SYNTHESIS AND CHARACTERIZATION
OF WATER SOLUBLE POLYMERS

by

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ABSTRACT: This thesis has been written in three parts.

Part I deals with the rheological response of dilute solutions of high molecular weight polyacrylamides at low shear rates. The non-Newtonian effects were found to be significant for polyacrylamides with number average molecular weights exceeding 10^6. The molecular weight average-intrinsic viscosity relationship most widely used in literature was found to be valid when the intrinsic viscosity was measured at high shear rates where the polymer solutions approached Newtonian behaviour. A new relationship was developed relating the number average molecular weight to the intrinsic viscosity extrapolated to zero shear rate.

Part II is an experimental investigation of the free-radical chain polymerization of acrylamide in water with potassium persulfate initiator. Conditions were such that the polymers produced had a number average molecular weight in excess of one million. Molecular weight averages were measured by viscometry, accounting for the non-Newtonian effects by the methods developed in Part I. Values for the transfer constants to the monomer and to the initiator were estimated at 25 °C and 40 °C and compared to the literature values.

In Part III, a new method was developed to estimate the reactivity ratios from composition-conversion data, based on non-linear regression. Previously published experimental data for the copolymerization of acrylic acid and acrylamide were analysed by the new method, and the results compared to those reported by the original investigators. Composition-conversion data were collected for this copolymerization system at intermediate conversion levels and over a limited range of compositions. Values for the reactivity ratios at 40°C were obtained from these data by the new algorithm, and compared to the literature values.

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I. Molecular Weight Determination of Acrylamide Polymers Using Intrinsic Viscosity Measurements

I.1 Introduction

Polymer molecules of high molecular weight possess the unique capacity to greatly increase the viscosity of the liquid in which they are dissolved, even when present at concentrations which are quite low. This is a manifestation of the voluminous character of randomly coiled long chain molecules. The higher the molecular weight within a given series of linear polymer homologs, the greater the increase in viscosity produced by a given weight concentration of polymer(1).

The dependence of the viscosity on molecular weight must be established empirically in each individual case by comparison with molecular weights determined by one of the absolute methods (osmotic pressure, light scattering, etc.). On the other hand, the measurement of viscosity is very much simpler than the execution of any of these absolute methods.

All previous investigations of the acrylamide polymer (kinetics of its synthesis, its various applications, etc.) have relied almost exclusively on viscosity measurements for its molecular weight determination. The importance of viscosity measurements as a quick and easy method for the molecular weight determination of polyacrylamides is enhanced by the fact that Ishige showed that gel permeation chromatography had limited resolution for the high molecular weight ends of these polymers$^{(2)}$. However, the commercial availability of glass packing material with pore diameters as large as 3 microns (E. Merck, Darmstadt, Germany) has substantially extended the resolution of GPC columns to higher molecular weight polymers. On the other hand, GPC has not yet been proved fruitful in the case of polyelectrolytes because of the dissociation of these molecules and its influence on coil size$^{(41,12)}$.

I.2 Theoretical Background and Literature Review

I.2.1 Intrinsic Viscosity

The development of the theoretical basis of the use of viscosity measurements for the determination of molecular weight of polymers have been largely developed by P.J. Flory and his coworkers$^{(1,3,4,5)}$.

The relative viscosity η_r is defined as the viscosity of the polymer solution divided by the viscosity of the pure solvent

$$\eta_r = \frac{\eta}{\eta_s} \qquad \text{(I-1)}$$

The specific viscosity η_{sp} is defined as

$$\begin{aligned} \eta_{sp} &= \eta_r - 1 \\ &= \frac{\eta - \eta_s}{\eta_s} \qquad \text{(I-2)} \end{aligned}$$

The specific viscosity expresses the incremental viscosity attributable to the polymeric solute. Therefore, the ratio $\frac{\eta_{sp}}{C}$, where C is the concentration of the polymer in solution, is a measure of the specific capacity of the polymer to increase the relative viscosity. The intrinsic viscosity $[\eta]$ is defined as the limiting value of this ratio at infinite dilution

$$[\eta] \equiv \left(\frac{\eta_{sp}}{C}\right)_{C\to 0} \equiv \left(\frac{\eta_r - 1}{C}\right)_{C\to 0} \qquad \text{(I-3)}$$

The concentration C is customarily expressed in grams per deciliter, $[\eta]$ being given in deciliters per gram.

Alternatively, if we express the concentration dependence of the relative viscosity as a virial equation of the form

$$\eta_r \equiv \frac{\eta}{\eta_s} = 1 + k_1 C + k_2 C^2 + \dots \qquad \text{(I-4)}$$

Then, from its definition in Eq. (I-3), the intrinsic viscosity is identical to the second virial coefficient k_1.

The intrinsic viscosity may also be defined as follows(6)

$$[\eta] \equiv \left(\frac{\ln \eta_r}{C}\right)_{C\to 0} \qquad \text{(I-5)}$$

Series expansion of the natural logarithm demonstrates the equivalence of Eq. (I-3) and Eq. (I-5).

I.2.1.1 The Determination of the Intrinsic Viscosity

The determination of the intrinsic viscosity requires the measurement of the polymer solution viscosities at different concentrations and the extrapolation to infinite dilution. But the procedure is relatively simple because plots of $\frac{\eta_{sp}}{C}$ and $\frac{\ln \eta_r}{C}$ versus C usually are very nearly linear for $\eta_r < 2$ (1). And it has been pointed out that the slopes of these plots for a given polymer-solvent system vary approximately as the square of the intrinsic viscosity(7). Thus the equation proposed by Huggins(8)

$$\frac{\eta_{sp}}{C} = [\eta] + k' [\eta]^2 C \qquad \text{(I-6)}$$

where k' is approximatley constant for a series of polymer homologs in a given solvent. Usually, but not always, k' is in the range from 0.35 to 0.40. It can also be shown that(1)

$$\frac{\ln \eta_r}{C} = [\eta] + k'' [\eta]^2 C \qquad \text{(I-7)}$$

where $k'' = k' - \frac{1}{2}$

Generally k" is negative and smaller in magnitude than k', hence $\frac{\ln \eta_r}{C}$ changes less rapidly with concentration than does $\frac{\eta_{sp}}{C}$. For this reason extrapolation of $\frac{\ln \eta_r}{C}$ is somewhat preferred over extrapolation of $\frac{\eta_{sp}}{C}$.

Polyelectrolytes exhibit a very ~~dif~~ferent behaviour than the one described above.

I.2.2 The Capillary Viscometer

This is, by far, the most widely used apparatus for the determination of the intrinsic viscosity of polymers. This is mainly due to the fact that capillary viscometers allow all the viscosity measurements at the different concentrations to be done using the same polymer solution by dilution in situ.

An energy balance about a capillary viscometer gives(9)

$$H = F_f + F_c + F_e \qquad \text{(I-8)}$$

where H is the driving fluid head (the vertical distance between the two menisci), and F_f is the friction developed in the capillary.

In a properly designed viscometer the flow will always be viscous and F_f may be calculated by Poiseuille's equation

$$F_f = \frac{8\ L\ V\ \eta}{\rho\ g\ \pi\ r^4\ t} \qquad \text{(I-9)}$$

where r is the radius of the capillary

L is the length of the capillary

η is the viscosity of the liquid

ρ is the density of the liquid

g is the gravitational acceleration

V is the volume of the liquid passed through the capillary in time t

The terms F_c and F_e in Eq. (I-8) are the friction forces due to turbulence caused by the contraction of the stream as it enters the capillary and the expansion of the stream as it leaves the capillary, respectively. Because both F_c and F_e have been correlated to the kinetic energy that the flowing fluid has when inside the capillary, they can be expressed as

$$F_c + F_e = \frac{m\,U^2}{g} \qquad \text{(I-10)}$$

where m is the kinetic energy correction coefficient

U is the average velocity inside the capillary and is equal to $\frac{V}{\pi r^2 t}$

Substituting from (I-9) and (I-10) into Eq. (I-8) and solving for the kinematic viscosity ν we get

$$\nu \equiv \frac{\eta}{\rho} = \left(\frac{\pi g H r^4}{8 L V}\right) t - \left(\frac{m V}{8 \pi L}\right) \frac{1}{t} \qquad \text{(I-11)}$$

or $$\nu = Ct - \frac{B}{t} \qquad \text{(I-11-A)}$$

Only C is a constant for long capillary viscometers whereas B is a constant only if m is a constant. But m increases with increasing Reynolds number and changes according to the shape of the capillary entrance and exit.

Cannon et al. have experimentally investigated the kinetic energy contribution to the total friction forces and suggested an equation of the form

$$\nu = Ct - \frac{E}{t^2} \qquad \text{(I-12)}$$

with E remaining constant over a wide range of Reynolds number(10).

I.2.3 Relationship between Intrinsic Viscosity and Molecular Weight

I.2.3.1 Empirical Approach

The relationship between the logarithm of the intrinsic viscosities of any series of fractionated linear polymer homologs and the logarithm of their molecular weights have been found to be linear over wide ranges of molecular weights$^{(1)}$. This suggests the form

$$[\eta] = k' M^a \qquad (I-13)$$

where k' and a are constants.

The exponent a varies with both the polymer and the solvent. It does not fall below 0.50 in any case and seldom exceeds about 0.80, the notable exception being polyelectrolytes in the absence of added salts. k' and a also vary somewhat with temperature.

Although Eq. (I-13) is empirical in origin, the more complicated theoretical expressions to be developed in the next section can be closely approximated by this simple equation over wide ranges of molecular weights.

In case of unfractionated polymers with a wide molecular weight distribution, Flory$^{(1)}$ showed that the following expression must be used in place of Eq. (I-13)

$$[\eta] = k' \bar{M}_v^a \qquad (I-14)$$

where $\bar{M}_v$ is the viscosity average molecular weight given by

$$\bar{M}_v = \left[\sum_i w_i \ M_i^a\right]^{\frac{1}{a}} = \left[\frac{\sum N_i \ M_i^{1+a}}{\sum N_i \ M_i}\right]^{\frac{1}{a}} \qquad (I-15)$$

where $w_i = \frac{C_i}{C}$ is the weight fraction of species i in the whole polymer and N_i is the number of molecules of this species.

The viscosity average molecular weight depends on the nature of the intrinsic viscosity-molecular weight relationship in each particular case as represented by the exponent a of the empirical relationship, Eq. (I-13). For polymers having "the most probable" distribution, it was shown that$^{(11)}$

$$\overline{M}_n : \overline{M}_v : \overline{M}_w = 1 : \left[(1+a)\,\Gamma(1+a)\right]^{\frac{1}{a}} : 2 \qquad \text{(I-16)}$$

where $\Gamma(1+a)$ is the gamma function of (1+a). As a varies from 0.50 to 1.0, $\frac{\overline{M}_v}{\overline{M}_n}$ for this particular molecular weight distribution increases from 1.67 to 2.0. In general, the viscosity average molecular weight will always be considerably closer to the weight average than the number average for any distribution likely to be encountered in a high polymer$^{(1)}$. It is necessary, however, that the molecular species included fall within the range over which the empirical equation (I-13) applies with sufficient accuracy.

I.2.3.2 Theoretical Approach$^{(1,3)}$ - Molecular Theories of Polymer Rheology at Low Concentrations

A number of successful developments have been made in the treatment of rheological response based upon mathematical models of the structure and dynamics of long chain molecules. These models use the physics of molecules— as opposed to the physics of continua—in attempting to describe this response. Dilute polymer solutions are usually treated as two-phase systems consisting of mechanical elements (the polymer molecules) embedded in a continuum (the solvent). The solvent is imagined to exert forces upon the polymer in much the same way that a fluid exerts forces upon a small suspended particle . As was pointed out by Middleman(13), this two-phase approach has led to some successful theories, although fundamentally improper, since solvent molecules are not really microscopic in comparison with the monomer elements.

The general procedure for calculating the dissipation of energy due to the presence of a perturbing phase was first given by Einstein(14). He considered the perturbation to a simple shear flow due to the presence of a single solid sphere of neutral density. By assuming that in a dilute suspension of spheres this single sphere calculation would still be valid for each individual sphere, Einstein arrived at the following expression for the viscosity of a suspension relative to the viscosity of the suspended fluid

$$\frac{\eta}{\eta_s} = 1 + 2.5\ \Phi \qquad \text{(I-17)}$$

where Φ is the volume fraction of spheres.

Debye(15) introduced the concept of the "Free Draining Polymer" where the individual monomer units do not interact with each other, nor do they distort the flow field. But when a monomer unit moves relative to the solvent, a frictional retardation is felt which is proportional to the relative viscosity, Debye showed that the centre of gravity will translate with the fluid velocity at that point and, in addition, the molecule will rotate with a frequency equal to half the shear rate. The analysis of such a model produces the result that the intrinsic viscosity should be directly proportional to the molecular weight, i.e.

$$[\eta] = K_1 M \qquad \text{(I-18)}$$

This equation is known as Staudinger's Viscosity Rule.

Deviations from Eq. (I-18) are common and attributed to the fact that the polymer molecule is not "freely drained". Hence the concept of a "Shielding Effect" was introduced, whereby peripheral monomer units are imagined to be able to shield interior monomer units from the external flow(16,17). Analysis of this model leads to the result

$$[\eta] = K_2 M^{\alpha} \qquad \text{(I-19)}$$

where α is a function of the amount of "shielding". At the limit of complete shielding, α equals 0.50. This behaviour is associated with the action of a poor solvent. These results agree with observation, but as Flory(1) points out, some of the parameters remain quantitatively undefined.

Following the treatment of Debye and Bueche(16), Flory considered the motion of the solvent with reference to the polymer molecule(1,3). Near the molecule's centre the solvent is very nearly stationary, but as we move outward its velocity increases. The molecule also rotates with an angular velocity equal to half the rate of shear of the surrounding solvent. The polymer molecule is considered to consist of a swarm of segments distributed on the average about the molecular centre of gravity in accordance with the Gaussian formula

$$x_j = x\left(\frac{\beta_o'}{\pi^{1/2}}\right)^3 \exp(-\beta_o'^2 s_j^2)\ 4\pi s_j\ \delta s_j \qquad \text{(I-20)}$$

where x_j is the number of segments occuring in the spherical shell of radius s_j from the centre of gravity and of thickness δs_j. The subscript o refers to the molecule in the unperturbed state, i.e. in absence of intramolecular interaction. The parameter of the Gaussian distribution β_o' is related to $(\overline{s_o^2})^{1/2}$, the root-mean-square distance from the molecule's centre of gravity averaged over all the segments in the unperturbed state (i.e. the radius of gyration of the unperturbed molecule) and $(\overline{r_o^2})^{1/2}$, the unperturbed root-mean-square end-to-end distance of the polymer molecule by the equation

$$\beta_o' = \left(\frac{3}{2\,\overline{s_o^2}}\right)^{1/2} = \frac{3}{\left(\overline{r_o^2}\right)^{1/2}} \qquad \text{(I-21)}$$

The single polymer molecule in a dilute solution is subject to the osmotic action of the surrounding solvent which tends to swell it to a larger average size than it would otherwise assume. Therefore the chain molecule is spread to a less probable configuration. An elastic reaction consequently develops. At equilibrium, the elastic force is in balance with the osmotic force which tends to swell the molecule. Defining α as the factor by which the linear dimensions of the molecule are altered as a consequence of the swelling action of the solvent on the polymer molecule in infinitely dilute solutions, we get at equilibrium

$$\beta_0' = \alpha \beta' \qquad \text{(I-22)}$$

The solution viscosity, being a friction characteristic, depends on the size of the molecular domain. Hence it is intimately related to the molecular configuration, including the intramolecular expansion factor . Analysing this model, Flory(1,3) arrives at the following result

$$\alpha^5 - \alpha^3 = c' \left(1 - \frac{\theta}{T}\right) M^{1/2} \qquad \text{(I-23)}$$

where c' and θ depend on the heat and entropy of dilution parameters characterizing the given polymer-solvent pair. θ is the ideal temperature at which α equals unity and the molecular dimensions are unperturbed by intramolecular forces. It represents the lowest temperature for complete miscibility in a given solvent at the limit of infinite molecular weight. In a good solvent, the molecule may expand considerably beyond its unperturbed size and $\alpha > 1$.

For polymers having molecular weights in excess of about 10,000 Flory shows that his model leads to -

$$[\eta] = \Phi \frac{(\overline{r^2})^{3/2}}{M} \tag{I-24}$$

where Φ is a universal constant, independent of the characteristics of the given chain molecule beyond the requirement that its spatial form be that characteristic of a randomly coiled chain molecule. From Eq.(I-21) and Eq.(I-22) it is clear that

$$(\overline{r^2})^{1/2} = \alpha\,(\overline{r_o^2})^{1/2} \tag{I-25}$$

Hence Eq.(I-24) may be written as

$$[\eta] = \Phi\left(\frac{\overline{r_o^2}}{M}\right)^{3/2} M^{1/2}\,\alpha^3 \tag{I-26}$$

and since $\frac{\overline{r_o^2}}{M}$ is independent of M for a linear polymer of a given unit structure,

$$[\eta] = K\, M^{1/2}\,\alpha^3 \tag{I-27}$$

where,
$$K = \Phi\left(\frac{\overline{r_o^2}}{M}\right)^{3/2}$$

K should be a constant independent of the molecular weight of the polymer and of the solvent. It may however vary with temperature inasmuch as the unperturbed molecular extension $\frac{\overline{r_o^2}}{M}$ may change with temperature.

I.2.3.3 Relationship between Theoretical and Empirical Approaches

The intrinsic viscosity of a linear polymer was found to be expressed by the empirical relationship

$$[\eta] = K' M^a \qquad \text{(I-13)}$$

And Flory's model predicts

$$[\eta] = K M^{1/2} \alpha^3 \qquad \text{(I-27)}$$

Also theory predicts the dependence of α^3, the volume expansion factor in good solvent, on the molecular weight of the polymer as

$$\alpha^5 - \alpha^3 = c' (1 - \frac{\theta}{T}) M^{1/2} \qquad \text{(I-23)}$$

This last relationship can be represented satisfactorily over considerable ranges of M by a power dependence(1)

$$\alpha^3 \sim M^{a'} \qquad \text{(I-28)}$$

From equations (I-13), (I-27) and (I-28) it is clear that

$$a = \frac{1}{2} + a' \qquad \text{(I-29)}$$

The better the solvent, the larger will be the right hand side of equation(I-23) and the larger a' required in Eq.(I-28). If the right hand side of Eq.(I-23) is sufficiently large, α^3 could be neglected compared to α^5 and we get $\alpha \sim M^{1/10}$. Then, a' = 0.30 and a = 0.80, which is an upper limit according to the theory of randomly coiled linear polymers. The lower limit occurs at the theta temperature, when $\alpha = 1$, a' = 0 and a = 0.50.

I.2.4 Shear Rate Dependence of the Intrinsic Viscosities Of High Polymers

All the analyses of dilute solution polymer viscosity described above in Section I.2.3 omit consideration of the effect of shear rate on the response of the molecule. But it has been observed quite early that even dilute solutions of high molecular weight polymers exhibit non-Newtonian behaviour(18). Therefore the need arises for finding a standard method for measuring the intrinsic viscosity of a polymer, so that it becomes independent of the instrument used in its measurement.

Several capillary viscometer designs have been proposed in the literature for measuring the shear rate dependence of the polymer solution viscosities at several concentrations, hence the intrinsic viscosity as a function of shear rate(19,20,21,22). From the velocity distribution for the laminar flow of a Newtonian fluid in a capillary, it can be shown that the maximum shear rate occurs at the wall and is given by(21)

$$\dot{\gamma}_w = \frac{r\ H\ g\,\rho}{2\ L\ \eta} \qquad \text{(I-30)}$$

where r and L are the radius and length of the capillary, respectively. H is the average distance between the upper and lower liquid levels during the measurement, g is the acceleration of gravity, ρ the liquid density, and η the liquid viscosity.

All the viscometers described in the above-mentioned papers depend on changing the average hydrostatic head H to vary the shear rate. This is accomplished either by providing several efflux bulbs at different heights above the capillary(19,20,21), or, alternatively, by applying different external pressures on the liquid in the viscometer by means of a manostat(22).

Fox, Fox, and Flory(19) found that for dilute solutions of polyisobutylene fractions, the logarithm of the specific viscosity $\ln(\eta_{sp})$ decreased linearly with the rate of shear over a wide range of shear rates . They defined the "Shear Coefficient" $\phi = 100 \dfrac{d(\ln \eta_{sp})}{d\dot{\gamma}}$ and found it to be independent of concentration at low concentrations. For molecular weights exceeding several million, they found the shear coefficient to be approximated by the empirical expression

$$\phi = 110 \frac{[\eta]^2}{M} \qquad \text{(I-31)}$$

However for dilute solutions of polyisobutylene of very high molecular weight (ca. 15×10^6), they found that $\ln \eta_{sp}$ decreases non-linearly with $\dot{\gamma}$, decreasing with increasing shear rate. The authors draw attention to the important fact that the ratio of $\dfrac{\eta_{sp}}{C}$ at zero shear rate to its value as ordinarily measured in a viscometer operating at a standard shear rate increases as the concentration is decreased, because the shear rate decreases with increasing concentration, owing to the increase in viscosity. Therefore ordinary extrapolation to infinite dilution applied to measurements made with a single viscometer fails to reduce the magnitude of the error arising from non-Newtonian flow. This is especially important for high molecular weight polymers in good solvents.

Krigbaum and Flory(21) made similar observations when measuring the viscosities at four shear rates of four polystyrene fractions in benzene. Again, the variation of the specific viscosity with shear rate could be expressed by

$$\ln \eta_{sp} = \left(\ln \eta_{sp}\right)_{\dot{\gamma}=0} - \frac{\phi}{100}\,\dot{\gamma} \qquad \text{(I-32)}$$

They also found that $\ln \eta_{sp}$ was no longer a linear function of shear rate for the highest molecular weight fraction studied (6,970,000), ϕ increasing with diminishing shear rate.

The fact that some of the viscosity data are not linear with respect to shear rate has led to several attempts to find a suitable change of variables that will reduce this relationship to a linear one and therefore make the extrapolation to zero shear rate less arbitrary.

Katchalsky and Sternberg(23) studied polymethacrylic acid solutions in a Bingham-type viscometer with a variable pressure system to control the rate of shear. They found the shear stress to decrease non-linearly with the shear rate up to a shear rate of 2 x $10^4(\text{sec})^{-1}$. They assumed the apparent viscosity to be an even function of shear rate of the form

$$\eta = \eta_o \left[1 - a\dot{\gamma}^2 \right] \qquad \text{(I-33)}$$

where η and η_o are the apparent viscosities of the solution at a rate of shear of $\dot{\gamma}$ and zero, respectively, and a is a constant. From Eq. (I-33) they derived the following relationship for the flow through a capillary

$$\frac{t_s}{t} = \frac{\eta_s}{\eta_o} \left[1 + \frac{a\ P^2\ r^2}{3\eta_o^2\ L^2} \right] \qquad \text{(I-34)}$$

where t_s and t are the flow times of the pure solvent and solution, repectively. P is the hydrostatic head of liquid, viz. ρgH, r the capillary radius and L the capillary length.

If follows from Eq. (I-34) that if a series of measurements is performed on a solution in different capillaries of varying lengths and radii, or in the same capillary under different heads of liquid, the resulting plot of $\frac{t_s}{t}$, i.e. the reciprocal of the relative viscosity, against $\frac{P^2\ r^2}{L^2}$ will be a straight line. The intercept of this line gives the reciprocal of the relative viscosity at zero shear rate. The authors pointed out that the viscosity measurements carried out at an arbitrary and undefined shearing stress will depend on the instrument used and the experimental conditions.

However, the authors presented a very limited set of experimental results to test their model. They measured the viscosities of a polymethacrylic acid at two concentrations and at three different shear rates for each concentration. A straight line was found to fit each set of three points.

Golub(23) critically examined the above paper by Katchalsky and Sternberg. He investigated the shear dependence of Alfin polyisoprene in dilute benzene solutions over a wide range of molecular weights and shear rates. He found that the intrinsic viscosity depended strongly on the rate of shear, the effect increasing with molecular weight. He found the shear dependence was best expressed by an equation involving both a linear and a quadratic function of the gradient i.e.

$$\eta = \eta_o \left[1 - a\dot{\gamma} + b\dot{\gamma}^2 \right] \qquad \text{(I-35)}$$

And, for small gradients, he assumed that this may be reduced to a simpler form

$$\eta = \eta_o \left[1 - a\dot{\gamma} \right] \qquad \text{(I-35-A)}$$

By using a derivation similar to that of Katchalsky and Sternberg(23), an equation analogous to Eq. (I-34) was obtained, but involving a linear, rather than a quadratic, function of $(\frac{P\,r}{L})$

$$\frac{t_s}{t} = \frac{\eta_s}{\eta_o} \left[1 - \frac{a\,P\,r}{2\,\eta_o L} \right] \qquad \text{(I-36)}$$

According to this equation the plot of $\frac{1}{\eta_r}$ versus $\frac{P\,r}{L}$ should be a straight line with the intercept giving the reciprocal of the relative viscosity at zero shear rate. Golub then showed that his experimental data fitted the above equation. But when plotted according to a Katchalsky's plot

Eq. (I-34), they showed a downward curvature at low gradients. Ignoring this curvature resulted in viscosity values consistently smaller than the ones provided by Eq. (I-36). It is interesting to note that Golub chose, as a measure of the consistancy of Eq. (I-34) and Eq. (I-36), to compare the respective results obtained from these plots to the results obtained from what he called "conventional viscosity shear rate curves" of $\frac{\ln \eta_r}{C}$ versus rate of shear. These plots were curved at low shear rates and had to be extrapolated "by eye" to zero shear rates.

All previous investigators chose to correct for the shear rate effects by extrapolating to zero shear rate. However, two alternative approaches have been suggested.

1. To make all the viscosity measurements at an arbitrary but finite shear rate. Tripp, Conrad, and Mares(24) chose this approach in their investigation of cellulose solutions. They adjusted all their viscosity data to a mean velocity gradient of 500 sec.^{-1}. In the discussion of the results of the present thesis it will be shown that this approach may not properly correct for shear rate effects.
2. To extrapolate the viscosity data to infinite rate of shear. Davies(18) measured the viscosities of dilute benzene solutions of polymethyl methacrylate and polystyrene at two different temperatures. He found all the viscosities to be non-Newtonian

especially at low temperatures and high molecular weights. However he found that there was a tendency to Newtonian behaviour at high shear rates. Therefore he concluded that if experiments were carried out at sufficiently high rates of shear, the non-Newtonian effects will be eliminated, and a good basis would exist for comparing the viscosities of the different polymer solutions.

This approach is consistent with Flory's statement that the "Shear Coefficient , proportional to $d(\ln \eta_{sp})/d\dot{\gamma}$ increases with diminishing shear rate(19,21). It also agrees with the experimental observations made on different polymer solutions in many of the previously mentioned investigations(22,23).

I.2.5 Intrinsic Viscosity Data for Polyacrylamide

The only investigation of the effect of the rate of shear on the measured intrinsic viscosity of polyacrylamide solutions was made by Bruce and Schwarz(25). They used a Weissenberg rheogonometer to measure the solution viscosities of a commercial non-ionic acrylamide polymer (Dow Separam MGL) at different shear rates. The effect of the shear rate was pronounced and the intrinsic viscosity extrapolated to zero shear rate was found to be 18.2 dl/g. Furthermore their data indicated clearly that the intrinsic viscosity approached a constant limiting value at high enough shear rates, which would validate Davies approach(18) with respect to acrylamide polymers.

The following are the most widely used equations relating the average molecular weight of acrylamide polymers with their intrinsic viscosities in water solutions at 25 °C. These equations were developed by Collinson, Dainton and McNaughton(26) and by Scholtan(27), respectively

$$[\eta] = 6.80 \times 10^{-4}(\bar{M}_n)^{0.66} \qquad \text{(I-37)}$$

$$[\eta] = 6.31 \times 10^{-5}(\bar{M}_w)^{0.80} \qquad \text{(I-38)}$$

It may be noted that these equations were derived from polymers having molecular weights less than 3×10^5 and 5×10^5, respectively. Therefore the authors' neglect of the effect of the rate of shear on the intrinsic viscosities was probably justified.

Subsequent investigators have consistently used these relationships to describe acrylamide polymers of several million molecular weight averages without correcting for shear effects nor providing the information necessary to compute the rates of shear at which their viscosity measurements were made. The following are some of these papers.

Investigations of the kinetics of synthesis of the acrylamide polymer from its monomer using different initiating systems have been reported(28-33) where the average molecular weights computed from Eq. (I-37) or Eq. (I-38) were as high as 7×10^6. Also some of the most recent papers on the application of acrylamide in different fields such as flocculation(34) and paper making(35) characterized the polymers used by Eq. (I-37) with $\bar{M}_n$ exceeding 6 x 10^6 in each case. Also, a recent investigation of the degradation of polyacrylamide in aqueous solution by high speed stirring(36) used Eq. (I-38) to find the molecular weight of the original polymer to exceed 5 x 10^6.

Considering the body of information presented in the preceding section, pointing to the important effect of the rate of shear on the measured intrinsic viscosities of high molecular weight polymers, it is a remarkable fact that this effect has been so consistently ignored in the previous investigations of high molecular weight polyacrylamide.

Therefore the present study was undertaken to investigate the effect of shear rate on the measured intrinsic viscosities of high molecular weight polyacrylamides. All the acrylamide polymers prepared for the kinetic study detailed in Part II of this thesis were used for this purpose.

The final objectives of this experimental study are :

1. To estimate the importance of correcting for the non-Newtonian effects on the measured intrinsic viscosity and to evaluate the reliability of the values of the intrinsic viscosities reported in the literature that were measured without taking these effects into consideration.

2. To specify standard techniques for measuring the intrinsic viscosities so that their values are independent of the instrument used and of experimental conditions.

I.3 Experimental Set-Up and Procedures

I.3.1 Materials Used

The polyacrylamides used were all synthesized in water solution from recrystallized acrylamide monomer as will be detailed in Part II of this thesis. The initiator used was recrystallized potassium persulfate, except for the two polymers "Standard A" and "Standard B" where the initiator was 4,4' azobis-4-cyanovaleric acid.

The water used as a solvent in polymerization and to dissolve the polymers for viscosity measurements was distilled twice, the second time out of an alkaline permanganate solution.

I.3.2 Apparatus

A Cannon-Ubbelohde four-bulb shear dilution viscometer(37) (size 50, Serial No. S 489) provided by the Cannon Instrument Company in State College, Pennsylvania was used throughout this investigation (Fig.I.1). The viscometer has four efflux bulbs (E_1 to E_4) providing approximately a five-fold variation in the mean hydrostatic head between the uppermost bulb (E_1) and the lowermost one (E_4). The capillary (H) is 0.044 cm in diameter and about 22 cm in length.

The "suspended-level" device, whereby the bulb I at the bottom of the capillary is connected directly to the atmosphere through tube K, makes the average hydrostatic

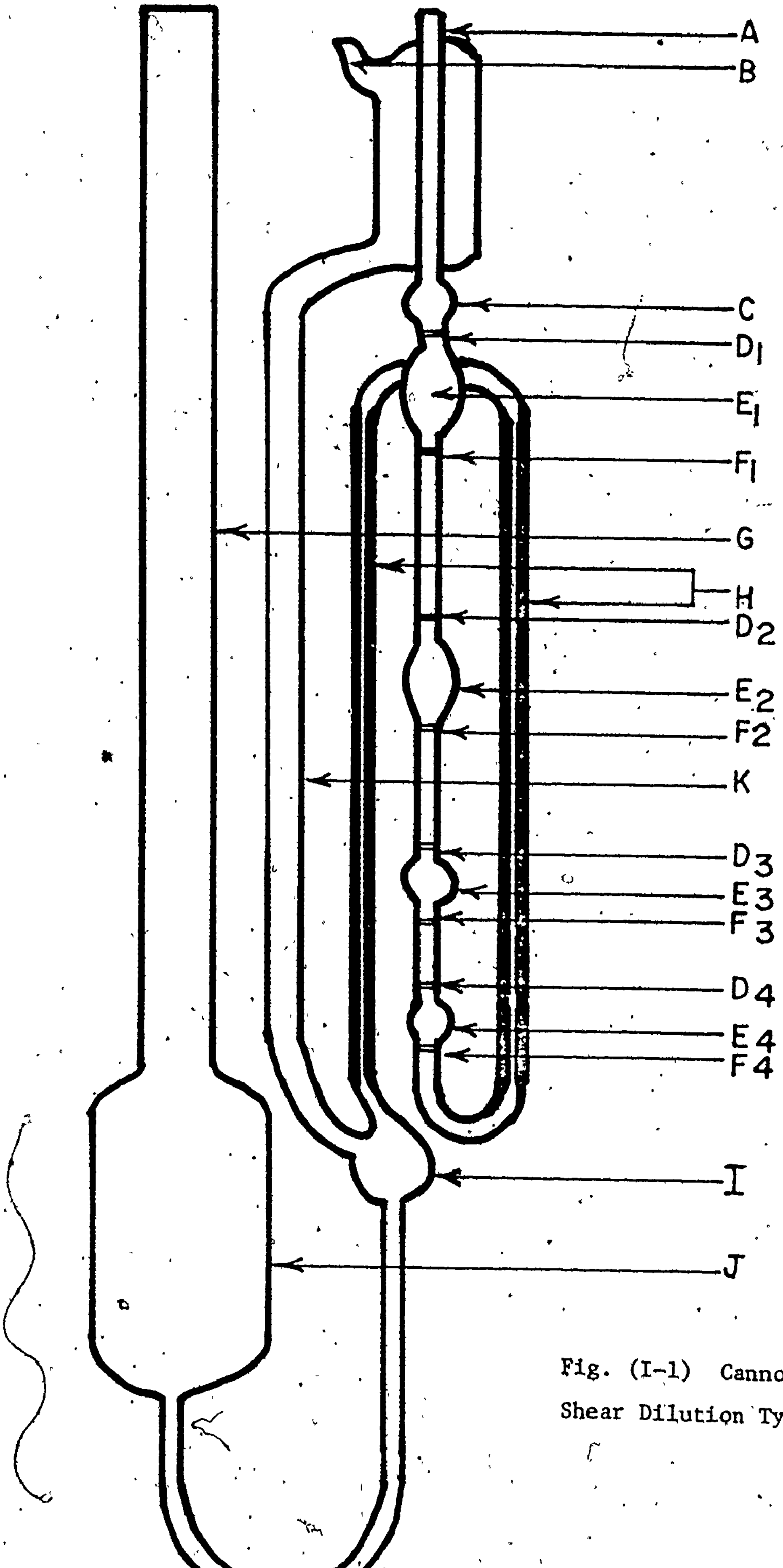


Fig. (I-1) Cannon-Ubbelohde Four-Bulb Shear Dilution Type Capillary Viscometer head for each of the four bulbs independent of the amount of liquid present in reservoir J, as opposed to the standard Ostwald viscometer. The size of reservoir J permits a five-fold decrease from the original concentration. The design of the viscometer also provides for mechanical strength and resistance to breakage.

I.3.3 Procedure

The viscometer was set in a constant temperature water bath operating at 25±0.1°C. The temperature control was achieved by means of a Haake portable immersion circulating pump equipped with adjustable heating capacity, cooling coil and thermoregulator.

Vertical alignment was ensured by using a burette support assembly consisting of two clamps and a support stand to hold the viscometer inside the bath. Vertical alignment was also periodically checked by means of a plumb-line.

The procedure for viscosity measurements was as follows.

A. Polymer Solutions

These were prepared by weighing the polymer and dissolving it in twice distilled water by heating at 40°C in an oven. The samples were heated for a minimum of 24 hours, but the higher molecular weight polymers required heating periods of longer duration (up to 3 days for the highest molecular weight polymers). No mechanical stirring was used at all during the dissolution of the polymer samples, as it has been reported that stirring causes the degradation of high molecular weight acrylamide polymers (2,36).

B. Viscosity Measurements

The following steps were followed in measuring the intrinsic viscosity of each polymer :

1. A 5 ml. sample of the polymer solution at the highest required concentration was charged directly from a pipette, through tube G, into the lower reservoir J of the viscometer.

2. The viscometer was then inserted into the constant temperature bath and clamped to the support stand in a vertical position.

3. Approximately 20 minutes were allowed for the sample to reach the temperature of the bath.

4. A finger was placed over tube B and suction applied to tube A until the liquid reached the centre of bulb C. Suction was then removed from tube A and the finger removed from tube B. The remaining solution then dropped immediately from the lower end of the capillary into bulb I.

5. The liquid sample was allowed to flow freely down, and the efflux time required for the meniscus to pass from etch mark D to etch mark F for each of the four bulbs was recorded to the nearest 0.1 seconds using a Precision Scientific Company electric stopwatch with a direct reading counter.

6. When required, steps 4 and 5 were repeated to check on possible polymer degradation.

7. The sample was then diluted by adding a measured volume of the twice distilled water from the pipette directly into reservoir J. This was mixed with the original sample by applying a slight pressure to tube A while placing a finger over tube B.

8. Steps 3 to 6 were repeated at the new concentration.

9. Steps 3 to 8 were repeated for all the concentrations necessary for the intrinsic viscosity calculations.

I.3.4 Calibration of the Viscometer

The complete equation to be used for the accurate use of the viscometer is Eq. (I-11-A)

$$\nu = Ct - \frac{B}{t} \qquad \text{(I-11-A)}$$

~~But, as~~ has been pointed out before, it is much more convenient when the term $(\frac{B}{t})$, due to the kinetic energy contribution, may be ignored, so that the time of flow t becomes directly proportional to the kinematic viscosity . Therefore it was necessary to estimate the parameters B and C of Eq. (I-11-A) to specify the conditions under which the second term on the right side of the equation may be ignored.

To evaluate B and C two liquids whose viscosities and densities are accurately known must be used to calibrate the viscometer. The first standard used was twice-distilled water. The water's viscosity and density at 25°C were taken as(38)

$$\eta = 0.8937 \text{ centipoises}$$

$$\rho = 0.99708 \text{ g/cm}^3$$

Therefore, $\nu \equiv \frac{\eta}{\rho} = 0.8963$ centistokes

The second viscosity standard was a Newtonian oil supplied by the Cannon Instrument Company, State College, Pennsylvania. The standard was labelled S-3 (No. 73101) with the following specifications at 25°C

$$\eta = 3.493 \text{ centipoises}$$

$$\rho = 0.8368 \text{ g/cm}^3$$

$$\nu = 4.174 \text{ centistokes}$$

In Appendix (I-1) the detailed efflux-time measurements through the four bulbs for each of these two liquids are listed. Ten different readings were done in the case of water and five readings for Standard S-3. Reproducibility was excellent and the flow times were averaged for each bulb. The average times were substituted into Eq. (I-11-A) and the equation solved for the parameters B and C. Table I-1 summarizes these results.

From Eq. (I-11-A) it is clear that the kinetic energy becomes less important as the time of flow increases. Therefore, from the values of B and C in Table (I-1) it is possible to compute for each bulb a "critical time" above which the kinetic energy term will be less than an arbitrary fraction of the viscous term. Choosing this fraction to be 0.02

Table (I-1) Calibration Constants for the Four-Bulb Viscometer

Bulb No.	Average Flow Time (Seconds)		C $\left(\frac{\text{Centistokes}}{\text{Second}}\right)$	B (Centistokes x Sec.)
	Water	S-3		
1	222.19	1047.15	0.003984	-2.470
2	203.99	961.18	0.004340	-2.245
3	229.74	1078.87	0.003867	-1.818
4	202.34	926.48	0.004509	3.244

(two per cent), the critical times for the four bulbs were found to be as follows.

Bulb No.	Critical Time (Seconds)
1	176
2	161
3	153
4	190

As these times are less than the times of flow of water, as presented in Table (I-1), it is clear that for all the polymer solutions, whose efflux times will exceed those of pure water, the kinetic energy correction term will be much less than 2% of the viscous term and a simplified version of Eq. (I-11-A) may be used

$$\nu = C\ t \qquad \text{(I-39)}$$

Furthermore, it has been observed that the presence of polyacrylamide in water at the low concentrations used in intrinsic viscosity determinations (in the order of 0.1 g/dl) causes no significant change in the density of the water(2).

In this case, Eq.(I-39) simplifies to

$$\eta = C' \cdot t \qquad \text{(I-40)}$$

Therefore the relative viscosity, or the ratio of the solution viscosity to that of the pure solvent can be expressed as

$$\eta_r \equiv \frac{\eta}{\eta_s} = \frac{t}{t_s} \qquad \text{(I-41)}$$

Where t is the time of flow of the polymer solution and t_s that of the pure solvent through each of the bulbs.

I.3.5 Estimation of the Shear Rates

To obtain an expression for the estimation of the shear rate associated with each efflux bulb, it is necessary to combine the simplified form of Eq.(I-11), where the second term on the right side of the equation (the kinetic energy term) is neglected, and Eq.(I-30) expressing the rate of shear at the wall of a capillary for viscous flow. Substituting for η from the former equation into the latter, we obtain

$$\dot{\gamma}_w = \frac{4\,V}{\pi\,r^3}\,\frac{1}{t} \qquad \text{(I-42)}$$

Therefore, to obtain the shear rate at the wall of the capillary, the "Shear Rate Constant" defined as $\frac{4\,V}{\pi\,r^3}$ must be divided by the efflux time through the bulb in question. Table (I-2) summarizes the values of the shear rate constants for the four bulbs, computed from values for the efflux volumes and the capillary diameter provided by the manufacturer.

Table (I-2) Shear Rate Constants for the Four Bulbs of the Viscometer

Bulb No.	Capillary Diameter (cm)	Efflux Volume (cm^3)	Shear Rate Constant
1	0.044	1.42	170,000
2	0.044	0.80	96,000
3	0.044	0.58	69,000
4	0.044	0.29	35,000

I.3.6 Polymer Degradation

It was necessary to ascertain that the polymers in solution did not degrade during the viscosity measurements. The first possible cause for polymer degradation is the shear they are subjected to in the capillary. To check for this possibility, some efflux-time readings, chosen at random, were repeated several times before diluting the sample to the lower concentration. Invariably the times of flow were reproducible to within 1% without any consistent drift of the times measured. Therefore it was concluded that the shear rates involved in this viscometer are too low to cause any detectable degradation ofthe polymer molecules.

The second possibility was that the polymers degraded with time while sitting in solution. This was particularly important because the viscosity measurements for each polymer sample extended over a period of several hours. To check for this possibility, some of the efflux-time readings were repeated after letting the solution sit in the viscometer inside the constant temperature bath overnight. Reproducibility was again excellent and it was concluded that the solutions' viscosities were independent of time during the viscosity measurements.

I.3.7 Reproducibility

To check for reproducibility, especially with respect to the errors inherent in preparing the polymer solutions, the intrinsic viscosities of two polymers (25-05-05-E) and (40-05-05-F) were measured each for two solutions prepared independently of each other. The agreement between each pair of duplicate measurements was excellent.

Details of all the viscosity measurements performed, including the above-mentioned duplicates, are listed in Appendix (I-1).

I.4 Results and Discussion

Figures (I-2) to (I-9) represent some typical viscosity data for the polymers investigated. The behaviour shown in these graphs is representative of that of all the polymers listed in Appendix (I-1) and span the whole molecular weight range investigated.

The viscosity data are plotted as the natural logarithm of the relative viscosity, the latter calculated from Eq. (I-41), versus the rate of shear at the wall of the capillary as calculated from Eq. (I-42) with the values from Table (I-2). Each point on these graphs represents the flow through one of the viscometer's four efflux bulbs, and each set of four points representing the data at a single concentration of polymer solution are connected by a single curve.

These figures reveal the following important flow characteristics of the polyacrylamide solutions.

1. The viscosities of these solutions are strong functions of the rate of shear even at the low concentrations encountered in the estimation of the intrinsic viscosities.

2. The rate of change of the viscosity with shear rate decreases with decreasing concentration for any particular polymer.

3. The rate of change of the viscosity with shear rate decreases with increasing shear rate, the solutions approaching Newtonian behaviour at high enough shear rates.

4. At the same concentration, the non-Newtonian

Fig. (I-2) Flow Data for Polymer (25-05-01-G)

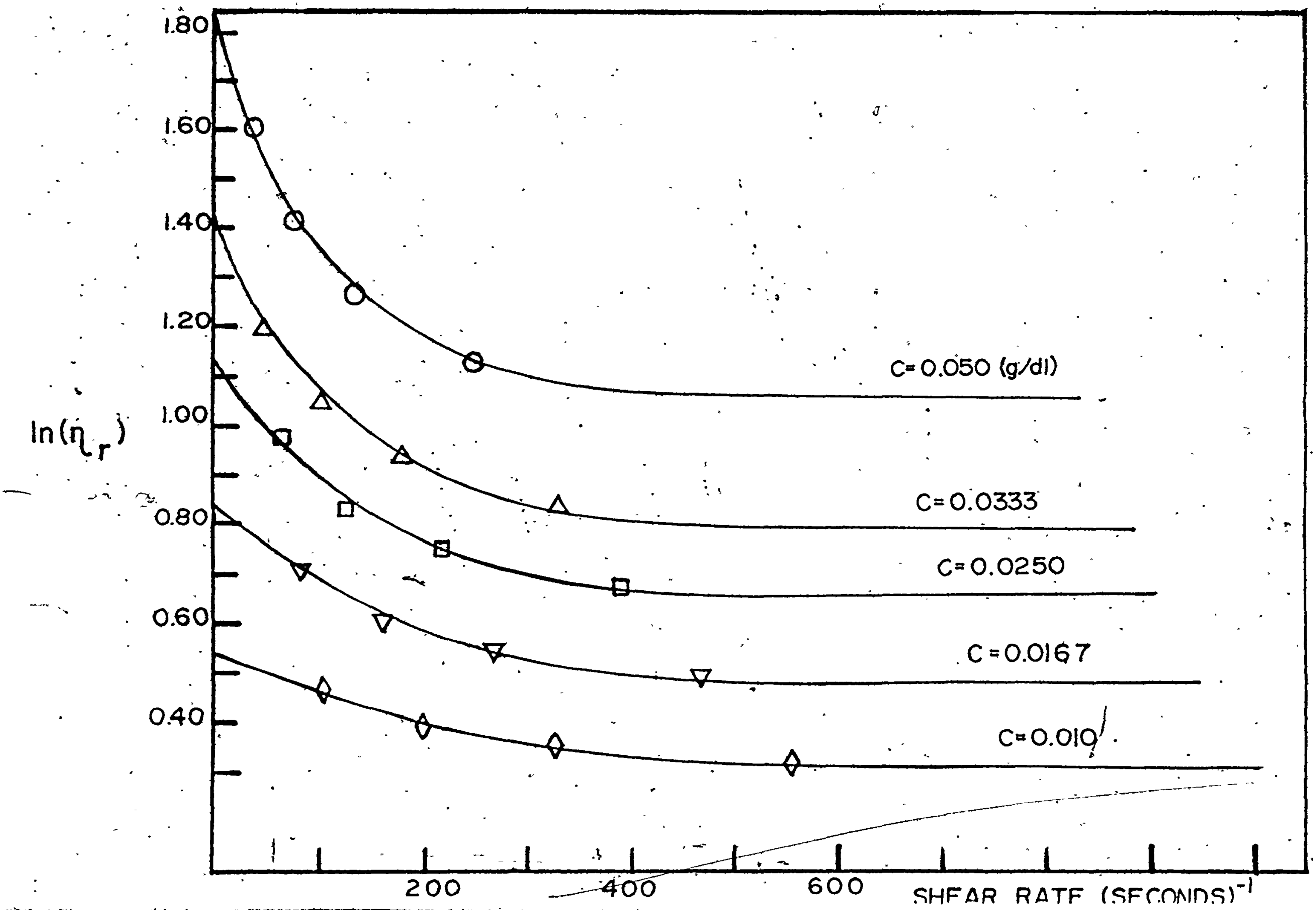


Fig. (I-3) Flow Data for Polymer (25-20-10-I)

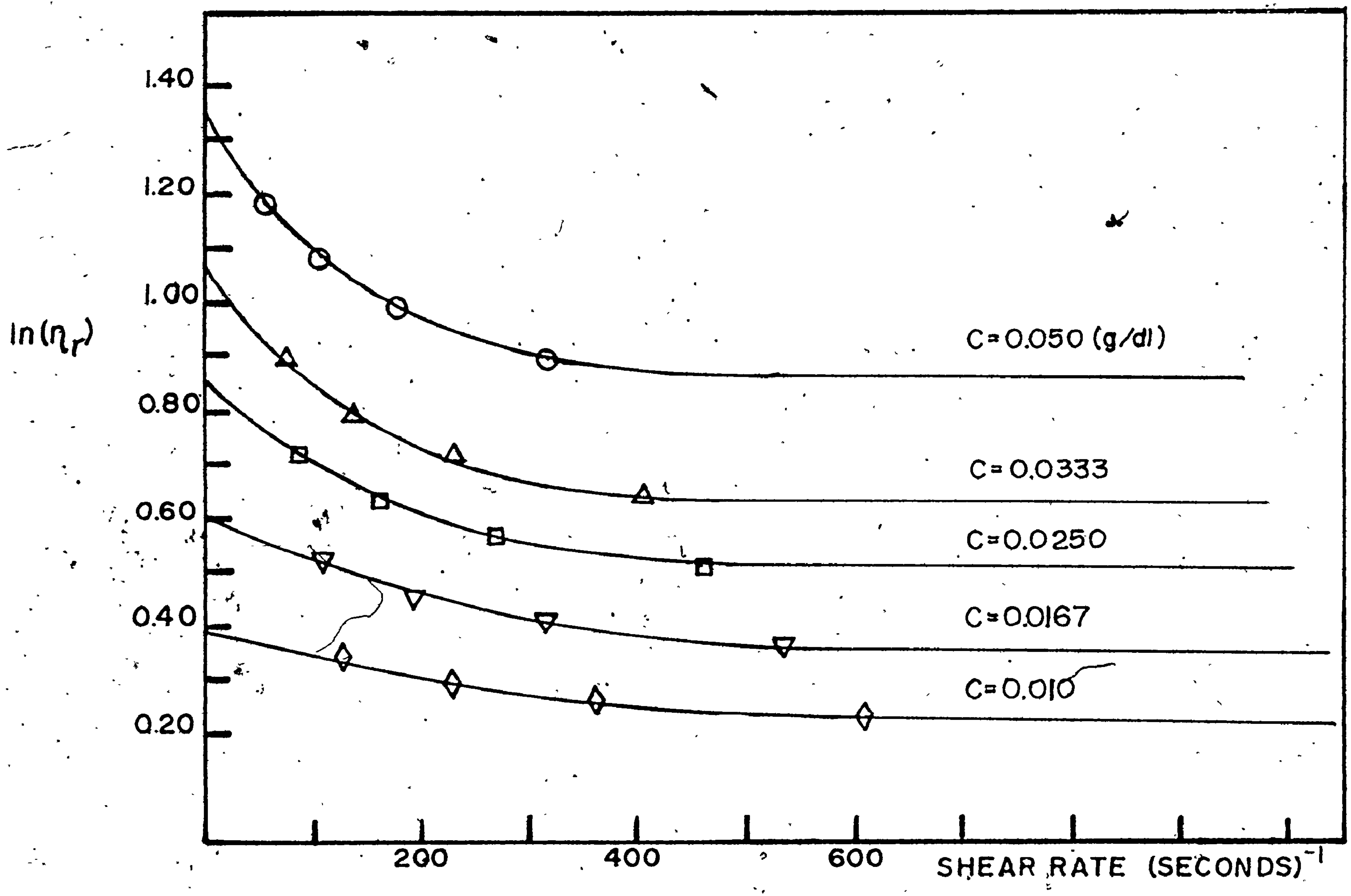


Fig. (I-4) Flow Data for Polymer (25-05-05-A)

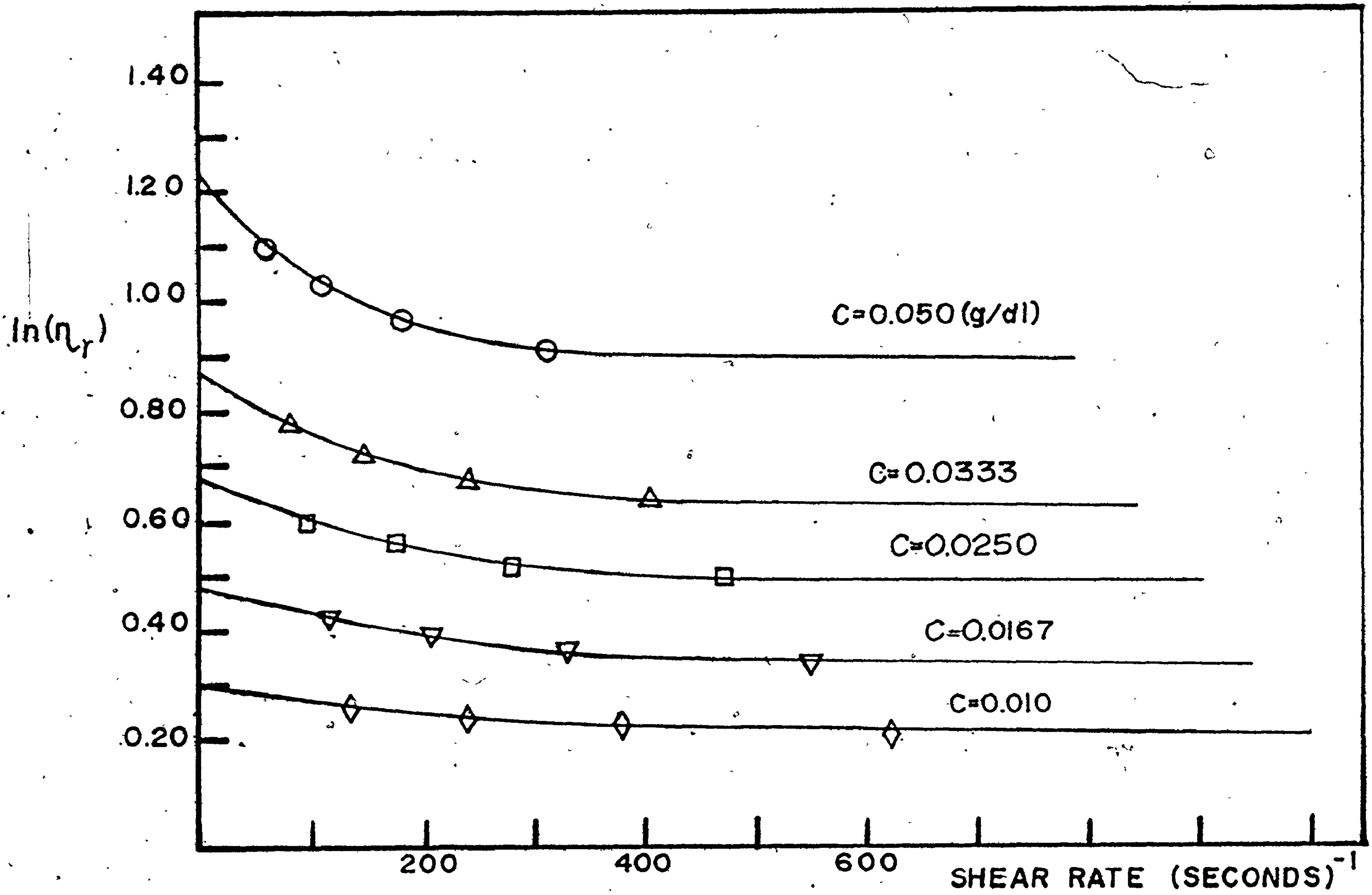


Fig. (I-5) Flow Data for Polymer (40-05-01-D)

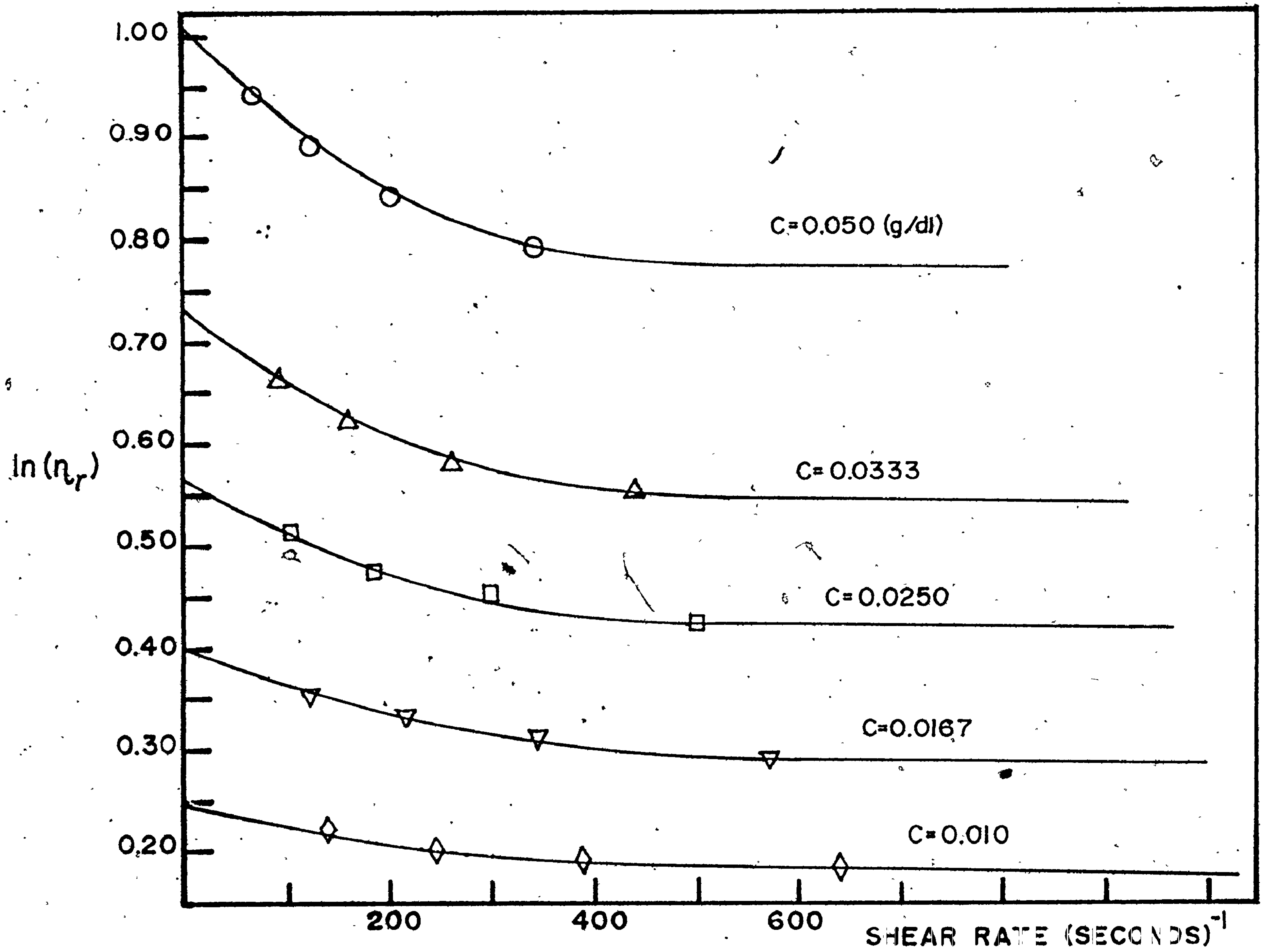
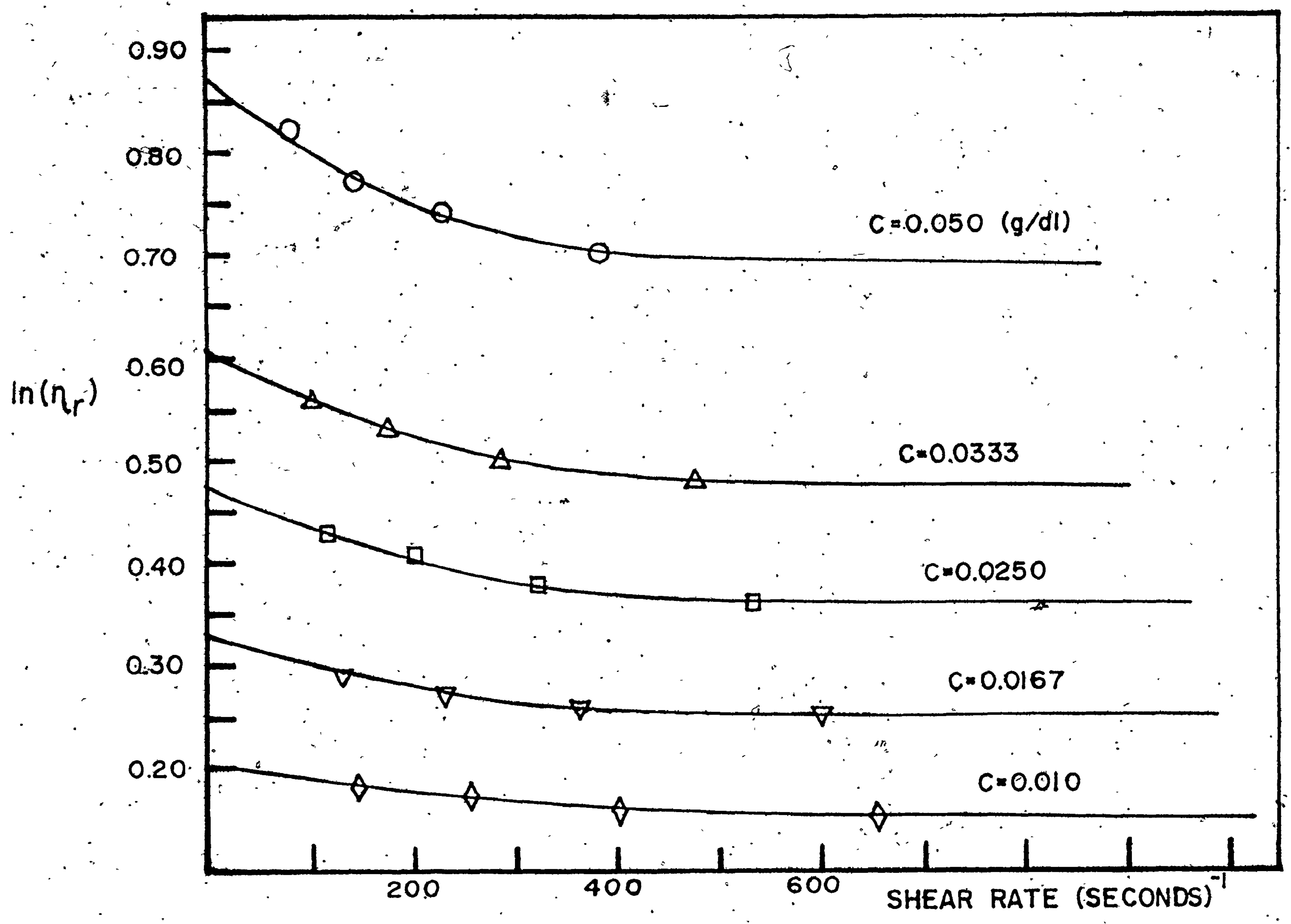


Fig. (I-6) Flow Data for Polymer (25-02-10-C)



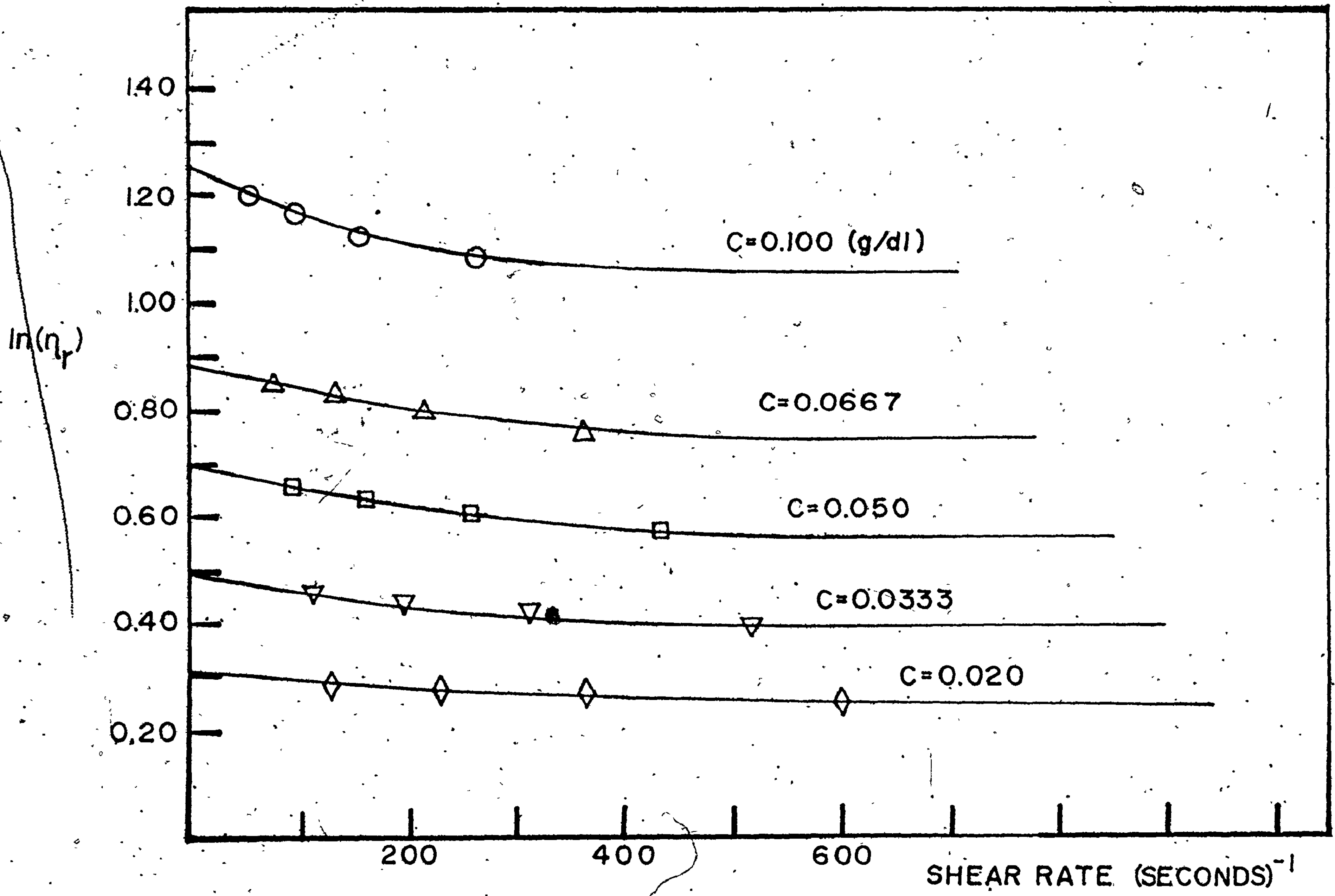


Fig. (I-7) Flow Data for Polymer (40-05-05-A)

Fig. (I-8) Flow Data for Polymer (40-02-05-A)

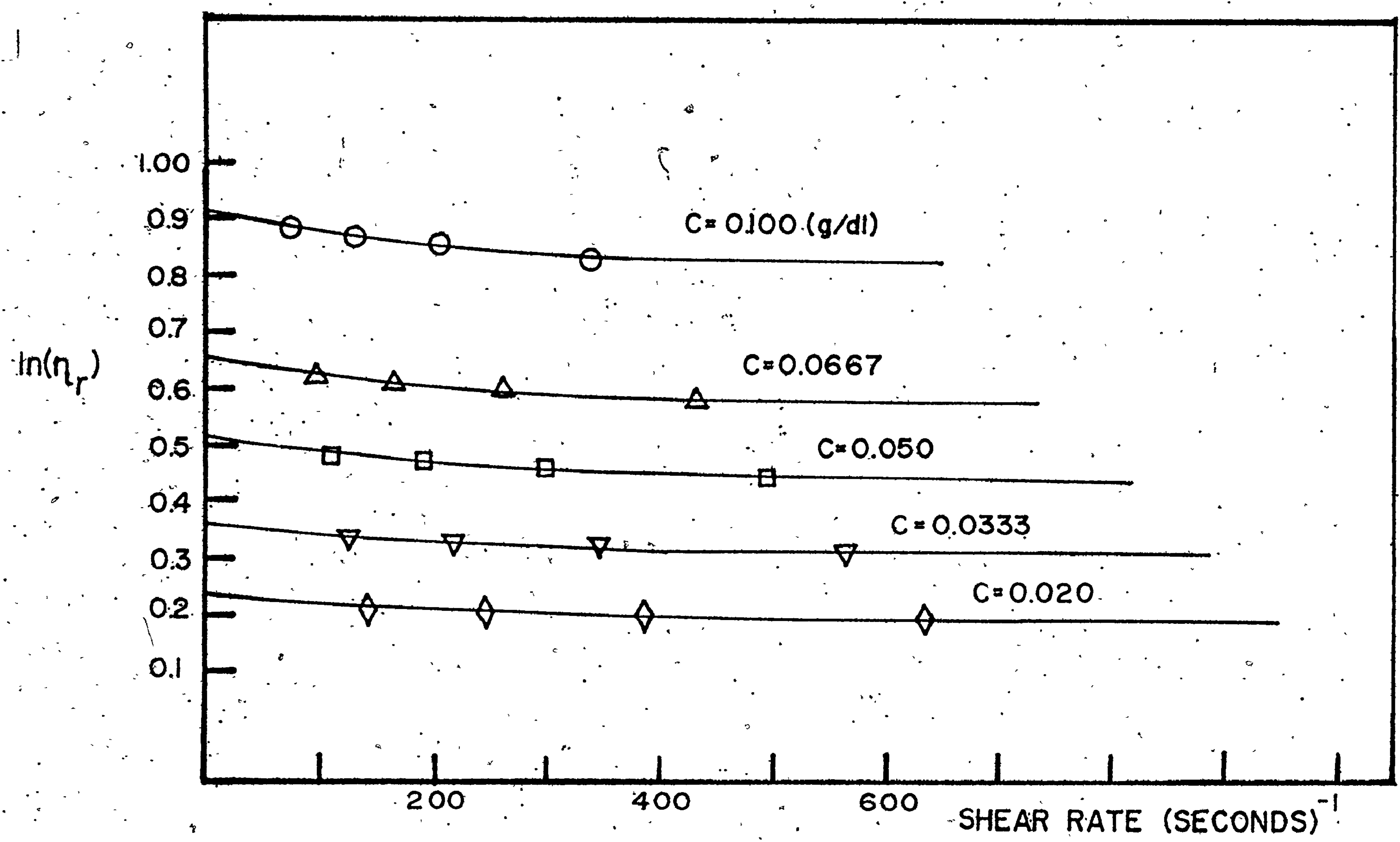
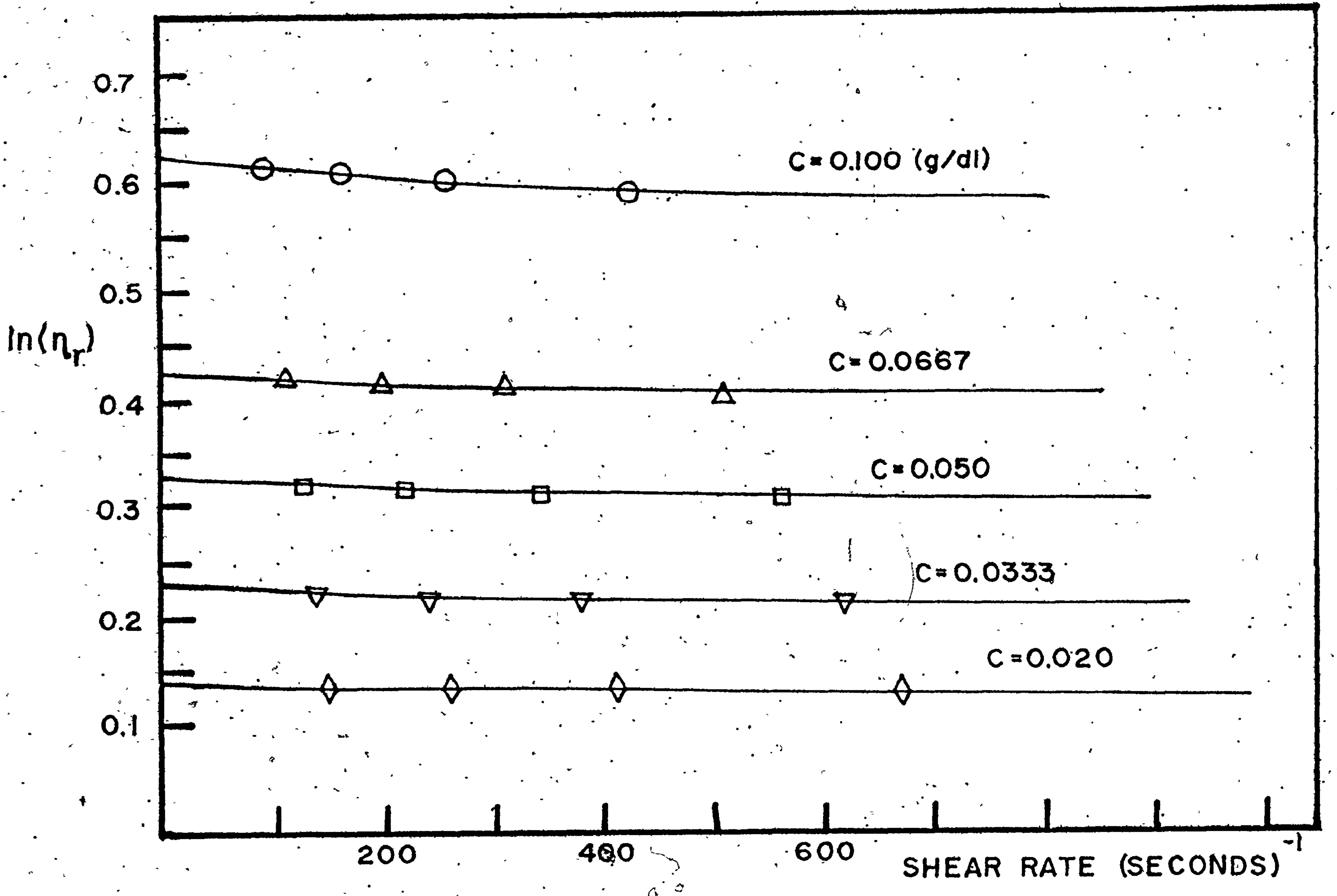


Fig. (I-9) Flow Data for Polymer (40-05-25-B)



behaviour of the polymer's solution is more pronounced the higher the solution viscosity at this concentration, i.e. the higher the molecular weight of the polymer.

The following is a discussion of the important implications, regarding the use of the intrinsic viscosities as a measure of molecular weight averages, inferred from the above observations.

1. The shape of the ($\ln \eta_r$) versus γ curves suggests immediately that two of the methods mentioned in the literature for shear rate correction are valid for the polyacrylamide-water system, viz. either to extrapolate the data to zero shear rate or extrapolate them to high enough shear rates where the non-Newtonian behaviour is minimal.

2. The above-mentioned extrapolations would clearly be less arbitrary if the viscosity-shear rate data for each concentration could be reduced to a straight line by a suitable change of variables.

Therefore the plots suggested by Katchalsky, Eq. (I-34), and the ones suggested by Golub, Eq. (I-36), were prepared for several polymers. Figures (I-10) and (I-11) show these plots for the viscosity data of polymer (25-05-01-G) shown in Fig. (I-2) and listed in Appendix (I-1). The value of the parameter $(\frac{Pr}{L})$ for each of the four bulbs of the viscometer, needed to construct these plots, were obtained as follows. By combining equations (I-30) and (I-42), both expressing the value of the shear rate at the wall of the capillary,

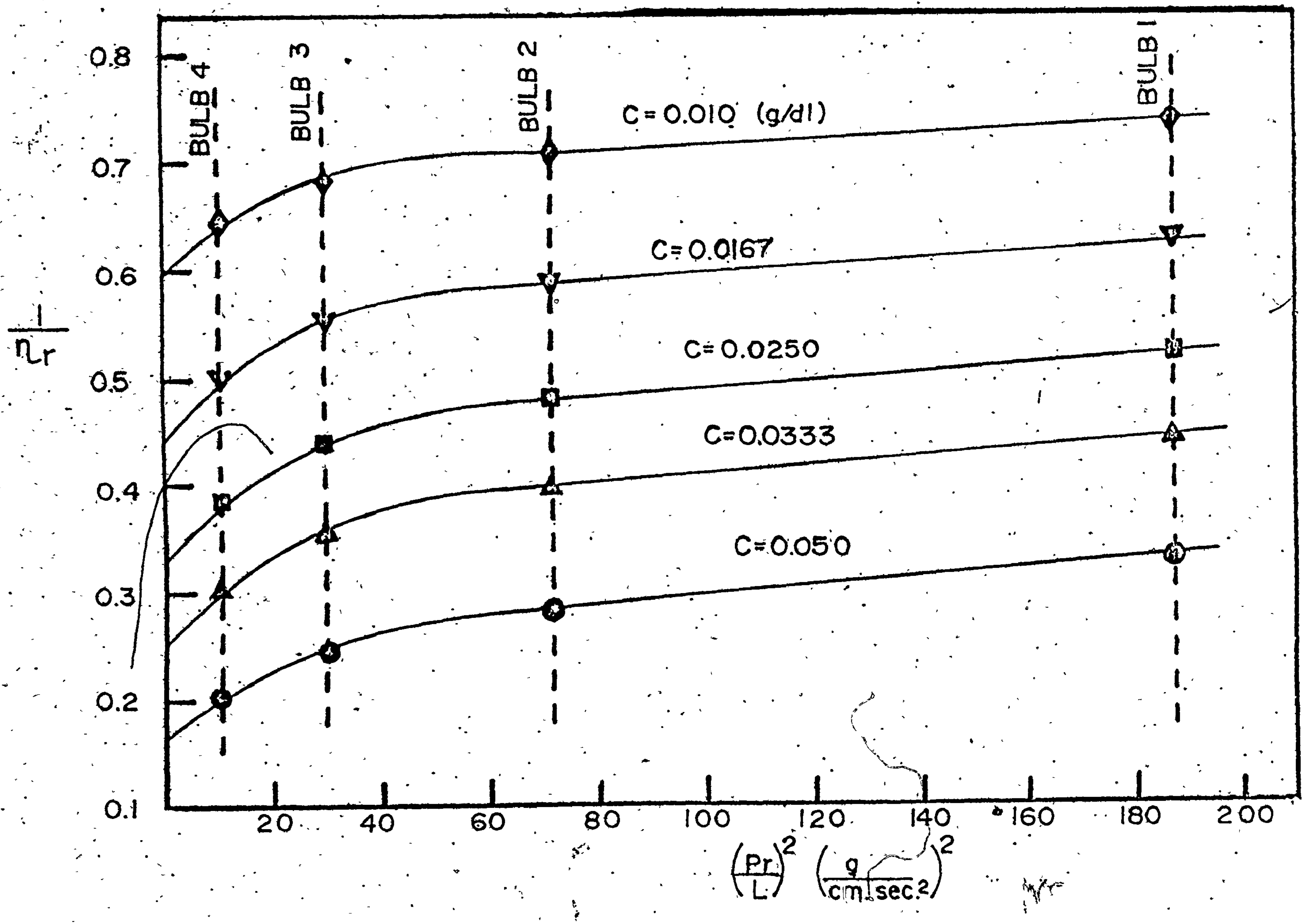
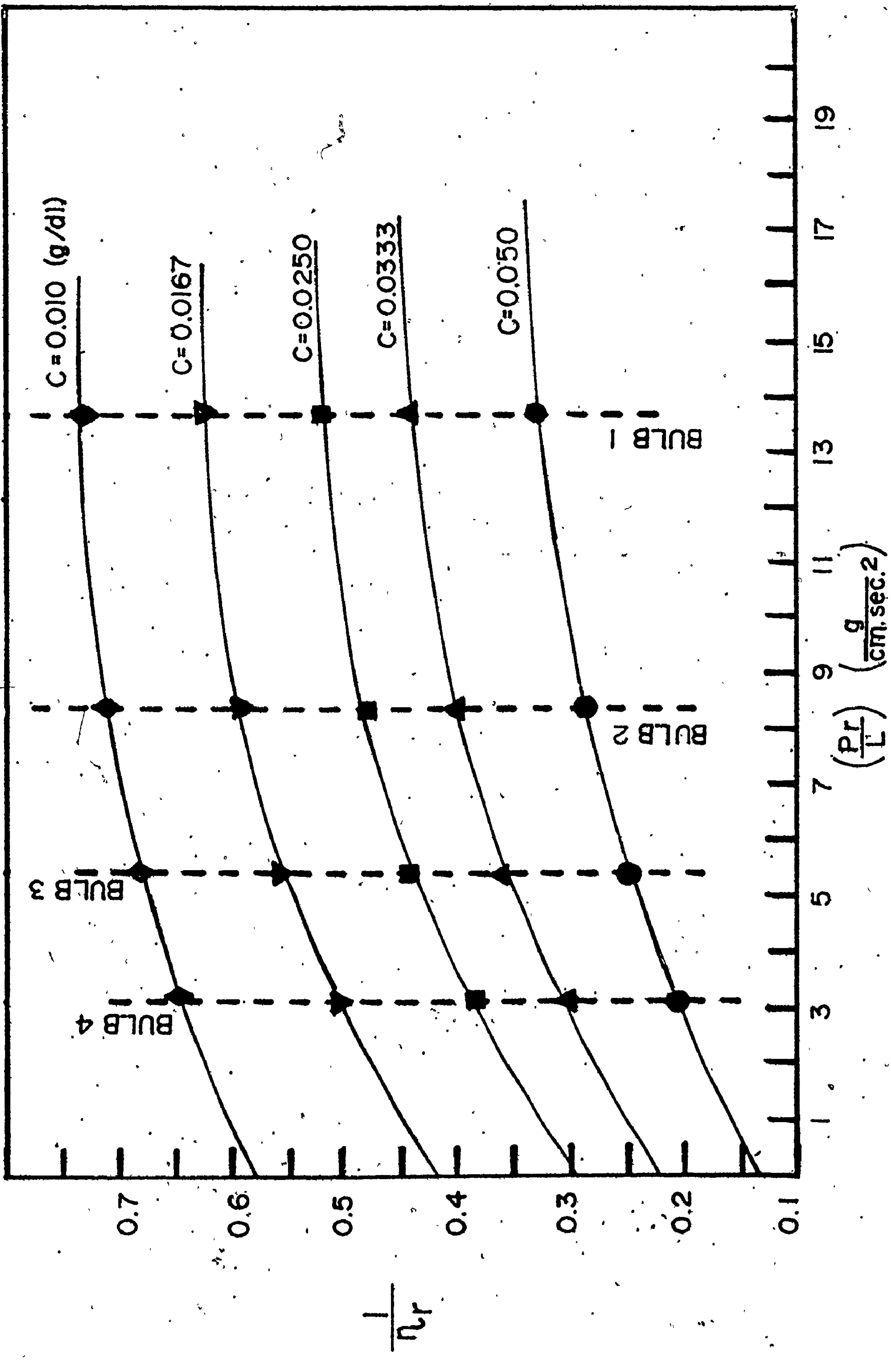


Fig. (I-10) Katchalsky's Plot for Polymer (25-05-01-G)

Fig. (I-11) Golub's Plot for Polymer (25-05-01-G)



we obtain

$$\frac{Pr}{L} = 2\left(\frac{4\dot{V}}{\pi r^3}\right)\frac{\eta}{t} \qquad \text{(I-44)}$$

Therefore for each bulb, by using the value of the parameter $\frac{\eta}{t}$ obtained from the flow data of pure water in Table (I-1) and the value of the "Shear Rate Constant" $\frac{4\dot{V}}{\pi r^3}$ from Table (I-2), the parameter $\frac{Pr}{L}$ for bulbs No. 1 through 4 was found to be equal to 13.7, 8.4, 5.4, and 3.1, respectively, with the units of $\left(\frac{g}{\text{cm. sec.}^2}\right)$.

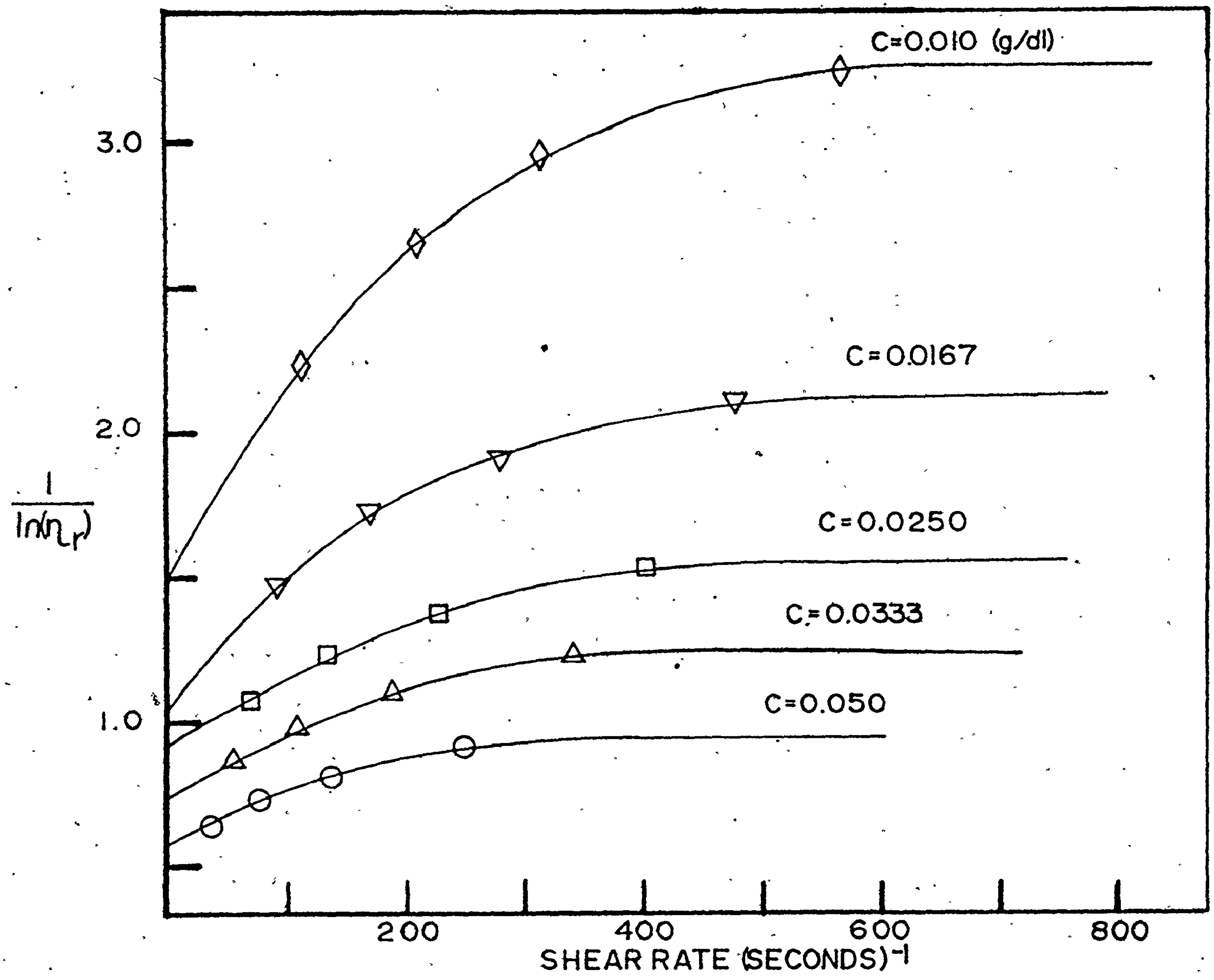
It is clear from Figures (I-10) and (I-11) that neither plot succeeds in reducing the flow data to a straight line. The uncertainties associated with extrapolating any of these plots to zero shear rate will be comparable to those associated with the extrapolation of the original curves in Fig. (I-2).

Another attempt was made to linearize the flow data as follows. In his book on statistical analysis, Himmelblau(39) suggests methods for linearization of functions of different shapes. The general shape of the ($\ln \eta_r$) versus $\dot{\gamma}$ plots in Figures (I-2) to (I-9) may be approximated, according to Himmelblau, by the following equation

$$\frac{1}{\ln \eta_r} = A + B\dot{\gamma} \qquad \text{(I-43)}$$

with A and B as constants. Therefore a plot of $\frac{1}{\ln \eta_r}$ versus $\dot{\gamma}$ should approximate a straight line. Fig. (I-12) shows such a plot for Polymer (25-05-01-G). Evidently this

Fig. (I-12) Himmelblau's Plot for Polymer (25-05-01-G)



method also fails in reducing the data to a straight line.

Therefore it was decided to extrapolate the viscosity data "by eye" to both high and zero shear rates, as shown in Figures (I-2) to (I-9). The validity of this approach is demonstrated by the fact that Golub(22) used the results obtained from such plots, which he called "conventional viscosity-shear rate curves" to test the accuracy of the results obtained from both his own and Katchalsky's linearized plots. This clearly indicates that Golub had more confidence in the results obtained from these conventional plots than in those obtained from the linearized ones.

However, it must be recognized that the uncertainty inherent in the values of the viscosities at zero shear rate obtained in this manner is more substantial than the viscosities at high shear rates due to the strong curvature of the plots at low shear rates, which makes the extrapolation procedure more arbitrary.

Therefore, values for ln η_r at both limits of shear rate were obtained in this manner for all the polymers. These are listed in Appendix (I-1). Then plots of $\frac{\eta_{sp}}{C}$ and $\frac{\ln \eta_r}{C}$ versus the concentration C were prepared for both zero and high shear rates. They were extrapolated to zero concentration to obtain values for the intrinsic viscosities at zero shear rate $[\eta]_0$ and at high shear rates $[\eta]_\infty$. These values for all the polymers are listed in Appendix (I-1) and the above procedure is illustrated in Figures (I-13) to (I-20) for the polymers

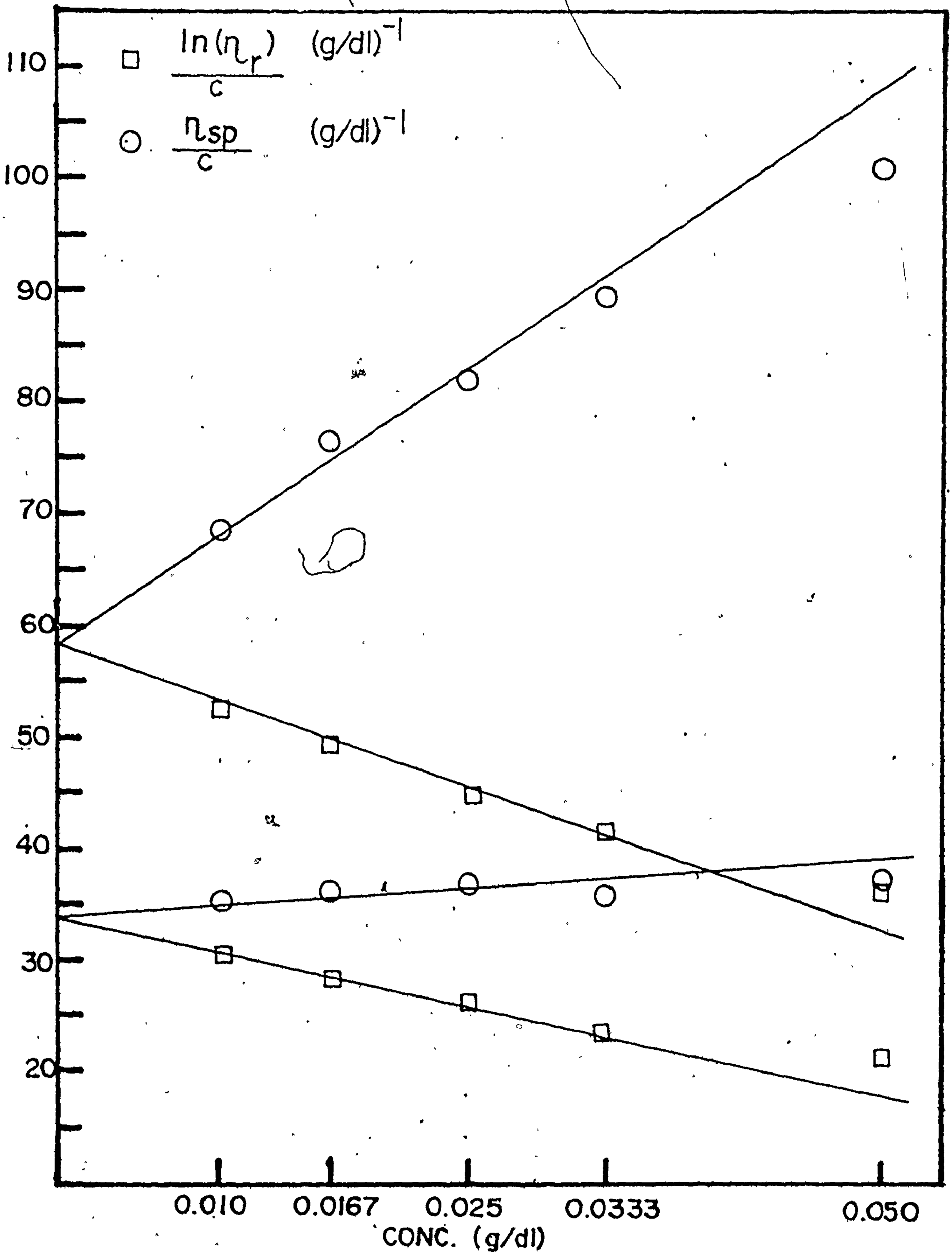
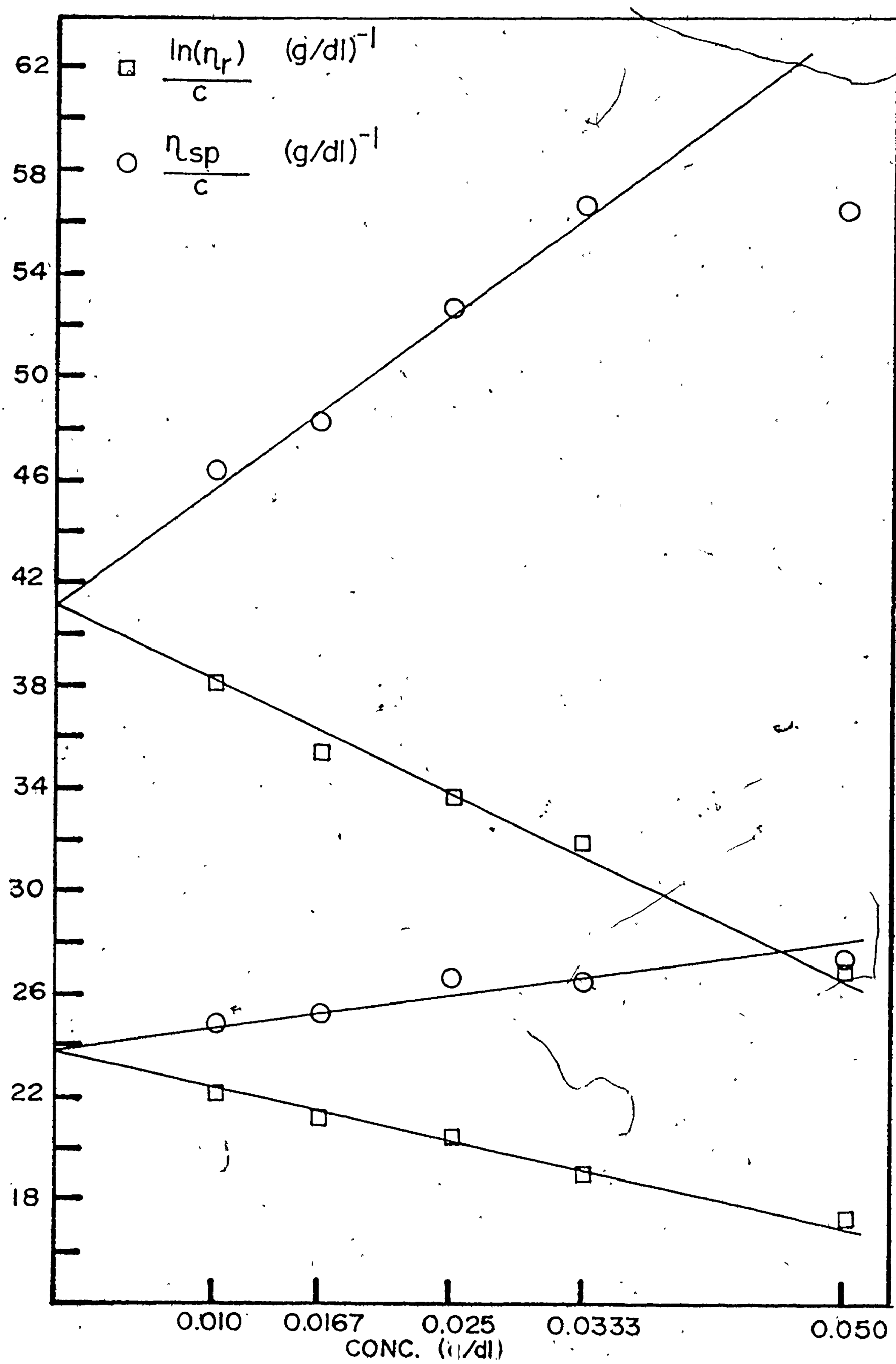


Fig. (I-13) Intrinsic Viscosities for Polymer (25-05-01-G)

I-5



62
58
54
50
46
42
38
34
30
26
22
18
$\frac{\ln(\eta_r)}{c}$ $(g/dl)^{-1}$
$\frac{\eta_{sp}}{c}$ $(g/dl)^{-1}$
0.010
0.0167
0.025
0.0333
0.050
CONC. (g/dl)

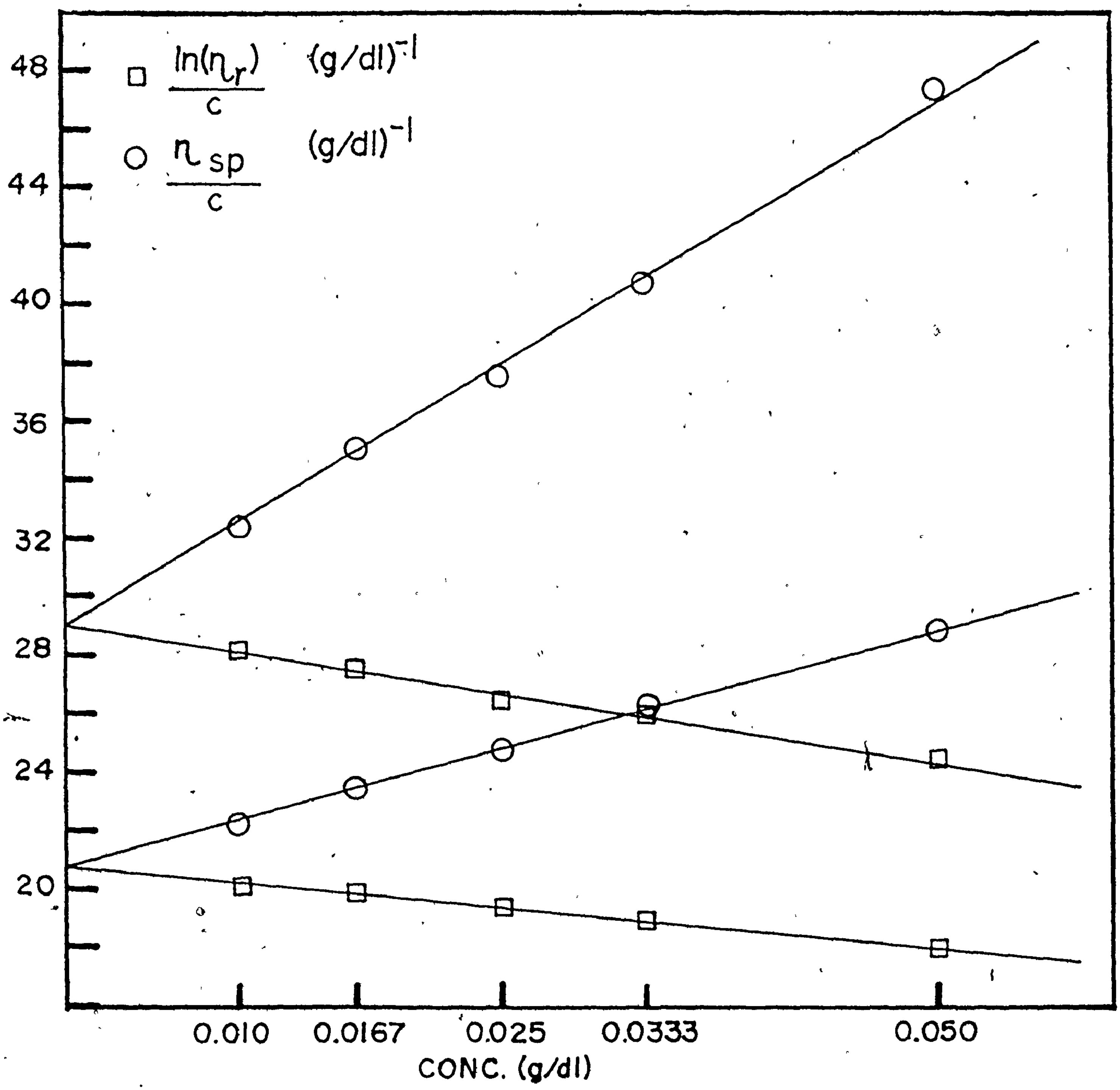


Fig. (I-15) Intrinsic Viscosities for Polymer (25-05-05-A)

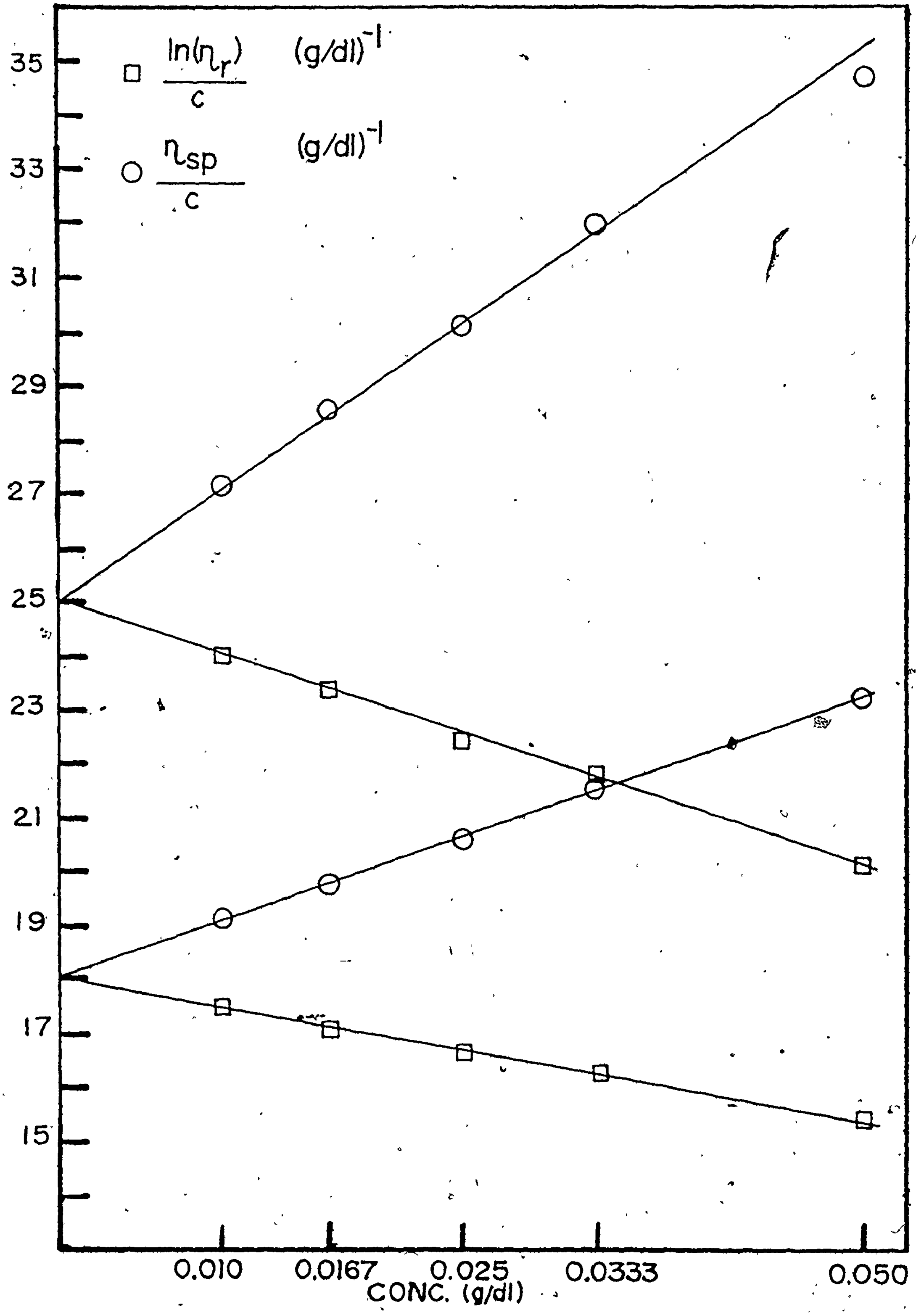


Fig. (I-16) Intrinsic Viscosities for Polymer (40-05-01-D)

Fig. (I-17) Intrinsic Viscosities for Polymer (25-02-10-6)

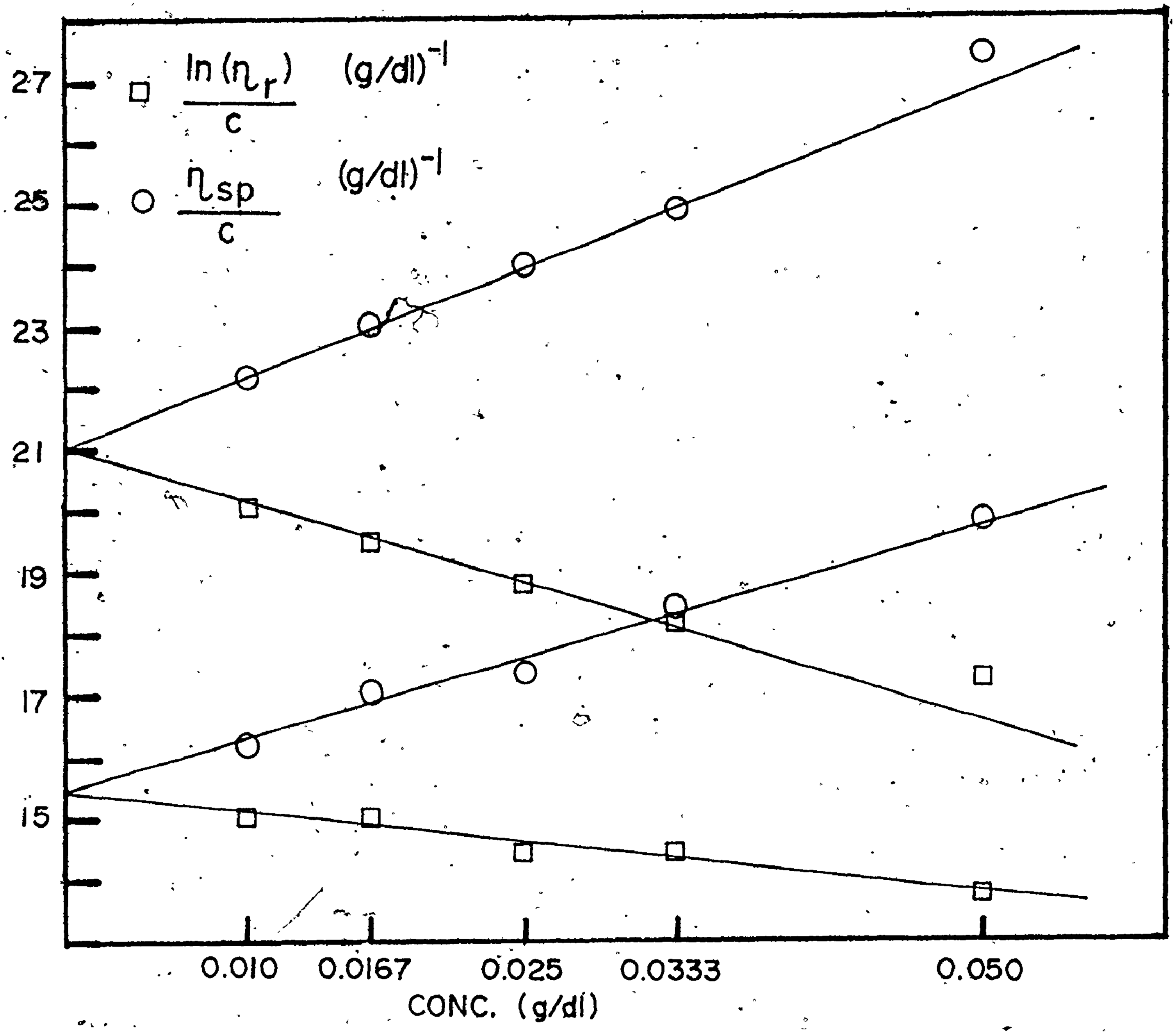


Fig. (I-18) Intrinsic Viscosities for Polymer (40-05-05-A)

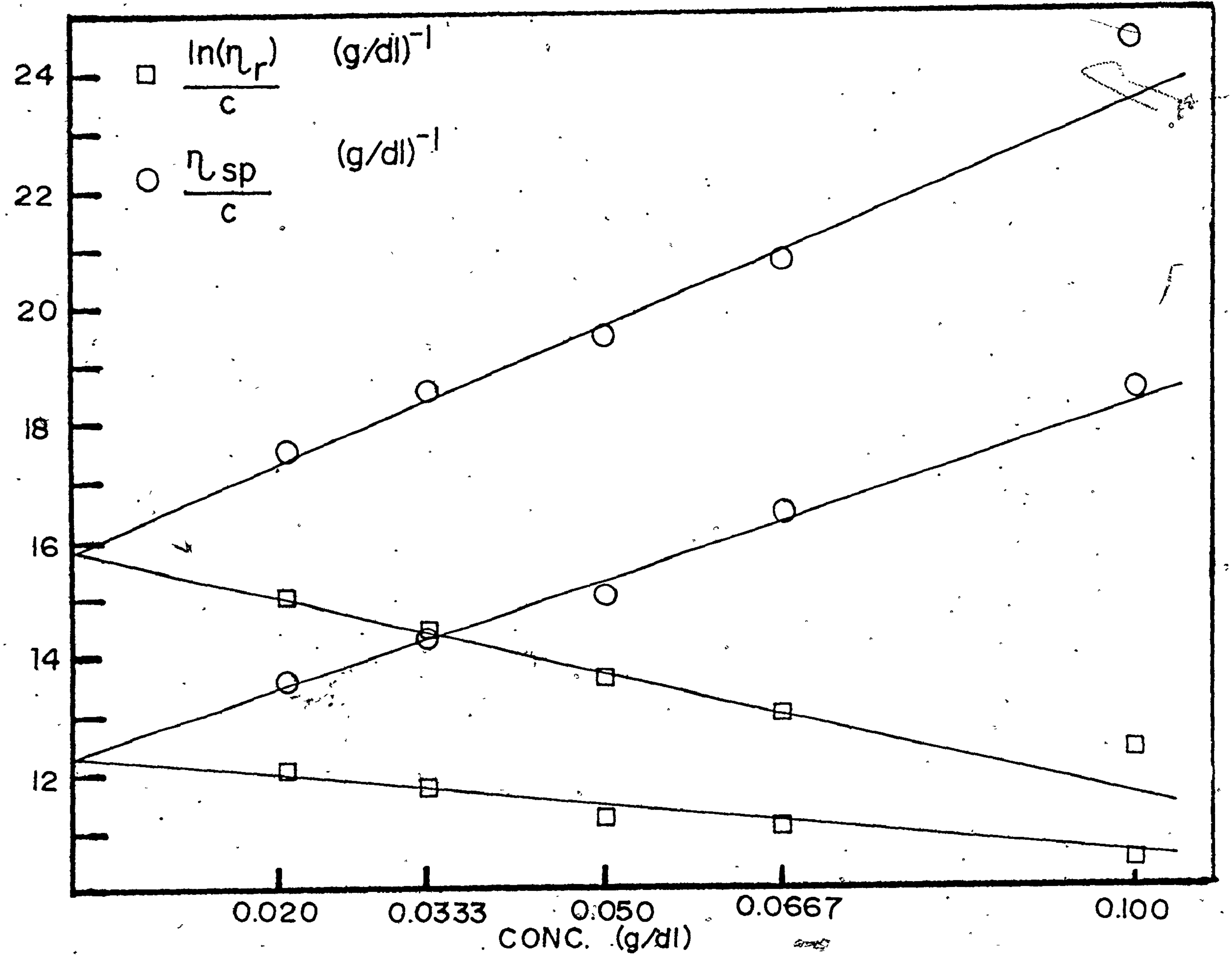


Fig. (I-19) Intrinsic Viscosities for Polymer (40-02-05-A)

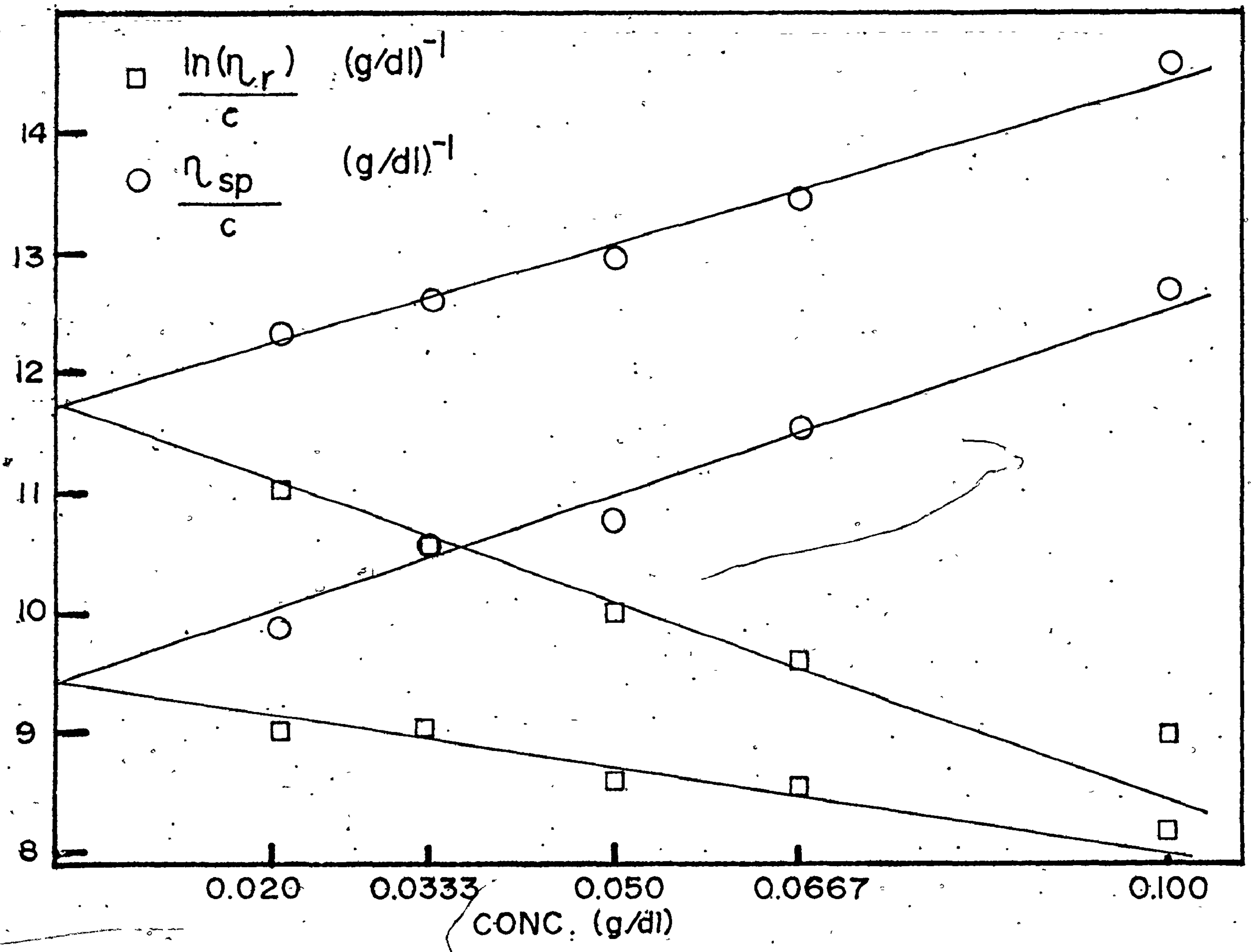
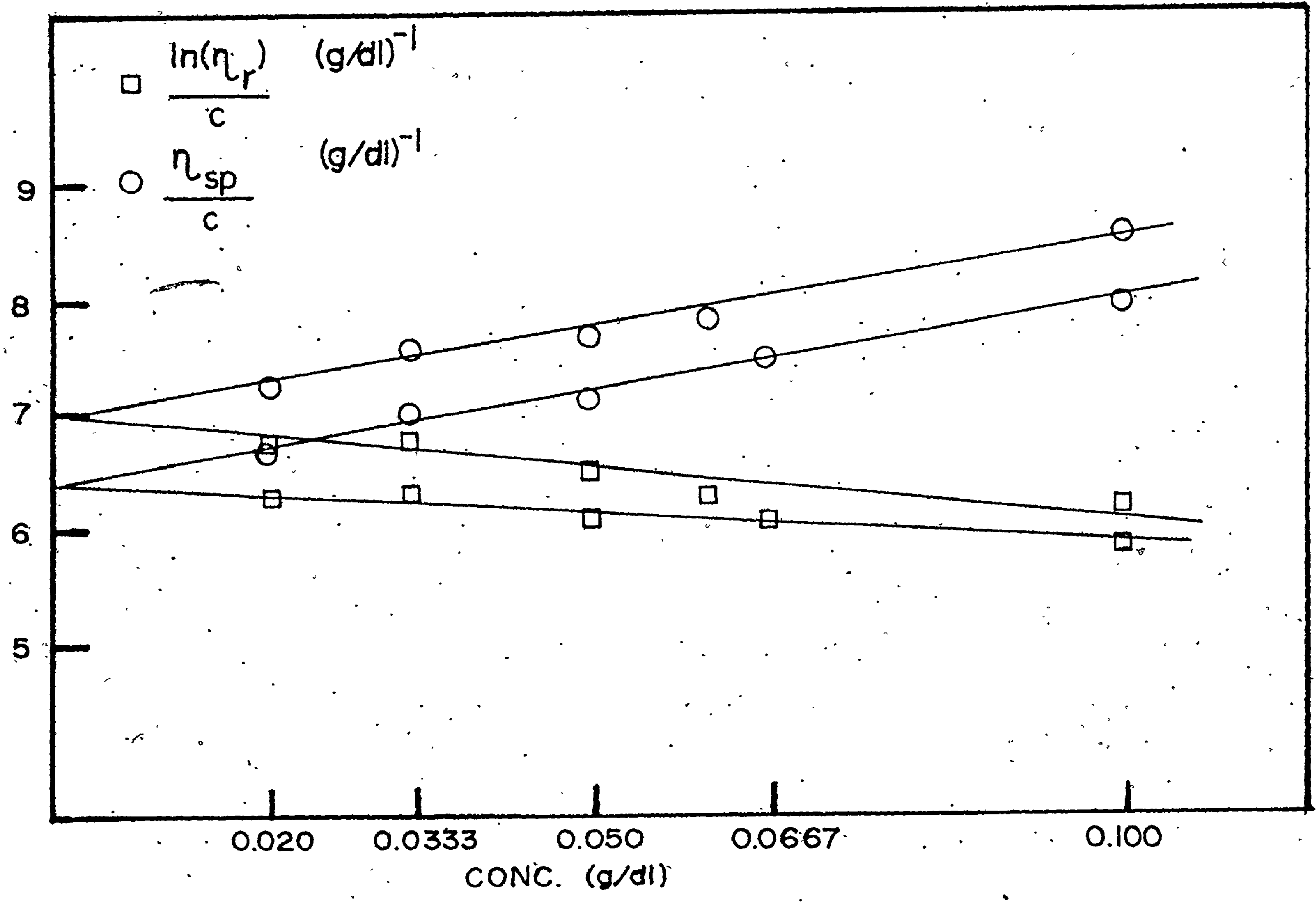


Fig. (I-20) Intrinsic Viscosities for Polymer (40-05-25-B)

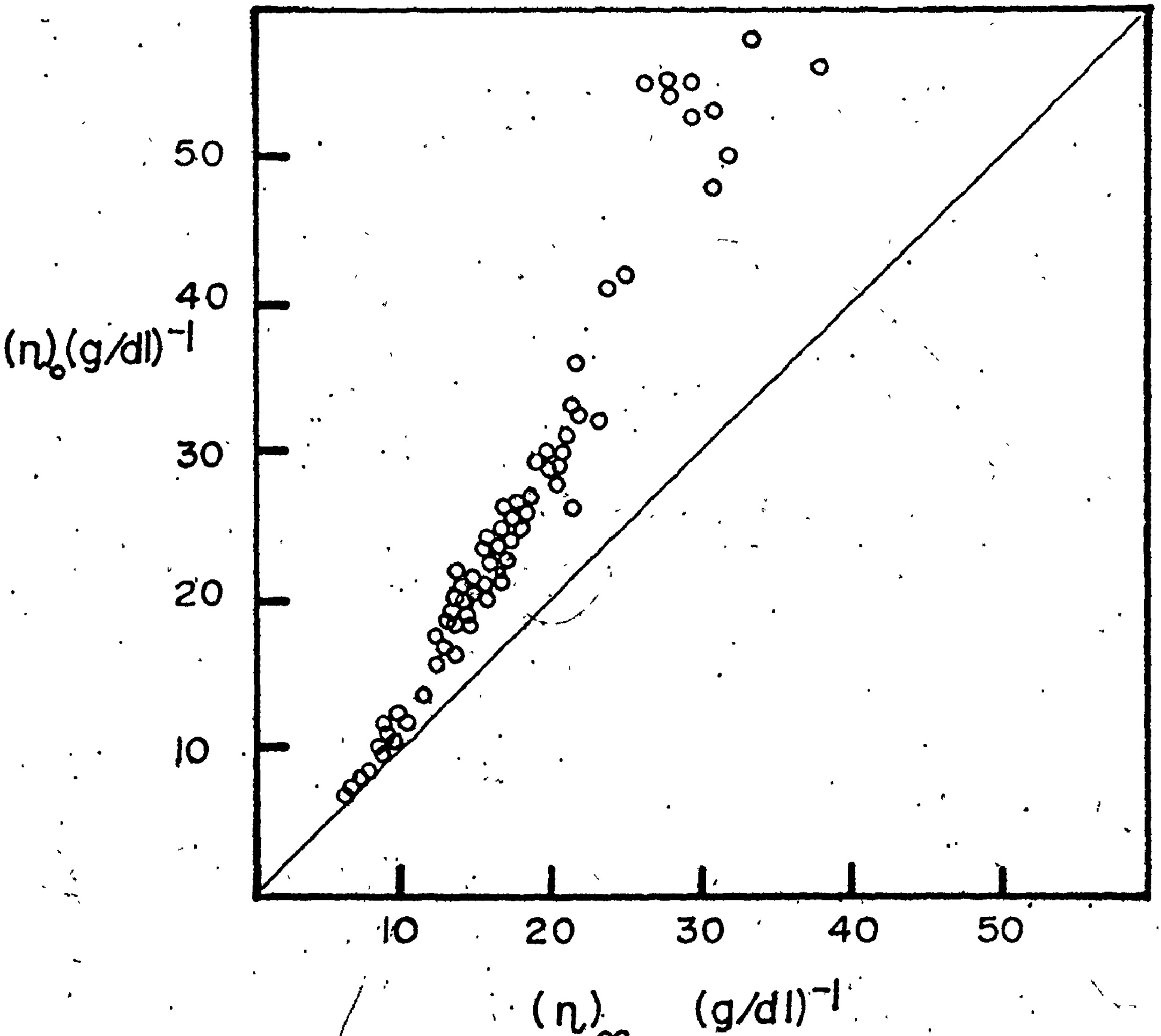


whose viscosity data are shown in figures (I-2) to (I-9).

3. Figures (I-13) to (I-20) and the intrinsic viscosities listed in Appendix (I.1) clearly show that the effect of the rate of shear on the intrinsic viscosities of acrylamide polymers becomes more pronounced for the higher molecular weight polymers. This is evidenced by the fact that the ratio $\frac{[\eta]_0}{[\eta]_\infty}$ becomes increasingly greater than unity the higher $[\eta]_0$ and $[\eta]_\infty$ are. This is consistent with the observations made by previous investigators on other polymer-solvent systems, as was detailed in Section I.2.4. of this thesis. Fig.(I.21) illustrates this fact clearly, where $[\eta]_0$ is plotted versus $[\eta]_\infty$ for all the polymers tested, together with a line of 45° slope representing Newtonian behaviour.

4. Consider Fig.(I.2) representing the viscosity data for Polymer(25-05-01-G) that has one of the highest molecular weights encountered in the present investigation. It is clear that trying to estimate the intrinsic viscosity of such a polymer by a traditional single-bulb viscometer, with no provisions for the variation of the rate of shear would be equivalent to trying to estimate an intrinsic viscosity from the data obtained from only one of the four bulbs of the viscometer used in the present investigation. Fig.(I.2) makes it quite obvious that the intrinsic viscosity obtained in this manner would depend strongly on the shear flow characteristics of the instrument used. The magnitude of this uncertainty may be as high as the magnitude

Fig. (I-21) Intrinsic Viscosities at Zero Shear Rate vs. Intrinsic Viscosities at High Shear Rates



of the ratio $\frac{[\eta]_0}{[\eta]_\infty}$, which is equal to 1.73 for this particular polymer.

The uncertainty in the magnitude of the molecular weight average for such a high molecular weight polymer will be compounded by the fact that the ratio of the molecular weights, computed from either Eq. (I-37) or Eq. (I-38), will be equal to the ratio $\frac{[\eta]_0}{[\eta]_\infty}$ raised to the power 1.52 or the power 1.25, respectively, according to which of the equations is used. In other words, for Polymer (25-05-01-G), whereas the intrinsic viscosity may vary by a factor of 1.73 with shear rate, the corresponding variations in molecular weight average are $(1.73)^{1.52} = 2.30$ from Eq. (I-37) and $(1.73)^{1.25} = 1.98$ from Eq. (I-38).

5. It may not be argued that using a single bulb viscometer would be equivalent to making all the viscosity measurements at an arbitrary but finite shear rate, as suggested by Tripp, Conrad, and Mares(24). As Figures (I-2) to (I-9) clearly indicate, for the same polymer, as the viscosity decreases with each subsequent dilution, the shear rate at which any one of the bulbs operates increases. Also, for different polymers of different molecular weights, the viscosities of solutions of the same concentration will vary greatly from one polymer to the other. Hence the viscometer will be operating at a different shear rate for each of the polymers.

This indicates that choosing a single shear rate for all the viscosity measurements is not feasible with a capillary viscometer, unless the viscometer is equipped with a device to control the rate of shear, such as the manostat used by Golub(22). This approach, however, may be practicable in connection with Cone-and-Plate and Couette viscometers.

6. Consider Figure (I-9), representing the viscosity data for Polymer (40-05-25-B) which has one of the lowest molecular weights encountered in the present investigation. The intrinsic viscosity of this polymer extrapolated to zero shear rate and high shear rate were found to be 7.0 and 6.4, respectively, in Figure (I-20). It is clear that this polymer's solutions conformed very closely to Newtonian behaviour. As the molecular weights of the other polymers increased, they deviated more and more from Newtonian characteristics. Using Eq. (I-37) we find that $\overline{M}_n$ for this polymer is of the order of 10^6. Therefore this may be regarded as a critical molecular weight, above which the non-Newtonian aspects of the behaviour of the polymers' solutions may not be ignored, even at the low concentrations encountered in intrinsic viscosity measurements.

Thus data in the numerous papers mentioned in Section (I-2-E) of this thesis, where the intrinsic viscosities of acrylamide polymers of several million molecular weight averages were reported without accounting for the shear rate effects and without providing the information necessary to estimate the rates of shear at which their measurements were made, have very little value, as these intrinsic viscosities depend on the instruments used. And, as we have shown, this will result in uncertainties in the molecular weights computed of more than 100% for the higher molecular weight polymers.

I.4.1 The Intrinsic Viscosity - Molecular Weight Relationships

The considerable discrepancy between the value of the intrincic viscosity of a high molecular weight polyacrylamide when estimated at zero shear rate, and its value when estimated at high shear rates, gives rise to the following question : which value for the intrinsic viscosity should be used in the empirical relations Eq. (I-37) and Eq. (I-38)?

To answer this question it was necessary to obtain polymers for which one of these relationships had been proven valid through an independent measurement of the average molecular weight together with an intrinsic viscosity measurement. Then, if the shear rates at which the viscosity measurements were made can be estimated, it will be possible to answer the above-mentioned question.

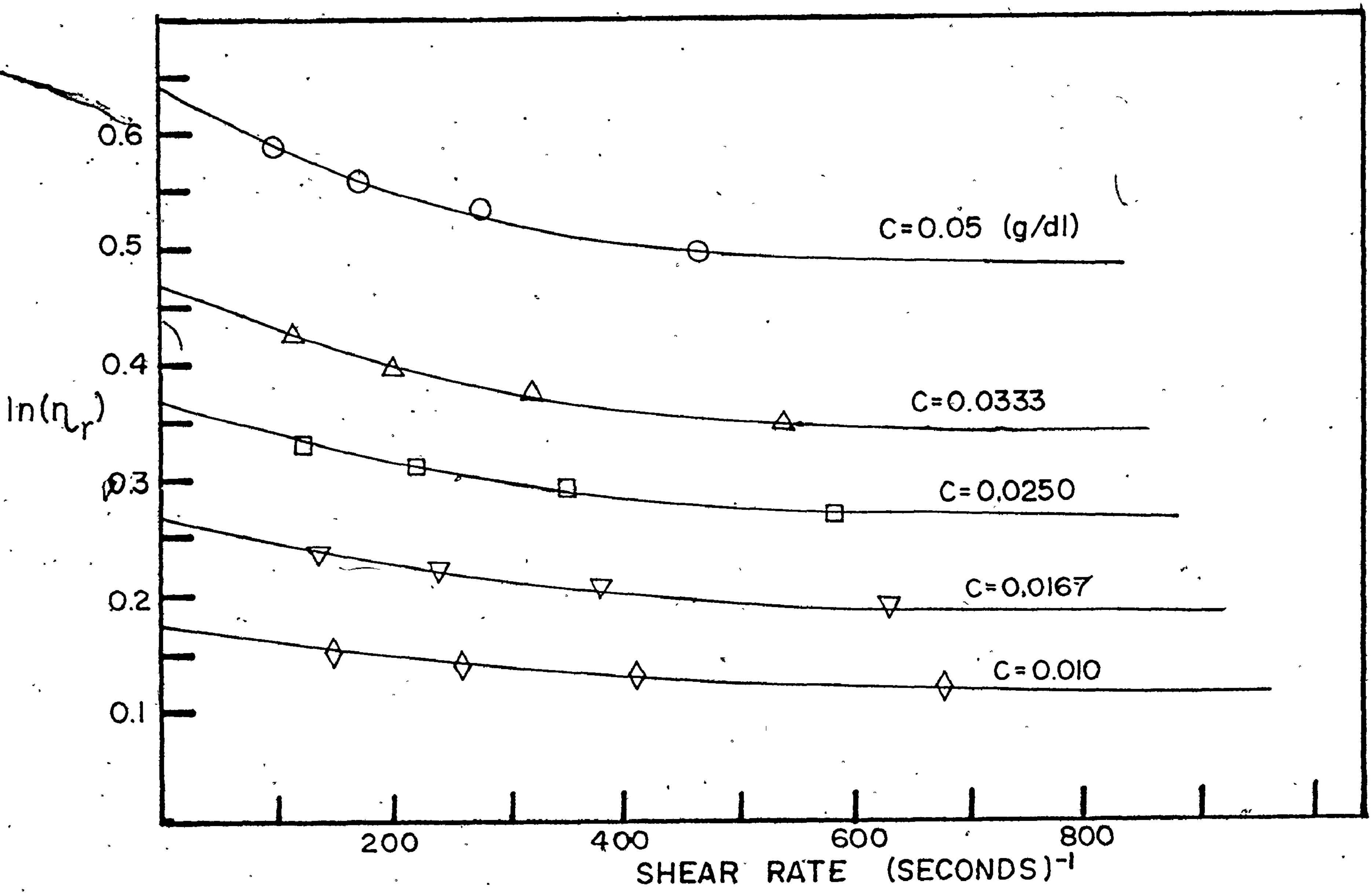
For this purpose two polyacrylamides were available that were synthesized by Ishige(2) in his study of the polymerization kinetics using the initiator 4,4' azobis-4-cyanovaleric acid (ACV). These polymers were synthesized in aqueous solution under isothermal conditions. The synthesis conditions are summarized in the following table.

Polymer	Monomer Conc. (Moles/l.)	ACV Conc. (Moles/l.)	Temperature (^{o}C)
Standard A	0.281	7.14×10^{-4}	40
Standard B	0.563	1.43×10^{-3}	50

The molecular weights of the polymers were measured by electron microscopy(2) and by gel permeation chromatograpgy(40). The number average molecular weights were found to be 2.52×10^{6} for Standard A, and 1.62×10^{6} for Standard B. Their intrinsic viscosities in water at 25°C were found to be 11.41 and 8.45, respectively. These values are in excellent agreement with Eq. (I-37) developed by Collinson, Dainton, and McNaughton(26). However, single bulb Cannon-Ubbelohde viscometers were used to measure the intrinsic viscosities with no provisions to correct for the shear rate effects.

Therefore, samples of Standard A and Standard B were dissolved in twice-distilled water, and their intrinsic viscosities were measured in the four-bulb variable shear viscometer, following the procedure outlined in Section (I-3) of this thesis. The details of the viscosity measurements and the intrinsic viscosity calculations are listed in Appendix (I-1) and Figures (I-22) to (I-25). The following table lists the intrinsic viscosities measured by Ishige(2) and those measured by the four-shear viscometer extrapolated to zero shear rate $[\eta]_{o}$ and to high shear rate $[\eta]_{\infty}$.

Fig. (I-22) Flow Data for Polymer (Standard-A)



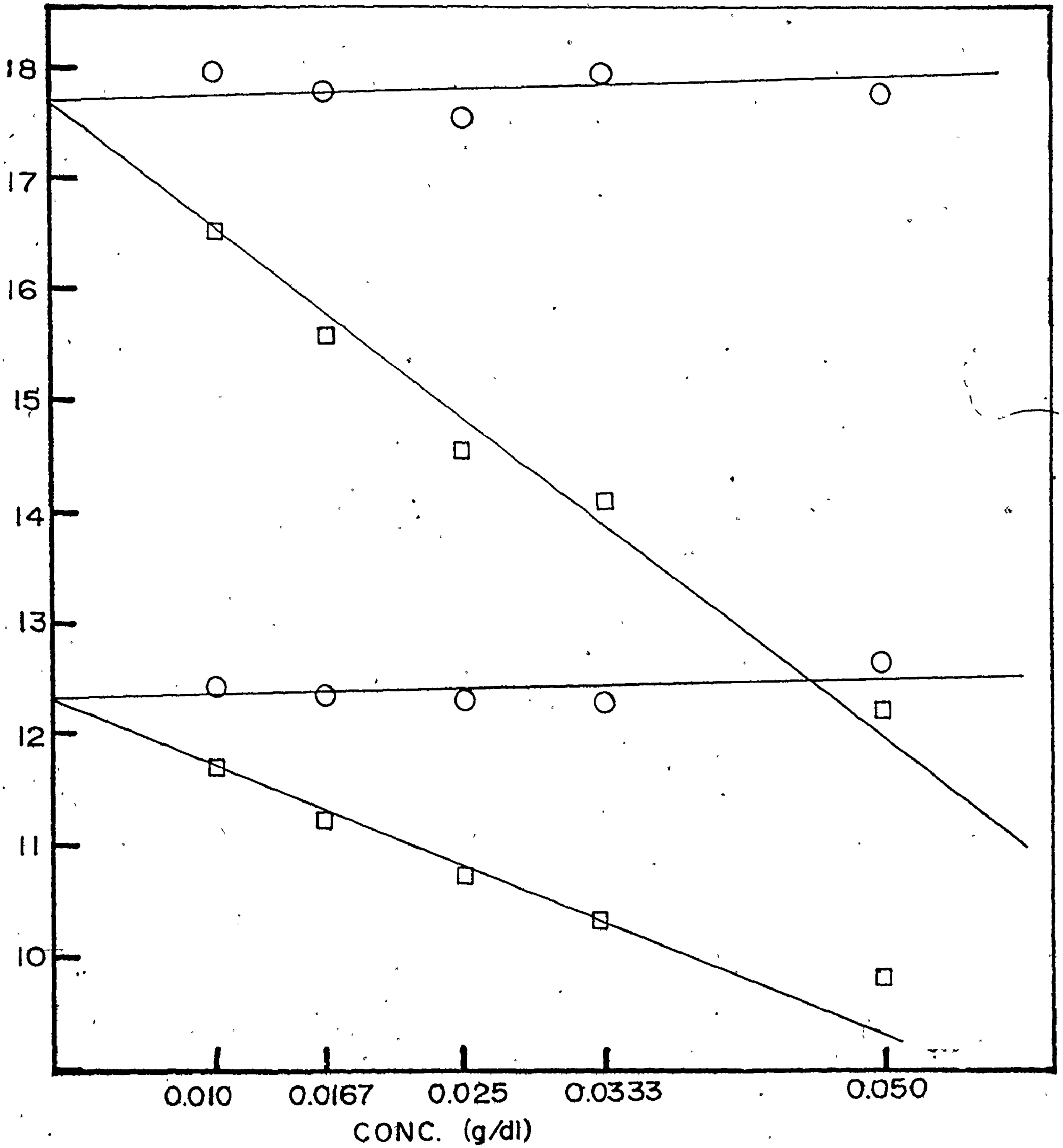


Fig. (I-23) Intrinsic Viscosities for Polymer (Standard-A)

Fig. (I-24) Flow Data for Polymer (Standard-B)

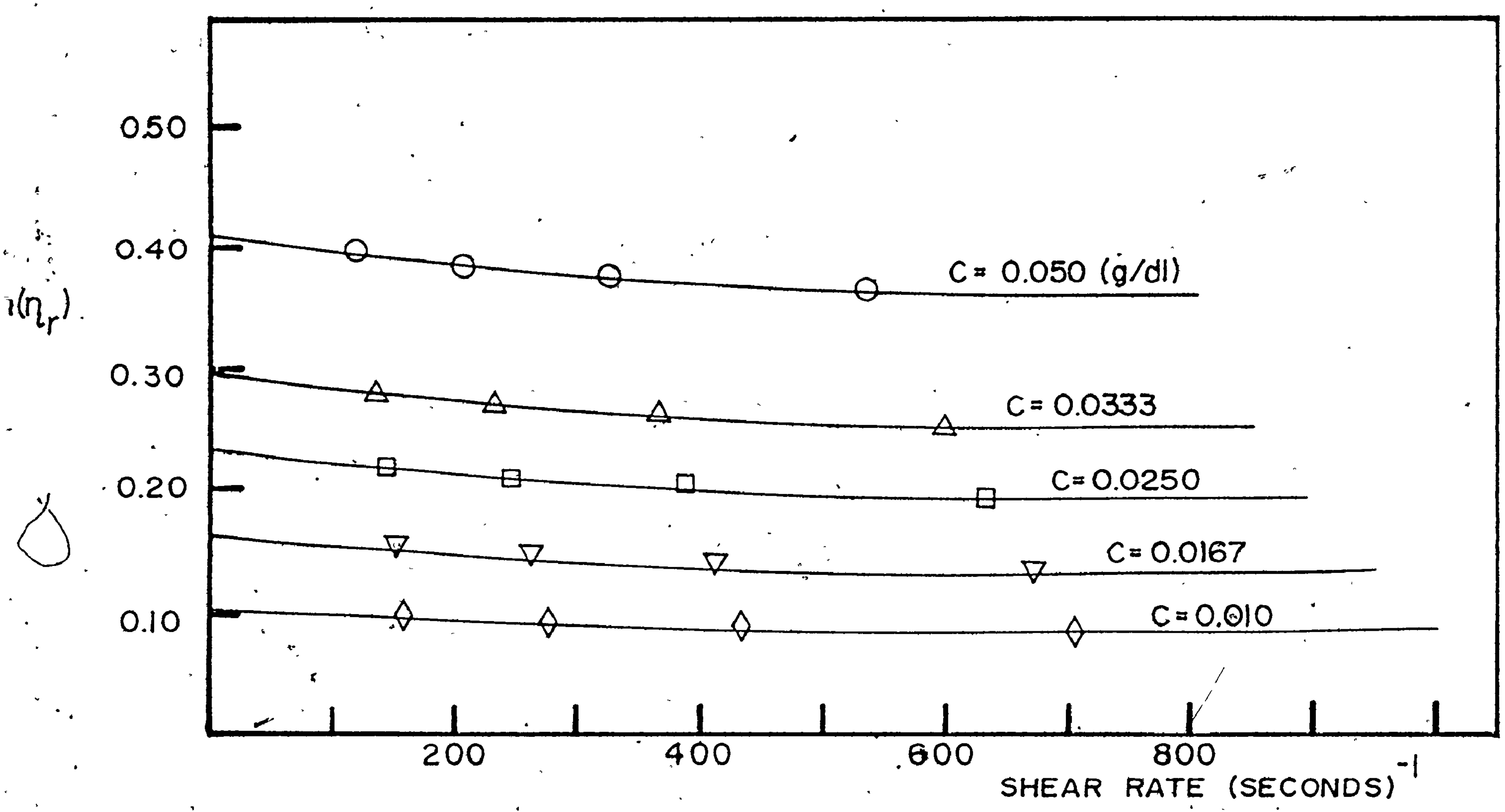
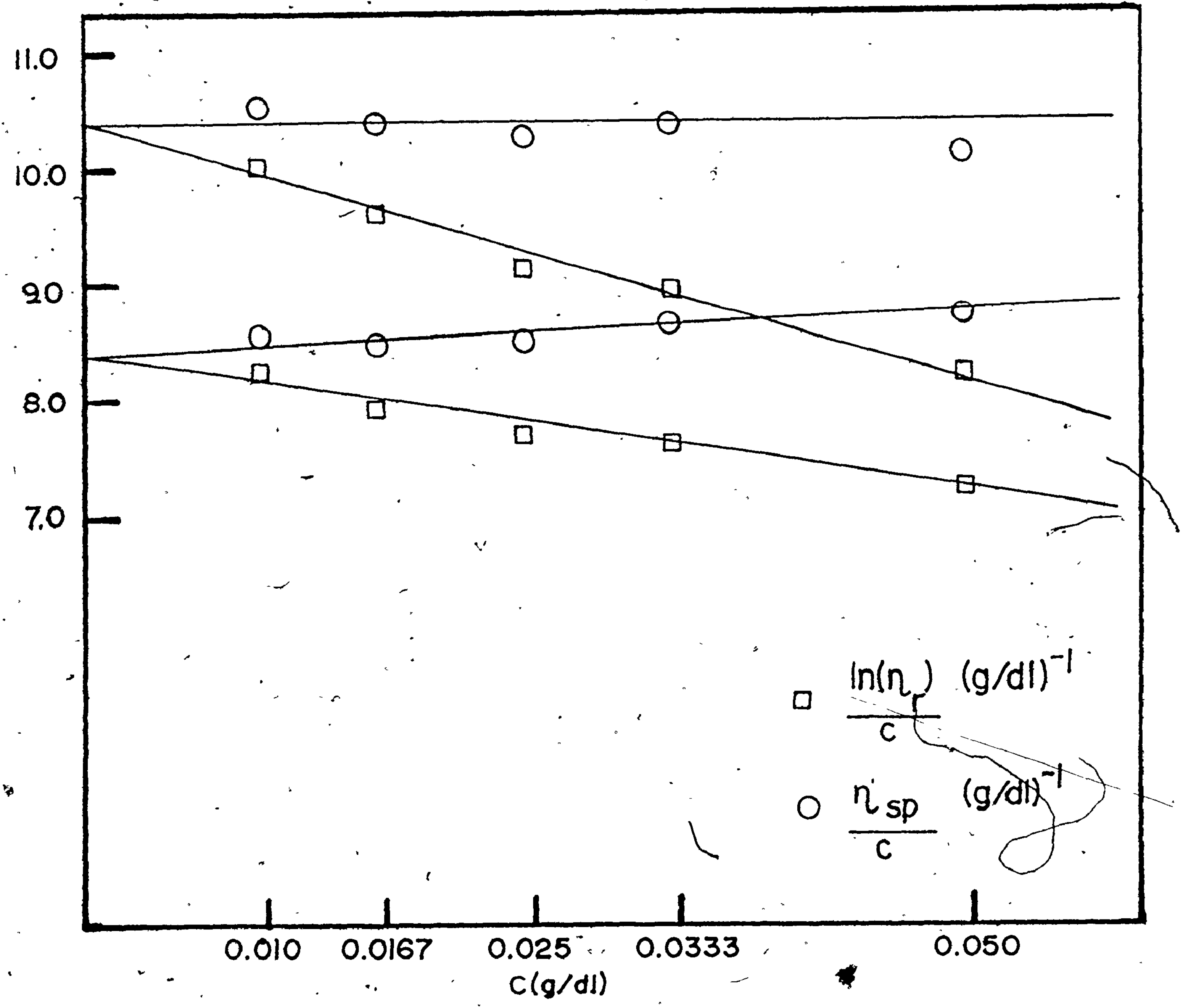


Fig. (I-25) Intrinsic Viscosities for Polymer (Standard-B)



	Standard A	Standard B
$[\eta]^{(2)}$	11.41	8.45
$[\eta]_0$	17.70	10.40
$[\eta]$	12.30	8.40

From the preceding table it is clear that the intrinsic viscosities reported by Ishige approximate closely the values for $[\eta]_\infty$ extrapolated to high shear rates. Indeed, by the following analysis of the specifications of the viscometers used by Ishige we shall prove that all the intrinsic viscosities measured in his investigation had to be a close, though fortuitous, approximation of $[\eta]_\infty$.

Ishige(2) used two Cannon-Ubbelohde single bulb capillary viscometers whose sizes and serial numbers were 50-A620 and 75-L181, respectively. The following specifications were kindly provided by the Cannon Instrument Company, State College, Pennsylvania.

Viscometer	Capillary Diameter (cm.)	Efflux Volume (cm^3)	Shear Rate Constant	Viscometer Constant (Centistokes/sec.)
50-A620	0.026	0.30	170,000	0.003882
75-L181	0.0305	0.30	110,000	0.008770
Bulb 1	0.044	1.42	170,000	0.003990

In the table above the last viscometer labelled Bulb 1 is the uppermost efflux bulb of the four-bulb viscometer (50-S489) used throughout the present investigation (bulb E_1 in Figure (I-1)). The shear rate constant was calculated as $\frac{4\ V}{\pi\ r^3}$, and used to obtain the shear rate at the wall of the capillary, according to Eq. (I-42). The viscometer constant is the parameter C in Eq. (I-39) and used to estimate the kinematic viscosity of the fluids. Substituting for the time of flow of any fluid in Eq. (I-42) in terms of its kinematic viscosity as obtained from Eq. (I-39) results in

$$\dot{\gamma}_w = \left(\frac{4\ V}{\pi\ r^3}\right) \frac{C}{\nu} \qquad \text{(I-45)}$$

Therefore for any fluid of viscosity ν, the rate of shear at the wall will be proportional to the product of the shear rate constant $\frac{4\ V}{\pi\ r^3}$ and the viscometer constant C.

Also, by comparing Eq. (I-11) and Eq. (I-11-A), it is clear that the viscometer constant C is equal to the quantity $\frac{\pi\ g\ H\ r^4}{8\ L\ V}$, substituting for C in Eq. (I-44) results in

$$\dot{\gamma}_w = \frac{g\ H\ r}{2\ L}\ \frac{1}{\nu} \qquad \text{(I-46)}$$

These quantities were computed for the three viscometers listed before and the results are as follows in Table (I-3).

As those results make clear, for any particular polymer solution, viscometer 50-A620 used by Ishige will operate at about the same wall shear rate associated with the uppermost bulb of the multi-bulb viscometer used in the present

Table (I-3)

Viscometer	$\frac{g\,H\,r}{2\,L} = \left(\frac{4\,V}{\pi\,r^3}\right) C$ (centistokes/sec.)
50-A620	660
75-L181	960
Bulb 1	680

investigation. Whereas viscometer 75-L181 will operate at a wall shear rate approximately 40 % larger than that level. Examination of the viscosity data shown in Figures (I-2) to (I-9) indicates that data obtained from the uppermost bulb of the viscometer closely approximate the values obtained after extrapolation to infinite rates of shear. Therefore both viscometers used by Ishige operated in this high shear rate range, and the intrinsic viscosity data reported in his work(2,33) should closely approximate $[\eta]_\infty$. This implies that the intrinsic viscosity-molecular weight relationship, Eq. (I-37), was proven by Ishige(2) and Abdel-Alim(40) to be valid for high molecular weight polyacrylamides when the intrinsic viscosity used is the one obtained from viscosity measurements extrapolated to high shear rates.

Therefore the viscosity average molecular weights of the polymers examined in the present investigation were calculated using Eq. (I-37) and the intrinsic viscosity at high shear rates $[\eta]_\infty$. These ~~results~~ are listed in Appendix (I-1) and the values used in Part II of this thesis to estimate the kinetic parameters of the solution polymerization of acrylamide in water with potassium persulfate initiator.

Plotting the logarithm of the molecular weight averages computed in this way versus the logarithm of the corresponding values of the intrinsic viscosities extrapolated to zero shear rate $[\eta]_o$, it is possible to estimate the parameters K' and a of Eq. (I-14) as applied to $[\eta]_o$. Figure (I-26) shows such a plot for all the polymers listed in Appendix (I-1). The solid line in this graph may be expressed as

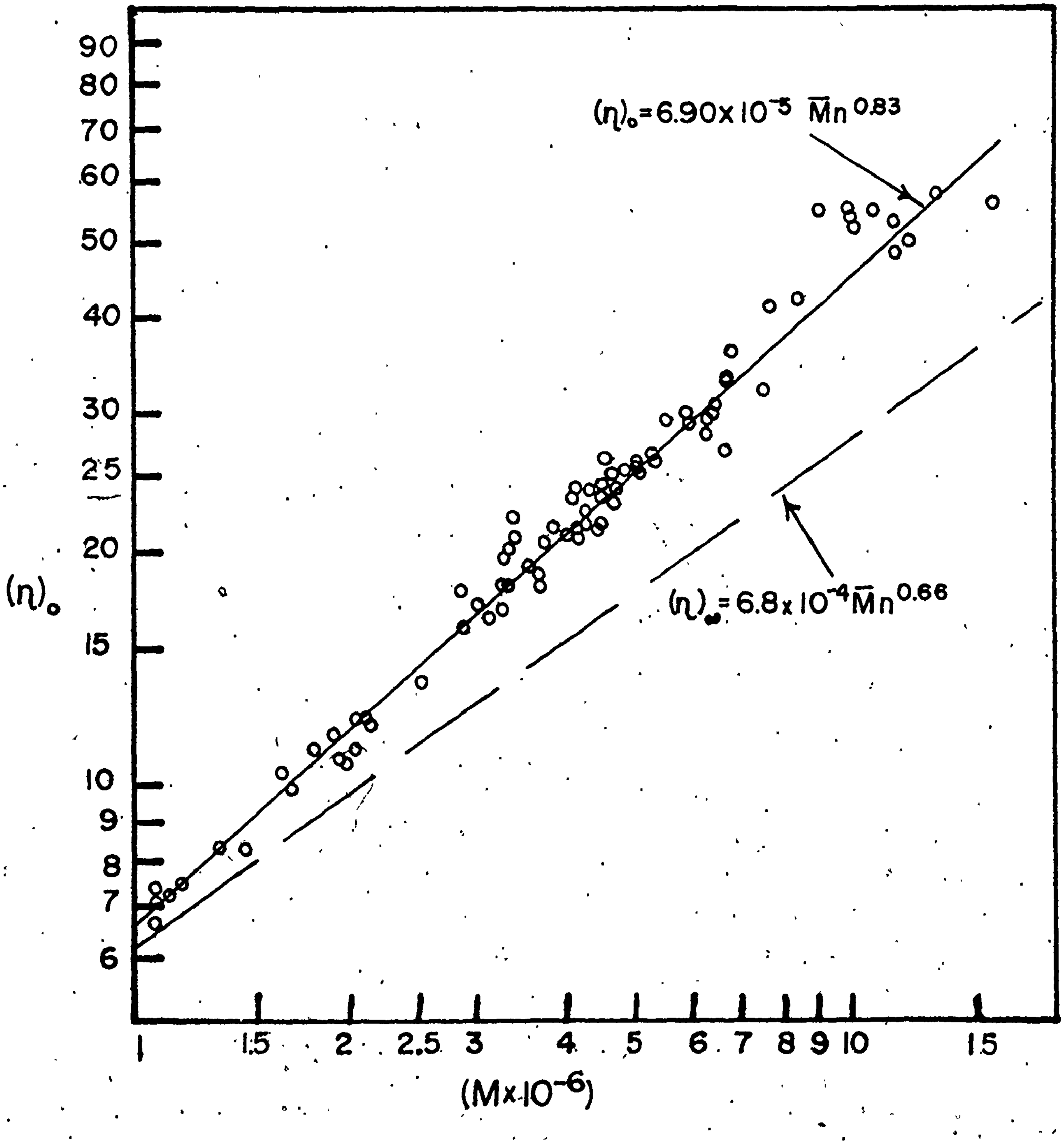
$$[\eta]_o = 6.9 \times 10^{-5}(\bar{M}_n)^{0.83} \qquad \text{(I-47)}$$

Comparing this equation with Eq. (I-37), which expresses the corresponding relationship between $[\eta]_\infty$ and $\bar{M}_n$, it may be concluded that the intrinsic viscosity at zero shear rate $[\eta]_o$ is a more sensitive measure for the molecular weight average than the intrinsic viscosity at high shear rates $[\eta]_\infty$. As the exponent to which the molecular weight average is raised is higher in value in Eq. (I-47) than in Eq. (I-37), then, for a specific change in the molecular weight average $\bar{M}_n$, $[\eta]_o$ will undergo a larger change in its value than $[\eta]_\infty$.

I.4.2 Use of Single-Bulb Viscometers in Intrinsic Viscosity Measurements

It has thus been demonstrated that intrinsic viscosities measured by using a multi-bulb variable shear rate viscometer are more accurate than the ones estimated by using the tradi-

Fig. (I-26) Relationship between Molecular Weight and Intrinsic Viscosity at Zero Shear Rate



tional single-bulb viscometer. But it must be pointed out that the length of time required for conducting the viscosity measurements necessary for calculating an intrinsic viscosity in a multi-bulb viscometer is approximately proportional to the number of bulbs. In other words, estimating an intrinsic viscosity for any of the polymers in the present investigation using the four-bulb viscometer took approximately four times longer than it would have taken using a single-bulb viscometer. This drawback is of special significance when dealing with polymers having extremely high molecular weight averages. These polymers exhibit very high viscosities and consume excessive amounts of time to flow through each of the bulbs. Therefore it may not be practicable to use the four-bulb viscometer for routine analyses in industrial plants e.g. for quality control. Therefore it would be desirable to specify conditions under which a single-bulb viscometer will yield reliable and consistent results.

It has been shown in the previous section that the intrinsic viscosities found by Ishige$^{(2)}$ using a conventional single-bulb viscometer approximated closely those found with the four-bulb viscometer when extrapolated to high shear rates.

The above observations immediately suggest that a careful selection of the viscometers'parameters (viz. the capillary radius, the hydrostatic head and the capillary length) will ensure that the shear rates will be high enough for the polymer solutions to approximate their Newtonian behaviour. This must hold true for all the concentrations and molecular weights involved in the analysis. This may be expressed more quantitatively by noting that both equations (I-45) and (I-46) express the rate of shear at the wall of the capillary in the following form

$$\dot{\gamma}_w = \frac{A}{\nu} \qquad \text{(I-48)}$$

where, $A = \frac{4\ V}{\pi\ r^3}$ $C = \frac{g\ H\ r}{2\ L}$

The rate of shear at the wall of the capillary, for any one liquid with kinematic viscosity ν, will be exclusively a function of the parameter A. Therefore the afore-mentioned condition reduces to the statement that the parameter A in Eq. (I-48) must be higher than a minimum level to ensure that $\dot{\gamma}_w$ will be high enough, for all the kinematic viscosities encountered, for the polymer solutions to approximate their Newtonian behaviour.

Whereas a lower limit is imposed on the rates of shear by the above condition, an upper limit is imposed by the fact that throughout our analysis, Eq. (I-39) is assumed valid. This implies that the kinetic-energy correction term, $\frac{B}{t}$ in Eq. (I-11-A) is negligible compared to the viscous flow term C t. As shown in the calibration of the present viscometer, Section (I.3.4), this requires that the flow time of all the liquids tested must exceed a minimum time, called "critical time". From Eq. (I-39) it is clear that imposing a minimum on the flow time of liquids of a certain kinematic viscosity ν is tantamount to imposing a maximum on the parameter C.

This, in turn, imposes a maximum on the parameter A and the wall shear rate, as Eq. (I-48) indicates.

The values of the viscometer's parameters satisfying the above two conditions have to be determined experimentally for each polymer-solvent system exhibiting non-Newtonian flow characteristics. It must also be kept in mind that for the same polymer-solvent system, the viscometer's specifications satisfying these conditions may vary if either the molecular weights of the polymers examined or the concentrations of the solutions used varied over a wide range, as these two factors affect the rheological response of the polymer solutions.

In the specific case of polyacrylamide-water system at 25°C, we have shown that a viscometer whose specifications approach those found in the uppermost bulb of the four-bulb viscometer 50-S489, or of any of the two viscometers used by Ishige(2) in his thesis (50-A620 or 75-L181), will satisfy the two above-mentioned conditions. This will apply for molecular weight averages of the polymers, as estimated from Eq. (I-37), between 10^6 to 10^7, and over a range of polymer solutions' concentrations of 0.1 g/dl to 0.01 g/dl. Therefore, from Table (I-3) it can be inferred that the minimum value of the parameter A in this case is in the order of 700 (centistokes/second). And from Table (I-1), the minimum time of flow for any liquid for a viscometer conforming to the specifications of bulb 1, to validate the use of Eq. (I-39), was found to be 176 seconds. Considering pure water as the liquid having the least viscosity to be used in this viscometer, and that water has a kinematic viscosity of 0.8963 centistokes at 25°C, from Eq. (I-39) it is clear that this implies a maximum for the parameter C of the order of 5 x 10^{-3} centistokes/second. The above results, combined with the definitions of the parameters A and C, Eq. (I-48) and Eq. (I-11), respectively, provide the following two inequalities that have to be satisfied

$$A = \frac{g\ H\ r}{2\ L} > 7\ (\mathrm{cm}^2/\mathrm{sec}^2) \qquad \text{(I-49)}$$

$$C = \frac{\pi g\ H\ r^4}{8\ L\ V} < 5 \times 10^{-5}\ (\mathrm{cm}^2/\mathrm{sec}^2) \qquad \text{(I-50)}$$

Finally, it is not likely that the data obtained from any single-bulb viscometer will provide a satisfactory approximation for the intrinsic viscosities at zero shear rate $[\eta]_0$ of high molecular weight polyacrylamides. This is due to the rapid rate of change of the apparent viscosities of these polymers with shear rate at low rates of shear, as evidenced by the extreme curvature at low shear rates of the ln η_r versus $\dot{\gamma}$ curves, Figures (I-2) to (I-9). Therefore, whenever $[\eta]_0$ is required, viscosity measurements at several shear rates have to be carried out, then extrapolated to zero rate of shear.

I.5 Conclusions

The rheological response of dilute solutions of high molecular weight polyacrylamides at low shear rates has been measured using a "Cannon-Ubbelohde Four-Bulb Shear Dilution Type Capillary Viscometer". These solutions were found to be highly non-Newtonian even at these low concentrations.

The solutions were found to approach Newtonian behaviour the lower the concentration, the lower the molecular weight and the higher the shear rates. The non-Newtonian effects were found to be significant for polyacrylamides with number-average molecular weights exceeding 10^6 (intrinsic viscosities higher than 6.0 to 7.0).

The molecular weight average-intrinsic viscosity relationship most widely used in the literature, Eq. (I-37), was found to be valid when the intrinsic viscosity was measured at high shear rates where the polymer solutions approach Newtonian behaviour. A new relationship was developed relating the number-average molecular weight to the intrinsic viscosity at zero shear rate, Eq. (I-47). The values of both the Mark-Houwink constants in this equation differed significantly from those in Eq. (I-37). This was attributed to the fact that the value of the intrinsic viscosity at zero shear rate is more sensitive to the change in molecular weights than the corresponding values of the intrinsic viscosity at high shear rates.

Attempts to render the flow data linear to facilitate extrapolation to zero and high shear rates were unsuccessful.

Conditions under which single-bulb viscometers may be used to obtain approximate values of the intrinsic viscosities at high shear rates were specified. On the other hand, it was shown that the intrinsic viscosities at zero shear rate for these high molecular weight polymers cannot be obtained from a single-bulb viscometer due to the excessive non-Newtonian effects at low shear rate.

The molecular weight data previously reported in the literature for polyacrylamides with molecular weight averages of several million was found wanting due to the fact that the non-Newtonian aspects of these polymers' solutions were completely ignored and assumed negligible. This assumption has been found groundless in the present investigation.

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Appendix (I-1) Flow Data in the Four Bulb Viscometer

Calibration of the Four-Bulb Cannon-Ubbelohde Shear Dilution Viscometer

Size : 50

Serial No. : S489

1. Distilled Water at 25°C

Flow Times (Seconds)

Bulb 1	Bulb 2	Bulb 3	Bulb 4
222.25	204.05	229.90	202.30
222.25	204.10	229.60	202.50
222.40	204.05	229.70	202.20
222.10	203.95	229.85	202.55
222.05	203.90	229.55	202.25
222.10	203.90	229.75	202.50
222.15	204.00	229.75	202.30
222.10	204.00	229.85	202.30
222.20	204.05	229.75	202.25
222.30	203.90	229.65	202.25

2. Viscosity Standard S-3 (No. 73101) at 25°C

Flow Times (Seconds)

Bulb 1	Bulb 2	Bulb 3	Bulb 4
1047.40	961.60	1079.50	926.40
1047.00	961.35	1078.40	927.30
1047.10	960.70	1078.40	925.70
1046.75	960.75	1079.20	925.50
1047.50	961.50	1078.85	927.50

POLYMER: Standard-A $[\eta]_0 = 17.70 \ (g/dl)^{-1}$

$\bar{M}_n = 2.82 \times 10^6$ $[\eta]_\infty = 12.30 \ (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	364.3	346.3	401.6	364.8	Time (Seconds)
	466.0	277.0	172.0	96.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	1.640	1.698	1.748	1.803	η_r
	0.495	0.529	0.558	0.589	$\ln(\eta_r)$
0.0333	314.5	296.4	341.2	308.2	Time
	541.0	324.0	202.0	114.0	$\dot{\gamma}$
	1.415	1.453	1.485	1.523	η_r
	0.347	0.374	0.396	0.421	$\ln(\eta_r)$
0.0250	290.8	272.6	312.5	281.6	Time
	585.0	352.0	221.0	124.0	$\dot{\gamma}$
	1.309	1.336	1.360	1.392	η_r
	0.269	0.290	0.308	0.331	$\ln(\eta_r)$
0.0167	267.8	249.7	285.2	255.5	Time
	635.0	384.0	242.0	137.0	$\dot{\gamma}$
	1.205	1.224	1.241	1.263	η_r
	0.187	0.202	0.216	0.233	$\ln(\eta_r)$
0.010	249.7	231.7	263.2	234.7	Time
	681.0	414.0	262.0	149.0	$\dot{\gamma}$
	1.124	1.136	1.146	1.160	η_r
	0.117	0.127	0.136	0.148	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.635	12.70	17.74	0.490	9.80	12.65
0.0333	0.465	14.09	17.94	0.340	10.30	12.27
0.0250	0.363	14.52	17.51	0.268	10.72	12.29
0.0167	0.260	15.57	17.78	0.187	11.20	12.31
0.010	0.165	16.50	17.94	0.117	11.70	12.41

POLYMER: Standard-B $\quad [\eta]_o$ = 10.40 $(g/dl)^{-1}$

$\bar{M}_n$ = 1.58×10^6 $\quad [\eta]_\infty$ = 8.40 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	318.8	296.6	337.3	300.2	Time (Seconds)
	533.0	324.0	205.0	117.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	1.435	1.454	1.468	1.483	η_r
	0.361	0.374	0.384	0.394	$\ln(\eta_r)$
0.0333	285.2	264.7	300.4	266.9	Time
	596.0	363.0	230.0	131.0	$\dot{\gamma}$
	1.284	1.298	1.308	1.319	η_r
	0.250	0.261	0.268	0.277	$\ln(\eta_r)$
0.0250	269.4	249.3	282.7	250.8	Time
	631.0	385.0	244.0	140.0	$\dot{\gamma}$
	1.212	1.222	1.231	1.239	η_r
	0.192	0.201	0.207	0.215	$\ln(\eta_r)$
0.0167	253.5	234.4	265.4	235.0	Time
	671.0	410.0	260.0	149.0	$\dot{\gamma}$
	1.141	1.149	1.155	1.161	η_r
	0.132	0.139	0.144	0.150	$\ln(\eta_r)$
0.010	241.4	222.7	251.4	222.4	Time
	704.0	431.0	274.0	157.0	$\dot{\gamma}$
	1.086	1.092	1.094	1.099	η_r
	0.083	0.088	0.090	0.095	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.408	8.16	10.08	0.360	7.20	8.67
0.0333	0.294	8.91	10.36	0.250	7.58	8.61
0.0250	0.228	9.12	10.24	0.192	7.68	8.47
0.0167	0.160	9.58	10.39	0.132	7.90	8.45
0.010	0.100	10.00	10.52	0.082	8.20	8.55

POLYMER: 25-20-10-A $[\eta]_o$ = 36.0 $(g/dl)^{-1}$

$\bar{M}_n = 6.77 \times 10^6$ $[\eta]_\infty$ = 21.7 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	553.7	550.6	675.5	665.7	Time (Seconds)
	307.0	174.0	102.0	53.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.49	2.70	2.94	3.29	η_r
	0.91	0.99	1.08	1.19	$\ln(\eta_r)$
0.0333	428.5	415.9	498.3	479.3	Time
	397.0	231.0	138.0	73.0	$\dot{\gamma}$
	1.93	2.04	2.17	2.37	η_r
	0.66	0.71	0.77	0.86	$\ln(\eta_r)$
0.0250	371.8	354.7	418.3	396.7	Time
	457.0	271.0	165.0	88.0	$\dot{\gamma}$
	1.67	1.74	1.82	1.96	η_r
	0.51	0.55	0.60	0.67	$\ln(\eta_r)$
0.0167	318.7	300.7	350.5	326.1	Time
	533.0	319.0	197.0	107.0	$\dot{\gamma}$
	1.43	1.47	1.53	1.61	η_r
	0.36	0.39	0.42	0.48	$\ln(\eta_r)$
0.010	277.7	259.8	299.5	273.5	Time
	612.0	370.0	230.0	128.0	$\dot{\gamma}$
	1.25	1.27	1.30	1.35	η_r
	0.22	0.24	0.27	0.30	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.32	26.40	54.87	0.90	18.0	29.19
0.0333	0.98	29.43	49.98	0.65	19.52	27.49
0.0250	0.78	31.20	47.26	0.51	20.40	26.61
0.0167	0.54	32.34	42.87	0.35	20.96	25.09
0.010	0.34	34.00	40.49	0.21	21.00	23.37

POLYMER: 25-20-10-B $[\eta]_0 = 33.0$ $(g/dl)^{-1}$

$\bar{M}_n = 6.68 \times 10^6$ $[\eta]_\infty = 21.5$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	526.9	521.4	632.7	610.3	Time (Seconds)
	323.0	184.0	109.0	57.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.37	2.56	2.75	3.02	η_r
	0.86	0.94	1.01	1.10	$\ln(\eta_r)$
0.0333	410.5	398.1	475.0	451.4	Time
	414.0	241.0	145.0	78.0	$\dot{\gamma}$
	1.85	1.95	2.07	2.23	η_r
	0.61	0.67	0.73	0.80	$\ln(\eta_r)$
0.0250	357.8	343.0	404.6	380.5	Time
	475.0	280.0	171.0	92.0	$\dot{\gamma}$
	1.61	1.68	1.76	1.88	η_r
	0.48	0.52	0.57	0.63	$\ln(\eta_r)$
0.0167	309.1	293.1	341.4	315.4	Time
	550.0	328.0	202.0	111.0	$\dot{\gamma}$
	1.39	1.44	1.49	1.56	η_r
	0.33	0.36	0.40	0.44	$\ln(\eta_r)$
0.010	273.1	255.9	294.6	268.1	Time
	622.0	375.0	234.0	131.0	$\dot{\gamma}$
	1.23	1.25	1.28	1.32	η_r
	0.21	0.23	0.25	0.25	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.26	25.20	50.51	0.84	16.80	26.33
0.0333	0.92	27.63	45.32	0.61	18.32	25.24
0.0250	0.72	28.80	42.18	0.48	19.20	24.64
0.0167	0.49	29.34	37.86	0.33	19.76	23.41
0.010	0.31	31.00	36.34	0.20	20.00	22.14

POLYMER: 25-20-10-C $[\eta]_o = 33.0$ $(g/dl)^{-1}$

$\bar{M}_n$ = 6.68×10^6 $[\eta]_\infty = 21.5$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	523.7	520.2	634.3	616.4	Time (Seconds)
	325.0	185.0	109.0	57.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.36	2.55	2.76	3.05	η_r
	0.86	0.94	1.02	1.11	$\ln(\eta_r)$
0.0333	407.7	397.1	475.9	454.1	Time
	417.0	242.0	145.0	77.0	$\dot{\gamma}$
	1.83	1.95	2.07	2.24	η_r
	0.61	0.67	0.73	0.81	$\ln(\eta_r)$
0.0250	356.2	342.3	405.3	382.0	Time
	477.0	280.0	170.0	92.0	$\dot{\gamma}$
	1.60	1.68	1.76	1.89	η_r
	0.47	0.52	0.57	0.64	$\ln(\eta_r)$
0.0167	308.1	292.3	341.5	316.3	Time
	552.0	328.0	202.0	111.0	$\dot{\gamma}$
	1.39	1.43	1.49	1.56	η_r
	0.33	0.36	0.40	0.45	$\ln(\eta_r)$
0.010	272.5	255.7	294.7	268.9	Time
	624.0	375.0	234.0	130.0	$\dot{\gamma}$
	1.23	1.25	1.28	1.33	η_r
	0.20	0.23	0.25	0.28	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.26	25.20	50.51	0.84	16.80	26.33
0.0333	0.92	27.63	45.32	0.61	18.32	25.24
0.0250	0.72	28.80	42.18	0.48	19.20	24.64
0.0167	0.49	29.34	37.86	0.33	19.76	23.41
0.010	0.31	31.00	36.34	0.20	20.00	22.14

POLYMER: 25-20-10-D $[\eta]_0 = 28.0$ $(g/dl)^{-1}$

$\bar{M}_n = 6.21 \times 10^6$ $[\eta]_\infty = 20.5$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	516.6	500.9	599.5	574.4	Time (Seconds)
	329.0	192.0	115.0	61.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.33	2.46	2.61	2.84	η_r
	0.84	0.90	0.96	1.04	$\ln(\eta_r)$
0.0333	403.4	383.5	450.1	422.4	Time
	421.0	250.0	153.0	83.0	$\dot{\gamma}$
	1.82	1.88	1.96	2.09	η_r
	0.60	0.63	0.67	0.74	$\ln(\eta_r)$
0.0250	351.9	330.65	385.2	355.6	Time
	483.0	290.0	179.0	98.0	$\dot{\gamma}$
	1.58	1.62	1.68	1.76	η_r
	0.46	0.48	0.52	0.56	$\ln(\eta_r)$
0.0167	304.8	284.4	327.7	299.4	Time
	558.0	338.0	211.0	117.0	$\dot{\gamma}$
	1.37	1.39	1.43	1.48	η_r
	0.32	0.33	0.36	0.39	$\ln(\eta_r)$
0.010	269.4	250.3	286.4	258.3	Time
	631.0	384.0	241.0	136.0	$\dot{\gamma}$
	1.21	1.23	1.25	1.28	η_r
	0.19	0.20	0.22	0.24	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.15	23.00	43.16	0.82	16.40	25.41
0.0333	0.83	24.92	38.84	0.60	18.02	24.69
0.0250	0.63	25.20	35.10	0.46	18.40	23.36
0.0167	0.44	26.35	33.10	0.32	19.16	22.58
0.010	0.27	27.00	31.00	0.19	19.00	20.92

POLYMER: 25-20-10-E $[\eta]_0$ = 32.0 $(g/dl)^{-1}$

$\bar{M}_n$ = 7.50×10^6 $[\eta]_\infty$ = 23.2 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	555.8	542.9	653.7	630.9	Time (Seconds)
	306.0	177.0	106.0	55.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$.
	2.50	2.66	2.85	3.12	η_r
	0.92	0.98	1.05	1.14	$\ln(\eta_r)$
0.0333	426.1	407.2	480.8	452.5	Time
	399.0	236.0	144.0	77.0	$\dot{\gamma}$
	1.92	2.00	2.09	2.24	η_r
	0.65	0.69	0.74	0.80	$\ln(\eta_r)$
0.0250	368.4	347.4	405.4	377.4	Time
	461.0	276.0	170.0	93.0	$\dot{\gamma}$
	1.66	1.77	1.76	1.87	η_r
	0.51	0.53	0.57	0.62	$\ln(\eta_r)$
0.0167	315.6	294.9	340.6	312.1	Time
	539.0	326.0	203.0	112.0	$\dot{\gamma}$
	1.42	1.45	1.48	1.54	η_r
	0.35	0.37	0.39	0.43	$\ln(\eta_r)$
0.010	275.7	256.0	293.5	265.5	Time
	617.0	375.0	235.0	132.0	$\dot{\gamma}$
	1.24	1.25	1.28	1.31	η_r
	0.22	0.23	0.24	0.27	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.24	24.80	49.11	0.90	18.00	29.19
0.0333	0.88	26.43	42.37	0.65	19.52	27.49
0.0250	0.68	27.20	38.96	0.50	20.00	25.95
0.0167	0.49	29.34	37.86	0.35	20.96	25.09
0.010	0.30	30.00	34.99	0.22	22.00	24.61

POLYMER: 25-20-10-F
$\bar{M}_n$ = 9.02×10^6

$[\eta]_0 = 55.0 \ (g/dl)^{-1}$
$[\eta]_\infty = 26.2 \ (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	565.5	571.8	711.5	710.8	Time (Seconds)
	301.0	168.0	97.0	49.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.55	2.80	3.10	3.51	η_r
	0.93	1.03	1.13	1.26	$\ln(\eta_r)$
0.0333	438.1	434.7	531.2	520.7	Time
	388.0	221.0	130.0	67.0	$\dot{\gamma}$
	1.97	2.13	2.31	2.57	η_r
	0.68	0.76	0.84	0.95	$\ln(\eta_r)$
0.0250	380.3	372.2	449.5	436.9	Time
	447.0	258.0	154.0	80.0	$\dot{\gamma}$
	1.71	1.82	1.96	2.16	η_r
	0.54	0.60	0.67	0.77	$\ln(\eta_r)$
0.0167	326.0	314.2	374.1	357.8	Time
	521.0	306.0	184.0	98.0	$\dot{\gamma}$
	1.47	1.54	1.63	1.77	η_r
	0.38	0.43	0.49	0.57	$\ln(\eta_r)$
0.010	284.2	269.6	315.7	295.1	Time
	598.0	356.0	219.0	119.0	$\dot{\gamma}$
	1.28	1.32	1.37	1.46	η_r
	0.25	0.28	0.32	0.38	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.42	28.40	62.74	0.91	18.20	29.69
0.0333	1.10	33.03	60.19	0.67	20.12	28.66
0.0250	0.92	36.80	60.37	0.54	21.60	28.64
0.0167	0.68	40.72	58.32	0.38	22.75	27.68
0.010	0.45	45.00	56.83	0.24	24.00	27.12

POLYMER: 25-20-10-G $[\eta]_0 = 26.8$ $(g/dl)^{-1}$

$\bar{M}_n = 6.68 \times 10^6$ $[\eta]_\infty = 21.5$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	442.1	429.6	510.7	479.2	Time (Seconds)
	385.0	223.0	135.0	73.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	1.99	2.11	2.22	2.37	η_r
	0.69	0.74	0.80	0.86	$\ln(\eta_r)$
0.0333	361.1	347.8	408.7	378.2	Time
	470.0	276.0	169.0	93.0	$\dot{\gamma}$
	1.63	1.71	1.78	1.87	η_r
	0.49	0.53	0.58	0.63	$\ln(\eta_r)$
0.0250	325.0	309.7	361.5	332.7	Time
	523.0	310.0	191.0	105.0	$\dot{\gamma}$
	1.46	1.52	1.57	1.64	η_r
	0.38	0.42	0.45	0.50	$\ln(\eta_r)$
0.0167	290.1	273.8	316.9	289.4	Time
	586.0	351.0	218.0	121.0	$\dot{\gamma}$
	1.31	1.34	1.38	1.43	η_r
	0.27	0.29	0.32	0.36	$\ln(\eta_r)$
0.010	262.9	245.8	282.0	254.7	Time
	647.0	391.0	245.0	137.0	$\dot{\gamma}$
	1.18	1.20	1.23	1.26	η_r
	0.17	0.19	0.20	0.23	$\ln(\eta_r)$

	$\dot{\gamma} \rightarrow 0$			$\dot{\gamma} \rightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.96	19.20	32.23	0.68	13.60	19.48
0.0333	0.70	21.02	30.44	0.48	14.41	18.50
0.0250	0.55	22.00	29.33	0.38	15.20	18.49
0.0167	0.39	23.35	28.56	0.27	16.17	18.56
0.010	0.25	25.00	28.40	0.17	17.00	18.53

POLYMER: 25-20-10-H　　$[\eta]_0$ = 42.00 $(g/dl)^{-1}$
$\bar{M}_n$ = 8.40×10^6　　$[\eta]_\infty$ = 25.00 $(g/dl)^{-1}$

CONC.	FLOW DATA				
(g/dl)	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	1094.3	1153.6	1457.9	1441.8	Time (Seconds)
	155.0	83.0	47.0	24.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	4.93	5.66	6.35	7.13	η_r
	1.59	1.73	1.85	1.96	$\ln(\eta_r)$
0.0667	724.3	749.3	937.8	925.7	Time
	235.0	128.0	74.0	38.0	$\dot{\gamma}$
	3.26	3.67	4.08	4.57	η_r
	1.18	1.30	1.41	1.52	$\ln(\eta_r)$
0.050	571.5	581.5	722.0	711.5	Time
	297.0	165.0	96.0	49.0	$\dot{\gamma}$
	2.57	2.85	3.14	3.52	η_r
	0.94	1.05	1.15	1.26	$\ln(\eta_r)$
0.0333	442.7	440.3	537.2	525.2	Time
	384.0	218.0	128.0	67.0	$\dot{\gamma}$
	1.99	2.16	2.34	2.60	η_r
	0.69	0.77	0.85	0.95	$\ln(\eta_r)$
0.020	348.7	339.0	405.1	387.6	Time
	487.0	283.0	170.0	90.0	$\dot{\gamma}$
	1.57	1.66	1.76	1.92	η_r
	0.45	0.51	0.57	0.65	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	2.10	21.00	71.66	1.48	14.80	33.93
0.0667	1.68	25.19	65.45	1.12	16.79	30.96
0.050	1.46	29.20	66.12	0.92	18.40	30.19
0.0333	1.06	31.83	56.65	0.68	20.42	29.25
0.020	0.70	35.00	50.69	0.44	22.00	27.64

POLYMER: 25-20-10-I

$\bar{M}_n$ = 7.69 x 10^6

$[\eta]_o$ = 41.00 $(g/dl)^{-1}$

$[\eta]_\infty$ = 23.60 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	542.8	547.5	673.5	656.4	Time (Seconds)
	313.0	175.0	102.0	53.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.44	2.68	2.93	3.24	η_r
	0.89	0.99	1.08	1.18	$\ln(\eta_r)$
0.0333	423.2	418.6	507.6	490.4	Time
	402.0	229.0	136.0	71.0	$\dot{\gamma}$
	1.90	2.05	2.21	2.42	η_r
	0.64	0.72	0.79	0.89	$\ln(\eta_r)$
0.0250	369.5	360.7	432.8	414.3	Time
	460.0	266.0	159.0	84.0	$\dot{\gamma}$
	1.66	1.77	1.88	2.05	η_r
	0.51	0.57	0.63	0.72	$\ln(\eta_r)$
0.0167	318.3	306.0	361.6	340.2	Time
	534.0	313.0	191.0	103.0	$\dot{\gamma}$
	1.43	1.50	1.57	1.68	η_r
	0.36	0.41	0.45	0.52	$\ln(\eta_r)$
0.010	279.3	264.4	307.3	283.1	Time
	609.0	363.0	225.0	124.0	$\dot{\gamma}$
	1.26	1.30	1.34	1.40	η_r
	0.23	0.26	0.29	0.34	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.34	26.80	56.38	0.86	17.20	27.26
0.0333	1.06	31.83	56.65	0.63	18.92	26.35
0.0250	0.84	33.60	52.65	0.51	20.40	26.61
0.0167	0.59	35.33	48.14	0.35	20.96	25.09
0.010	0.38	38.00	46.23	0.22	22.00	24.61

POLYMER: 25-20-10-J $[\eta]_o$ = 21.4 $(g/dl)^{-1}$

$\bar{M}_n$ = 3.86×10^6 $[\eta]_\infty$ = 15.0 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	416.9 408.0 1.88 0.63	399.8 240.0 1.96 0.67	467.3 148.0 2.03 0.71	428.2 82.0 2.12 0.75	Time (Seconds) $\dot{\gamma}$ $(Seconds)^{-1}$ η_r $\ln(\eta_r)$
0.0333	344.3 494.0 1.55 0.44	326.4 294.0 1.60 0.47	378.2 182.0 1.65 0.50	344.1 102.0 1.70 0.53	Time $\dot{\gamma}$ η_r $\ln(\eta_r)$
0.0250	311.2 546.0 1.40 0.34	293.3 327.0 1.44 0.36	338.1 204.0 1.47 0.39	306.1 114.0 1.51 0.41	Time $\dot{\gamma}$ η_r $\ln(\eta_r)$
0.0167	280.6 606.0 1.26 0.23	262.4 366.0 1.29 0.25	300.5 230.0 1.31 0.27	270.3 129.0 1.34 0.29	Time $\dot{\gamma}$ η_r $\ln(\eta_r)$
0.010	257.2 661.0 1.16 0.15	239.0 402.0 1.17 0.16	272.1 254.0 1.18 0.17	243.0 144.0 1.20 0.18	Time $\dot{\gamma}$ η_r $\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.81	16.20	24.96	0.615	12.30	16.99
0.0333	0.575	17.27	23.34	0.435	13.06	16.37
0.0250	0.45	18.00	22.73	0.34	13.60	16.20
0.0167	0.33	19.76	23.41	0.23	13.77	15.49
0.010	0.20	20.00	22.14	0.145	14.50	15.60

POLYMER: 25-05-10-A $\qquad [\eta]_0 = 30.00\ (g/dl)^{-1}$

$\bar{M}_n = 5.89 \times 10^6 \qquad [\eta]_\infty = 19.80\ (g/dl)^{-1}$

CONC.	FLOW DATA				
(g/dl)	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	499.0	490.1	590.3	565.6	Time (Seconds)
	341.0	196.0	117.0	62.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.25	2.40	2.57	2.80	η_r
	0.81	0.88	0.94	1.03	$\ln(\eta_r)$
0.0333	392.4	379.0	448.7	420.6	Time
	433.0	253.0	154.0	83.0	$\dot{\gamma}$
	1.77	1.86	1.95	2.08	η_r
	0.57	0.62	0.67	0.73	$\ln(\eta_r)$
0.0250	344.8	329.3	386.8	359.3	Time
	493.0	292.0	178.0	97.0	$\dot{\gamma}$
	1.55	1.61	1.68	1.78	η_r
	0.44	0.48	0.52	0.57	$\ln(\eta_r)$
0.0167	301.4	284.9	330.5	302.9	Time
	564.0	337.0	209.0	116.0	$\dot{\gamma}$
	1.36	1.40	1.44	1.50	η_r
	0.30	0.33	0.36	0.40	$\ln(\eta_r)$
0.010	268.4	251.2	288.3	260.7	Time
	633.0	382.0	239.0	134.0	$\dot{\gamma}$
	1.21	1.23	1.26	1.29	η_r
	0.19	0.21	0.23	0.25	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.13	22.60	41.91	0.79	15.80	24.07
0.0333	0.81	24.32	37.47	0.56	16.82	22.54
0.0250	0.64	25.60	35.86	0.44	17.60	22.11
0.0167	0.45	26.95	34.03	0.30	17.96	20.95
0.010	0.28	28.00	32.31	0.19	19.00	20.92

POLYMER: 25-05-10-B $[\eta]_0$ = 26.3 $(g/dl)^{-1}$

$\bar{M}_n$ = 5.31×10^6 $[\eta]_\infty$ = 18.5 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	488.3	471.5	559.2	526.3	Time (Seconds)
	348.0	204.0	123.0	67.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.20	2.31	2.43	2.60	η_r
	0.79	0.84	0.89	0.96	$\ln(\eta_r)$
0.0333	384.6	366.2	428.2	395.8	Time
	442.0	262.0	161.0	88.0	$\dot{\gamma}$
	1.73	1.80	1.86	1.96	η_r
	0.55	0.59	0.62	0.67	$\ln(\eta_r)$
0.0250	338.5	319.5	370.7	339.4	Time
	502.0	300.0	186.0	103.0	$\dot{\gamma}$
	1.52	1.57	1.61	1.68	η_r
	0.42	0.45	0.48	0.52	$\ln(\eta_r)$
0.0167	296.4	277.8	319.5	289.6	Time
	573.0	346.0	216.0	121.0	$\dot{\gamma}$
	1.33	1.36	1.39	1.43	η_r
	0.29	0.31	0.33	0.36	$\ln(\eta_r)$
0.010	265.1	246.8	281.9	253.2	Time
	641.0	389.0	245.0	138.0	$\dot{\gamma}$
	1.19	1.21	1.23	1.25	η_r
	0.18	0.19	0.20	0.22	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.05	21.00	37.15	0.78	15.60	23.63
0.0333	0.75	22.52	33.54	0.55	16.52	22.02
0.0250	0.58	23.20	31.44	0.42	16.80	20.88
0.0167	0.41	24.55	30.35	0.29	17.37	20.15
0.010	0.25	25.00	28.40	0.18	18.00	19.72

POLYMER: 25-05-10-C $[\eta]_0 = 26.3 \quad (g/dl)^{-1}$

$\bar{M}_n = 5.31 \times 10^6$ $[\eta]_\infty = 18.5 \quad (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	490.3	472.9	561.0	527.6	Time (Seconds)
	347.0	203.0	123.0	66.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.21	2.32	2.44	2.61	η_r
	0.79	0.84	0.89	0.96	$\ln(\eta_r)$
0.0333	386.5	367.4	429.6	398.9	Time
	440.0	261.0	161.0	88.0	$\dot{\gamma}$
	1.74	1.80	1.87	1.97	η_r
	0.55	0.59	0.63	0.68	$\ln(\eta_r)$
0.0250	340.0	320.7	372.0	341.9	Time
	500.0	299.0	185.0	102.0	$\dot{\gamma}$
	1.53	1.57	1.62	1.69	η_r
	0.43	0.45	0.48	0.52	$\ln(\eta_r)$
0.0167	297.3	278.4	320.6	290.9	Time
	572.0	345.0	215.0	120.0	$\dot{\gamma}$
	1.34	1.36	1.40	1.44	η_r
	0.29	0.31	0.33	0.36	$\ln(\eta_r)$
0.010	265.4	247.3	282.3	253.9	Time
	641.0	388.0	244.0	138.0	$\dot{\gamma}$
	1.19	1.21	1.23	1.25	η_r
	0.18	0.19	0.21	0.23	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.05	21.00	37.15	0.78	15.60	23.63
0.0333	0.75	22.52	33.54	0.55	16.52	22.02
0.0250	0.58	23.20	31.44	0.42	16.80	20.80
0.0167	0.41	24.55	30.35	0.29	17.37	20.15
0.010	0.25	25.00	28.40	0.18	18.00	19.72

POLYMER: 25-05-10-D $[\eta]_0 \doteq 25.5$ $(g/dl)^{-1}$

$\bar{M}_n = 5.10 \times 10^6$ $[\eta]_\infty = 18.0$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	460.3	444.7	526.5	491.6	Time (Seconds)
	369.0	216.0	131.0	71.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.07	2.18	2.29	2.43	η_r
	0.73	0.78	0.83	0.89	$\ln(\eta_r)$
0.0333	368.0	351.6	412.2	380.3	Time
	462.0	273.0	167.0	92.0	$\dot{\gamma}$
	1.66	1.72	1.79	1.88	η_r
	0.50	0.54	0.58	0.63	$\ln(\eta_r)$
0.0250	328.0	310.7	361.1	331.2	Time
	518.0	309.0	191.0	106.0	$\dot{\gamma}$
	1.48	1.52	1.57	1.64	η_r
	0.39	0.42	0.45	0.49	$\ln(\eta_r)$
0.0167	290.8	273.4	314.9	286.3	Time
	585.0	351.0	219.0	122.0	$\dot{\gamma}$
	1.31	1.34	1.37	1.41	η_r
	0.27	0.29	0.32	0.35	$\ln(\eta_r)$
0.010	262.9	245.2	280.4	252.2	Time
	647.0	392.0	246.0	139.0	$\dot{\gamma}$
	1.18	1.20	1.22	1.25	η_r
	0.17	0.18	0.20	0.22	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.97	19.40	32.76	0.72	14.40	21.09
0.0333	0.70	21.02	30.44	0.50	15.02	19.48
0.0250	0.54	21.60	28.64	0.39	15.60	19.08
0.0167	0.39	23.35	28.56	0.27	16.17	18.56
0.010	0.24	24.00	27.12	0.17	17.00	18.53

POLYMER: 25-05-10-E $[\eta]_0 = 25.5$ $(g/dl)^{-1}$
$\bar{M}_n = 5.10 \times 10^6$ $[\eta]_\infty = 18.0$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
	465.9	451.35	535.7	500.1	Time (Seconds)
0.050	365.0	213.0	129.0	70.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.10	2.21	2.33	2.47	η_r
	0.74	0.79	0.85	0.90	$\ln(\eta_r)$
	373.6	358.4	421.1	389.4	Time
0.0333	455.0	268.0	164.0	90.0	$\dot{\gamma}$
	1.68	1.76	1.83	1.92	η_r
	0.52	0.56	0.61	0.65	$\ln(\eta_r)$
	331.9	315.5	367.3	337.5	Time
0.0250	512.0	304.0	188.0	104.0	$\dot{\gamma}$
	1.49	1.55	1.60	1.67	η_r
	0.40	0.44	0.47	0.51	$\ln(\eta_r)$
	293.3	276.6	319.4	291.3	Time
0.0167	580.0	347.0	216.0	120.0	$\dot{\gamma}$
	1.32	1.36	1.39	1.44	η_r
	0.28	0.30	0.33	0.36	$\ln(\eta_r)$
	264.7	247.1	282.9	255.6	Time
0.010	642.0	388.0	244.0	137.0	$\dot{\gamma}$
	1.19	1.21	1.23	1.26	η_r
	0.18	0.19	0.21	0.23	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.97	19.40	32.76	0.72	14.40	21.09
0.0333	0.70	21.02	30.44	0.50	15.02	19.48
0.0250	0.54	21.60	28.64	0.39	15.60	19.08
0.0167	0.39	23.35	28.56	0.27	16.17	18.56
0.010	0.24	24.00	27.12	0.17	17.00	18.53

POLYMER: 25-05-10-F

$\bar{M}_n$ = 5.27×10^6

$[\eta]_o$ = 26.5 $(g/dl)^{-1}$

$[\eta]_\infty$ = 18.4 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	434.1	420.4	495.7	457.5	Time (Seconds)
	392.0	228.0	139.0	77.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	1.95	2.06	2.16	2.26	η_r
	0.67	0.72	0.77	0.82	$\ln(\eta_r)$
0.0333	358.0	343.2	402.0	369.8	Time
	475.0	280.0	172.0	95.0	$\dot{\gamma}$
	1.61	1.68	1.75	1.83	η_r
	0.48	0.52	0.56	0.60	$\ln(\eta_r)$
0.0250	322.1	306.9	357.1	327.2	Time
	528.0	313.0	193.0	107.0	$\dot{\gamma}$
	1.45	1.50	1.55	1.62	η_r
	0.37	0.41	0.44	0.48	$\ln(\eta_r)$
0.0167	288.7	272.5	314.7	286.4	Time
	589.0	352.0	219.0	122.0	$\dot{\gamma}$
	1.30	1.34	1.37	1.42	η_r
	0.26	0.29	0.31	0.35	$\ln(\eta_r)$
0.010	262.4	245.4	281.6	253.9	Time
	648.0	391.0	245.0	138.0	$\dot{\gamma}$
	1.18	1.20	1.23	1.25	η_r
	0.17	0.19	0.20	0.23	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.88	17.60	28.22	0.66	13.20	18.70
0.0333	0.66	19.82	28.07	0.48	14.41	18.50
0.0250	0.54	21.60	28.64	0.39	15.60	19.08
0.0167	0.39	23.35	28.56	0.27	16.17	18.56
0.010	0.24	24.00	27.12	0.17	17.00	18.53

POLYMER: 25-02-10-A $[\eta]_o$ = 19.6 (g/dl)$^{-1}$

$\bar{M}_n$ = 3.29 x 10^6 $[\eta]_\infty$ = 13.5 (g/dl)$^{-1}$

CONC.	FLOW DATA				
(g/dl)	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	389.7	370.3	428.4	387.4	Time (Seconds)
	436.0	259.0	161.0	90.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	1.75	1.82	1.86	1.91	η_r
	0.56	0.60	0.62	0.65	$\ln(\eta_r)$
0.0333	330.0	311.9	359.5	324.2	Time
	515.0	308.0	192.0	108.0	$\dot{\gamma}$
	1.49	1.53	1.56	1.60	η_r
	0.40	0.42	0.45	0.47	$\ln(\eta_r)$
0.0250	302.2	284.0	326.4	293.6	Time
	563.0	338.0	211.0	119.0	$\dot{\gamma}$
	1.36	1.39	1.42	1.45	η_r
	0.31	0.33	0.35	0.37	$\ln(\eta_r)$
0.0167	275.3	257.5	294.3	263.8	Time
	617.0	373.0	234.0	133.0	$\dot{\gamma}$
	1.24	1.26	1.28	1.30	η_r
	0.21	0.23	0.25	0.27	$\ln(\eta_r)$
0.010	254.2	236.3	269.0	240.1	Time
	669.0	406.0	257.0	146.0	$\dot{\gamma}$
	1.14	1.16	1.17	1.19	η_r
	0.13	0.15	0.16	0.17	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.685	13.70	19.68	0.555	11.10	14.85
0.0333	0.505	15.17	19.73	0.40	12.01	14.77
0.0250	0.400	16.00	19.67	0.31	12.40	14.54
0.0167	0.290	17.37	20.15	0.21	12.57	13.99
0.010	0.180	18.00	19.72	0.13	13.00	13.88

POLYMER: 25-02-10-B $\quad [\eta]_0 = 23.3 \ (g/dl)^{-1}$

$\bar{M}_n = 4.06 \times 10^6 \quad [\eta]_\infty = 15.5 \ (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	449.2	429.4	504.2	465.8	Time (Seconds)
	378.0	224.0	137.0	75.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.02	2.11	2.19	2.30	η_r
	0.70	0.74	0.79	0.83	$\ln(\eta_r)$
0.0333	361.0	341.0	395.6	362.0	Time
	471.0	282.0	174.0	97.0	$\dot{\gamma}$
	1.62	1.67	1.72	1.79	η_r
	0.49	0.51	0.54	0.58	$\ln(\eta_r)$
0.0250	321.4	302.0	348.2	316.2	Time
	529.0	318.0	198.0	111.0	$\dot{\gamma}$
	1.45	1.48	1.52	1.56	η_r
	0.37	0.39	0.42	0.45	$\ln(\eta_r)$
0.0167	285.4	266.6	305.2	274.7	Time
	596.0	360.0	226.0	127.0	$\dot{\gamma}$
	1.28	1.31	1.33	1.36	η_r
	0.25	0.27	0.28	0.31	$\ln(\eta_r)$
0.010	258.9	240.4	273.7	244.6	Time
	657.0	399.0	252.0	143.0	$\dot{\gamma}$
	1.17	1.18	1.19	1.21	η_r
	0.15	0.16	0.18	0.19	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.89	17.80	28.70	0.69	13.80	19.87
0.0333	0.645	19.55	27.45	0.48	14.55	18.67
0.025	0.505	20.20	26.28	0.365	14.60	17.62
0.0167	0.350	20.96	25.09	0.25	14.97	17.01
0.010	0.220	22.00	24.61	0.15	15.00	16.18

POLYMER: 25-02-10-C $[\eta]_0 = 21.0 \ (g/dl)^{-1}$

$\bar{M}_n = 4.02 \times 10^6$ $[\eta]_\infty = 15.4 \ (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	446.3	425.5	497.1	457.9	Time (Seconds)
	381.0	226.0	139.0	76.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.01	2.09	2.16	2.26	η_r
	0.70	0.74	0.77	0.82	$\ln(\eta_r)$
0.0333	358.3	337.9	390.4	354.7	Time
	475.0	284.0	177.0	99.0	$\dot{\gamma}$
	1.61	1.66	1.70	1.75	η_r
	0.48	0.50	0.53	0.56	$\ln(\eta_r)$
0.0250	319.5	299.4	344.5	310.8	Time
	532.0	321.0	200.0	113.0	$\dot{\gamma}$
	1.44	1.47	1.50	1.54	η_r
	0.36	0.38	0.41	0.43	$\ln(\eta_r)$
0.0167	284.2	264.9	302.5	271.6	Time
	598.0	362.0	228.0	129.0	$\dot{\gamma}$
	1.28	1.30	1.32	1.34	η_r
	0.25	0.26	0.27	0.29	$\ln(\eta_r)$
0.010	258.7	239.7	272.0	242.3	Time
	657.0	400.0	254.0	144.0	$\dot{\gamma}$
	1.16	1.18	1.18	1.20	η_r
	0.15	0.16	0.17	0.18	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.865	17.30	27.50	0.69	13.80	19.87
0.0333	0.60	18.18	24.91	0.475	14.39	18.42
0.0250	0.47	18.80	24.00	0.360	14.40	17.33
0.0167	0.325	19.46	23.00	0.250	14.97	17.01
0.010	0.20	20.00	22.14	0.15	15.00	16.18

POLYMER: 25-02-10-D

$\bar{M}_n = 3.82 \times 10^6$

$[\eta]_o = 21.5 \ (g/dl)^{-1}$

$[\eta]_\infty = 14.9 \ (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	428.6	409.8	478.4	438.6	Time (Seconds)
	397.0	234.0	144.0	80.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	1.93	2.01	2.08	2.17	η_r
	0.66	0.77	0.73	0.77	$\ln(\eta_r)$
0.0333	349.6	330.8	382.5	348.0	Time
	486.0	290.0	180.0	101.0	$\dot{\gamma}$
	1.57	1.62	1.66	1.72	η_r
	0.45	0.48	0.51	0.54	$\ln(\eta_r)$
0.0250	314.2	295.2	340.8	307.9	Time
	541.0	325.0	202.0	114.0	$\dot{\gamma}$
	1.41	1.45	1.48	1.52	η_r
	0.35	0.37	0.39	0.42	$\ln(\eta_r)$
0.0167	281.3	262.5	300.3	270.0	Time
	604.0	366.0	230.0	130.0	$\dot{\gamma}$
	1.27	1.29	1.31	1.33	η_r
	0.24	0.25	0.27	0.29	$\ln(\eta_r)$
0.010	256.8	238.3	271.3	242.1	Time
	662.0	403.0	254.0	145.0	$\dot{\gamma}$
	1.16	1.17	1.18	1.20	η_r
	0.14	0.16	0.17	0.18	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.825	16.50	25.64	0.65	13.00	18.31
0.0333	0.590	17.88	24.36	0.45	13.64	17.22
0.0250	0.455	18.20	23.05	0.35	14.00	16.76
0.0167	0.315	18.86	22.17	0.238	14.25	16.09
0.010	0.195	19.50	21.53	0.145	14.50	15.60

POLYMER: 25-02-10-E $[\eta]_0$ = 24.0 $(g/dl)^{-1}$

$\bar{M}_n$ = 4.10×10^6 $[\eta]_\infty$ = 15.6 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	655.3	642.5	763.7	711.0	Time (Seconds)
	259.0	149.0	90.0	49.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$
	2.95	3.15	3.32	3.51	η_r
	1.08	1.15	1.20	1.26	$\ln(\eta_r)$
0.0667	485.2	472.0	558.0	518.1	Time
	350.0	203.0	124.0	68.0	$\dot{\gamma}$
	2.18	2.31	2.43	2.56	η_r
	0.78	0.84	0.89	0.94	$\ln(\eta_r)$
0.050	412.1	397.9	468.5	434.0	Time
	413.0	241.0	147.0	81.0	$\dot{\gamma}$
	1.85	1.95	2.04	2.14	η_r
	0.62	0.67	0.71	0.76	$\ln(\eta_r)$
0.0333	347.1	332.2	389.1	358.6	Time
	490.0	289.0	177.0	98.0	$\dot{\gamma}$
	1.56	1.63	1.69	1.77	η_r
	0.45	0.49	0.53	0.57	$\ln(\eta_r)$
0.020	297.7	281.9	327.0	299.5	Time
	571.0	340.0	211.0	117.0	$\dot{\gamma}$
	1.34	1.38	1.42	1.48	η_r
	0.29	0.32	0.35	0.39	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	1.32	13.20	27.43	1.03	10.30	18.01
0.0667	1.00	14.99	25.76	0.76	11.39	17.07
0.050	0.82	16.40	25.41	0.61	12.20	16.81
0.0333	0.61	18.32	25.24	0.44	13.21	16.60
0.020	0.41	20.50	25.34	0.28	14.00	16.16

POLYMER: 25-02-10-F $[\eta]_0$ = 22.00 $(g/dl)^{-1}$

$\bar{M}_n$ = 3.39×10^6 $[\eta]_\infty$ = 13.75 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	376.3	356.7	411.2	370.0	Time (Seconds)
	452.0	269.0	168.0	95.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	1.69	1.75	1.79	1.83	η_r
	0.53	0.56	0.58	0.60	$\ln(\eta_r)$
0.0333	324.1	305.7	351.7	316.4	Time
	525.0	314.0	196.0	111.0	$\dot{\gamma}$
	1.46	1.50	1.53	1.56	η_r
	0.38	0.40	0.43	0.45	$\ln(\eta_r)$
0.0250	298.7	280.8	322.1	289.0	Time
	569.0	342.0	214.0	121.0	$\dot{\gamma}$
	1.34	1.38	1.40	1.43	η_r
	0.30	0.32	0.34	0.36	$\ln(\eta_r)$
0.0167	273.7	256.1	292.8	262.7	Time
	621.0	375.0	236.0	133.0	$\dot{\gamma}$
	1.23	1.26	1.27	1.30	η_r
	0.21	0.23	0.24	0.26	$\ln(\eta_r)$
0.010	253.7	236.0	268.8	239.9	Time
	670.0	407.0	257.0	146.0	$\dot{\gamma}$
	1.14	1.16	1.17	1.19	η_r
	0.13	0.15	0.16	0.17	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.635	12.70	17.74	0.525	10.50	13.81
0.0333	0.485	14.56	18.74	0.375	11.26	13.66
0.0250	0.380	15.20	18.49	0.300	12.00	13.99
0.0167	0.280	16.77	19.35	0.205	12.28	13.62
0.010	0.180	18.00	19.72	0.130	13.00	13.88

POLYMER: 25-05-01-A $\quad [\eta]_o = 50.0 \ (g/dl)^{-1}$

$\bar{M}_n = 12.2 \times 10^6 \quad [\eta]_\infty = 32.0 \ (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.150	2710.1	3341.9	4840.6	5426.4	Time (Seconds)
	63.0	29.0	14.0	6.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	12.20	16.38	21.07	26.82	η_r
	2.50	2.80	3.05	3.29	$\ln(\eta_r)$
0.100	1431.7	1644.9	2283.2	2528.2	Time
	119.0	58.0	30.0	14.0	$\dot{\gamma}$
	6.44	8.06	9.94	12.49	η_r
	1.86	2.09	2.30	2.53	$\ln(\eta_r)$
0.075	1000.8	1102.8	1491.7	1630.0	Time
	170.0	87.0	46.0	21.0	$\dot{\gamma}$
	4.50	5.41	6.49	8.06	η_r
	1.51	1.69	1.87	2.09	$\ln(\eta_r)$
0.050	680.0	714.7	931.0	992.4	Time
	250.0	134.0	74.0	35.0	$\dot{\gamma}$
	3.06	3.50	4.05	4.90	η_r
	1.12	1.25	1.40	1.59	$\ln(\eta_r)$
0.030	472.8	472.8	588.3	599.7	Time
	360.0	203.0	117.0	58.0	$\dot{\gamma}$
	2.13	2.32	2.56	2.96	η_r
	0.76	0.84	0.94	1.09	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.150	3.46	23.07	205.45	2.26	15.07	57.22
0.100	2.72	27.20	141.80	1.74	17.40	46.97
0.075	2.30	30.67	119.66	1.46	19.47	44.08
0.050	1.80	36.00	100.99	1.10	22.00	40.08
0.030	1.24	41.33	81.85	0.76	25.33	37.94

POLYMER: 25-05-01-B $[\eta]_o$ = 53.0 (g/dl)$^{-1}$

$\bar{M}_n$ = 11.6 x 10^6 $[\eta]_\infty$ = 31.0 (g/dl)$^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	1469.6	1707.1	2426.7	2796.9	Time (Seconds)
	116.0	56.0	28.0	12.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	6.61	8.37	10.56	13.82	η_r
	1.89	2.12	2.36	2.63	$\ln(\eta_r)$
0.0667	907.5	1007.5	1370.2	1532.7	Time
	187.0	95.0	50.0	23.0	$\dot{\gamma}$
	4.08	4.94	5.96	7.57	η_r
	1.41	1.60	1.79	2.02	$\ln(\eta_r)$
0.050	695.0	732.0	961.1	1042.9	Time
	245.0	131.0	72.0	34.0	$\dot{\gamma}$
	3.13	3.59	4.18	5.15	η_r
	1.14	1.28	1.43	1.64	$\ln(\eta_r)$
0.0333	512.8	520.1	660.6	690.8	Time
	331.0	185.0	104.0	51.0	$\dot{\gamma}$
	2.31	2.55	2.88	3.41	η_r
	0.84	0.94	1.06	1.23	$\ln(\eta_r)$
0.020	392.6	381.1	460.3	454.7	Time
	433.0	252.0	150.0	77.0	$\dot{\gamma}$
	1.77	1.87	2.00	2.25	η_r
	0.57	0.63	0.69	0.81	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.10	2.94	29.40	179.16	1.86	18.60	54.24
0.0667	2.31	34.48	135.44	1.40	20.90	45.60
0.050	1.86	37.20	108.47	1.15	23.00	43.16
0.0333	1.38	41.82	90.15	0.82	24.85	38.50
0.020	0.95	47.50	79.29	0.55	27.50	36.66

POLYMER: 25-05-01-C $\quad [\eta]_o$ = 48.0 (g/dl)$^{-1}$

$\bar{M}_n$ = 11.6 x 10^6 $\quad [\eta]_\infty$ = 31.0 (g/dl)$^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	1326.8	1485.5	2016.0	2185.8	Time (Seconds)
	128.0	65.0	34.0	16.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	5.97	7.28	8.78	10.80	η_r
	1.79	1.99	2.17	2.38	$\ln(\eta_r)$
0.0667	832.9	889.15	1162.6	1231.0	Time
	204.0	108.0	59.0	28.0	$\dot{\gamma}$
	3.75	4.36	5.06	6.08	η_r
	1.32	1.47	1.62	1.81	$\ln(\eta_r)$
0.050	641.7	664.2	850.5	887.5	Time
	265.0	144.0	81.0	39.0	$\dot{\gamma}$
	2.89	3.26	3.70	4.39	η_r
	1.06	1.18	1.31	1.48	$\ln(\eta_r)$
0.0333	487.4	486.2	602.8	613.2	Time
	349.0	197.0	114.0	57.0	$\dot{\gamma}$
	2.19	2.38	2.62	3.03	η_r
	0.79	0.87	0.96	1.11	$\ln(\eta_r)$
0.020	372.1	358.4	428.0	415.0	Time
	457.0	268.0	161.0	84.0	$\dot{\gamma}$
	1.67	1.76	1.86	2.05	η_r
	0.52	0.56	0.62	0.72	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.10	2.62	26.20	127.36	1.60	16.00	39.53
0.0667	2.06	30.75	102.18	1.26	18.81	37.69
0.050	1.68	33.60	87.31	1.02	20.40	35.46
0.0333	1.30	39.39	80.89	0.76	23.03	34.49
0.020	0.83	41.50	64.67	0.51	25.50	33.26

POLYMER: 25-05-01-D
$\bar{M}_n$ = 15.9 x 10^6

$[\eta]_o$ = 56.0 $(g/dl)^{-1}$
$[\eta]_\infty$ = 38.0 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	575.6	575.5	709.5	706.7	Time (Seconds)
	295.0	167.0	97.0	50.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.59	2.82	3.09	3.45	η_r
	0.95	1.04	1.13	1,25	$\ln(\eta_r)$
0.0333	444.4	433.5	523.6	511.8	Time
	383.0	221.0	132.0	68.0	$\dot{\gamma}$
	2.00	2.12	2.28	2.53	η_r
	0.69	0.75	0.82	0.93	$\ln(\eta_r)$
0.0250	384.9	370.7	443.6	429.7	Time
	442.0	259.0	156.0	81.0	$\dot{\gamma}$
	1.73	1.82	1.93	2.12	η_r
	0.55	0.60	0.66	0.75	$\ln(\eta_r)$
0.0167	329.7	312.5	368.6	349.6	Time
	516.0	307.0	187.0	100.0	$\dot{\gamma}$
	1.48	1.53	1.60	1.73	η_r
	0.39	0.43	0.47	0.55	$\ln(\eta_r)$
0.010	287.2	270.1	314.6	293.3	Time
	592.0	355.0	219.0	119.0	$\dot{\gamma}$
	1.29	1.32	1.37	1.45	η_r
	0.26	0.28	0.31	0.37	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.38	27.60	59.50	0.93	18.60	30.69
0.0333	1.09	32.73	59.29	0.67	20.12	28.66
0.0250	0.89	35.60	57.40	0.54	21.60	28.64
0.0167	0.70	41.92	60.70	0.39	23.35	28.56
0.010	0.46	46.00	58.41	0.25	25.00	28.40

POLYMER: 25-05-01-E
$\bar{M}_n$ = 9.98×10^6

$[\eta]_0 = 55.0 \ (g/dl)^{-1}$
$[\eta]_\infty = 28.0 \ (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	639.7	656.5	831.0	853.7	Time (Seconds)
	266.0	146.0	83.0	41.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.88	3.22	3.62	4.22	η_r
	1.06	1.17	1.29	1.44	$\ln(\eta_r)$
0.0333	479.4	476.2	585.7	585.6	Time
	355.0	202.0	118.0	60.0	$\dot{\gamma}$
	2.16	2.33	2.55	2.89	η_r
	0.77	0.85	0.94	1.06	$\ln(\eta_r)$
0.0250	409.3	399.5	483.1	473.3	Time
	415.0	240.0	143.0	74.0	$\dot{\gamma}$
	1.84	1.96	2.10	2.34	η_r
	0.61	0.67	0.74	0.85	$\ln(\eta_r)$
0.0167	342.7	328.1	389.1	371.4	Time
	496.0	293.0	177.0	94.0	$\dot{\gamma}$
	1.54	1.61	1.69	1.84	η_r
	0.43	0.48	0.53	0.61	$\ln(\eta_r)$
0.010	292.4	275.9	321.8	299.8	Time
	581.0	348.0	214.0	117.0	$\dot{\gamma}$
	1.32	1.35	1.40	1.48	η_r
	0.27	0.30	0.34	0.39	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.05	1.61	32.20	80.06	1.05	21.00	37.15
0.0333	1.26	38.18	76.53	0.76	23.03	34.49
0.025	1.06	42.40	75.45	0.60	24.00	32.88
0.0167	0.77	46.11	69.45	0.41	24.55	30.35
0.010	0.51	51.00	66.53	0.27	27.00	31.00

POLYMER: 25-05-01-F
$\bar{M}_n$ = 10.2 x 10^6

$[\eta]_0$ = 52.5 $(g/dl)^{-1}$
$[\eta]_\infty$ = 28.5 $(g/dl)^{-1}$

CONC.	FLOW DATA				
(g/dl)	Bulb 1'	Bulb 2	Bulb 3	Bulb 4	
0.050	643.4	665.6	850.0	881.8	Time (Seconds)
	264.0	144.0	81.0	40.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.90	3.26	3.70	4.36	η_r
	1.06	1.18	1.31	1.47	$\ln(\eta_r)$
0.0333	483.4	483.7	600.1	606.0	Time
	352.0	198.0	115.0	58.0	$\dot{\gamma}$
	2.18	2.37	2.61	3.00	η_r
	0.78	0.86	0.96	1.10	$\ln(\eta_r)$
0.0250	413.0	405.5	493.9	489.7	Time
	412.0	237.0	140.0	71.0	$\dot{\gamma}$
	1.86	1.99	2.15	2.42	η_r
	0.62	0.69	0.77	0.88	$\ln(\eta_r)$
0.0167	344.8	331.7	395.3	380.6	Time
	493.0	289.0	174.0	92.0	$\dot{\gamma}$
	1.55	1.63	1.72	1.88	η_r
	0.44	0.49	0.54	0.63	$\ln(\eta_r)$
0.010	293.9	277.6	326.6	303.5	Time
	578.0	346.0	211.0	115.0	$\dot{\gamma}$
	1.32	1.36	1.42	1.50	η_r
	0.28	0.31	0.35	0.41	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.66	33.20	85.19	1.02	20.40	35.46
0.0333	1.245	37.73	74.94	0.77	23.30	35.14
0.025	1.03	41.20	72.04	0.615	24.60	33.99
0.0167	0.71	42.51	61.92	0.43	25.75	32.17
0.010	0.485	48.50	62.42	0.27	27.00	31.00

POLYMER: 25-05-01-G $[\eta]_0 = 58.0$ $(g/dl)^{-1}$

$\bar{M}_n = 13.1 \times 10^6$ $[\eta]_\infty = 33.5$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	681.4	718.3	937.4	1004.1	Time (Seconds)
	249.0	134.0	74.0	35.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	3.07	3.52	4.08	4.96	η_r
	1.12	1.26	1.41	1.60	$\ln(\eta_r)$
0.0333	505.7	512.9	645.7	666.8	Time
	336.0	187.0	107.0	52.0	$\dot{\gamma}$
	2.28	2.51	2.81	3.30	η_r
	0.82	0.92	1.03	1.19	$\ln(\eta_r)$
0.0250	429.3	425.8	524.0	528.5	Time
	396.0	225.0	132.0	66.0	$\dot{\gamma}$
	1.93	2.09	2.28	2.61	η_r
	0.66	0.74	0.82	0.96	$\ln(\eta_r)$
0.0167	357.9	346.2	415.1	404.3	Time
	475.0	277.0	166.0	87.0	$\dot{\gamma}$
	1.61	1.70	1.81	2.00	η_r
	0.48	0.53	0.59	0.69	$\ln(\eta_r)$
0.010	303.1	286.7	335.7	316.6	Time
	561.0	335.0	206.0	111.0	$\dot{\gamma}$
	1.36	1.41	1.46	1.56	η_r
	0.31	0.34	0.38	0.45	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.80	36.00	100.99	1.05	21.00	37.15
0.0333	1.38	41.44	89.34	0.78	23.42	35.48
0.0250	1.11	44.40	81.37	0.65	26.00	36.62
0.0167	0.82	49.10	76.08	0.47	28.14	35.93
0.010	0.52	52.00	68.20	0.30	30.00	34.99

POLYMER: 25-05-01-H $[\eta]_0 = 54.0 \quad (g/dl)^{-1}$

$\bar{M}_n = 9.98 \times 10^6$ $[\eta]_\infty = 28.0 \quad (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	625.3	657.9	845.8	870.5	Time (Seconds)
	272.0	146.0	82.0	40.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$
	2.81	3.22	3.68	4.30	η_r
	1.03	1.17	1.30	1.46	$\ln(\eta_r)$
0.0333	472.8	480.5	604.3	612.7	Time
	360.0	200.0	114.0	57.0	$\dot{\gamma}$
	2.13	2.36	2.63	3.03	η_r
	0.76	0.86	0.97	1.11	$\ln(\eta_r)$
0.0250	403.1	402.8	497.0	496.6	Time
	422.0	238.0	139.0	70.0	$\dot{\gamma}$
	1.81	1.97	2.16	2.45	η_r
	0.60	0.68	0.77	0.90	$\ln(\eta_r)$
0.0167	339.8	331.7	400.0	389.2	Time
	500.0	289.0	173.0	90.0	$\dot{\gamma}$
	1.53	1.63	1.74	1.92	η_r
	0.42	0.49	0.55	0.65	$\ln(\eta_r)$
0.010	291.4	278.6	328.3	309.9	Time
	583.0	345.0	210.0	113.0	$\dot{\gamma}$
	1.31	1.37	1.43	1.53	η_r
	0.27	0.31	0.36	0.43	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.63	32.60	82.80	0.94	18.80	31.20
0.0333	1.31	39.34	81.27	0.75	22.52	33.54
0.0250	1.06	42.40	75.45	0.59	23.60	32.16
0.0167	0.78	46.71	70.75	0.41	24.55	30.35
0.010	0.50	50.00	64.87	0.26	26.00	29.69

POLYMER: 25-05-01-I $[\eta]_o = 55.0$ $(g/dl)^{-1}$

$\bar{M}_n = 10.8 \times 10^6$ $[\eta]_\infty = 29.5$ $(g/dl)^{-1}$

CONC.	FLOW DATA				
(g/dl)	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	649.3	671.7	854.8	882.1	Time (Seconds)
	262.0	143.0	81.0	40.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.92	3.29	3.72	4.36	η_r
	1.07	1.19	1.13	1.47	$\ln(\eta_r)$
0.0333	485.3	487.0	603.1	605.4	Time
	350.0	197.0	114.0	58.0	$\dot{\gamma}$
	2.18	2.39	2.63	2.99	η_r
	0.78	0.87	0.97	1.10	$\ln(\eta_r)$
0.0250	411.3	404.6	492.1	485.9	Time
	413.0	237.0	140.0	72.0	$\dot{\gamma}$
	1.85	1.98	2.14	2.40	η_r
	0.62	0.68	0.76	0.88	$\ln(\eta_r)$
0.0167	344.7	331.8	395.0	378.9	Time
	493.0	289.0	175.0	92.0	$\dot{\gamma}$
	1.55	1.63	1.72	1.87	η_r
	0.44	0.49	0.54	0.63	$\ln(\eta_r)$
0.010	293.9	278.1	324.6	303.4	Time
	578.0	345.0	213.0	115.0	$\dot{\gamma}$
	1.32	1.36	1.41	1.50	η_r
	0.28	0.31	0.35	0.41	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.66	33.20	85.19	1.00	20.00	34.37
0.0333	1.30	39.04	80.16	0.75	22.52	33.54
0.025	1.05	42.00	74.31	0.60	24.00	32.88
0.0167	0.76	45.51	68.16	0.43	25.75	32.17
0.010	0.49	49.00	63.23	0.27	27.00	31.00

POLYMER: 25-05-05-A $[\eta]_0$ = 29.0 $(g/dl)^{-1}$
$\bar{M}_n$ = 6.30×10^6 $[\eta]_\infty$ = 20.7 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	548.3	532.0	634.6	599.5	Time (Seconds)
	310.0	180.0	109.0	58.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$
	2.47	2.61	2.76	2.96	η_r
	0.90	0.96	1.02	1.09	$\ln(\eta_r)$
0.0333	418.2	399.0	468.0	436.0	Time
	407.0	241.0	147.0	80.0	$\dot{\gamma}$
	1.84	1.96	2.04	2.15	η_r
	0.63	0.67	0.71	0.77	$\ln(\eta_r)$
0.0250	361.2	341.4	397.1	365.7	Time
	471.0	281.0	174.0	96.0	$\dot{\gamma}$
	1.63	1.67	1.73	1.81	η_r
	0.49	0.51	0.55	0.59	$\ln(\eta_r)$
0.0167	309.0	290.4	334.7	304.2	Time
	549.0	331.0	206.0	115.0	$\dot{\gamma}$
	1.39	1.42	1.46	1.50	η_r
	0.33	0.35	0.38	0.41	$\ln(\eta_r)$
0.010	272.5	253.8	290.5	260.9	Time
	624.0	378.0	238.0	134.0	$\dot{\gamma}$
	1.23	1.24	1.26	1.29	η_r
	0.20	0.22	0.23	0.25	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.21	24.20	47.07	0.89	17.80	28.70
0.0333	0.85	25.76	40.60	0.62	18.79	26.03
0.0250	0.66	26.40	37.39	0.48	19.20	24.64
0.0167	0.46	27.54	34.97	0.33	19.76	23.41
0.010	0.28	28.00	32.31	0.20	20.00	22.14

POLYMER: 25-05-05-B $[\eta]_o$ = 30.6 $(g/dl)^{-1}$
$\bar{M}_n$ = 6.44×10^6 $[\eta]_\infty$ = 21.0 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	514.1	507.8	614.0	588.3	Time (Seconds)
	331.0	189.0	112.0	59.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$
	2.31	2.49	2.67	2.91	η_r
	0.84	0.91	0.98	1.07	$\ln(\eta_r)$
0.0333	402.0	390.3	464.8	438.8	Time
	423.0	246.0	148.0	80.0	$\dot{\gamma}$
	1.81	1.91	2.02	2.17	η_r
	0.59	0.65	0.70	0.77	$\ln(\eta_r)$
0.0250	352.4	338.3	398.7	372.8	Time
	482.0	284.0	173.0	94.0	$\dot{\gamma}$
	1.59	1.66	1.74	1.84	η_r
	0.46	0.51	0.55	0.61	$\ln(\eta_r)$
0.0167	306.4	290.6	338.3	311.5	Time
	555.0	330.0	204.0	112.0	$\dot{\gamma}$
	1.38	1.42	1.47	1.54	η_r
	0.32	0.35	0.39	0.43	$\ln(\eta_r)$
0.010	271.5	254.6	293.1	265.7	Time
	626.0	377.0	235.0	132.0	$\dot{\gamma}$
	1.22	1.25	1.28	1.31	η_r
	0.20	0.22	0.24	0.27	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.17	23.40	44.44	0.82	16.40	25.41
0.0333	0.86	25.83	40.94	0.59	17.72	24.14
0.0250	0.66	26.40	37.39	0.46	18.40	23.36
0.0167	0.47	28.14	35.93	0.32	19.16	22.58
0.010	0.29	29.00	33.64	0.20	20.00	22.14

POLYMER: 25-05-05-C $[\eta]_o$ = 26.0 $(g/dl)^{-1}$

$\bar{M}_n$ = 5.31×10^6 $[\eta]_\infty$ = 18.5 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	504.0	487.1	578.9	546.2	Time (Seconds)
	337.0	197.0	119.0	64.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.27	2.39	2.52	2.70	η_r
	0.82	0.87	0.92	0.99	$\ln(\eta_r)$
0.0333	393.4	373.3	436.5	404.3	Time
	432.0	257.0	158.0	87.0	$\dot{\gamma}$
	1.77	1.83	1.90	2.00	η_r
	0.57	0.60	0.64	0.69	$\ln(\eta_r)$
0.0250	343.4	323.9	375.4	344.5	Time
	495.0	296.0	184.0	102.0	$\dot{\gamma}$
	1.55	1.59	1.63	1.70	η_r
	0.44	0.46	0.49	0.53	$\ln(\eta_r)$
0.0167	298.4	279.6	321.6	292.0	Time
	570.0	343.0	215.0	120.0	$\dot{\gamma}$
	1.34	1.37	1.40	1.44	η_r
	0.29	0.32	0.34	0.37	$\ln(\eta_r)$
0.010	265.6	246.9	282.1	253.7	Time
	640.0	389.0	245.0	138.0	$\dot{\gamma}$
	1.20	1.21	1.23	1.25	η_r
	0.18	0.19	0.21	0.23	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.07	21.40	38.31	0.805	16.10	24.73
0.0333	0.76	23.03	34.49	0.567	17.18	23.12
0.0250	0.585	23.40	31.80	0.440	17.60	22.11
0.0167	0.40	23.95	29.45	0.290	17.37	20.15
0.010	0.25	25.00	28.40	0.180	18.00	19.72

POLYMER: 25-05-05-D $[\eta]_o = 29.3$ $(g/dl)^{-1}$

$\bar{M}_n = 5.53 \times 10^6$ $[\eta]_\infty = 19.0$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	488.9	475.4	567.8	537.2	Time (Seconds)
	348.0	202.0	122.0	65.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.20	2.33	2.47	2.66	η_r
	0.79	0.85	0.90	0.98	$\ln(\eta_r)$
0.0333	387.8	372.3	438.8	408.3	Time
	438.0	258.0	157.0	86.0	$\dot{\gamma}$
	1.75	1.82	1.91	2.02	η_r
	0.56	0.60	0.65	0.70	$\ln(\eta_r)$
0.0250	341.9	325.2	380.4	351.9	Time
	497.0	295.0	181.0	99.0	$\dot{\gamma}$
	1.54	1.59	1.66	1.74	η_r
	0.43	0.47	0.50	0.55	$\ln(\eta_r)$
0.0167	300.15	283.1	328.0	300.3	Time
	566.0	339.0	210.0	117.0	$\dot{\gamma}$
	1.35	1.39	1.43	1.48	η_r
	0.30	0.33	0.36	0.39	$\ln(\eta_r)$
0.010	268.5	251.2	288.6	260.9	Time
	633.0	382.0	239.0	134.0	$\dot{\gamma}$
	1.21	1.23	1.26	1.29	η_r
	0.19	0.21	0.23	0.25	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.07	21.40	38.31	0.77	15.40	23.20
0.0333	0.78	23.42	35.48	0.55	16.52	22.02
0.0250	0.61	24.40	33.62	0.425	17.00	21.18
0.0167	0.43	25.75	32.17	0.30	17.96	20.95
0.010	0.27	27.00	31.00	0.18	18.00	19.72

POLYMER: 25-05-05-E $[\eta]_o$ = 29.0 $(g/dl)^{-1}$

$\bar{M}_n$ = 5.90×10^6 $[\eta]_\infty$ = 20.0 $(g/dl)^{-1}$

CONC.	FLOW DATA				
(g/dl)	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	987.7	1005.8	1242.3	1203.3	Time (Seconds)
	172.0	95.0	56.0	29.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$
	4.45	4.93	5.41	5.95	η_r
	1.49	1.60	1.69	1.78	$\ln(\eta_r)$
0.0667	637.7	631.1	763.7	730.6	Time
	267.0	152.0	90.0	48.0	$\dot{\gamma}$
	2.87	3.09	3.32	3.61	η_r
	1.05	1.13	1.20	1.28	$\ln(\eta_r)$
0.050	506.5	491.6	585.1	551.6	Time
	336.0	195.0	118.0	63.0	$\dot{\gamma}$
	2.28	2.41	2.55	2.73	η_r
	0.82	0.88	0.93	1.00	$\ln(\eta_r)$
0.0333	396.8	378.5	443.4	412.1	Time
	428.0	254.0	156.0	85.0	$\dot{\gamma}$
	1.79	1.86	1.93	2.04	η_r
	0.58	0.62	0.66	0.71	$\ln(\eta_r)$
0.020	320.3	301.7	349.4	319.8	Time
	531.0	318.0	198.0	109.0	$\dot{\gamma}$
	1.44	1.48	1.52	1.58	η_r
	0.37	0.39	0.42	0.46	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	1.91	19.10	57.53	1.43	14.30	31.79
0.0667	1.40	20.99	45.81	1.05	15.74	27.85
0.050	1.09	21.80	39.49	0.82	16.40	25.41
0.0333	0.79	23.72	36.14	0.58	17.42	23.60
0.020	0.52	26.00	34.10	0.37	18.50	22.39

POLYMER: 25-05-05-E(duplicate) $[\eta]_o$ = 30.0 (g/dl)$^{-1}$

$\bar{M}_n$ = 6.26 x 10^6 $[\eta]_\infty$ = 20.8 (g/dl)$^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	504.5	491.1	586.7	556.7	Time (Seconds)
	337.0	195.0	118.0	63.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.27	2.41	2.55	2.75	η_r
	0.82	0.88	0.94	1.01	$\ln(\eta_r)$
0.0333	395.6	379.0	446.4	416.5	Time
	430.0	253.0	155.0	84.0	$\dot{\gamma}$
	1.78	1.86	1.94	2.06	η_r
	0.58	0.62	0.66	0.72	$\ln(\eta_r)$
0.0250	347.7	330.2	285.6	257.4	Time
	489.0	291.0	179.0	98.0	$\dot{\gamma}$
	1.56	1.62	1.68	1.77	η_r
	0.45	0.48	0.52	0.57	$\ln(\eta_r)$
0.0167	303.3	285.4	330.1	302.0	Time
	560.0	336.0	209.0	116.0	$\dot{\gamma}$
	1.37	1.40	1.44	1.49	η_r
	0.31	0.34	0.36	0.40	$\ln(\eta_r)$
0.010	270.2	252.7	289.6	262.7	Time
	629.0	380.0	238.0	133.0	$\dot{\gamma}$
	1.22	1.24	1.26	1.30	η_r
	0.20	0.21	0.23	0.26	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.10	22.00	40.08	0.81	16.20	24.96
0.0333	0.80	24.02	36.80	0.58	17.42	23.60
0.025	0.63	25.20	35.10	0.45	18.00	22.73
0.0167	0.45	26.95	34.03	0.31	18.56	21.76
0.010	0.28	28.00	32.31	0.195	19.50	21.53

POLYMER: 25-05-20-A

$\bar{M}_n = 3.40 \times 10^6$

$[\eta]_0 = 20.8 \quad (g/dl)^{-1}$

$[\eta]_\infty = 13.8 \quad (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	622.7	604.4	713.2	657.3	Time (Seconds)
	273.0	159.0	97.0	53.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.80	2.96	3.10	3.25	η_r
	1.03	1.09	1.13	1.18	$\ln(\eta_r)$
0.0667	465.1	448.5	526.0	483.9	Time
	366.0	214.0	131.0	72.0	$\dot{\gamma}$
	2.09	2.20	2.29	2.39	η_r
	0.74	0.79	0.83	0.87	$\ln(\eta_r)$
0.050	398.1	380.5	444.6	408.5	Time
	427.0	252.0	155.0	86.0	$\dot{\gamma}$
	1.79	1.87	1.94	2.02	η_r
	0.58	0.62	0.66	0.70	$\ln(\eta_r)$
0.0333	336.5	319.7	371.0	338.4	Time
	505.0	300.0	186.0	103.0	$\dot{\gamma}$
	1.51	1.57	1.61	1.67	η_r
	0.42	0.45	0.48	0.51	$\ln(\eta_r)$
0.020	290.5	273.3	314.9	285.9	Time
	585.0	351.0	219.0	122.0	$\dot{\gamma}$
	1.31	1.34	1.37	1.41	η_r
	0.27	0.29	0.32	0.35	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	1.24	12.40	24.56	0.98	9.80	16.64
0.0667	0.93	13.94	23.01	0.73	10.94	16.12
0.050	0.75	15.00	22.34	0.57	11.40	15.37
0.0333	0.55	16.52	22.02	0.41	12.31	15.22
0.020	0.37	18.50	22.39	0.26	13.00	14.85

POLYMER: 25-05-25-B $[\eta]_o$ = 22.5 $(g/dl)^{-1}$

$\bar{M}_n$ = 4.26 x 10^6 $[\eta]_\infty$ = 16.0 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	478.9	458.6	540.2	503.8	Time (Seconds)
	355.0	209.0	128.0	70.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.16	2.25	2.35	2.49	η_r
	0.77	0.81	0.85	0.91	$\ln(\eta_r)$
0.0333	378.0	357.1	415.5	381.3	Time
	450.0	269.0	166.0	92.0	$\dot{\gamma}$
	1.70	1.75	1.81	1.88	η_r
	0.53	0.56	0.59	0.63	$\ln(\eta_r)$
0.0250	333.0	312.4	360.7	328.8	Time
	511.0	307.0	191.0	106.0	$\dot{\gamma}$
	1.50	1.53	1.57	1.62	η_r
	0.40	0.43	0.45	0.49	$\ln(\eta_r)$
0.0167	291.5	271.9	311.7	280.7	Time
	583.0	353.0	221.0	125.0	$\dot{\gamma}$
	1.31	1.33	1.36	1.39	η_r
	0.27	0.29	0.31	0.33	$\ln(\eta_r)$
0.010	261.5	242.7	276.4	247.1	Time
	650.0	395.0	250.0	142.0	$\dot{\gamma}$
	1.18	1.19	1.20	1.22	η_r
	0.16	0.17	0.18	0.20	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.985	19.70	33.56	0.76	15.20	22.77
0.0333	0.680	20.61	29.51	0.525	15.91	20.92
0.0250	0.530	21.20	27.96	0.40	16.00	19.67
0.0167	0.355	21.26	25.52	0.27	16.17	18.56
0.010	0.220	22.00	26.61	0.16	16.00	17.35

POLYMER: 25-05-25-C $[\eta]_o = 22.5$ $(g/dl)^{-1}$

$\bar{M}_n = 4.26 \times 10^6$ $[\eta]_\infty = 16.0$ $(g/dl)^{-1}$

CONC.	FLOW DATA				
(g/dl)	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	467.2	446.8	525.8	490.8	Time (Seconds)
	364.0	215.0	131.0	71.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.10	2.19	2.29	2.43	η_r
	0.74	0.78	0.83	0.89	$\ln(\eta_r)$
0.0333	370.0	349.7	406.2	372.6	Time
	459.0	275.0	170.0	94.0	$\dot{\gamma}$
	1.67	1.71	1.77	1.84	η_r
	0.51	0.54	0.57	0.61	$\ln(\eta_r)$
0.0250	327.4	307.2	354.6	321.8	Time
	519.0	313.0	195.0	109.0	$\dot{\gamma}$
	1.47	1.51	1.54	1.59	η_r
	0.39	0.41	0.43	0.46	$\ln(\eta_r)$
0.0167	289.1	269.9	308.6	278.1	Time
	588.0	356.0	224.0	126.0	$\dot{\gamma}$
	1.30	1.32	1.34	1.37	η_r
	0.26	0.28	0.30	0.32	$\ln(\eta_r)$
0.010	261.0	242.3	275.6	246.1	Time
	651.0	396.0	250.0	142.0	$\dot{\gamma}$
	1.17	1.19	1.20	1.22	η_r
	0.16	0.17	0.18	0.20	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.965	19.30	32.50	0.71	14.20	20.68
0.0333	0.670	20.30	28.92	0.50	15.50	19.66
0.0250	0.500	20.00	25.95	0.385	15.40	18.78
0.0167	0.355	21.26	25.52	0.255	15.27	17.39
0.010	0.220	22.00	24.61	0.155	15.50	16.77

POLYMER: 25-05-25-D $[\eta]_o$ = 18.6 $(g/dl)^{-1}$

$\bar{M}_n$ = 3.67×10^6 $[\eta]_\infty$ = 14.5 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	768.9	756.5	906.4	84.9	Time (Seconds)
	221.0	127.0	76.0	41.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$
	3.46	3.71	3.95	4.20	η_r
	1.24	1.31	1.37	1.43	$\ln(\eta_r)$
0.0667	529.0	511.2	603.9	558.9	Time
	321.0	118.0	114.0	63.0	$\dot{\gamma}$
	2.38	2.51	2.63	2.76	η_r
	0.87	0.92	0.97	1.02	$\ln(\eta_r)$
0.050	435.2	415.3	485.2	445.4	Time
	391.0	231.0	142.0	79.0	$\dot{\gamma}$
	1.96	2.04	2.11	2.20	η_r
	0.67	0.71	0.75	0.79	$\ln(\eta_r)$
0.0333	352.5	332.3	383.6	348.7	Time
	482.0	289.0	180.0	100.0	$\dot{\gamma}$
	1.59	1.63	1.67	1.72	η_r
	0.46	0.49	0.51	0.54	$\ln(\eta_r)$
0.020	295.7	276.3	316.0	283.8	Time
	575.0	347.0	218.0	123.0	$\dot{\gamma}$
	1.33	1.35	1.38	1.40	η_r
	0.29	0.30	0.32	0.34	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	1.51	15.10	35.27	1.19	11.90	22.87
0.0667	1.09	16.34	29.60	0.86	12.89	20.44
0.050	0.85	17.00	26.79	0.66	13.20	18.70
0.0333	0.57	17.12	23.07	0.45	13.51	17.07
0.020	0.36	18.00	21.67	0.28	14.00	16.16

POLYMER: 25-05-25-E $[\eta]_o$ = 23.8 $(g/dl)^{-1}$

$\bar{M}_n$ = 4.38×10^6 $[\eta]_\infty$ = 16.3 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	445.0	427.5	503.3	466.6	Time (Seconds)
	382.0	225.0	137.0	75.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.00	2.10	2.19	2.31	η_r
	0.69	0.74	0.78	0.84	$\ln(\eta_r)$
0.0333	360.0	342.1	398.0	364.7	Time
	472.0	281.0	173.0	96.0	$\dot{\gamma}$
	1.62	1.68	1.73	1.80	η_r
	0.48	0.52	0.55	0.59	$\ln(\eta_r)$
0.0250	321.9	303.8	351.2	320.3	Time
	528.0	316.0	196.0	109.0	$\dot{\gamma}$
	1.45	1.49	1.53	1.58	η_r
	0.37	0.40	0.42	0.46	$\ln(\eta_r)$
0.0167	286.7	268.4	308.7	278.6	Time
	593.0	358.0	224.0	126.0	$\dot{\gamma}$
	1.29	1.32	1.34	1.38	η_r
	0.25	0.27	0.29	0.32	$\ln(\eta_r)$
0.010	260.5	242.3	276.4	247.9	Time
	652.0	396.0	250.0	141.0	$\dot{\gamma}$
	1.17	1.19	1.20	1.22	η_r
	0.16	0.17	0.18	0.20	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.915	18.30	29.94	0.680	13.60	19.48
0.0333	0.645	19.37	27.21	0.480	14.41	18.50
0.0250	0.510	20.40	26.61	0.365	14.60	17.62
0.0167	0.360	21.56	25.95	0.255	15.27	17.39
0.010	0.225	22.50	25.23	0.160	16.00	17.35

POLYMER: 25-05-25-F $[\eta]_o$ = 20.5 $(g/dl)^{-1}$

$\bar{M}_n$ = 3.71×10^6 $[\eta]_\infty$ = 14.6 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	419.2	400.0	466.9	427.3	Time (Seconds)
	406.0	240.0	148.0	82.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	1.89	1.96	2.03	2.11	η_r
	0.64	0.67	0.71	0.75	$\ln(\eta_r)$
0.0333	344.6	326.0	376.8	342.0	Time
	493.0	294.0	183.0	102.0	$\dot{\gamma}$
	1.55	1.60	1.64	1.69	η_r
	0.44	0.47	0.49	0.52	$\ln(\eta_r)$
0.0250	311.0	292.0	336.0	303.0	Time
	546.0	329.0	205.0	115.0	$\dot{\gamma}$
	1.40	1.43	1.46	1.50	η_r
	0.34	0.36	0.38	0.40	$\ln(\eta_r)$
0.0167	279.6	261.0	298.3	267.7	Time
	608.0	368.0	231.0	131.0	$\dot{\gamma}$
	1.26	1.28	1.30	1.32	η_r
	0.23	0.25	0.26	0.28	$\ln(\eta_r)$
0.010	256.3	237.9	270.5	241.1	Time
	663.0	404.0	255.0	145.0	$\dot{\gamma}$
	1.15	1.17	1.18	1.19	η_r
	0.14	0.15	0.16	0.17	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.81	16.20	24.96	0.62	12.40	17.18
0.0333	0.59	17.72	24.14	0.435	13.06	16.36
0.0250	0.44	17.60	22.11	0.335	13.40	15.92
0.0167	0.305	18.26	21.35	0.230	13.77	15.48
0.010	0.195	19.50	21.53	0.14	14.00	15.03

POLYMER: 40-20-05-A $[\eta]_0 = 21.3$ $(g/dl)^{-1}$

$\bar{M}_n = 4.47 \times 10^6$ $[\eta]_\infty = 16.5$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	456.4	437.9	513.7	472.8	Time (Seconds)
	372.0	219.0	134.0	74.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.05	2.15	2.24	2.34	η_r
	0.72	0.76	0.80	0.85	$\ln(\eta_r)$
0.0333	364.4	345.9	401.7	366.2	Time
	467.0	278.0	172.0	96.0	$\dot{\gamma}$
	1.64	1.70	1.75	1.81	η_r
	0.49	0.53	0.56	0.59	$\ln(\eta_r)$
0.0250	324.05	305.2	351.7	318.3	Time
	525.0	315.0	196.0	110.0	$\dot{\gamma}$
	1.46	1.50	1.53	1.57	η_r
	0.38	0.40	0.43	0.45	$\ln(\eta_r)$
0.0167	287.5	268.8	307.8	276.1	Time
	591.0	357.0	224.0	127.0	$\dot{\gamma}$
	1.29	1.32	1.34	1.36	η_r
	0.26	0.28	0.29	0.31	$\ln(\eta_r)$
0.010	260.6	242.0	275.3	245.7	Time
	652.0	397.0	251.0	142.0	$\dot{\gamma}$
	1.17	1.19	1.20	1.21	η_r
	0.16	0.17	0.18	0.19	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.92	18.40	30.19	0.70	14.00	20.28
0.0333	0.63	18.92	26.35	0.495	14.86	19.23
0.0250	0.485	19.40	24.97	0.375	15.00	18.20
0.0167	0.335	20.06	23.83	0.257	15.39	17.55
0.010	0.205	20.50	22.75	0.160	16.00	17.35

POLYMER: 40-20-05-B

$\bar{M}_n \cong 5.01 \times 10^6$

$[\eta]_o = 26.0$ $(g/dl)^{-1}$

$[\eta]_\infty = 17.8$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	894.6	909.6	1118.3	1077.1	Time (Seconds)
	190.0	106.0	62.0	32.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$
	4.03	4.46	4.87	5.32	η_r
	1.39	1.49	1.58	1.67	$\ln(\eta_r)$
0.0667	605.9	601.3	728.6	694.8	Time
	281.0	160.0	95.0	50.0	$\dot{\gamma}$
	2.73	2.95	3.17	3.43	η_r
	1.00	1.08	1.15	1.23	$\ln(\eta_r)$
0.050	484.9	474.9	569.6	541.3	Time
	351.0	202.0	121.0	65.0	$\dot{\gamma}$
	2.81	2.33	2.48	2.68	η_r
	0.78	0.85	0.91	0.98	$\ln(\eta_r)$
0.0333	384.0	368.7	434.7	406.1	Time
	443.0	260.0	159.0	86.0	$\dot{\gamma}$
	1.73	1.81	1.89	2.01	η_r
	0.55	0.59	0.64	0.70	$\ln(\eta_r)$
0.020	313.7	296.7	344.7	316.4	Time
	542.0	324.0	200.0	111.0	$\dot{\gamma}$
	1.41	1.45	1.50	1.56	η_r
	0.34	0.37	0.41	0.45	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	1.81	18.10	51.10	1.32	13.20	27.43
0.0667	1.33	19.94	41.69	0.98	14.69	24.95
0.050	1.08	21.60	38.89	0.77	15.40	23.20
0.0333	0.78	23.42	35.48	0.54	16.22	21.50
0.020	0.48	24.00	30.80	0.33	16.50	19.55

POLYMER: 40-20-05-C $[\eta]_0 = 25.0$ $(g/dl)^{-1}$
$\bar{M}_n = 4.67 \times 10^6$ $[\eta]_\infty = 17.0$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	849.1	853.0	1031.9	973.7	Time (Seconds)
	200.0	113.0	67.0	36.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	3.82	4.18	4.49	4.81	η_r
	1.34	1.43	1.50	1.57	$\ln(\eta_r)$
0.0667	579.4	573.7	689.0	647.3	Time
	293.0	167.0	100.0	54.0	$\dot{\gamma}$
	2.61	2.81	3.00	3.20	η_r
	0.96	1.03	1.10	1.16	$\ln(\eta_r)$
0.050	470.1	459.1	546.3	511.4	Time
	362.0	209.0	126.0	68.0	$\dot{\gamma}$
	2.12	2.25	2.38	2.53	η_r
	0.75	0.81	0.87	0.93	$\ln(\eta_r)$
0.0333	376.6	362.7	426.6	395.6	Time
	451.0	265.0	162.0	88.0	$\dot{\gamma}$
	1.69	1.78	1.86	1.96	η_r
	0.53	0.58	0.62	0.67	$\ln(\eta_r)$
0.020	310.5	294.6	341.7	312.6	Time
	548.0	326.0	202.0	112.0	$\dot{\gamma}$
	1.40	1.44	1.49	1.54	η_r
	0.33	0.37	0.40	0.43	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	1.66	16.60	42.59	1.29	12.90	26.33
0.0667	1.25	18.74	37.34	0.95	14.24	23.77
0.050	1.01	20.20	34.91	0.74	14.80	21.92
0.0333	0.72	21.62	31.66	0.52	15.62	20.48
0.020	0.46	23.00	29.20	0.32	16.00	18.86

POLYMER: 40-20-05-D $[\eta]_o = 22.8$ $(g/dl)^{-1}$
$\bar{M}_n = 4.67 \times 10^6$ $[\eta]_\infty = 17.0$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	471.9	453.9	535.0	498.0	Time (Seconds)
	360.0	211.0	129.0	70.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.12	2.23	2.33	2.46	η_r
	0.75	0.80	0.85	0.90	$\ln(\eta_r)$
0.0333	373.7	354.7	412.55	378.9	Time
	455.0	271.0	167.0	92.0	$\dot{\gamma}$
	1.68	1.74	1.80	1.87	η_r
	0.52	0.55	0.59	0.63	$\ln(\eta_r)$
0.0250	330.4	311.3	359.4	327.6	Time
	515.0	308.0	192.0	107.0	$\dot{\gamma}$
	1.49	1.53	1.59	1.62	η_r
	0.40	0.42	0.45	0.48	$\ln(\eta_r)$
0.0167	291.0	272.0	311.8	281.3	Time
	584.0	353.0	221.0	124.0	$\dot{\gamma}$
	1.31	1.33	1.36	1.39	η_r
	0.27	0.29	0.31	0.33	$\ln(\eta_r)$
0.010	262.6	243.9	277.7	248.1	Time
	647.0	394.0	248.0	141.0	$\dot{\gamma}$
	1.18	1.20	1.21	1.23	η_r
	0.17	0.18	0.19	0.20	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.965	19.30	32.50	0.73	14.60	21.50
0.0333	0.69	20.72	29.84	0.515	15.47	20.23
0.0250	0.515	20.60	26.95	0.40	16.00	19.67
0.0167	0.36	21.56	25.96	0.265	15.87	18.17
0.010	0.22	22.00	24.61	0.165	16.50	17.94

POLYMER: 40-20-05-E

$\bar{M}_n$ = 4.47×10^6

$[\eta]_o = 23.5$ $(g/dl)^{-1}$

$[\eta]_\infty = 16.5$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	457.4	438.7	515.9	478.5	Time (Seconds)
	372.0	219.0	134.0	73.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.06	2.15	2.25	2.36	η_r
	0.72	0.77	0.81	0.86	$\ln(\eta_r)$
0.0333	366.2	347.8	404.6	370.8	Time
	464.0	276.0	171.0	94.0	$\dot{\gamma}$
	1.65	1.70	1.76	1.83	η_r
	0.50	0.53	0.57	0.61	$\ln(\eta_r)$
0.0250	325.6	306.9	354.4	322.1	Time
	522.0	313.0	195.0	109.0	$\dot{\gamma}$
	1.47	1.50	1.54	1.59	η_r
	0.38	0.41	0.43	0.46	$\ln(\eta_r)$
0.0167	288.7	270.2	310.0	279.4	Time
	589.0	355.0	223.0	125.0	$\dot{\gamma}$
	1.30	1.32	1.35	1.38	η_r
	0.26	0.28	0.30	0.32	$\ln(\eta_r)$
0.010	261.4	242.9	276.6	247.9	Time
	650.0	395.0	249.0	141.0	$\dot{\gamma}$
	1.18	1.19	1.20	1.23	η_r
	0.16	0.17	0.19	0.20	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.935	18.70	30.94	0.705	14.10	20.48
0.0333	0.685	20.57	29.54	0.495	14.86	19.23
0.0250	0.505	20.20	26.28	0.375	15.00	18.20
0.0167	0.355	21.26	25.52	0.257	15.39	17.55
0.010	0.225	22.50	25.23	0.160	16.00	17.35

POLYMER: 40-20-05-F
$\bar{M}_n$ = 4.14 x 10^6

$[\eta]_o$ = 21.2 $(g/dl)^{-1}$
$[\eta]_\infty$ = 15.7 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	424.9	408.2	478.2	439.2	Time (Seconds)
	400.0	235.0	144.0	80.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$
	1.91	2.00	2.08	2.17	η_r
	0.65	0.69	0.73	0.78	$\ln(\eta_r)$
0.0333	349.1	332.3	385.7	351.5	Time
	487.0	289.0	179.0	100.0	$\dot{\gamma}$
	1.57	1.63	1.68	1.74	η_r
	0.45	0.49	0.52	0.55	$\ln(\eta_r)$
0.0250	314.9	297.1	342.8	310.8	Time
	540.0	323.0	201.0	113.0	$\dot{\gamma}$
	1.42	1.46	1.49	1.54	η_r
	0.35	0.38	0.40	0.43	$\ln(\eta_r)$
0.0167	282.6	264.5	303.3	272.6	Time
	602.0	363.0	228.0	128.0	$\dot{\gamma}$
	1.27	1.30	1.32	1.35	η_r
	0.24	0.26	0.28	0.30	$\ln(\eta_r)$
0.010	257.8	239.8	272.8	243.9	Time
	660.0	400.0	253.0	144.0	$\dot{\gamma}$
	1.16	1.18	1.19	1.21	η_r
	0.15	0.16	0.17	0.19	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.86	17.20	27.26	0.63	12.60	17.55
0.0333	0.60	18.02	24.69	0.44	13.21	16.60
0.0250	0.47	18.80	24.00	0.35	14.00	16.76
0.0167	0.33	19.76	23.41	0.24	14.37	16.24
0.010	0.20	20.00	22.14	0.15	15.00	16.18

POLYMER: 40-20-05-G
$\bar{M}_n = 3.33 \times 10^6$

$[\eta]_0 = 20.2$ $(g/dl)^{-1}$
$[\eta]_\infty = 13.6$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	684.5	669.8	792.1	729.7	Time (Seconds)
	248.0	143.0	87.0	48.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	3.08	3.28	3.45	3.61	η_r
	1.13	1.19	1.24	1.28	$\ln(\eta_r)$
0.0667	492.9	478.3	562.5	515.9	Time
	345.0	201.0	123.0	68.0	$\dot{\gamma}$
	2.22	2.34	2.45	2.55	η_r
	0.80	0.85	0.90	0.94	$\ln(\eta_r)$
0.050	412.8	396.2	462.7	423.9	Time
	412.0	242.0	149.0	83.0	$\dot{\gamma}$
	1.86	1.94	2.01	2.10	η_r
	0.62	0.66	0.70	0.74	$\ln(\eta_r)$
0.0333	342.4	324.9	376.6	341.9	Time
	497.0	295.0	183.0	102.0	$\dot{\gamma}$
	1.54	1.59	1.64	1.69	η_r
	0.43	0.47	0.49	0.52	$\ln(\eta_r)$
0.020	291.5	273.4	314.1	283.6	Time
	583.0	351.0	220.0	123.0	$\dot{\gamma}$
	1.31	1.34	1.37	1.40	η_r
	0.27	0.29	0.31	0.34	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	1.35	13.50	28.57	1.06	10.60	18.86
0.0667	1.01	15.14	26.17	0.78	11.69	17.71
0.050	0.81	16.20	24.96	0.61	12.20	16.81
0.0333	0.57	17.12	23.07	0.42	12.61	15.67
0.020	0.37	18.50	22.39	0.26	13.00	14.85

POLYMER: 40-05-05-A
$\bar{M}_n$ = 2.86 x 10^6

$[\eta]_o$ = 15.8 $(g/dl)^{-1}$
$[\eta]_\infty$ = 12.3 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	651.1	626.9	730.7	662.6	Time (Seconds)
	261.0	153.0	94.0	53.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.93	3.07	3.18	3.27	η_r
	1.08	1.12	1.16	1.19	$\ln(\eta_r)$
0.0667	469.3	448.1	519.2	469.0	Time
	362.0	214.0	133.0	75.0	$\dot{\gamma}$
	2.11	2.20	2.26	2.32	η_r
	0.75	0.79	0.82	0.84	$\ln(\eta_r)$
0.050	394.4	373.1	429.9	386.9	Time
	431.0	257.0	160.0	90.0	$\dot{\gamma}$
	1.78	1.83	1.87	1.91	η_r
	0.57	0.60	0.63	0.65	$\ln(\eta_r)$
0.0333	329.3	309.1	353.8	316.9	Time
	516.0	311.0	195.0	110.0	$\dot{\gamma}$
	1.48	1.52	1.54	1.57	η_r
	0.39	0.42	0.43	0.45	$\ln(\eta_r)$
0.020	283.4	263.7	300.1	267.5	Time
	600.0	364.0	230.0	131.0	$\dot{\gamma}$
	1.28	1.29	1.31	1.32	η_r
	0.24	0.26	0.27	0.28	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	1.24	12.40	24.56	1.05	10.50	18.58
0.0667	0.87	13.04	20.79	0.74	11.09	16.43
0.050	0.68	13.60	19.48	0.56	11.20	15.01
0.0333	0.48	14.41	18.50	0.39	11.71	14.32
0.020	0.30	15.00	17.49	0.24	12.00	13.56

POLYMER: 40-05-05-B $[\eta]_o = 18.0$ $(g/dl)^{-1}$

$\bar{M}_n = 3.29 \times 10^6$ $[\eta]_\infty = 13.5$ $(g/dl)^{-1}$

CONC.	FLOW DATA				
(g/dl)	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	697.0	679.8	801.4	735.1	Time (Seconds)
	244.0	141.0	86.0	48.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	3.14	3.33	3.49	3.63	η_r
	1.14	1.20	1.25	1.29	$\ln(\eta_r)$
0.0667	496.8	479.7	561.0	511.4	Time
	342.0	200.0	123.0	68.0	$\dot{\gamma}$
	2.24	2.35	2.44	2.53	η_r
	0.80	0.86	0.89	0.93	$\ln(\eta_r)$
0.050	415.2	395.5	462.6	421.1	Time
	409.0	243.0	149.0	83.0	$\dot{\gamma}$
	1.87	1.94	2.01	2.08	η_r
	0.63	0.66	0.70	0.73	$\ln(\eta_r)$
0.0333	342.8	324.8	375.6	340.6	Time
	496.0	296.0	184.0	103.0	$\dot{\gamma}$
	1.54	1.59	1.63	1.68	η_r
	0.43	0.47	0.49	0.52	$\ln(\eta_r)$
0.020	292.4	274.0	314.2	283.2	Time
	581.0	350.0	220.0	124.0	$\dot{\gamma}$
	1.32	1.34	1.37	1.40	η_r
	0.27	0.30	0.31	0.34	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	1.32	13.20	27.43	1.10	11.00	20.04
0.0667	0.98	14.69	24.95	0.77	11.54	17.39
0.050	0.77	15.40	23.20	0.62	12.40	17.18
0.0333	0.54	16.22	21.50	0.42	12.61	15.67
0.020	0.34	17.00	20.25	0.26	13.00	14.85

POLYMER: 40-05-05-C

$\bar{M}_n = 3.67 \times 10^6$

$[\eta]_o = 18.0 \quad (g/dl)^{-1}$

$[\eta]_\infty = 14.5 \quad (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	413.9	395.2	461.1	422.1	Time (Seconds)
	411.0	243.0	150.0	83.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$
	1.86	1.94	2.01	2.09	η_r
	0.62	0.66	0.70	0.74	$\ln(\eta_r)$
0.0333	340.5	321.8	372.0	337.6	Time
	499.0	298.0	186.0	104.0	$\dot{\gamma}$
	1.53	1.58	1.62	1.67	η_r
	0.43	0.46	0.48	0.51	$\ln(\eta_r)$
0.0250	308.0	289.1	332.2	299.7	Time
	552.0	332.0	208.0	117.0	$\dot{\gamma}$
	1.39	1.42	1.45	1.48	η_r
	0.33	0.35	0.37	0.39	$\ln(\eta_r)$
0.0167	277.4	258.9	295.5	265.2	Time
	613.0	371.0	234.0	132.0	$\dot{\gamma}$
	1.25	1.27	1.29	1.31	η_r
	0.22	0.24	0.25	0.27	$\ln(\eta_r)$
0.010	254.7	236.1	267.9	238.7	Time
	667.0	407.0	258.0	147.0	$\dot{\gamma}$
	1.15	1.16	1.17	1.18	η_r
	0.14	0.15	0.15	0.17	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.80	16.00	24.51	0.61	12.20	16.81
0.0333	0.55	16.52	22.02	0.43	12.91	16.13
0.0250	0.41	16.40	20.27	0.33	13.20	15.64
0.0167	0.29	17.37	20.15	0.22	13.17	14.74
0.010	0.175	17.50	19.12	0.14	14.00	15.03

POLYMER: 40-05-05-D $[\eta]_0 = 16.8$ $(g/dl)^{-1}$

$\bar{M}_n = 3.29 \times 10^6$ $[\eta]_\infty = 13.5$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	714.9	697.0	821.7	754.9	Time (Seconds)
	238.0	138.0	84.0	46.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	3.22	3.42	3.58	3.73	η_r
	1.77	1.23	1.27	1.32	$\ln(\eta_r)$
0.0667	499.9	482.3	564.8	516.0	Time
	340.0	199.0	122.0	68.0	$\dot{\gamma}$
	2.25	2.36	2.46	2.55	η_r
	0.81	0.86	0.90	0.94	$\ln(\eta_r)$
0.050	414.6	394.9	457.7	415.2	Time
	410.0	243.0	151.0	84.0	$\dot{\gamma}$
	1.87	1.94	1.99	2.05	η_r
	0.62	0.66	0.69	0.72	$\ln(\eta_r)$
0.0333	340.7	321.2	369.5	332.2	Time
	499.0	299.0	187.0	105.0	$\dot{\gamma}$
	1.53	1.57	1.61	1.64	η_r
	0.43	0.45	0.48	0.50	$\ln(\eta_r)$
0.020	289.2	269.9	308.1	275.4	Time
	588.0	356.0	224.0	127.0	$\dot{\gamma}$
	1.30	1.32	1.34	1.36	η_r
	0.26	0.28	0.29	0.31	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	1.38	13.80	29.75	1.13	11.30	20.96
0.0667	1.00	14.99	25.76	0.79	11.84	18.04
0.050	0.76	15.20	22.77	0.61	12.20	16.81
0.0333	0.53	15.92	20.99	0.42	12.61	15.67
0.020	0.32	16.00	18.86	0.26	13.00	14.85

POLYMER: 40-05-05-E $\quad [\eta]_o = 16.5 \quad (g/dl)^{-1}$

$\bar{M}_n = 3.11 \times 10^6 \quad [\eta]_\infty = 13.0 \quad (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	653.0	628.4	731.0	659.3	Time (Seconds)
	260.0	153.0	94.0	53.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.94	3.08	3.18	3.26	η_r
	1.08	1.13	1.16	1.18	$\ln(\eta_r)$
0.0667	472.8	451.8	523.0	470.2	Time
	360.0	212.0	132.0	74.0	$\dot{\gamma}$
	2.13	2.22	2.28	2.32	η_r
	0.76	0.80	0.82	0.84	$\ln(\eta_r)$
0.050	398.2	377.4	434.8	391.6	Time
	427.0	254.0	159.0	89.0	$\dot{\gamma}$
	1.79	1.85	1.89	1.94	η_r
	0.58	0.62	0.64	0.66	$\ln(\eta_r)$
0.0333	332.5	313.0	358.9	321.6	Time
	511.0	307.0	192.0	109.0	$\dot{\gamma}$
	1.50	1.53	1.56	1.59	η_r
	0.40	0.43	0.45	0.46	$\ln(\eta_r)$
0.020	285.7	266.4	303.8	271.5	Time
	595.0	360.0	227.0	129.0	$\dot{\gamma}$
	1.29	1.31	1.32	1.34	η_r
	0.25	0.27	0.28	0.29	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	1.23	12.30	24.21	1.06	10.60	18.86
0.0667	0.88	13.19	21.15	0.75	11.24	16.75
0.050	0.70	14.00	20.28	0.58	11.60	15.72
0.0333	0.49	14.71	18.99	0.40	12.01	14.77
0.020	0.31	15.50	18.17	0.25	12.50	14.20

POLYMER: 40-05-05-F $[\eta]_0 = 19.0 \quad (g/dl)^{-1}$

$\bar{M}_n = 3.51 \times 10^6$ $[\eta]_\infty = 14.2 \quad (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	432.9	412.8	481.9	441.8	Time (Seconds)
	393.0	233.0	143.0	79.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	1.95	2.02	2.10	2.18	η_r
	0.67	0.70	0.74	0.78	$\ln(\eta_r)$
0.0333	350.9	331.7	383.9	348.7	Time
	484.0	289.0	180.0	100.0	$\dot{\gamma}$
	1.58	1.63	1.67	1.72	η_r
	0.46	0.49	0.51	0.54	$\ln(\eta_r)$
0.0250	314.2	295.1	339.2	306.1	Time
	541.0	325.0	203.0	114.0	$\dot{\gamma}$
	1.41	1.45	1.48	1.51	η_r
	0.35	0.37	0.39	0.41	$\ln(\eta_r)$
0.0167	280.6	261.6	298.5	267.7	Time
	606.0	367.0	231.0	131.0	$\dot{\gamma}$
	1.26	1.28	1.30	1.32	η_r
	0.23	0.25	0.26	0.28	$\ln(\eta_r)$
0.010	256.0	237.5	269.7	240.0	Time
	664.0	404.0	256.0	146.0	$\dot{\gamma}$
	1.15	1.16	1.17	1.19	η_r
	0.14	0.15	0.16	0.17	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.85	17.00	26.79	0.66	13.20	18.70
0.0333	0.593	17.97	24.53	0.455	13.79	17.46
0.0250	0.435	17.40	21.80	0.35	14.00	16.76
0.0167	0.310	18.56	21.76	0.23	13.77	15.49
0.010	0.190	19.00	20.92	0.14	14.00	15.03

POLYMER: 40-05-05-F(duplicate) $[\eta]_0 = 18.0$ $(g/dl)^{-1}$
$\bar{M}_n$ = 3.25×10^6 $[\eta]_\infty = 13.5$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	421.9	401.8	467.6	426.7	Time (Seconds)
	403.0	239.0	148.0	82.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	1.90	1.97	2.04	2.11	η_r
	0.64	0.68	0.71	0.75	$\ln(\eta_r)$
0.0333	343.5	324.5	375.2	339.9	Time
	495.0	296.0	184.0	103.0	$\dot{\gamma}$
	1.55	1.59	1.63	1.68	η_r
	0.44	0.46	0.49	0.52	$\ln(\eta_r)$
0.0250	309.4	290.0	332.5	299.1	Time
	549.0	331.0	208.0	117.0	$\dot{\gamma}$
	1.39	1.42	1.45	1.48	η_r
	0.33	0.35	0.37	0.39	$\ln(\eta_r)$
0.0167	278.0	258.8	294.8	264.0	Time
	612.0	371.0	234.0	133.0	$\dot{\gamma}$
	1.25	1.27	1.28	1.30	η_r
	0.22	0.24	0.25	0.27	$\ln(\eta_r)$
0.010	254.7	235.9	267.6	237.8	Time
	667.0	407.0	258.0	147.0	$\dot{\gamma}$
	1.15	1.16	1.16	1.18	η_r
	0.14	0.15	0.15	0.16	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.82	16.40	25.41	0.63	12.60	17.55
0.0333	0.57	17.27	23.28	0.435	13.18	16.51
0.025	0.418	16.72	20.76	0.325	13.00	15.36
0.0167	0.30	17.96	20.95	0.22	13.17	14.74
0.010	0.175	17.50	19.12	0.14	14.00	15.03

POLYMER: 40-05-05-G $\quad [\eta]_o = 17.0 \quad (g/dl)^{-1}$

$\bar{M}_n = 3.04 \times 10^6 \quad [\eta]_\infty = 12.8 \quad (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	413.9	393.9	457.7	417.4	Time (Seconds)
	411.0	244.0	151.0	84.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	1.86	1.93	1.99	2.06	η_r
	0.62	0.66	0.69	0.72	$\ln(\eta_r)$
0.0333	339.8	320.2	368.8	333.2	Time
	500.0	300.0	187.0	105.0	$\dot{\gamma}$
	1.53	1.57	1.61	1.65	η_r
	0.42	0.45	0.47	0.50	$\ln(\eta_r)$
0.0250	302.5	282.8	323.4	289.8	Time
	562.0	340.0	213.0	121.0	$\dot{\gamma}$
	1.36	1.39	1.41	1.43	η_r
	0.31	0.33	0.34	0.36	$\ln(\eta_r)$
0.0167	274.0	254.9	290.0	258.7	Time
	620.0	377.0	238.0	135.0	$\dot{\gamma}$
	1.23	1.25	1.26	1.28	η_r
	0.21	0.22	0.23	0.25	$\ln(\eta_r)$
0.010	252.9	234.3	265.5	235.7	Time
	672.0	410.0	260.0	149.0	$\dot{\gamma}$
	1.14	1.15	1.16	1.16	η_r
	0.13	0.14	0.14	0.15	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.76	15.20	22.77	0.61	12.20	16.81
0.0333	0.543	16.45	21.85	0.415	12.58	15.59
0.0250	0.390	15.60	19.08	0.31	12.40	14.54
0.0167	0.277	16.59	19.11	0.21	12.57	13.99
0.010	0.165	16.50	17.94	0.13	13.00	13.88

POLYMER: 40-02-05-A $[\eta]_0 = 11.7$ $(g/dl)^{-1}$
$\bar{M}_n = 1.90 \times 10^6$ $[\eta]_\infty = 9.4$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	505.3	474.9	543.1	485.5	Time (Seconds)
	336.0	202.0	127.0	72.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.274	2.328	2.364	2.399	η_r
	0.822	0.845	0.860	0.875	$\ln(\eta_r)$
0.0667	392.8	367.9	419.6	373.9	Time
	433.0	261.0	164.0	94.0	$\dot{\gamma}$
	1.768	1.804	1.826	1.848	η_r
	0.570	0.590	0.602	0.614	$\ln(\eta_r)$
0.050	344.2	320.9	365.3	324.6	Time
	494.0	299.0	189.0	109.0	$\dot{\gamma}$
	1.549	1.573	1.590	1.604	η_r
	0.438	0.453	0.464	0.473	$\ln(\eta_r)$
0.0333	299.7	278.1	315.6	280.0	Time
	567.0	345.0	219.0	125.0	$\dot{\gamma}$
	1.349	1.363	1.374	1.384	η_r
	0.299	0.310	0.318	0.325	$\ln(\eta_r)$
0.020	267.9	247.15	279.7	247.5	Time
	635.0	388.0	247.0	141.0	$\dot{\gamma}$
	1.206	1.212	1.217	1.223	η_r
	0.187	0.192	0.197	0.201	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.90	9.00	14.60	0.82	8.20	12.70
0.0667	0.64	9.60	13.44	0.57	8.55	11.52
0.050	0.50	10.00	12.97	0.43	8.60	10.75
0.0333	0.35	10.51	12.58	0.30	9.01	10.51
0.020	0.22	11.00	12.30	0.18	9.00	9.86

POLYMER: 40-02-05-B $[\eta]_o$ = 11.8 $(g/dl)^{-1}$

$\bar{M}_n$ = 2.15×10^6 $[\eta]_\infty$ = 10.2 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	351.7	328.6	374.3	332.6	Time (Seconds)
	483.0	292.0	184.0	105.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	1.58	1.61	1.63	1.64	η_r
	0.46	0.48	0.49	0.50	$\ln(\eta_r)$
0.0333	304.2	282.9	321.6	285.1	Time
	559.0	339.0	215.0	123.0	$\dot{\gamma}$
	1.37	1.39	1.40	1.41	η_r
	0.31	0.33	0.34	0.34	$\ln(\eta_r)$
0.0250	282.2	261.6	296.3	262.3	Time
	602.0	367.0	233.0	133.0	$\dot{\gamma}$
	1.27	1.28	1.29	1.30	η_r
	0.24	0.25	0.26	0.26	$\ln(\eta_r)$
0.0167	261.6	241.8	273.3	241.7	Time
	650.0	397.0	252.0	145.0	$\dot{\gamma}$
	1.18	1.18	1.19	1.20	η_r
	0.16	0.17	0.17	0.18	$\ln(\eta_r)$
0.010	245.5	226.3	255.6	226.0	Time
	692.0	424.0	270.0	155.0	$\dot{\gamma}$
	1.10	1.11	1.11	1.12	η_r
	0.10	0.10	0.11	0.11	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.52	10.40	13.64	0.46	9.20	11.68
0.0333	0.36	10.81	13.01	0.315	9.46	11.12
0.0250	0.275	11.00	12.66	0.24	9.60	10.85
0.0167	0.185	11.08	12.17	0.16	9.58	10.39
0.010	0.115	11.50	12.19	0.10	10.00	10.52

POLYMER: 40-02-05-C $[\eta]_o = 13.6$ $(g/dl)^{-1}$

$\bar{M}_n = 2.51 \times 10^6$ $[\eta]_\infty = 11.3$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	367.0	344.7	394.7	352.8	Time (Seconds)
	463.0	279.0	175.0	99.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	1.65	1.69	1.72	1.74	η_r
	0.50	0.52	0.54	0.56	$\ln(\eta_r)$
0.0333	313.1	292.6	333.7	297.0	Time
	543.0	328.0	207.0	118.0	$\dot{\gamma}$
	1.41	1.43	1.45	1.47	η_r
	0.34	0.36	0.37	0.38	$\ln(\eta_r)$
0.0250	288.5	268.3	305.2	270.9	Time
	589.0	358.0	226.0	129.0	$\dot{\gamma}$
	1.30	1.32	1.33	1.34	η_r
	0.26	0.27	0.28	0.29	$\ln(\eta_r)$
0.0167	265.6	245.9	278.8	247.2	Time
	640.0	390.0	247.0	142.0	$\dot{\gamma}$
	1.19	1.21	1.21	1.22	η_r
	0.18	0.19	0.19	0.20	$\ln(\eta_r)$
0.010	247.9	228.9	258.9	229.2	Time
	686.0	419.0	267.0	153.0	$\dot{\gamma}$
	1.12	1.12	1.13	1.13	η_r
	0.11	0.11	0.12	0.12	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.58	11.60	15.72	0.50	10.00	12.97
0.0333	0.41	12.42	15.36	0.34	10.30	12.27
0.0250	0.31	12.40	14.54	0.26	10.40	11.88
0.0167	0.215	12.87	14.36	0.175	10.48	11.45
0.010	0.13	13.00	13.88	0.11	11.00	11.63

POLYMER: 40-02-05-D $\quad [\eta]_o$ = 11.7 $(g/dl)^{-1}$

$\bar{M}_n$ = 1.90×10^6 $\quad [\eta]_\infty$ = 9.4 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	503.0	472.6	539.6	481.7	Time (Seconds)
	338.0	203.0	128.0	73.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$
	2.264	2.317	2.349	2.381	η_r
	0.817	0.840	0.854	0.867	$\ln(\eta_r)$
0.0667	390.7	365.7	417.0	570.8	Time
	435.0	263.0	165.0	94.0	$\dot{\gamma}$
	1.793	1.793	1.815	1.838	η_r
	0.564	0.584	0.596	0.606	$\ln(\eta_r)$
0.050	343.2	319.1	362.7	322.4	Time
	495.0	301.0	190.0	109.0	$\dot{\gamma}$
	1.545	1.564	1.579	1.593	η_r
	0.435	0.447	0.457	0.466	$\ln(\eta_r)$
0.0333	299.0	277.3	314.5	279.4	Time
	569.0	346.0	219.0	125.0	$\dot{\gamma}$
	1.346	1.360	1.369	1.381	η_r
	0.297	1.307	0.314	0.323	$\ln(\eta_r)$
0.020	266.4	246.3	278.6	246.8	Time
	638.0	390.0	248.0	142.0	$\dot{\gamma}$
	1.199	1.207	1.213	1.220	η_r
	0.181	0.188	0.193	0.199	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.90	9.00	14.60	0.82	8.20	12.70
0.0667	0.64	9.60	13.44	0.57	8.55	11.52
0.050	0.50	10.00	12.97	0.43	8.60	10.75
0.0333	0.35	10.50	12.58	0.30	9.01	10.51
0.020	0.22	11.00	12.30	0.18	9.00	9.86

POLYMER: 40-02-05-E $\quad [\eta]_o = 12.1 \ (g/dl)^{-1}$

$\bar{M}_n = 2.09 \times 10^6 \quad [\eta]_\infty = 10.0 \ (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	540.3	510.6	586.3	524.5	Time (Seconds)
	315.0	188.0	118.0	67.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.432	2.503	2.552	2.592	η_r
	0.889	0.917	0.937	0.952	$\ln(\eta_r)$
0.0667	410.7	386.75	442.7	395.1	Time
	414.0	248.0	156.0	89.0	$\dot{\gamma}$
	1.848	1.896	1.927	1.953	η_r
	0.614	0.640	0.656	0.699	$\ln(\eta_r)$
0.050	355.9	332.8	379.6	338.5	Time
	478.0	288.0	182.0	103.0	$\dot{\gamma}$
	1.602	1.631	1.652	1.673	η_r
	0.471	0.489	0.502	0.515	$\ln(\eta_r)$
0.0333	306.45	285.1	324.1	287.9	Time
	555.0	337.0	213.0	122.0	$\dot{\gamma}$
	1.379	1.298	1.411	1.423	η_r
	0.322	0.335	0.344	0.353	$\ln(\eta_r)$
0.020	270.9	250.9	283.9	251.6	Time
	628.0	383.0	243.0	139.0	$\dot{\gamma}$
	1.219	1.230	1.236	1.244	η_r
	0.198	0.207	0.212	0.218	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.98	9.80	16.64	0.87	8.70	13.87
0.0667	0.68	10.19	14.60	0.605	9.07	12.46
0.050	0.53	10.60	13.98	0.465	9.30	11.84
0.0333	0.37	11.11	13.45	0.320	9.61	11.33
0.020	0.23	11.50	12.93	0.195	9.75	10.77

POLYMER: 40-02-05-F $[\eta]_0 = 11.1 \ (g/dl)^{-1}$

$\bar{M}_n = 2.02 \times 10^6$ $[\eta]_\infty = 9.8 \ (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	524.5	493.9	565.6	504.9	Time (Seconds)
	324.0	194.0	122.0	69.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.360	2.421	2.462	2.495	η_r
	0.859	0.884	0.901	0.914	$\ln(\eta_r)$
0.0667	403.3	378.6	432.4	385.3	Time
	422.0	254.0	160.0	91.0	$\dot{\gamma}$
	1.815	1.856	1.882	1.904	η_r
	0.596	0.618	0.632	0.644	$\ln(\eta_r)$
0.050	350.6	327.4	372.7	331.8	Time
	485.0	293.0	185.0	106.0	$\dot{\gamma}$
	1.578	1.605	1.622	1.640	η_r
	0.456	0.473	0.484	0.495	$\ln(\eta_r)$
0.0333	303.45	282.0	320.2	284.7	Time
	560.0	340.0	215.0	123.0	$\dot{\gamma}$
	1,366	1.382	1.394	1.407	η_r
	0.312	0.324	0.332	0.341	$\ln(\eta_r)$
0.020	269.2	249.1	282.0	249.6	Time
	632.0	385.0	245.0	140.0	$\dot{\gamma}$
	1.212	1.221	1.227	1.234	η_r
	0.192	0.200	0.205	0.210	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.94	9.40	15.60	0.83	8.30	12.93
0.0667	0.665	9.97	14.16	0.585	8.77	11.92
0.050	0.51	10.20	13.31	0.455	9.10	11.52
0.0333	0.35	10.51	12.58	0.31	9.31	10.91
0.020	0.215	10.75	11.99	0.19	9.50	10.46

POLYMER: 40-05-01-A

$\bar{M}_n$ = 4.80×10^6

$[\eta]_0 = 25.5$ $(g/dl)^{-1}$

$[\eta]_\infty = 17.3$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	493.4	477.7	568.8	538.4	Time (Seconds)
	345.0	201.0	121.0	65.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$
	2.22	2.34	2.48	2.66	η_r
	0.80	0.85	0.91	0.98	$\ln(\eta_r)$
0.0333	388.6	369.8	433.4	403.7	Time
	438.0	260.0	159.0	87.0	$\dot{\gamma}$
	1.75	1.81	1.89	2.00	η_r
	0.56	0.59	0.63	0.69	$\ln(\eta_r)$
0.0250	341.9	322.2	374.6	345.9	Time
	497.0	298.0	184.0	101.0	$\dot{\gamma}$
	1.54	1.58	1.63	1.71	η_r
	0.43	0.46	0.49	0.54	$\ln(\eta_r)$
0.0167	299.0	279.6	322.7	294.7	Time
	569.0	243.0	214.0	119.0	$\dot{\gamma}$
	1.35	1.37	1.40	1.46	η_r
	0.30	0.32	0.34	0.38	$\ln(\eta_r)$
0.010	267.1	248.6	284.5	256.7	Time
	636.0	386.0	243.0	136.0	$\dot{\gamma}$
	1.20	1.22	1.24	1.27	η_r
	0.18	0.20	0.21	0.24	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.09	21.80	39.49	0.78	15.60	23.63
0.0333	0.75	22.52	33.53	0.55	16.52	22.02
0.025	0.59	23.60	32.16	0.41	16.40	20.27
0.0167	0.40	23.95	29.45	0.28	16.77	19.35
0.010	0.25	25.00	28.40	0.17	17.00	18.53

POLYMER: 40-05-01-B $[\eta]_o$ = 24.0 $(g/dl)^{-1}$

$\bar{M}_n$ = 4.67 x 10^6 $[\eta]_\infty$ = 17.0 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	461.8	445.0	523.7	483.8	Time (Seconds)
	368.0	216.0	132.0	72.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.08	2.18	2.28	2.39	η_r
	0.73	0.78	0.82	0.87	$\ln(\eta_r)$
0.0333	370.9	353.9	412.1	376.8	Time
	458.0	271.0	167.0	93.0	$\dot{\gamma}$
	1.67	1.73	1.79	1.86	η_r
	0.51	0.55	0.58	0.62	$\ln(\eta_r)$
0.0250	329.3	311.7	360.7	327.7	Time
	516.0	308.0	191.0	107.0	$\dot{\gamma}$
	1.48	1.53	1.57	1.62	η_r
	0.39	0.42	0.45	0.48	$\ln(\eta_r)$
0.0167	290.8	272.7	315.4	282.7	Time
	585.0	352.0	220.0	124.0	$\dot{\gamma}$
	1.31	1.34	1.36	1.40	η_r
	0.27	0.29	0.31	0.33	$\ln(\eta_r)$
0.010	262.8	244.8	279.2	250.4	Time
	647.0	392.0	247.0	140.0	$\dot{\gamma}$
	1.18	1.20	1.22	1.24	η_r
	0.17	0.18	0.19	0.21	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.94	18.80	31.20	0.71	14.20	20.68
0.0333	0.685	20.57	29.54	0.50	15.02	19.48
0.0250	0.53	21.20	27.96	0.385	15.40	18.78
0.0167	0.36	21.56	25.96	0.265	15.87	18.17
0.010	0.23	23.00	25.86	0.165	16.50	17.94

POLYMER: 40-05-01-C $\quad [\eta]_0 = 21.5 \quad (g/dl)^{-1}$

$\bar{M}_n = 4.47 \times 10^6 \quad [\eta]_\infty = 16.5 \quad (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	850.9	851.7	1031.6	975.9	Time (Seconds)
	200.0	113.0	67.0	36.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	3.83	4.18	4.49	4.82	η_r
	1.34	1.43	1.50	1.57	$\ln(\eta_r)$
0.0667	572.7	559.7	666.5	622.4	Time
	297.0	172.0	104.0	56.0	$\dot{\gamma}$
	2.58	2.74	2.90	3.08	η_r
	0.95	1.01	1.07	1.12	$\ln(\eta_r)$
0.050	461.5	444.0	522.7	483.7	Time
	368.0	216.0	132.0	72.0	$\dot{\gamma}$
	2.08	2.18	2.28	2.39	η_r
	0.73	0.78	0.82	0.87	$\ln(\eta_r)$
0.0333	368.4	350.0	407.0	372.2	Time
	461.0	274.0	170.0	94.0	$\dot{\gamma}$
	1.66	1.72	1.77	1.84	η_r
	0.51	0.54	0.57	0.61	$\ln(\eta_r)$
0.020	304.3	285.8	328.4	296.7	Time
	559.0	336.0	210.0	118.0	$\dot{\gamma}$
	1.37	1.40	1.43	1.47	η_r
	0.31	0.34	0.36	0.38	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	1.62	16.20	40.53	1.27	12.70	25.61
0.0667	1.19	17.84	34.29	0.93	13.94	23.01
0.050	0.93	18.60	30.69	0.72	14.40	21.09
0.0333	0.67	20.12	28.66	0.51	15.32	19.98
0.020	0.40	20.00	24.59	0.31	15.50	18.17

POLYMER: 40-05-01-D

$\bar{M}_n$ = 5.10 x 10^6

$[\eta]_o$ = 25.0 $(g/dl)^{-1}$

$[\eta]_{\dot{\infty}}$ = 18.0 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	490.4	472.3	558.2	520.5	Time (Seconds)
	347.0	203.0	124.0	67.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.21	2.32	2.43	2.57	η_r
	0.79	0.84	0.89	0.94	$\ln(\eta_r)$
0.0333	385.1	365.7	426.1	390.9	Time
	442.0	263.0	162.0	90.0	$\dot{\gamma}$
	1.73	1.79	1.85	1.93	η_r
	0.55	0.58	0.62	0.66	$\ln(\eta_r)$
0.0250	338.4	318.7	368.8	336.0	Time
	502.0	301.0	187.0	104.0	$\dot{\gamma}$
	1.52	1.56	1.61	1.66	η_r
	0.42	0.45	0.47	0.51	$\ln(\eta_r)$
0.0167	296.6	277.6	318.8	287.7	Time
	573.0	346.0	216.0	122.0	$\dot{\gamma}$
	1.34	1.36	1.39	1.42	η_r
	0.29	0.31	0.33	0.35	$\ln(\eta_r)$
0.010	265.7	247.0	281.5	251.9	Time
	640.0	389.0	245.0	140.0	$\dot{\gamma}$
	1.20	1.21	1.23	1.24	η_r
	0.18	0.19	0.20	0.22	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	1.005	20.10	34.64	0.77	15.40	23.20
0.0333	0.725	21.77	31.97	0.54	16.22	21.50
0.025	0.56	22.40	30.03	0.415	16.60	20.57
0.0167	0.39	23.35	28.56	0.285	17.07	19.75
0.010	0.24	24.00	27.12	0.175	17.50	19.12

POLYMER: 40-05-01-E　　$[\eta]_o$ = 24.0 $(g/dl)^{-1}$

$\bar{M}_n$ = 4.67 x 10^6　　$[\eta]_\infty$ = 17.0 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	463.1	446.6	527.0	489.7	Time (Seconds)
	367.0	215.0	131.0	71.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.08	2.19	2.29	2.42	η_r
	0.73	0.78	0.83	0.88	$\ln(\eta_r)$
0.0333	370.8	353.3	412.3	378.8	Time
	458.0	272.0	167.0	92.0	$\dot{\gamma}$
	1.67	1.73	1.79	1.87	η_r
	0.51	0.55	0.58	0.63	$\ln(\eta_r)$
0.0250	329.3	311.5	360.7	329.6	Time
	516.0	308.0	191.0	106.0	$\dot{\gamma}$
	1.48	1.53	1.57	1.63	η_r
	0.39	0.42	0.45	0.49	$\ln(\eta_r)$
0.0167	291.4	273.5	314.4	284.7	Time
	583.0	351.0	219.0	123.0	$\dot{\gamma}$
	1.31	1.34	1.37	1.41	η_r
	0.27	0.29	0.31	0.34	$\ln(\eta_r)$
0.010	263.4	245.4	280.0	251.3	Time
	645.0	391.0	246.0	139.0	$\dot{\gamma}$
	1.19	1.20	1.22	1.24	η_r
	0.17	0.18	0.20	0.22	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.94	18.80	31.20	0.71	14.20	20.68
0.0333	0.685	20.57	29.54	0.50	15.02	19.48
0.025	0.53	21.20	27.96	0.385	15.40	18.78
0.0167	0.36	21.56	25.96	0.265	15.87	18.17
0.010	0.230	23.00	25.86	0.165	16.50	17.94

POLYMER: 40-05-01-F $[\eta]_0 = 21.5$ $(g/dl)^{-1}$

$\bar{M}_n \geqq 4.26 \times 10^6$ $[\eta]_\infty = 16.0$ $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	429.8	412.7	483.9	445.2	Time (Seconds)
	396.0	233.0	143.0	79.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	1.93	2.02	2.11	2.20	η_r
	0.66	0.70	0.74	0.79	$\ln(\eta_r)$
0.0333	351.3	333.7	387.5	353.6	Time
	484.0	288.0	178.0	99.0	$\dot{\gamma}$
	1.58	1.64	1.69	1.75	η_r
	0.46	0.49	0.52	0.56	$\ln(\eta_r)$
0.0250	315.6	297.7	343.4	311.3	Time
	539.0	322.0	201.0	112.0	$\dot{\gamma}$
	1.42	1.46	1.49	1.54	η_r
	0.35	0.38	0.40	0.43	$\ln(\eta_r)$
0.0167	282.6	264.6	303.3	273.0	Time
	602.0	363.0	228.0	128.0	$\dot{\gamma}$
	1.27	1.30	1.32	1.35	η_r
	0.24	0.26	0.28	0.30	$\ln(\eta_r)$
0.010	257.7	239.5	272.7	243.7	Time
	660.0	401.0	253.0	144.0	$\dot{\gamma}$
	1.16	1.17	1.19	1.20	η_r
	0.15	0.16	0.17	0.19	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.86	17.20	27.26	0.66	13.20	18.70
0.0333	0.60	18.02	24.69	0.46	13.81	17.54
0.0250	0.46	18.40	23.36	0.35	14.00	16.76
0.0167	0.32	19.16	22.58	0.24	14.37	16.24
0.010	0.20	20.00	22.14	0.15	15.00	16.18

POLYMER: 40-05-01-G $[\eta]_o = 20.8 \quad (g/dl)^{-1}$

$\bar{M}_n = 4.18 \times 10^6$ $[\eta]_\infty = 15.8 \quad (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	447.0	427.0	500.1	461.7	Time (Seconds)
	380.0	225.0	138.0	76.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.01	2.09	2.18	2.28	η_r
	0.70	0.74	0.78	0.82	$\ln(\eta_r)$
0.0333	359.7	340.5	394.5	359.2	Time
	473.0	282.0	175.0	97.0	$\dot{\gamma}$
	1.62	1.67	1.72	1.78	η_r
	0.48	0.51	0.54	0.57	$\ln(\eta_r)$
0.0250	321.0	301.6	347.6	314.9	Time
	530.0	318.0	199.0	111.0	$\dot{\gamma}$
	1.44	1.48	1.51	1.56	η_r
	0.37	0.39	0.41	0.44	$\ln(\eta_r)$
0.0167	285.5	266.7	305.2	274.2	Time
	595.0	360.0	226.0	128.0	$\dot{\gamma}$
	1.28	1.31	1.33	1.36	η_r
	0.25	0.27	0.28	0.30	$\ln(\eta_r)$
0.010	258.9	240.5	273.6	244.4	Time
	657.0	399.0	252.0	143.0	$\dot{\gamma}$
	1.17	1.18	1.19	1.21	η_r
	0.15	0.16	0.17	0.19	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.87	17.40	27.74	0.69	13.80	19.87
0.0333	0.63	18.92	26.35	0.48	14.41	18.50
0.0250	0.48	19.20	24.64	0.37	14.80	17.91
0.0167	0.32	19.16	22.58	0.25	14.97	17.01
0.010	0.20	20.00	22.14	0.15	15.00	16.18

POLYMER: 40-05-01-H $\quad [\eta]_o = 26.2 \quad (g/dl)^{-1}$

$\bar{M}_n = 4.55 \times 10^6 \quad [\eta]_\infty = 16.7 \quad (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	788.6	782.3	932.9	862.8	Time (Seconds)
	216.0	123.0	74.0	41.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	3.55	3.83	4.06	4.26	η_r
	1.27	1.34	1.40	1.45	$\ln(\eta_r)$
0.0667	550.0	540.0	640.0	591.2	Time
	309.0	178.0	108.0	59.0	$\dot{\gamma}$
	2.48	2.65	2.79	2.92	η_r
	0.91	0.97	1.02	1.07	$\ln(\eta_r)$
0.050	452.3	440.0	518.8	479.2	Time
	376.0	218.0	133.0	73.0	$\dot{\gamma}$
	2.04	2.16	2.26	2.37	η_r
	0.71	0.77	0.81	0.86	$\ln(\eta_r)$
0.0333	367.6	353.4	413.8	381.2	Time
	462.0	272.0	167.0	92.0	$\dot{\gamma}$
	1.65	1.73	1.80	1.88	η_r
	0.50	0.55	0.59	0.63	$\ln(\eta_r)$
0.020	307.0	291.5	338.2	309.0	Time
	554.0	329.0	204.0	113.0	$\dot{\gamma}$
	1.38	1.43	1.47	1.53	η_r
	0.32	0.36	0.39	0.42	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	1.52	15.20	35.72	1.21	12.10	23.53
0.0667	1.14	17.09	31.89	0.90	13.49	21.88
0.050	0.94	18.80	31.20	0.71	14.20	20.68
0.0333	0.68	20.42	29.25	0.50	15.02	19.48
0.020	0.45	22.50	28.42	0.31	15.50	18.17

POLYMER: 40-05-15-A $\qquad [\eta]_0 = 9.9 \quad (g/dl)^{-1}$

$\bar{M}_n = 1.66 \times 10^6 \qquad [\eta]_\infty = 8.6 \quad (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	467.1	440.0	504.5	452.2	Time (Seconds)
	364.0	218.0	137.0	77.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.10	2.15	2.20	2.23	η_r
	0.74	0.77	0.79	0.80	$\ln(\eta_r)$
0.0667	371.4	348.3	380.0	355.7	Time
	458.0	276.0	173.0	98.0	$\dot{\gamma}$
	1.67	1.71	1.73	1.76	η_r
	0.51	0.53	0.55	0.56	$\ln(\eta_r)$
0.050	329.1	306.7	349.4	311.6	Time
	517.0	313.0	197.0	112.0	$\dot{\gamma}$
	1.48	1.50	1.52	1.54	η_r
	0.39	0.41	0.42	0.43	$\ln(\eta_r)$
0.0333	290.6	269.7	306.4	272.1	Time
	585.0	356.0	225.0	129.0	$\dot{\gamma}$
	1.31	1.32	1.33	1.34	η_r
	0.27	0.28	0.29	0.30	$\ln(\eta_r)$
0.020	262.4	242.4	274.8	243.2	Time
	648.0	396.0	251.0	144.0	$\dot{\gamma}$
	1.18	1.19	1.20	1.20	η_r
	0.17	0.17	0.18	0.18	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.83	8.30	12.93	0.735	7.35	10.85
0.0667	0.585	8.77	11.92	0.51	7.65	9.97
0.050	0.45	9.00	11.37	0.39	7.80	9.54
0.0333	0.31	9.31	10.91	0.27	8.11	9.31
0.020	0.19	9.50	10.46	0.17	8.50	9.27

POLYMER: 40-05-15-B
$\bar{M}_n$ = 1.99 x 10^6

$[\eta]_0$ = 10.7 $(g/dl)^{-1}$
$[\eta]_\infty$ = 9.7 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	504.5	473.9	541.6	483.1	Time (Seconds)
	337.0	203.0	127.0	72.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$
	2.270	2.323	2.357	2.388	η_r
	0.820	0.843	0.858	0.870	$\ln(\eta_r)$
0.0667	392.0	367.1	418.4	372.1	Time
	434.0	262.0	165.0	94.0	$\dot{\gamma}$
	1.764	1.800	1.812	1.839	η_r
	0.568	0.588	0.599	0.609	$\ln(\eta_r)$
0.050	434.4	320.3	364.6	325.9	Time
	495.0	300.0	189.0	107.0	$\dot{\gamma}$
	1.546	1.570	1.587	1.611	η_r
	0.435	0.451	0.462	0.477	$\ln(\eta_r)$
0.0333	299.9	277.7	317.0	279.8	Time
	567.0	346.0	218.0	125.0	$\dot{\gamma}$
	1.350	1.361	1.380	1.383	η_r
	0.300	0.308	0.322	0.324	$\ln(\eta_r)$
0.020	267.2	246.9	279.1	246.8	Time
	636.0	389.0	247.0	142.0	$\dot{\gamma}$
	1.203	1.211	1.215	1.220	η_r
	0.184	0.191	0.195	0.199	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.89	8.90	14.35	0.805	8.05	12.37
0.0667	0.62	9.30	12.88	0.56	8.40	11.25
0.050	0.49	9.80	12.65	0.43	8.60	10.75
0.0333	0.335	10.06	11.95	0.30	9.10	10.51
0.020	0.205	10.25	11.38	0.185	9.25	10.16

POLYMER: 40-05-15-C
$\bar{M}_n$ = 1.96 x 10^6

$[\eta]_o$ = 10.8 $(g/dl)^{-1}$
$[\eta]_\infty$ = 9.6 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	515.2	485.2	556.1	497.3	Time (Seconds)
	330.0	198.0	124.0	70.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	2.319	2.379	2.421	2.458	η_r
	0.841	0.866	0.884	0.899	$\ln(\eta_r)$
0.0667	397.7	372.7	425.2	378.4	Time
	428.0	258.0	162.0	92.0	$\dot{\gamma}$
	1.790	1.827	1.851	1.870	η_r
	0.582	0.603	0.616	0.626	$\ln(\eta_r)$
0.050	347.0	324.0	368.8	327.5	Time
	490.0	296.0	187.0	107.0	$\dot{\gamma}$
	1.562	1.588	1.605	1.619	η_r
	0.446	0.463	0.473	0.482	$\ln(\eta_r)$
0.0333	301.5	280.5	317.7	281.8	Time
	564.0	343.0	217.0	124.0	$\dot{\gamma}$
	1.357	1.373	1.383	1.393	η_r
	0.305	0.317	0.324	0.331	$\ln(\eta_r)$
0.020	268.4	248.2	280.7	248.6	Time
	633.0	387.0	246.0	141.0	$\dot{\gamma}$
	1.208	1.217	1.222	1.229	η_r
	0.189	0.196	0.200	0.206	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.925	9.25	15.22	0.83	8.30	12.93
0.0667	0.645	9.67	13.58	0.575	8.62	11.65
0.050	0.50	10.00	12.97	0.44	8.80	11.05
0.0333	0.34	10.21	12.16	0.305	9.16	10.71
0.020	0.21	10.50	11.68	0.185	9.25	10.16

POLYMER: 40-05-15-D $[\eta]_o$ = 12.3 $(g/dl)^{-1}$

$\bar{M}_n$ = 2.05×10^6 $[\eta]_\infty$ = 9.9 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	483.9	454.4	518.9	463.9	Time (Seconds)
	351.0	211.0	133.0	75.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	2.18	2.23	2.26	2.29	η_r
	0.78	0.80	0.81	0.83	$\ln(\eta_r)$
0.0667	387.1	362.7	413.5	367.2	Time
	439.0	265.0	167.0	95.0	$\dot{\gamma}$
	1.74	1.78	1.80	1.81	η_r
	0.56	0.58	0.59	0.60	$\ln(\eta_r)$
0.050	342.75	320.6	365.2	324.7	Time
	496.0	299.0	189.0	108.0	$\dot{\gamma}$
	1.54	1.57	1.59	1.60	η_r
	0.433	0.452	0.46	0.47	$\ln(\eta_r)$
0.0333	301.7	281.2	320.0	284.5	Time
	563.0	341.0	216.0	123.0	$\dot{\gamma}$
	1.36	1.38	1.39	1.41	η_r
	0.31	0.32	0.33	0.34	$\ln(\eta_r)$
0.020	269.9	250.8	284.7	252.6	Time
	630.0	383.0	242.0	139.0	$\dot{\gamma}$
	1.21	1.23	1.24	1.25	η_r
	0.19	0.21	0.22	0.22	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.86	8.60	13.63	0.77	7.70	11.60
0.0667	0.62	9.30	12.88	0.555	8.32	11.12
0.050	0.485	9.70	12.48	0.43	8.60	10.75
0.0333	0.345	10.36	12.37	0.305	9.16	10.71
0.020	0.22	11.00	12.30	0.19	9.50	10.46

POLYMER: 40-05-15-E
$\bar{M}_n$ = 1.78×10^6

$[\eta]_0 = 11.1 \ (g/dl)^{-1}$
$[\eta]_\infty = 9.0 \ (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.050	342.9	320.4	366.2	326.8	Time (Seconds)
	496.0	300.0	188.0	107.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	1.54	1.57	1.59	1.62	η_r
	0.43	0.45	0.47	0.48	$\ln(\eta_r)$
0.0333	298.7	277.9	316.5	281.8	Time
	569.0	345.0	218.0	124.0	$\dot{\gamma}$
	1.34	1.36	1.38	1.39	η_r
	0.30	0.31	0.32	0.33	$\ln(\eta_r)$
0.0250	278.5	258.4	292.6	260.1	Time
	610.0	372.0	236.0	135.0	$\dot{\gamma}$
	1.25	1.27	1.27	1.29	η_r
	0.23	0.24	0.24	0.25	$\ln(\eta_r)$
0.0167	258.8	239.4	270.9	239.7	Time
	657.0	401.0	255.0	146.0	$\dot{\gamma}$
	1.16	1.17	1.18	1.18	η_r
	0.15	0.16	0.16	0.17	$\ln(\eta_r)$
0.010	244.1	225.0	254.1	225.0	Time
	696.0	427.0	272.0	156.0	$\dot{\gamma}$
	1.10	1.10	1.11	1.11	η_r
	0.094	0.098	0.101	0.106	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.050	0.51	10.20	13.31	0.42	8.40	10.44
0.0333	0.35	10.61	12.70	0.295	8.94	10.40
0.025	0.26	10.40	11.88	0.225	9.00	10.09
0.0167	0.18	10.78	11.81	0.15	8.98	9.69
0.010	0.11	11.00	11.63	0.09	9.00	9.42

POLYMER: 40-05-25-A

$\bar{M}_n = 1.06 \times 10^6$

$[\eta]_0 = 7.4 \quad (g/dl)^{-1}$

$[\eta]_\infty = 6.4 \quad (g/dl)^{-1}$

CONC.	FLOW DATA				
(g/dl)	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	395.6	366.6	414.6	367.3	Time (Seconds)
	430.0	262.0	166.0	95.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	1.780	1.797	1.805	1.815	η_r
	0.577	0.586	0.590	0.596	$\ln(\eta_r)$
0.0667	329.9	305.3	344.9	304.9	Time
	515.0	314.0	200.0	115.0	$\dot{\gamma}$
	1.485	1.497	1.501	1.507	η_r
	0.395	0.403	0.406	0.410	$\ln(\eta_r)$
0.050	300.5	277.4	313.3	277.4	Time
	566.0	346.0	220.0	126.0	$\dot{\gamma}$
	1.352	1.360	1.364	1.371	η_r
	0.302	0.307	0.310	0.316	$\ln(\eta_r)$
0.0333	274.0	252.9	285.6	253.3	Time
	620.0	380.0	242.0	138.0	$\dot{\gamma}$
	1.233	1.240	1.243	1.252	η_r
	0.210	0.215	0.218	0.225	$\ln(\eta_r)$
0.020	251.8	231.6	261.1	230.8	Time
	675.0	415.0	264.0	152.0	$\dot{\gamma}$
	1.133	1.135	1.137	1.141	η_r
	0.125	0.127	0.128	0.132	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.605	6.05	8.31	0.575	5.75	7.77
0.0667	0.42	6.30	7.83	0.395	5.92	7.26
0.050	0.325	6.50	7.68	0.30	6.00	7.00
0.0333	0.230	6.91	7.77	0.205	6.16	6.83
0.020	0.14	7.00	7.51	0.125	6.25	6.66

POLYMER: 40-05-25-B $[\eta]_o$ = 7.0 $(g/dl)^{-1}$

$\bar{M}_n$ = 1.06 x 10^6 $[\eta]_\infty$ = 6.4 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	400.9	371.7	422.0	373.1	Time (Seconds)
	424.0	258.0	164.0	94.0	$\dot{\gamma}$ $(Seconds)^{-1}$
	1.804	1.822	1.837	1.844	η_r
	0.590	0.600	0.608	0.612	$\ln(\eta_r)$
0.0667	332.7	307.7	347.7	307.3	Time
	511.0	312.0	198.0	114.0	$\dot{\gamma}$
	1.497	1.508	1.513	1.519	η_r
	0.404	0.411	0.414	0.418	$\ln(\eta_r)$
0.050	302.3	279.1	315.2	278.4	Time
	562.0	344.0	219.0	126.0	$\dot{\gamma}$
	1.361	1.368	1.372	1.376	η_r
	0.308	0.313	0.316	0.319	$\ln(\eta_r)$
0.0333	274.2	252.5	284.95	251.7	Time
	620.0	380.0	242.0	139.0	$\dot{\gamma}$
	1.234	1.238	1.240	1.244	η_r
	0.210	0.213	0.215	0.218	$\ln(\eta_r)$
0.020	252.9	232.6	262.1	231.4	Time
	672.0	413.0	263.0	151.0	$\dot{\gamma}$
	1.138	1.140	1.141	1.144	η_r
	0.129	0.131	0.132	0.134	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.62	6.20	8.59	0.585	5.85	7.95
0.0667	0.42	6.30	7.83	0.405	6.07	7.49
0.050	0.325	6.50	7.68	0.305	6.10	7.13
0.0333	0.225	6.76	7.58	0.21	6.31	7.02
0.020	0.135	6.75	7.23	0.125	6.25	6.66

POLYMER: 40-05-25-C
$\bar{M}_n$ = 1.16 x 10^6

$[\eta]_0$ = 7.5 $(g/dl)^{-1}$
$[\eta]_\infty$ = 6.8 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	415.4	385.5	463.3	386.2	Time (Seconds)
	409.0	249.0	158.0	91.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$
	1.870	1.890	1.899	1.909	η_r
	0.626	0.636	0.641	0.646	$\ln(\eta_r)$
0.0667	341.4	315.8	356.9	315.6	Time
	498.0	304.0	193.0	111.0	$\dot{\gamma}$
	1.537	1.548	1.553	1.560	η_r
	0.430	0.437	0.441	0.445	$\ln(\eta_r)$
0.050	308.2	284.5	321.4	284.0	Time
	552.0	337.0	215.0	123.0	$\dot{\gamma}$
	1.387	1.395	1.399	1.404	η_r
	0.327	0.333	0.336	0.339	$\ln(\eta_r)$
0.0333	277.2	255.6	288.6	255.1	Time
	613.0	376.0	239.0	137.0	$\dot{\gamma}$
	1.248	1.253	1.256	1.261	η_r
	0.221	0.226	0.228	0.232	$\ln(\eta_r)$
0.020	254.4	234.2	264.1	233.1	Time
	668.0	410.0	261.0	150.0	$\dot{\gamma}$
	1.145	1.148	1.150	1.152	η_r
	0.136	0.138	0.139	0.142	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.655	6.55	9.25	0.625	6.25	8.68
0.0667	0.455	6.82	8.64	0.43	6.45	8.05
0.050	0.35	7.00	8.38	0.325	6.50	7.68
0.0333	0.24	7.21	8.15	0.22	6.61	7.39
0.020	0.145	7.25	7.80	0.135	6.75	7.23

POLYMER: 40-05-25-D $\quad [\eta]_0 = 8.3 \quad (g/dl)^{-1}$

$\bar{M}_n = 1.43 \times 10^6 \quad [\eta]_\infty = 7.8 \quad (g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	428.2	398.8	452.9	402.9	Time (Seconds)
	397.0	241.0	152.0	87.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	1.93	1.95	1.97	1.99	η_r
	0.66	0.67	0.68	0.69	$\ln(\eta_r)$
0.0667	349.4	324.4	367.7	326.4	Time
	486.0	296.0	188.0	107.0	$\dot{\gamma}$
	1.57	1.59	1.60	1.61	η_r
	0.45	0.46	0.47	0.48	$\ln(\eta_r)$
0.050	313.8	290.5	329.0	291.5	Time
	542.0	330.0	210.0	120.0	$\dot{\gamma}$
	1.41	1.42	1.43	1.44	η_r
	0.35	0.35	0.36	0.37	$\ln(\eta_r)$
0.0333	281.1	259.7	293.4	259.4	Time
	605.0	370.0	235.0	135.0	$\dot{\gamma}$
	1.27	1.27	1.28	1.28	η_r
	0.24	0.24	0.25	0.25	$\ln(\eta_r)$
0.020	256.4	236.5	266.9	235.6	Time
	663.0	406.0	259.0	149.0	$\dot{\gamma}$
	1.15	1.16	1.16	1.16	η_r
	0.14	0.15	0.15	0.15	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.71	7.10	10.34	0.655	6.55	9.25
0.0667	0.50	7.50	9.73	0.45	6.75	8.52
0.050	0.385	7.70	9.39	0.35	7.00	8.38
0.0333	0.26	7.81	8.92	0.24	7.21	8.15
0.020	0.16	8.00	8.68	0.15	7.50	8.09

POLYMER: 40-05-25~~E~~)
$\bar{M}_n$ = 1.06 x 10^6

$[\eta]_0$ = 7.0 $(g/dl)^{-1}$
$[\eta]_\infty$ = 6.4 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	393.2 432.0 1.770 0.571	364.4 263.0 1.786 0.580	412.3 167.0 1.795 0.585	365.2 96.0 1.805 0.590	Time (Seconds) $\dot{\gamma}$ $(\text{Seconds})^{-1}$ η_r $\ln(\eta_r)$
0.0667	329.0 517.0 1.481 0.393	304.2 316.0 1.491 0.400	344.0 201.0 1.497 0.404	304.4 115.0 1.504 0.408	Time $\dot{\gamma}$ η_r $\ln(\eta_r)$
0.050	299.5 568.0 1.348 0.299	276.6 347.0 1.356 0.305	312.5 221.0 1.360 0.308	276.3 127.0 1.366 0.312	Time $\dot{\gamma}$ η_r $\ln(\eta_r)$
0.0333	272.1 625.0 1.225 0.203	251.0 382.0 1.230 0.207	283.0 244.0 1.232 0.208	250.4 140.0 1.238 0.213	Time $\dot{\gamma}$ η_r $\ln(\eta_r)$
0.020	251.8 675.0 1.133 0.125	231.6 415.0 1.135 0.127	260.9 264.0 1.136 0.127	230.75 152.0 1.140 0.131	Time $\dot{\gamma}$ η_r $\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.61	6.10	8.40	0.57	5.70	7.68
0.0667	0.42	6.30	7.83	0.39	5.85	7.15
0.050	0.32	6.40	7.54	0.30	6.00	7.00
0.0333	0.22	6.61	7.39	0.203	6.10	6.76
0.020	0.135	6.75	7.23	0.125	6.25	6.66

POLYMER: 40-05-25-F $[\eta]_0$ = 8.3 $(g/dl)^{-1}$
$\bar{M}_n$ = 1.32×10^6 $[\eta]_\infty$ = 7.4 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	432.0	402.4	457.5	406.7	Time (Seconds)
	394.0	239.0	151.0	86.0	$\dot{\gamma}$ (Seconds)$^{-1}$
	1.944	1.973	1.991	2.010	η_r
	0.665	0.679	0.689	0.698	$\ln(\eta_r)$
0.0667	351.2	327.0	371.1	328.4	Time
	484.0	294.0	186.0	107.0	$\dot{\gamma}$
	1.581	1.603	1.615	1.623	η_r
	0.458	0.472	0.480	0.484	$\ln(\eta_r)$
0.050	315.8	292.65	331.5	293.5	Time
	538.0	328.0	208.0	119.0	$\dot{\gamma}$
	1.421	1.435	1.443	1.451	η_r
	0.352	0.361	0.367	0.372	$\ln(\eta_r)$
0.0333	282.4	261.1	294.7	261.2	Time
	602.0	368.0	234.0	134.0	$\dot{\gamma}$
	1.271	1.280	1.283	1.291	η_r
	0.240	0.247	0.249	0.255	$\ln(\eta_r)$
0.020	257.7	237.3	267.9	237.15	Time
	660.0	404.0	258.0	148.0	$\dot{\gamma}$
	1.160	1.164	1.166	1.172	η_r
	0.148	0.151	0.154	0.159	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.715	7.15	10.44	0.66	6.60	9.35
0.0667	0.49	7.35	9.48	0.455	6.82	8.64
0.050	0.38	7.60	9.25	0.35	7.00	8.38
0.0333	0.26	7.81	8.92	0.235	7.06	7.96
0.020	0.16	8.00	8.68	0.145	7.25	7.80

POLYMER: 40-05-25-G $[\eta]_o$ = 7.2 $(g/dl)^{-1}$
$\bar{M}_n$ = 1.13 x 10^6 $[\eta]_\infty$ = 6.7 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	406.3	377.1	427.1	378.7	Time (Seconds)
	418.0	255.0	162.0	92.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$
	1.829	1.849	1.859	1.872	η_r
	0.604	0.614	0.620	0.627	$\ln(\eta_r)$
0.0667	337.7	312.8	353.9	313.5	Time
	503.0	307.0	195.0	112.0	$\dot{\gamma}$
	1.520	1.533	1.540	1.549	η_r
	0.419	0.427	0.432	0.438	$\ln(\eta_r)$
0.050	305.0	281.7	318.4	282.0	Time
	557.0	341.0	217.0	124.0	$\dot{\gamma}$
	1.373	1.381	1.386	1.394	η_r
	0.317	0.323	0.326	0.332	$\ln(\eta_r)$
0.0333	276.1	254.6	287.4	254.4	Time
	616.0	377.0	240.0	138.0	$\dot{\gamma}$
	1.243	1.248	1.251	1.257	η_r
	0.217	0.222	0.224	0.229	$\ln(\eta_r)$
0.020	253.6	233.5	263.3	232.6	Time
	670.0	411.0	262.0	150.0	$\dot{\gamma}$
	1.141	1.415	1.416	1.150	η_r
	0.132	0.135	0.136	0.139	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.64	6.40	8.96	0.60	6.00	8.22
0.0667	0.45	6.75	8.52	0.415	6.22	7.71
0.050	0.335	6.70	7.96	0.31	6.20	7.27
0.0333	0.23	6.91	7.70	0.215	6.46	7.20
0.020	0.14	7.00	7.51	0.13	6.50	6.94

POLYMER: 40-05-25-H
$\bar{M}_n$ = 1.06 x 10^6

$[\eta]_o$ = 6.6 $(g/dl)^{-1}$
$[\eta]_\infty$ = 6.4 $(g/dl)^{-1}$

CONC. (g/dl)	FLOW DATA				
	Bulb 1	Bulb 2	Bulb 3	Bulb 4	
0.100	395.8	366.3	414.0	366.5	Time (Seconds)
	430.0	262.0	167.0	95.0	$\dot{\gamma}$ $(\text{Seconds})^{-1}$
	1.781	1.796	1.802	1.811	η_r
	0.577	0.585	0.589	0.594	$\ln(\eta_r)$
0.0667	330.6	305.5	345.4	305.4	Time
	514.0	314.0	200.0	115.0	$\dot{\gamma}$
	1.488	1.498	1.504	1.497	η_r
	0.397	0.404	0.408	0.404	$\ln(\eta_r)$
0.050	301.1	277.8	313.4	277.8	Time
	565.0	346.0	220.0	126.0	$\dot{\gamma}$
	1.355	1.362	1.364	1.362	η_r
	0.304	0.309	0.311	0.309	$\ln(\eta_r)$
0.0333	273.6	252.1	284.2	251.2	Time
	621.0	381.0	243.0	139.0	$\dot{\gamma}$
	1.231	1.236	1.237	1.231	η_r
	0.208	0.212	0.213	0.208	$\ln(\eta_r)$
0.020	252.6	232.4	261.9	231.5	Time
	673.0	413.0	263.0	151.0	$\dot{\gamma}$
	1.137	1.139	1.140	1.144	η_r
	0.128	0.130	0.131	0.135	$\ln(\eta_r)$

	$\dot{\gamma} \longrightarrow 0$			$\dot{\gamma} \longrightarrow \infty$		
Conc.	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$	$\ln(\eta_r)$	$\frac{\ln(\eta_r)}{C}$	$\frac{\eta_{sp}}{C}$
0.100	0.60	6.00	8.22	0.575	5.75	7.77
0.0667	0.41	6.15	7.60	0.395	5.92	7.26
0.050	0.315	6.30	7.41	0.305	6.10	7.13
0.0333	0.21	6.31	7.02	0.205	6.16	6.83
0.020	0.13	6.50	6.94	0.125	6.25	6.66

Appendix (I-2) On Estimating Number Average Molecular Weights from Intrinsic Viscosity Measurements.

For an unfractionated polymer with a wide molecular weight distribution, an intrinsic viscosity measurement will yield an estimate of its viscosity average molecular weight $\overline{M}_v$, according to equations (I-14) through (I-16). However, the estimation of the kinetic parameters in the free-radical polymerization model requires the knowledge of the number average molecular weight $\overline{M}_n$.

Although, in principle, $\overline{M}_n$ may be estimated by gel permeation chromatography (GPC), a previous attempt to do so for high molecular weight polyacrylamides was not satisfactory due to the limited resolution by the packing material of the high molecular weight tail of these polymers$^{(2,33)}$. The present attempts to estimate the molecular weight distributions of the synthesized polyacrylamides by GPC were also unsuccessful for the same reason, despite the use of the packing material recently developed by E. Merck Co., Darmstadt, Germany, with a mean pore diameter as high as 1400 nm. The columns were calibrated by the polyacrylamide standards A and B, synthesized by Abdel-Alim and Hamielec$^{(40)}$. When the calibration line thus obtained was used to estimate the molecular weight distribution of a polyacrylamide with a higher molecular weight average than these standards, such as any of those produced in Run (25-05-01), the polydispersity was found to be significantly less than 2.0, which is impossible according to the free-radical polymerization theory. This, together with the fact that the leading portions of the chromatograms for polymers with an estimated $\overline{M}_n$ ranging from 3.0×10^6 to 10.0×10^6 all started nearly at a constant retention volume, indicated that the hydrodynamic volumes of these polymers exceeded the exclusion limit of the GPC columns.

Two methods have been proposed in the literature to obtain $\overline{M}_n$ from a measurement of $[\eta]$. Both make use of the fact that the polyacrylamides obtained in isothermal free-radical polymerization in the absence of substantial amounts of a chain transfer agent will have a molecular weight distribution close to the Most Probable Distribution(1). The proof of the above statement is detailed in Part II of this thesis.

The first approach for obtaining $\overline{M}_n$ (29,30) makes use of the fact that the viscosity average molecular weight will always be considerably closer to the weight average than the number average, for any distribution likely to be encountered in a high polymer(1). Therefore, Eq.(I-38) is used to obtain $\overline{M}_w$ from the measured $[\eta]$. And, as the polydispersity of the Most Probable Distribution is 2.0, $\overline{M}_w$ is divided by 2.0 to obtain $\overline{M}_n$. Inspection of Eq.(I-38) with $(\overline{M}_w)^{0.80}$ replaced by $(2\,\overline{M}_n)^{0.80}$ reveals that the net effect of this method is to use the following expression to calculate $\overline{M}_n$,

$$[\eta] = 1.10 \times 10^{-4} \ \overline{M}_n^{0.80} \qquad \text{(I-A2-1)}$$

Other investigators have argued that a molecular weight exponent of 0.80 in Eq.(I-38) is high in view of the fact that water is not considered to be a "good" solvent for polyacrylamide(26). Furthermore, Ishige and Hamielec(2,33) have shown that Eq.(I-37) predicted values for $\overline{M}_n$ in close agreement with those obtained by electron mycroscopy and by light scattering for polyacrylamides with the Most Probable Distribution. Hence, several investigators chose to use Eq.(I-37) directly to estimate $\overline{M}_n$ for polyacrylamides with the Most Probable Distribution(28,31,33). This latter approach was adopted in the present investigation.

II. Kinetic Study of the Solution Polymerization of Acrylamide in Water Solution

II.1 Introduction : The Properties and Applications of Acrylamide and Its Polymers

Polyacrylamide is a product of the polymerization of the vinyl monomer acrylamide, $CH_2 = CHCONH_2$. The monomer is a white crystalline solid with a melting point of 84.5 ± 0.3 °C(1). Acrylamide undergoes the usual chemical reactions associated with the amide group and the double bond. The solid monomer is stable and does not need inhibition. Solutions of the monomer are fairly stable below 50°C(2). Comprehensive reviews of the methods of preparation of acrylamide monomer, its properties, physiological activity and uses have been compiled by MacWilliams(3) and by Leonard(4).

In the presence of free radicals, acrylamide polymerizes readily to high molecular weight polyacrylamide. The heat evolved in converting monomer to polymer was found to be 19.5 $(\frac{KCal}{mole})$(1). Common initiators are peroxides, azo compounds, persulfates, redox pairs, photochemical systems and x-rays. Polymerization in aqueous solution is generally the preferred method commercially(2). Methods of polymerization of limited commercial importance include solid-state polymerization initiated by ionizing radiation(6,7) and heterogeneous polymerization in which the polymer formed precipitates out from the reaction solution(8). A polymerization technique that is gaining in commercial importance is the so-called "Inverse Emulsion Polymerization". In this method the acrylamide is present in a concentrated aqueous solution dispersed in an organic medium in the form of small droplets with a surface active stabilizer used to prevent coagulation(9,10).

Polyacrylamide is a linear polymer with the normal head-to-tail structure. Special preparation conditions must be provided to effect significant amount of chain branching(11). Whereas acrylamide monomer is soluble in water and many organic solvents, the polymer however is unique among addition polymers in that it is virtually insoluble in common organic solvents, but appreciably soluble in water. Solutions of high molecular weight polyacrylamides in water are extremely viscous and their viscosities very sensitive to concentration, as evident in Part I of this thesis.

Polyacrylamides undergo the typical reactions of aliphatic amides. The most important of these reactions are those leading to ionic derivatives and those leading to insoluble crosslinked polymers. The most important ionic derivatives of polyacrylamide are its copolymers with acrylic acid. They may be produced by alkali or acid hydrolysis of polyacrylamide. However, they are more conveniently produced by the copolymerization of acrylamide with acrylic acid or its salts. Part III of this thesis will investigate this copolymerization system.

The applications of polyacrylamide and its copolymers with acrylic acid rely primarily on the following characteristics of these polymers(2) :

1. They are very high molecular weight, stable polymers.
2. They are water-soluble over a broad range of conditions and the copolymers are hydrophilic..
3. The polymers are adsorbed by particles or by extended surfaces and hydrogen bond strongly.
4. Crosslinking of the polymers can be effected.

The most important uses for polyacrylamide and acrylamide-acrylic acid copolymers are(12) :

1, Those associated with flocculating and settling of aqueous suspension, mainly in the treatment of waste-water(13).
2. Paper-treating resins.
3. Gelling or stabilizing for soils and muds.
4. Coatings, with acrylamide as a comonomer of the thermosetting acrylic resins.
5. In drilling fluids and secondary oil recovery in the petroleum production industry.

The chemical and physical properties of acrylamide polymers may be found in several references(14,15). The techniques for the chemical analysis of both the acrylamide monomer and its polymers and c[illegible]ymers have been detailed by Norris(16).

II.2 Theoretical Background and Literature Review

II.2.1 Aqueous Polymerization

Aqueous vinyl polymerization is essentially a free-radical chain process, as opposed to an ionic process. This is due to the fact that an ionic chain process that produces vinyl polymers is not sustainable in water due to rapid chain termination to produce H^+ or OH^- ions that are impotent as initiators of vinyl polymers(17).

Of all solvents, water is unique in having a chain-transfer constant of practically zero(18,19). This partly accounts for the high molecular weight polymers obtainable in aqueous polymerization(20).

II.2.2 Free-Radical Polymerization

A brief outline of the chemistry of free-radical polymerization will be presented in this section. This model has been described in detail in several textbooks. The following outline parallels the presentations of Odian(21) and Hamielec and Friis(22).

Radical chain polymerization is a chain reaction consisting of a sequence of three steps : initiation, propagation and termination. In some systems a transfer step may parallel the above three.

There are three major types of free-radical initiators employed in industrial polymerization. These are the chemical, thermal and radiation initiation. Only chemical initiation will be outlined here as it is the one relevent to the present investigation, and it is also the most widely used in industry. The usual case is the homolytic dissociation of initiator or catalyst species I to yield a pair of free radicals R_c^* which can rapidly react with a monomer molecule M to begin the propagation of the polymer chain

$$I \xrightarrow{k_d} 2\ R_c^* \qquad \text{(II-1)}$$

$$R_c^* + M \xrightarrow{k_{pc}} R_1^* \qquad \text{(II-2)}$$

where R_1^* is the propagating radical containing one monomer unit, often referred to as "initiator radical" or "primary radical". k_d is the first-order decomposition rate constant of the initiator.

Propagation consists of the growth of R_1^* by the successive additions of monomer molecules according to the general scheme

$$R_r^* + M \xrightarrow{k_p} R_{r+1}^* \qquad \text{(II-3)}$$

where k_p is the propagation rate constant.

Termination, with the annihilation of the radical centres, occurs by bimolecular reaction between radicals. Two radicals react with each other either by combination (coupling)

$$R_r^* + R_s^* \xrightarrow{k_{tc}} P_{r+s} \qquad \text{(II-4)}$$

or by disproportionation, in which a hydrogen radical is transferred from one radical centre to the other. The result is the formation of two dead polymer molecules, one with a terminal double bond

$$R_r^* + R_s^* \xrightarrow{k_{td}} P_r + P_s \qquad \text{(II-5)}$$

where P_i represents a dead polymer chain consisting of i monomer units.

Both modes of termination may occur simultaneously, with the overall termination rate constant

$$k_t = k_{tc} + k_{td} \qquad \text{(II-6)}$$

During the free radical initiated polymerization of an ethylenic monomer, transfer reactions may take place between the growing polymer chain and the initiator, monomer, solvent or polymer. These reactions may be represented as follows

$$R_r^* + I \xrightarrow{k_{fi}} P_r + I^*\text{(initiator)} \qquad \text{(II-7)}$$

$$R_r^* + M \xrightarrow{k_{fm}} P_r + M^*\text{(monomer)} \qquad \text{(II-8)}$$

$$R_r^* + S \xrightarrow{k_{fs}} P_r + S^*\text{(solvent)} \qquad \text{(II-9)}$$

$$R_r^* + P_s \xrightarrow{k_{fp}} P_r + R_s^*\text{(dead polymer)} \qquad \text{(II-10)}$$

where I^*, M^*, S^*, and R_s^* are called transfer radicals. The general mechanism proceeds by the transfer of a hydrogen or a halogen atom from an inactive molecule to the growing chain. The growing chain is terminated and the radical activity is transferred to the hydrogen or halogen donor.

In order to make an analysis of the above reactions tractable, the following assumptions are generally made :

1. All the above-reactions are elementary.
2. The intrinsic reactivity of a radical is independent of its molecular weight and of conversion. This permits the use of a single rate constant for each reaction which depends only upon temperature.
3. The average chain length is large. This implies that the monomer consumed in reactions other than propagation is negligible in the calculation of total monomer consumption and polymer production. This assumption is usually referred to as the long chain approximation (LCA).
4. The stationary state hypothesis SSH is valid for all radical species. This permits the reduction of a set of ordinary differential equations to a set of algebraic equations.
5. Volume contraction during the reaction is negligible.

Using the above assumptions, the set of chemical equations (II-1) to (II-10) is analysed in detail in Appendix (II-1). Only the resulting final expressions will be presented below.

II.2.2.1 Polymer Production Rate for a Batch Reactor

The above system of equations yields a rate of polymerization, defined as the rate of monomer consumption, equal to

$$R_p = -\frac{d\,[M]}{d\,t} = \left(\frac{k_p^2}{k_t}\right)^{0.5} (2\,f\,k_d\,[I])^{0.5}\,[M] \qquad \text{(II-11)}$$

where $[I]$ and $[M]$ are the concentrations of the ini monomer, respectively, and f denotes the initiator efficiency which is defined as the fraction of the radicals R_c^* produced in the homolysis reaction which initiate polymer chains.

Integration of Eq. (II-11) to express the conversion-time behaviour is straightforward, except for the polymer systems that exhibit the so-called "gel effect". In these systems, the increase in the polymer concentration in the reaction mixture with increasing conversion leads to an increase in viscosity, which results in a significant reduction of the translational and segmental diffusion of radical chains. Therefore, reactions involving long radical chains become diffusion controlled. In such systems k_t will fall appreciably with monomer conversion. To account for this effect, a relationship between k_t and conversion is required for a numerical integration of Eq. (II-11) to be performed.

II.2.2.2 Molecular Weights of Resulting Polymers

Considering the case where branching reactions and transfer to polymer are negligible, the following expression for the number-average chain length $\bar{r}_n$ is developed in Appendix (II-1)

$$\frac{1}{\bar{r}_n} = \frac{(2\ k_{td} + k_{tc})\ R_p}{2\ k_p^2\ [M]^2} + \frac{k_{fm}}{k_p} + \frac{k_{fi}}{k_p}\frac{[I]}{[M]} + \frac{k_{fs}}{k_p}\frac{[S]}{[M]} \qquad (II-12)$$

It is clear from Eq. (II-11) and Eq. (II-12) that although the transfer reactions do not alter the overall rate expression, their effect is to lower the molecular weight of the resulting polymer. Expressions for $\overline{r}_w$ and $[\eta]$ may be found in Appendix (II-1). These equations and their cumulative forms are very useful in polymer reactor model parameter estimation. They are especially useful for the development of a strategy for molecular weight control.

II.2.2.3 Deviations from the Rate Expression

A dependence of the rate R_p on the monomer concentration $[M]$ greater than first-order was observed early in the study of several polymerization systems, including polyacrylamide. This has been generally explained using a more complicated initiation mechanism leading to a monomer dependent initiation rate. The mechanisms proposed for this purpose may be classified into two main categories: the complex theory and the cage-effect theory.

The complex theory(23) proposes the formation of a complex between initiator and monomer, the rate of initiation is then determined by the rate of decomposition of the complex.

$$I + M \underset{}{\overset{K_c}{\rightleftharpoons}} I—M \qquad \text{(II-13)}$$

$$I—M \xrightarrow{k_1} M^* + R_c^* \qquad \text{(II-14)}$$

Making the usual assumptions, this model leads to an expression of the rate of polymerization given by

$$R_p = k_p \left(\frac{2\ k_1}{k_t} \right)^{1/2} \left(\frac{K_c}{1 + K_c\ [M]} \right)^{1/2} [I]^{1/2}\ [M]^{3/2} \qquad \text{(II-15)}$$

This equation describes a change in the order of the reaction with respect to the monomer concentration from 1.50 to 1.0 with increasing monomer concentration.

The Cage-Effect theory(24) proposes that when a catalyst decomposes into two radicals, the surrounding solvent molecules form a potential barrier to their separation by diffusion. The "caged" radicals may then recombine with each other, may react with a monomer molecule or may diffuse out of the cage. The following equations illustrate this kinetic scheme, where the parentheses indicate species contained in a solvent cage.

$$I \xrightarrow{k_d} (2\ R_c^*) \qquad \text{(II-16)}$$

$$(2\ R_c^*) \xrightarrow{k_R} I \qquad \text{(II-17)}$$

$$(R_c^*) \xrightarrow{k_D} R_c^* \qquad \text{(II-18)}$$

$$(R_c^*) + M \xrightarrow{k_x} R_1^* \qquad \text{(II-19)}$$

$$R_c^* + M \xrightarrow{k'_x} R_1^* \qquad \text{(II-20)}$$

$$2\ R_c^* \xrightarrow{k'_R} I \qquad \text{(II-21)}$$

The relative magnitude of the reaction rate constants will determine the dependence on the monomer concentration. If $k_D \ll k_x M$, and making the usual conventional assumptions, the following expression for the rate of polymerization arises

$$R_p \propto \left(\frac{k_x}{k_R + k_x [M]} \right)^{1/2} [I]^{1/2} [M]^{3/2} \qquad \text{(II-22)}$$

Again the dependence on monomer concentration varies from a power of 1.50 to 1.0 as the monomer concentration increases. Thus the interpretation of kinetic orders greater than unity in the cage-effect model hinges on the dominance of the reaction between caged radicals and monomer molecules in the cage wall, Eq. (II-19).

We may note that Eq. (II-15) and Eq. (II-22) are of the same form. The reason why the cage-effect theory was proposed is that efforts to detect the existence of a complex through melting point-composition relationships or by spectroscopic examination have been inconclusive; and although K_c, the equilibrium constant in Eq. (II-13), experimentally increases with temperature, the negative entropy changes usually accompanying complex formation would predict the opposite.

Finally, an alternative concept, associated with the cage-effect theory, has been proposed by Noyes(25) to explain the rate dependence on monomer concentration. We have shown that when a molecule is dissociated into two radicals in a liquid phase, the radicals may undergo "primary recombination" in the "cage" in which they were formed, Eq. (II-17). The fragments that escape from the "cage" undergo random diffusive displacements. If they re-encounter each other they undergo "secondary recombination" Eq. (II-21) or may combine with radicals from other dissociations. Noyes shows that a reactive free-radical scavenger—the monomer—present in low concentrations, may compete only with the secondary recombination of original partners from a dissociation. Primary recombination occurs too rapidly for competition, except in a medium that consists almost entirely of very reactive scavengers. If such competition with the secondary recombination process does occur, Noyes shows that the fraction of radicals reacting with the monomer that would otherwise have undergone secondary recombination, i.e. the increase in efficiency of initiation, varies approximately as the square root of the concentration of the monomer. Hence the total rate of initiation is given by

$$R_I = K_o + K_1 \left[M\right]^{1/2} \qquad \text{(II-23)}$$

where K_o and K_1 are constants. With this rate of initiation, the rate of polymerization becomes

$$R_P = \left(\frac{k_p}{k_t^{1/2}}\right) \left(K_o + K_1 \left[M\right]^{1/2}\right) \left[M\right] \qquad \text{(II-24)}$$

and this defines an exponential dependency on monomer concentration between 1.0 and 1.25. If $K_1 \gg K_o$, $R_p \propto \left[M\right]^{1.25}$, which is the experimental result found for polyacrylamide.

II.2.3 Kinetic Data for Acrylamide Polymerization

Kinetic studies of the polymerization of acrylamide have been made using a number of different initiator systems. These include radiation initiation with x-rays, γ-rays, and UV light, and chemical initiation with redox systems, peroxides persulfates and azo compounds. Polymerization was conducted either in solution or in the solid crystalline state. A listing of many of these studies has been provided by Ishige(20). The following is a review of some of those studies that are the most relevent to the present investigation.

Suen and Rossler(26) polymerized acrylamide, then they extracted all residual monomer by a series of alternate steps of precipitation in acetone and dissolution in water. Then, by titrating for the residual unsaturation in the polymer molecules and by estimating the degree of polymerization by viscometry, they established that every two polymer molecules possess one double bond. Hence they concluded that the termination step in the polymerization of acrylamide is to a large extent through disproportionation. This conclusion has been generally accepted by subsequent investigators. It has also been confirmed when some of these investigators found that kinetics based on termination by disproportionation gave better agreement between the measured and the predicted molecular weight distributions, than did those based on termination by combination.

The most comprehensive study carried out to elucidate the reaction mechanism of acrylamide polymerization, and to evaluate the individual rate constants associated with it, has been reported in a series of four papers by Dainton and different co-workers(28-31). Based on data at two temperatures (25°C and 40°C), they found the Arrhenius expression for the ratio $\frac{k_p}{k_t^{1/2}}$, in the units of $(\frac{l}{\text{mole sec}})^{1/2}$ as follows

$$\frac{k_p}{k_t^{1/2}} = 57.0 \exp(-\frac{1500}{2\,T}) \qquad \text{(II-25)}$$

where T is in (°K).

The ratio $(\frac{k_p}{k_t^{1/2}})$ exceeds that reported for any other monomer(2). This means the number of molecules of monomer polymerized per initiating event is much greater for acrylamide than for other monomers. It implies also that polymerization will be rapid and molecular weights high.

The values predicted by Eq. (II-25) have been generally accepted by subsequent investigators. Furthermore, in a later study(32), Dainton et.al. showed that although k_p and k_t both diminish by about one order of magnitude as the pH is changed from 1 to 13, the ratio $\frac{k_p}{k_t^{1/2}}$ remains almost constant.

The value of the ratio $\frac{k_{fm}}{k_p}$, associated with the transfer reaction to the monomer molecules, is not as unequivocally defined. When acrylamide was polymerized in aqueous solution by x and γ-ray initiation(28), Dainton et al. found $\frac{k_{fm}}{k_p}$ to be "not greater than 10^{-6}" at 25 °C. On the other hand, in the hydrogen peroxide photosensitized polymerization(30), $\frac{k_{fm}}{k_p}$ was found to be 1.2×10^{-5}, also at 25°C. Subsequent investigators have reported values for this ratio closer in magnitude to the latter of the above two values reported by Dainton.

Fadner and Morawetz(33) polymerized acrylamide in the crystalline state and reported values for $\frac{k_{fm}}{k_p}$ of 2×10^{-5} at 25°C and of 6×10^{-5} at 60°C. Using the initiator 4-4'-Dicyano-4-4' azo pentanoic acid, Cavell reports two slightly different values for this ratio at 25°C, 1.6×10^{-5} (34) and 2.0×10^{-5} (35). Other values for this ratio will be reported later in this section.

As mentioned before, water has a chain transfer constant of practically zero(18,19), and as no transfer agent was used in the present investigation, the last term of Eq. (II-12) may be neglected.

The transfer reaction to dead polymer was studied by radio tracer techniques(36). It was concluded that at reaction temperatures of 50°C or less branching was negligible, whereas a significant amount of branching was observed when polymerization was conducted at 78°C, indicating the importance of transfer to dead polymer at high temperatures.

It may be that in the great majority of the kinetic studies performed, the reactions were carried out in a batch reactor equipped with a dilatometer to measure the conversion history of the reaction. After the reaction was virtually complete, the polymers were recovered and their molecular weights measured. Therefore, none of these studies provide any information on how the molecular weights change with conversion. Furthermore, the molecular weights measured for polymers recovered at high conversions are the cumulative ones integrated over the reaction time, as indicated by Eq. (II-A1-28) through (II-A1-31) in Appendix (II-1). Therefore, fitting these molecular weights to Eq. (II-12) in order to estimate the reaction rate constants is not rigorously correct.

Two investigators have corrected for this shortcoming :

1. Ishige(5,20), by conducting the polymerization reactions in small glass ampoules that could be quenched consecutively at different time intervals, was able to measure the change of molecular weight averages with conversion. The initiator used in that study was 4-4' azobis-4-cyanovaleric acid. He found the molecular weight averages to remain almost constant with conversion, monomer concentration and initiator concentration. Only a change in temperature appreciably affected the molecular weights of the polymers produced. By examining Eq. (II-12) he concluded that the transfer reaction to monomer molecules was the prevailing one in controlling the molecular weights of the polymer. In other words, the term $\frac{k_{fm}}{k_p}$ is much greater than all the other terms on the right-hand side of Eq. (II-12). Ishige reports a value of $\frac{k_{fm}}{k_p}$ of 1.4×10^{-5} at 50°C.

2. Kwangfu studied the polymerization of acrylamide in different aqueous media using different initiating systems and reported his results in a series of six papers. With

sodium metaperiodate as initiator, and at a temperature of 40°C, the average degree of polymerization of the polymers produced remained constant with conversion in neutral and acid solutions (pH $\leq$ 7); whereas in alkaline solutions, the degree of polymerization increased remarkably as the polymerization proceeded(37). The chain transfer constant to monomer $\frac{k_{fm}}{k_p}$ was found to be 5.8×10^{-4} at a pH of 5.4 and 40°C(39). With potassium persulfate as initiator, the average molecular weights did not show a systematic change with either pH or conversion (up to 83% conversion), whereas when hydrogen peroxide was used as initiator, a dramatic increase of molecular weight with conversion was observed at all pH(42). Unfortunately, in the case of $K_2S_2O_8$ and H_2O_2 initiator, Kwangfu did not vary $[I]$ or $[M]$ to try to estimate the different groups of reaction rate constants in Eq. (II-12).

The dependence of the rate of polymerization R_p on monomer concentration $[M]$ and initiator concentration $[I]$ has been investigated for a large number of initiating systems(20). The square root dependency of R_p on $[I]$, predicted by Eq. (II-11) has been consistently observed in the absence of a linear terminator. The dependence of R_p on $[M]$ however was found to vary significantly depending on the particular initiator used. R_p was found to be proportional to $[M]^{\alpha}$, with α taking values between 1.0 and 2.5. No acceleration in the rate of polymerization was observed at intermediate conversions, indicating that the "gel effect" was not present in the case of solution polymerization of acrylamide.

Riggs and Rodriguez(43) investigated the polymerization of acrylamide with potassium persulfate ($K_2S_2O_8$) initiator. They used a dilatometric technique to collect conversion-time data. Their results were found to fit the following empirical rate expression

$$R_P = k_{1.25} \left[I\right]^{0.5} \left[M\right]^{1.25} \qquad (II-26)$$

with the constant $k_{1.25}$ conforming to the Arrhenius expression

$$k_{1.25} = 1.70 \times 10^{11} \exp\left(- \frac{16,900}{1.987\ T}\right) \qquad (II-27)$$

with T in (°K) and $k_{1.25}$ in $\left(\frac{1^{0.75}}{\text{mole}^{0.75}\ \text{min.}}\right)$. The range of variables investigated was as follows

$T = 30 - 50$ (°C)

$\left[M\right] = 0.05 - 0.40$ (Moles/l)

$\left[I\right] = 9.5 \times 10^{-4} - 5.2 \times 10^{-2}$ (Moles/l)

The authors considered both the complex theory and the cage effect theory to explain the exponential dependence of R_P on $\left[M\right]^{1.25}$. Though no conclusive evidence was found, they favored the cage-effect theory for the same energetic arguments advanced above in Section (II.2.2.3). But the authors conceded that weaknesses are present in both theories and that "the point is not clear".

The authors then proceeded to estimate, by viscometry, the molecular weight averages of those polymers recovered at the end of the polymerization. They found these averages difficult to measure and reproduce. Furthermore, their attempts to use those measured molecular weight averages are not satisfactory. The plots that the authors try to fit their data to (M_v versus $[M]_o$ for all $[I]_o$, and $M_v[M_o]^{-1.25}$ vs. $[I]_o$) cannot be derived from the free-radical polymerization model, Eq. (II-12), even when disregarding all transfer reactions. Also, the scatter in the above-mentioned plots was considerable, and the authors do not draw any conclusions from them. However, their results do show a definite trend for the measured molecular weight averages to increase with increasing $[M]_o$ and to decrease with increasing $[I]_o$. This would indicate, in this system, that the molecular weights of the formed polymers are not mainly determined by the transfer reaction to monomer. In other words, $\frac{k_{fm}}{k_p}$ is not the only significant term on the right-hand side of Eq. (II-12). This is contrary to what Ishige(20) found with 4-4'-azobis-4-cyanovaleric acid (ACV) initiator. This would seem to indicate that either the transfer reaction to $K_2S_2O_8$ is significant or that the rate of propagation k_p is much higher with $K_2S_2O_8$ as initiator than that with ACV. However, from the experimental rate data presented by Ishige(20) and Riggs and Rodriguez(43), R_p is comparable in both systems, with ACV giving a larger R_p than $K_2S_2O_8$. On the other hand, no information is given in the literature about the magnitude of the transfer constant $\frac{k_{fi}}{k_p}$ to the persulfate initiator during the polymerization of acrylamide. We may also note that a substantial transfer reaction to the initiator $K_2S_2O_8$ is in apparent contradiction with the observation made by Kwangfu, that the average degree of polymerization did not change with conversion when the polymerization reaction was carried out in neutral and acidic solutions with $K_2S_2O_8$ as initiator$^{(42)}$.

Examination of the above-mentioned studies leads to the following conclusions :

1. There are extensive and reliable data, collected mainly by dilatometry, relating the rate of polymerization of acrylamide to $[M]$ and $[I]$ for different initiating systems, including $K_2S_2O_8$. Any further contribution to this particular aspect of polymerization would centre on interpreting the fact that, for many of these initiating systems, R_p is proportional to $[M]$ raised to a power higher than 1.0; the value predicted by classical kinetics, Eq. (II-11). However, for polymer reactor design purposes, the conversion-time history can be predicted with reasonable accuracy for most initiating systems.

2. The situation is far from satisfactory with regard to the kinetic parameters necessary for the prediction and control of the molecular weights of the resulting polymers, Eq. (II-12). To illustrate this fact, the following table summarizes the values reported for $\frac{k_{fm}}{k_p}$ in the above-mentioned studies

$\frac{k_{fm}}{k_p}$	Temp. (°C)	Reference
$> 10^{-6}$	25	Collinson, Dainton, and McNaughton(28)
1.2×10^{-5}	25	Dainton and Tordoff(30)
1.6×10^{-5}	25	Cavell(34)
2.0×10^{-5}	25	Cavell and Gilson(35)
2.0×10^{-5}	25	Fadner and Morawetz(33)
6.0×10^{-5}	60	Fadner and Morawetz(33)
1.45×10^{-5}	50	Ishige(20)
5.8×10^{-4}	40	Kwangfu(39)

The values reported for $\frac{k_{fm}}{k_p}$ at 25°C vary by a factor of 20, and at the higher temperature level of 40-60°C the values vary by a factor of 10, and this latter variation cannot be explained by the variation of temperature from one investigation to the other. These uncertainties in the value of $\frac{k_{fm}}{k_p}$ would cause differences of several orders of magnitude in the predicted molecular weights of the resulting polymers, especially if the transfer to monomer is the most important one in determining these molecular weights, as Ishige reports(20).

3. Almost all of the studies mentioned above used viscometry to determine the average molecular weights of the polymers produced. No provisions were taken to correct for the non-Newtonian effects when estimating the intrinsic viscosities of polyacrylamides having molecular weight averages of several million(20,28,30,34). As we have proved in Part I

of this thesis, this practice may introduce a considerable error in the computed intrinsic viscosities, rendering the values of $\frac{k_{fm}}{k_p}$, based upon these viscosities doubtful.

4. The fact that no estimate of the transfer constant $\frac{k_{fi}}{k_p}$ to the initiator $K_2S_2O_8$ is available in the literature of acrylamide polymerization is a serious deficiency. $K_2S_2O_8$ is an important initiator, both when used alone and when used in redox systems. As pointed out, the transfer reaction to $K_2S_2O_8$ may account for the fact that Riggs and Rodriguez(43) found a dependence of the molecular weights on $[M]$ and $[I]$ while Ishige did not. And, as evident from Eq. (II-12), a knowledge of $\frac{k_{fi}}{k_p}$ is of utmost importance in polymer reactor design for the control of the molecular weights of the polymers produced.

5. It is important to resolve the apparent contradiction between the observation made by Kwangfu(42), viz. that with $K_2S_2O_8$ as initiator, the molecular weights of the polymers were independent of conversion, except in highly alkaline aqueous media; and that made by Riggs and Rodriguez(43), using the same initiator, that the molecular weights increased with increasing $[M]$ and decreased with increasing $[I]$.

Hence, in order to elucidate some of the contentious points mentioned above, the present experimental investigation was undertaken with the following objectives :

1. To monitor the variation of the degree of poly-

merization of the resulting polyacrylamide with $[M]$, $[K_2S_2O_8]$, conversion and temperature. The degree of polymerization is to be determined by the four-bulb viscometer, described in Part I, to correct for the shear rate effects.

2. From the above data, to estimate the value of the kinetic parameter $\frac{k_{fm}}{k_p}$ and compare it to the ones reported in the literature. Also, an estimate for $\frac{k_{fi}}{k_p}$ is to be found from the same data for the acrylamide - $K_2S_2O_8$ system, a value that is not available in the literature. The variation of both these kinetic parameters with temperature was also to be found.

3. To evaluate the reliability of the rate expression developed by Riggs and Rodriguez(45) for the acrylamide-$K_2S_2O_8$ system, Eq. (II-26), and that of the reaction-rate constant associated with the above expression, Eq. (II-27).

4. It was hoped that a precise determination of the above kinetic parameters would render the development of the free radical kinetic model complete for the acrylamide-$K_2S_2O_8$ aqueous polymerization systems. Hence this model could be used in the design simulation and optimization of reactors used in the industrial production of polyacrylamide. This implies the ability to predict conversion and molecular weight averages and distribution of the polymers formed up to high conversions. This would also help to evaluate the relative importance of the pertinent reaction variables- viz. temperature,

conversion, $[M]$ and $[I]$ in the control of the molecular weights of the resulting polymers.

5. Reaction conditions were chosen so that the molecular weight averages of the resulting polymers were fairly high ($\overline{M}_n > 10^6$). This implied high $[M]$, low $[I]$ and low temperature. These high molecular weight polyacrylamides are by far the most important commercially. Hence it was important to ascertain whether the kinetic model holds at these conditions.

II.2.4 The Kinetics of the Decomposition of Potassium Persulfate in Aqueous Media

The kinetics of the thermal decomposition of $K_2S_2O_8$ in aqueous solutions have been investigated by Kolthoff and Miller(44). They found that $K_2S_2O_8$ decomposes through two different reactions :

1. An uncatalysed symmetrical rupture of the O–O bond to form two sulfate free radicals

$$S_2O_8^{--} \xrightarrow{k_1} 2\ SO_4^{-*} \qquad \text{(II-28)}$$

2. An acid catalysed reaction involving the unsymmetrical rupture of the O–O bond of the $HS_2O_8^-$ ion to form a bisulfate ion and SO_4

$$S_2O_8^{--} + H^+ \xrightarrow{k_2} HS_2O_8^- \longrightarrow SO_4 + HSO_4^- \qquad \text{(II-29)}$$

The kinetics of the total thermal decomposition may be expressed by the following equation.

$$-\frac{d[S_2O_8^{--}]}{dt} = (k_1 + k_2[H^+])[S_2O_8^{--}] \qquad \text{(II-30)}$$

The reaction rate constants take the following values at 50 °C

$k_1 = 6.0 \times 10^{-5}$ (min)$^{-1}$

$k_2 = 3.5 \times 10^{-3}$ $(\frac{l}{\text{mole min}})$

The corresponding activation energies were found to be

$E_1 = 33.5$ (KCal/mole).

$E_2 = 26.0$ (KCal/mole)

From Eq.(II-30) and the values of k_1 and k_2 given, it is easy to demonstrate that reaction (II-29) will be negligible compared to reaction (II-28) in alkaline, neutral and dilute acid solutions. Only in acid solutions where $pH < 3$ does $K_2S_2O_8$ decompose through reaction (II-29) to an appreciable extent. And as the polymerization reactions in the present study were not carried out in such strongly acidic solutions, Eq.(II-29) may be neglected, and $K_2S_2O_8$ is considered to decompose according to the pseudo-first order rate expression

$$-\frac{d[S_2O_8^{--}]}{dt} = k_1[S_2O_8^{--}] \qquad \text{(II-31)}$$

Therefore, if X is the fractional conversion of $K_2S_2O_8$ at time t_X, the following expression holds

$$\ln\left(\frac{1}{1-X}\right) = k_1 t_X \qquad \text{(II-32)}$$

Two temperatures were used in the present investigation, viz. 25°C and 40°C. Denoting $t_{.02}$ as the time necessary for 2% of the original $K_2S_2O_8$ to decompose, this time was found to be as indicated in the following table :

T (°C)	k_1 (min.)$^{-1}$	$t_{.02}$ (hours)
25	7.7×10^{-7}	440
40	1.1×10^{-5}	31

As all polymerizations were terminated in a time less than $t_{.02}$ at each temperature, it is reasonable to assume that the concentration of $K_2S_2O_8$ remained virtually constant throughout the polymerization reactions. In other words, $K_2S_2O_8$ has such a long half-life that changes in its concentration during the polymerization reaction may be ignored. Therefore $[I]$ in equations (II-12) and (II-26) may be replaced by $[I]_o$, the original concentration of $K_2S_2O_8$ at time zero, without introducing a significant error into these equations.

It follows that Eq.(II-26) may be integrated analytically by separation of variables. Performing this integration and solving the resulting expression for the fractional conversion of the monomer we obtain

$$X = \frac{[M]_o - [M]}{[M]_o} = 1 - \left(\frac{k_{1.25} \, [I]_o^{0.50} \, [M]_o^{0.25} \, t}{4} + 1 \right)^{-4} \qquad \text{(II-33)}$$

This equation was used, together with the value of $k_{1.25}$ computed from Eq.(II-27) to describe the conversion-time behaviour predicted by the empirical relation, Eq.(II-26), developed by Riggs and Rodriguez(43). This was compared to the experimental conversion-time data obtained in the present investigation.

Finally, substituting the expression for the rate of polymerization R_p found by Riggs and Rodriguez, Eq.(II-26), into the expression for the instantaneous number-average chain length, Eq.(II-12), and after dropping the terms corresponding to termination via combination and transfer to solvent, the following equation is obtained

$$\frac{1}{\bar{r}_n} = \frac{k_{td}}{k_p^2} k_{1.25} \frac{[I]^{0.50}}{[M]^{0.75}} + \frac{k_{fm}}{k_p} + \frac{k_{fi}}{k_p} \frac{[I]}{[M]} \qquad \text{(II-34)}$$

Assuming $[I]$ to remain constant at its original value $[I]_o$ due to the long half-life of $K_2S_2O_8$, and substituting for $[M]$ in terms of conversion X, we get

$$\frac{1}{\bar{r}_n} = \frac{k_{td}}{k_p^2} k_{1.25} \frac{[I]_o^{0.50}}{[M]_o^{0.75}} \frac{1}{(1 - X)^{0.75}} + \frac{k_{fm}}{k_p} + \frac{k_{fi}}{k_p} \frac{[I]_o}{[M]_o} \frac{1}{(1 - X)} \qquad \text{(II-35)}$$

As pointed out in Appendix II.1, the cumulative average for all the polymers produced in a batch reactor up to any conversion X will be expressed by the following equation

$$\mathrm{Cum}\left[\frac{1}{\bar{r}_n}\right] = \frac{1}{X}\int_0^X \frac{1}{\bar{r}_n}\,dX \qquad \text{(II-36)}$$

Substituting Eq.(II-35) into Eq.(II-36), the above integration may be performed analytically to yield

$$\begin{aligned}\mathrm{Cum}\,\frac{1}{\bar{r}_n} &= 4\,k'\,\frac{[I]_o^{0.50}}{[M]_o^{0.75}}\,\frac{(1-(1-X)^{0.25})}{X} + C_M \\ &+ C_I\,\frac{[I]_o}{[M]_o}\,\frac{\ln[1/(1-X)]}{X}\end{aligned} \qquad \text{(II-37)}$$

where,

$$k' = \frac{k_{td}}{k_p^2}\,k_{1.25}$$

$$C_M = \frac{k_{fm}}{k_p}$$

$$C_I = \frac{k_{fi}}{k_p}$$

Equation (II-37) was used to estimate the values of the parameters C_M and C_I .

II.3 Experimental Set-Up and Procedures

II.3.1 Reagents

Acrylamide monomer was purchased from Eastman Kodak Company, Rochester, New York. It was purified by twice recrystallizing it out of chloroform, then washing it with benzene. The resulting crystals were then dried in a vacuum oven at room temperature for 24 hours. The purified acrylamide was stored, in the dark, in a dessicator over $CaSO_4$. Because of its hygroscopic nature, the monomer was periodically replaced in the vacuum oven at room temperature for several hours, before solutions were prepared for each experimental run.

The potassium persulfate initiator was purchased from Fisher Scientific Company, Fair Lawn, New Jersey. It was purified by recrystallizing it twice from twice-distilled water at 60°C. The crystals were then dried in a vacuum oven at room temperature for 24 hours. They were also stored in a dessicator, in the dark, over $CaSO_4$.

Water used as a polymerization medium, for viscosity measurements and for the final rinsing of glassware, was doubly distilled, the second distillation being from alkaline potassium permanganate in a Pyrex apparatus.

Other reagents were used as received.

II.3.2 Analytical Techniques

II.3.2.1 Conversion Measurements

Conversion of monomer to polymer was measured gravimetrically. The reaction was stopped by immersing the reaction ampoule in liquid nitrogen, then the ampoule was broken and its contents added to more than 10 times its volume of distilled water together with 10 ml. of a 0.1 gm/l aqueous solution of hydroquinone. After the reaction mixture was thoroughly mixed with the water and hydroquinone, the mixture was poured dropwise from a vessel provided with a teflon stopcock at its bottom, into methanol. Throughout the addition, methanol was stirred vigorously by a magnetic bar and stirrer. The volume of methanol used was at least ten times the total volume of aqueous solution poured into it.

The precipitated polymer was filtered on a pre-weighed, Pyrex brand, Gooch type, low-form glass filtering crucible equipped with a fritted disc of medium porosity having a nominal maximum pore size of 14 microns. The polymer was then washed several times with methanol and acetone. Then the crucible was placed in a vacuum oven kept at 40°C and dried to constant weight. The time needed for drying the polymers varied between about one and three days according to the amount of the polymer recovered and the physical state in which it was recovered (particle size, aggregation, etc.).

Conversion was calculated as the weight fraction of the recovered polymer to the weight of monomer initially present. All the conversion-time data collected in the present investigation are detailed in Appendix (II-2).

II.3.2.2 Molecular Weight Measurements

As described in Part I of this thesis, the number average molecular weight of the polymers collected were calculated from their measured intrinsic viscosities at high shear rates using the empirical relation $[\eta] = 6.80 \times 10^{-4} \bar{M}_n^{0.66}$. The four-bulb Cannon-Ubbelohde viscometer (size 50, No. S489), illustrated in Fig. (I-1), was used to correct for the non-Newtonian effects of the polymer solutions.

Sections (I-3) in Part I of this thesis details the description of the viscometer (I.3.2), its calibration (I.3.4) and the procedures followed in dissolving the polymers and in measuring their intrinsic viscosities (I.3.3). All the viscosity data collected in the course of this study are listed in Appendix (II-1).

II.3.3 Cleaning of Glassware

To obtain reliable rate data for polymerization reactions conducted in glass vessels, it is absolutely imperative to ensure the thorough cleanliness of these vessels(19,28), together with the high purity of the chemical reagents used. Also, it is generally recognized that solutions of high molecular weight polymers should be kept in very clean containers to eliminate the possibility of their molecular weights, and viscosities, being affected by any impurity present.

Therefore, all glassware used in this investigation that was to come in contact with either the monomer or the initiator solutions, or later with the polymer solutions (volumetric flasks, reaction ampoules, different flasks and beakers, glass rods, the four-bulb viscometer, etc.) was cleaned as follows :

1. The glassware was soaked for 24 hours in commercially available "Chromerge" cleaning solution (Manostat, New York, N.Y.) that contains chromium trioxide mixed with concentrated sulphuric acid.

2. The glassware was then rinsed repeatedly with distilled water, then left to soak in distilled water for two hours.

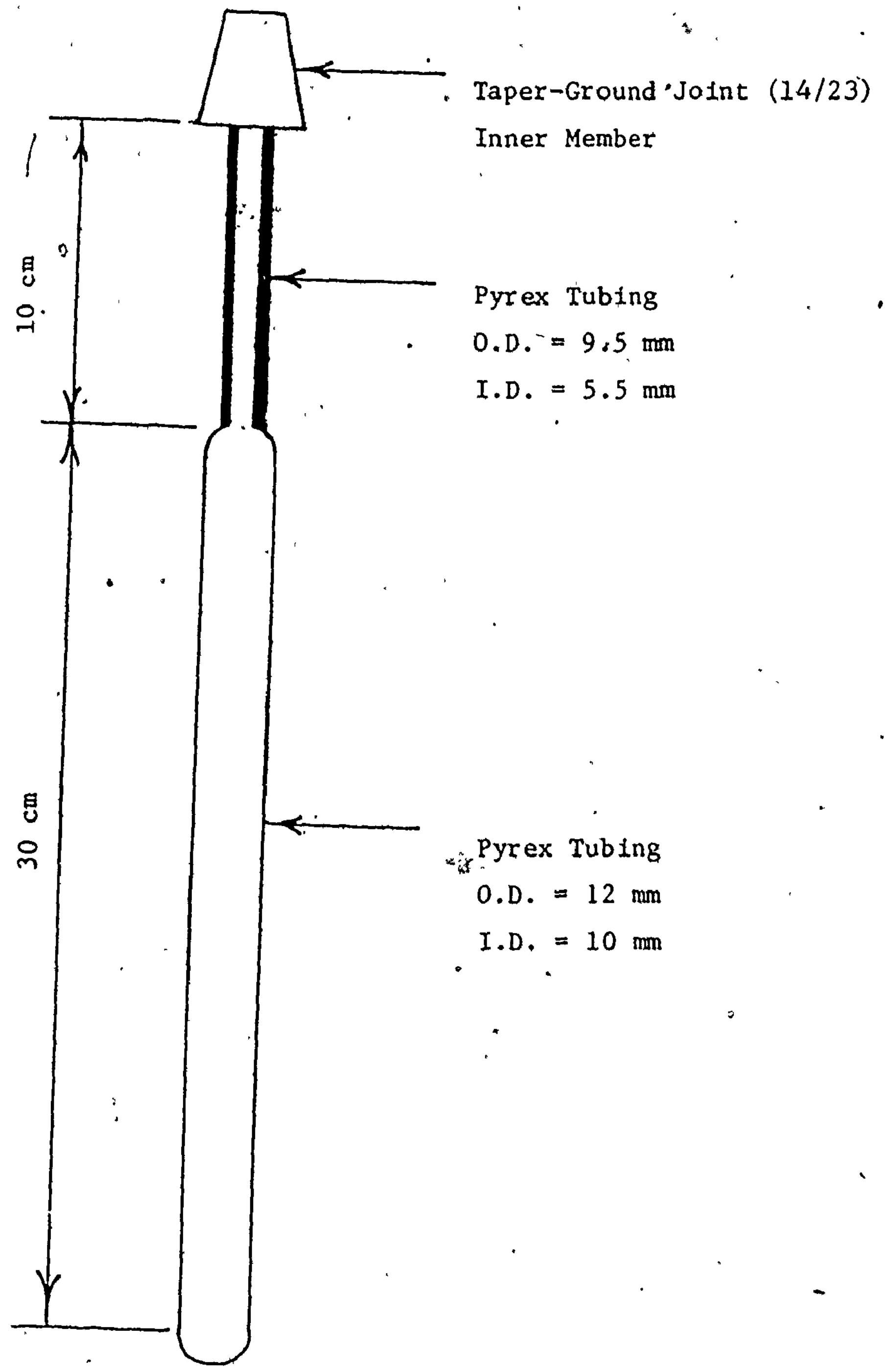
3. The glassware was then rinsed several more times with distilled water and finally rinsed once with the twice-distilled water used as a medium for polymerization.

4. The glassware was then left to dry in an oven.

II.3.4 The Reaction Vessels or Ampoules

The polymerization reactions were carried out in ampoules made of Pyrex glass tubing and equipped with a taper-ground joint at one end. The shape and dimensions of these ampoules are illustrated in Figure (II-1). The neck of the ampoule was made of thick-walled tubes to ensure easy sealing with a torch.

Fig. (II-I) The Pyrex Ampoules Used as Reaction Vessels



The use of ampoules with the dimensions shown in Figure (II-1) has been proven to be satisfactory in achieving isothermal conditions during the polymerization of acrylamide in the same range of variables (concentrations, temperature, etc.) used in the present study(20). This was done by comparing the conversion history of the polymerization reaction when conducted in ampoules identical in diameter to the one in Figure (II-1) with that of the same reaction when conducted in much thinner ampoules (O.D. = 6 mm, I.D. = 4 mm). No significant difference in the measured conversions was detected between the two methods. Hence it was concluded that isothermal conditions were achieved in both cases. The rates of polymerization in the present study are of the same order of magnitude, but somewhat smaller than those reported in the above study. Therefore it was safe to assume that isothermal conditions were also achieved in the present case.

II.3.5 Deaeration Apparatus and Procedures

It has been observed that freeze and thaw techniques commonly used for deaerating reaction ampoules in polymer chemistry were difficult to use for the polymerization of acrylamide since a considerable amount of polymerization occurred during the thawing steps(20,28). Dainton circumvented this difficulty by using a less rigorous freeze and thaw technique, viz. by reducing the number of freeze and thaw steps(28). Ishige opted for a technique whereby nitrogen gas was bubbled through the monomer solution and the initiator solution separately, then the two solutions were mixed in the required proportions in a deaerated reaction ampoule, which was then immediately sealed and transported to the constant temperature bath(20).

The second approach, used by Ishige, was chosen for the present investigation. The apparatus built for deaerating the monomer and initiator solutions is schematically shown in Figure (II-2). The apparatus consists of a vacuum line, a nitrogen line and two 50-ml. burettes (A and B in Figure (II-2)) containing the solutions to be deaerated. These burettes are connected to the vacuum and nitrogen lines and to one of the reaction ampoules at a time. Details of these connections for one of the burettes are shown in Figure (II-3).

The vacuum line consists of a single stage reciprocal type vacuum pump, a liquid nitrogen trap and a U-tube mercury manometer. The minimum absolute pressure produced in the line was about 10 mm Hg. This moderate vacuum was deliberately chosen to minimize water loss through evaporation.

The nitrogen line begins with a nitrogen gas pressurized cylinder (Canadian Liquid Air Ltd., Montreal, P.Q. - N_2 Grade L - 20 ppm max. O_2 content). The cylinder is equipped with a pressure gauge, a regulator, and a needle valve for fine control of the gas flow. The "nitrogen-head indicator", illustrated in Figure (II-2), follows the

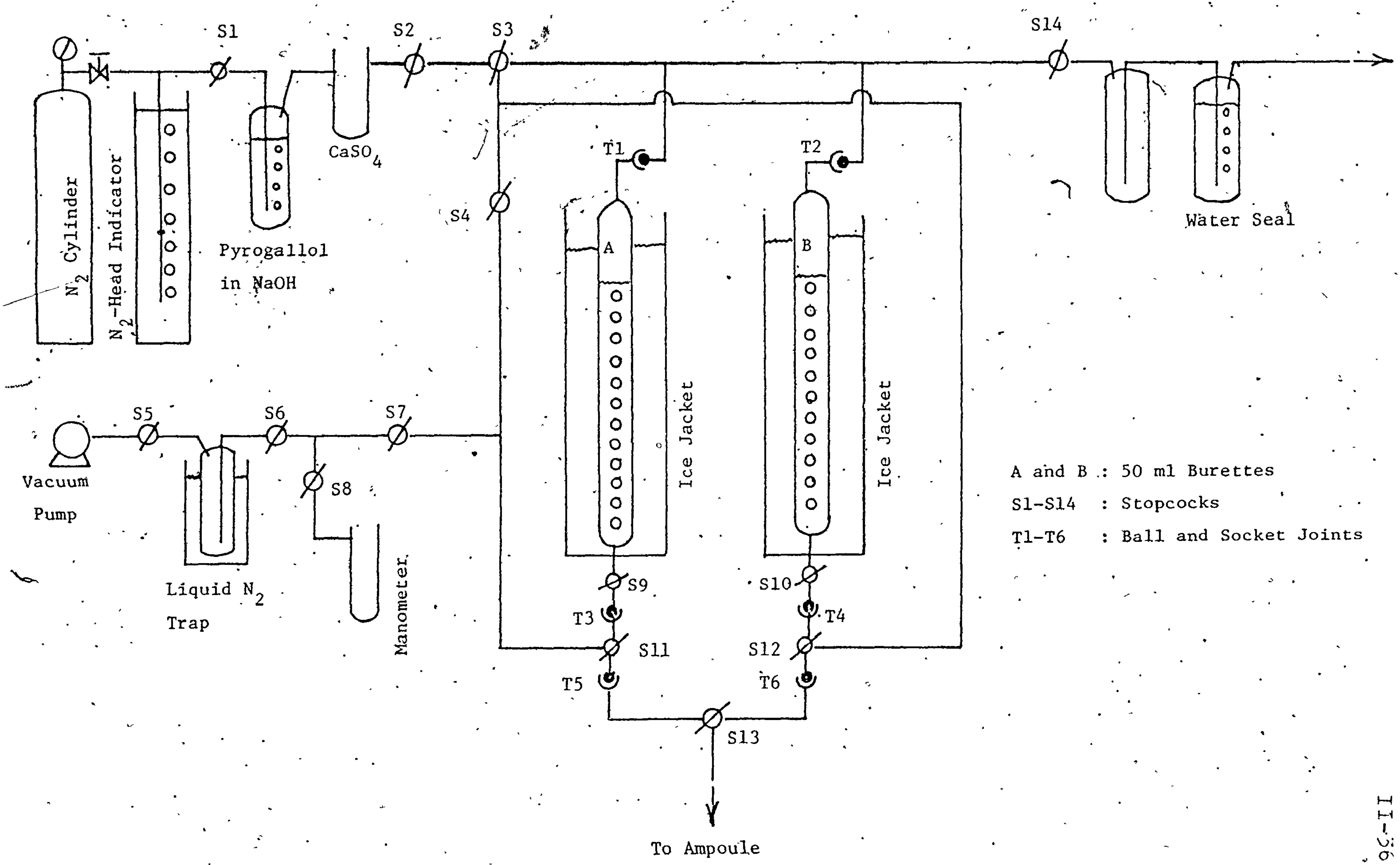
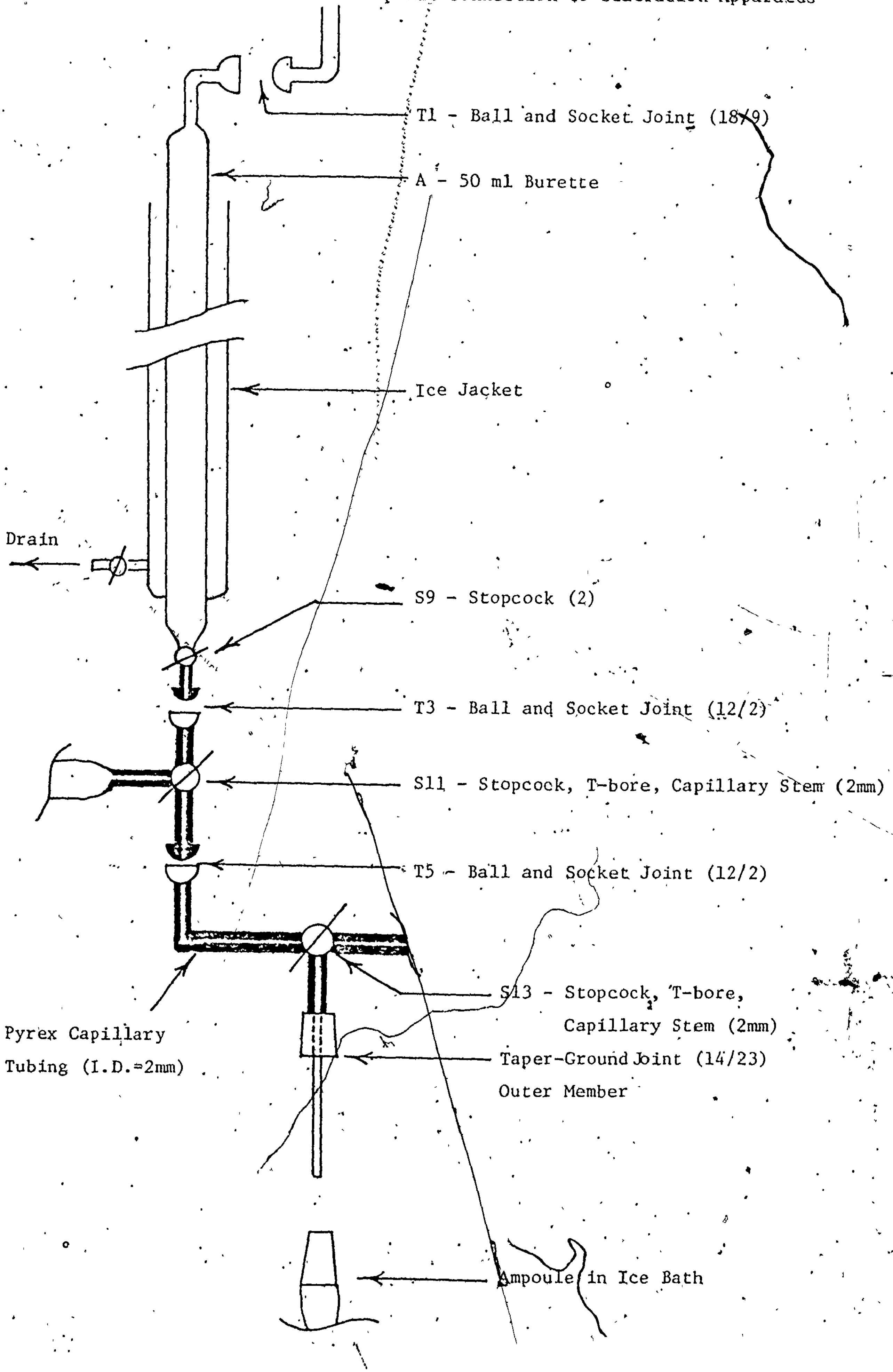


Fig. (II-2) Schematic Diagram of Deaeration Apparatus

Fig. (II-3) Burette and Ampoule Connection to Deaeration Apparatus



pressurized N_2-cylinder, and is nothing more than a T-tube immersed to a constant depth in water. It served the dual purpose of a fine indicator of the N_2 pressure in the line and as a safety escape valve. As will be pointed out later in this section, the ability to control and monitor the N_2 pressure inside the line within certain specified limits was essential for a successful deaeration process. The nitrogen was then bubbled through a 5 % solution of Pyrogallol in 2-N sodium hydroxide to eliminate all residual oxygen in the nitrogen gas. This gas was then passed through a U-tube filled with an indicating moisture absorbent (Dierite-$CaSO_4$). The emerging gas was used to deaerate the monomer and initiator solutions and the reaction ampoules.

By manipulating the fourteen stopcocks shown in Figure (II-2) either vacuum or N_2-gas may be applied to different parts of the deaerating apparatus.

The deaeration procedure was as follows :

1. The monomer and initiator solutions, at concentrations equal to twice those called for by the experiment, were charged in burettes A and B, respectively. The jackets surrounding these burettes were filled with a mixture of water and ice.

2. The air in all the tubes of the apparatus was replaced by nitrogen through alternate steps of application of vacuum and refilling with nitrogen gas. This was repeated five times.

3. Nitrogen was bubbled through the monomer and the initiator solutions for one hour. This has been proven to be adequate to eliminate induction periods[20,27]. During this step the pressure of the nitrogen gas had to be controlled accurately, for if this pressure became too high, flooding conditions occurred and the liquids were then carried over through the top of the burettes. On the other hand, if the nitrogen pressure fell below the head of liquid in the burettes, the solutions escaped through the bottom of the burettes. This was the reason why the "nitrogen-head indicator" was introduced to the nitrogen line.

4. One of the reaction ampoules was connected to the bottom of the line through the taper-ground joint as shown in Figure (II-3). The ampoule was then immersed in an ice-bath. The air in the ampoule was replaced by nitrogen through a step identical to step 2 above.

5. Known and equal volumes of the monomer solution and the initiator solution were introduced into the ampoule. For conversion measurements to be precise, it was essential that the volume of each solution introduced into the ampoule be known accurately. Hence, the following procedure was followed in filling the ampoules to eliminate "dead-volume" errors.

5-a. A moderate vacuum was applied to the ampoule and the capillary tubing between stopcocks S9 and S13.

5-b. The monomer solution from burette A was allowed to fill the volume between S9 and S11.

5-c. The reading on the scale of burette A was recorded (V_0, say).

5-d. By manipulating stopcock S13, the monomer solution was allowed to flow slowly into the ampoule. The flow was stopped when the reading on the scale of burette A indicated ($V_0 + V$), where V is the volume of the monomer solution required by the experiment.

5-e. Nitrogen gas was allowed to fill the tubes of the apparatus between S1 and S11 and by manipulating S11, N_2-gas was allowed to push the monomer solution remaining in the capillary between S11 and S13 into the ampoule.

5-g. Steps 5-a through 5-e were repeated for burette B to introduce an equal volume of the initiator concentration into the ampoule.

6. The neck of the ampoule was sealed-off by a torch. The ampoule was then shaken a few times and transferred into a thermostated bath maintained at the required reaction temperature. The same water-bath used for the viscometry measurements, and described in Section (I.3.3) of Part I of this thesis was used when the reaction temperature was 25°C. Whereas in the case of 40°C an oil-bath equipped at the bottom with an agitator plate, pulsated by a self-timing DC electromagnet to circulate the oil in the bath was used.

7. Steps 4 to 6 were repeated for all the reaction ampoules in each run.

II.3.6 Experimental Conditions

Following is the range of variables at which poly-merization reactions were carried out in the present investigation

Temperature, T : 25-40 (°C)

Initial Acrylamide Concentration, $[M]_o$:

0.20 - 2.0 (g moles/l)

Initial $K_2S_2O_8$ Concentration, $[I]_o$:

10^{-4} - 2.5 x 10^{-3} (g moles/l)

Conversion, X : 0.10 - 0.90 (approximately)

Each of the experimental runs will be designated by three hyphenated numbers of two digits each. The first number corresponds to the temperature in (°C), the second number equals $[M]_o$ x 10 in (g moles/l), whereas the third number indicates $[I]_o$ x 10^4 in (g moles/l). As an example, run No. 25-05-10 was conducted at 25°C with $[M]_o$ = 0.5 (g moles/l) and $[I]_o$ = 10^{-3} (g moles/l). Each polymer produced is designated by the three numbers corresponding to the run in which it was produced plus a letter used to distinguish between polymers produced at different conversion levels in the same run. For example, the polymers produced in the above-mentioned run No. 25-05-10 are designated by 25-05-10-A, 25-05-10-B, etc., in order of increasing conversion.

The choice of a relatively narrow range over which $[M]_o$ was varied requires an explanation. On the low end, because the capacity of the ampoule was limited to about

20 ml., $[M]_0$ could not be decreased much below 0.20 (g moles/l) and still recover enough polymer to analyse. Even at an $[M]_0$ of 0.20, not enough polymer was recovered at conversions below 20 - 30%. And as one of the main aims of this study was to monitor the molecular weight change with conversion, $[M]_0$ was not further decreased. On the other hand, $[M]_0$ could not be increased beyond 2.0 (g moles/l) for the following reason. After adding the quenched reaction mixture from the ampoule to ten times its volume of water inhibited by hydroquinone, the polymer mixture first swelled with water before gradually dissolving. At low conversions, the dissolution process was completed within 24 hours without the need for any mechanical stirring. On the other hand, for the polymer mixtures obtained at high conversions to dissolve, they had to be stirred for a considerable length of time. The time of stirring increases with $[M]_0$ as well as conversion. For $[M]_0 = 0.20$, dissolution was complete within a few hours of stirring even at the highest conversion. When $[M]_0 = 0.50$, the polymer mixtures obtained at conversions higher than about 80% required up to 2-3 days to dissolve. With $[M]_0 = 2.0$, even polymer mixtures recovered at about 40% conversion required several days of stirring whereas those obtained at conversions higher than approximately 80% required about two weeks of constant stirring to dissolve. These prolonged periods of stirring may introduce a serious error in the measured molecular weights. The effect of continuous

stirring of a polyacrylamide solution on its intrinsic viscosity has been reported by several investigators(20,45). They found the intrinsic viscosity decreased irreversibly by an amount proportional to the duration and the intensity of stirring. This was attributed to polymer molecules degrading under the effect of the shear rate applied to the solution. Therefore, in the present investigation, the largest uncertainty in the measured intrinsic viscosities is attributable to this dilution step, and this uncertainty is larger for higher conversions and $[M]_o$. Hence $[M]_o$ could not be increased much beyond 2.0 (g moles/l) without rendering the measured molecular weights, even those at moderate conversions, almost useless. Even with $[M]_o = 2.0$, it will be seen that the intrinsic viscosities obtained for the polymers recovered at the highest conversions are of doubtful value.

It must be emphasized that the step wherein the reaction mixture from the ampoule was diluted with water was absolutely necessary for a satisfactory polymer recovery process. Simple addition of the original polymer mixture to methanol resulted in the formation of a hard outer layer of polymer inside which the reaction mixture remained as a viscous monomer-polymer mixture in water. Attempts to dry these mixtures to constant weight in the vacuum oven were unsuccessful, as the weight kept on falling very slowly for more than a week. This is probably due to the slow rate of diffusion of water through the outer polymer layer.

Table (II-1) summarizes the experimental conditions for all the polymerization runs performed in the present investigation.

Table (II-1) Experimental Conditions for the Polymerization Runs

Run No.	Temperature (°C)	$[M]_o$ (g moles/l)	$[I]_o$ (g moles/l)
25-20-10	25	2.00	10^{-3}
25-05-10	25	0.50	10^{-3}
25-02-10	25	0.20	10^{-3}
25-05-01	25	0.50	10^{-4}
25-05-05	25	0.50	5.0×10^{-4}
25-05-25	25	0.50	2.5×10^{-3}
40-20-05	40	2.00	5.0×10^{-4}
40-05-05	40	0.50	5.0×10^{-4}
40-02-05	40	0.20	5.0×10^{-4}
40-05-01	40	0.50	10^{-4}
40-05-15	40	0.50	1.5×10^{-3}
40-05-25	40	0.50	2.5×10^{-3}

II-4 Results and Discussion

Appendix (II-2) is a summary of all the conversion and molecular weight measurements carried out during the present investigation. For each run, the following information is listed in consecutive columns of each table in the appendix.

1. The letter identifying the particular ampoule within the run.

2. The length of time, in hours, that the ampoule was left in the constant temperature bath, after the deaeration procedure, allowing the polymerization reaction to proceed before quenching it in liquid nitrogen.

3. The conversion, measured gravimetrically, as detailed in Section (II.3.2.1).

4. The predicted conversion, based on the empirical expression found by Riggs and Rodriguez, Eq. (II-26), and their corresponding reaction rate constant, Eq. (II-27). Furthermore, by assuming the $K_2S_2O_8$ concentration to remain constant during the course of the reaction, the integrated form of the polymerization rate expression was used, viz. Eq. (II-33).

5. The next two columns in the tables of Appendix (II-2) list the intrinsic viscosities of the polymers' solutions extrapolated to zero shear rate and to high shear rate, respectively. These were measured by the four-bulb capillary viscometer as detailed in Part I of this thesis. These

data are transcribed from Appendix (I-1).

6. The measured number average molecular weight as calculated from Eq. (I-37) using the intrinsic viscosities at high shear rates. The reason for this choice was stated in Section (1.4.1) of this thesis.

7. Finally, listed in the last ~~column~~ of each table, are the predicted cumulative number average molecular weights calculated from the free radical polymerization model as developed in Appendix (II-1). The integrated form of the expression, Eq. (II-37), was used, again assuming that the concentration of $K_2S_2O_8$ remained constant throughout the course of the polymerization reactions. The values of the kinetic parameters used in these calculations and the reasons for using them will be detailed below.

Figures (II-4) to (II-15) illustrate the above-mentioned data. In each figure, the lower curve is the conversion versus time relationship. The circles are the conversions measured experimentally, whereas the solid line is the predicted conversion history according to equations (II-33) and (II-27). The upper curve in each of these figures is the $\bar{M}_n$ versus time (hence, conversion) relationship. The squares are the average molecular weights measured by viscometry whereas the solid line is the predicted one according to Eq. (II-37).

II.4.1 Reproducibility

To ascertain that both the conversion measurements and the molecular weights of the resulting polymers are reproducible, the conditions in four of the experimental runs were duplicated, and, for each of these runs, three new polymers were produced at three different levels of conversion. These four runs were :

25-20-10

25-05-01

40-05-01

and 40-05-25

The data obtained from these duplicate tests are included in the tables of Appendix (II-2) with their respective runs, but under the heading of "Reproducibility Tests". These data are also included in Figures (II-4) to (II-15). The points representing these data are "filled in" to distinguish them from those obtained in the original runs.

II.4.2 The Rate Expression

First, the conversion-time data were examined to determine the expression for the polymerization rate R_p. This quantity is important not only to predict the conversion history (hence the production rate in industrial reactors, the heat to be dissipated per unit time, etc.) but also it enters directly into the expression of the average chain length of the resulting polymer chains, Eq. (II-12).

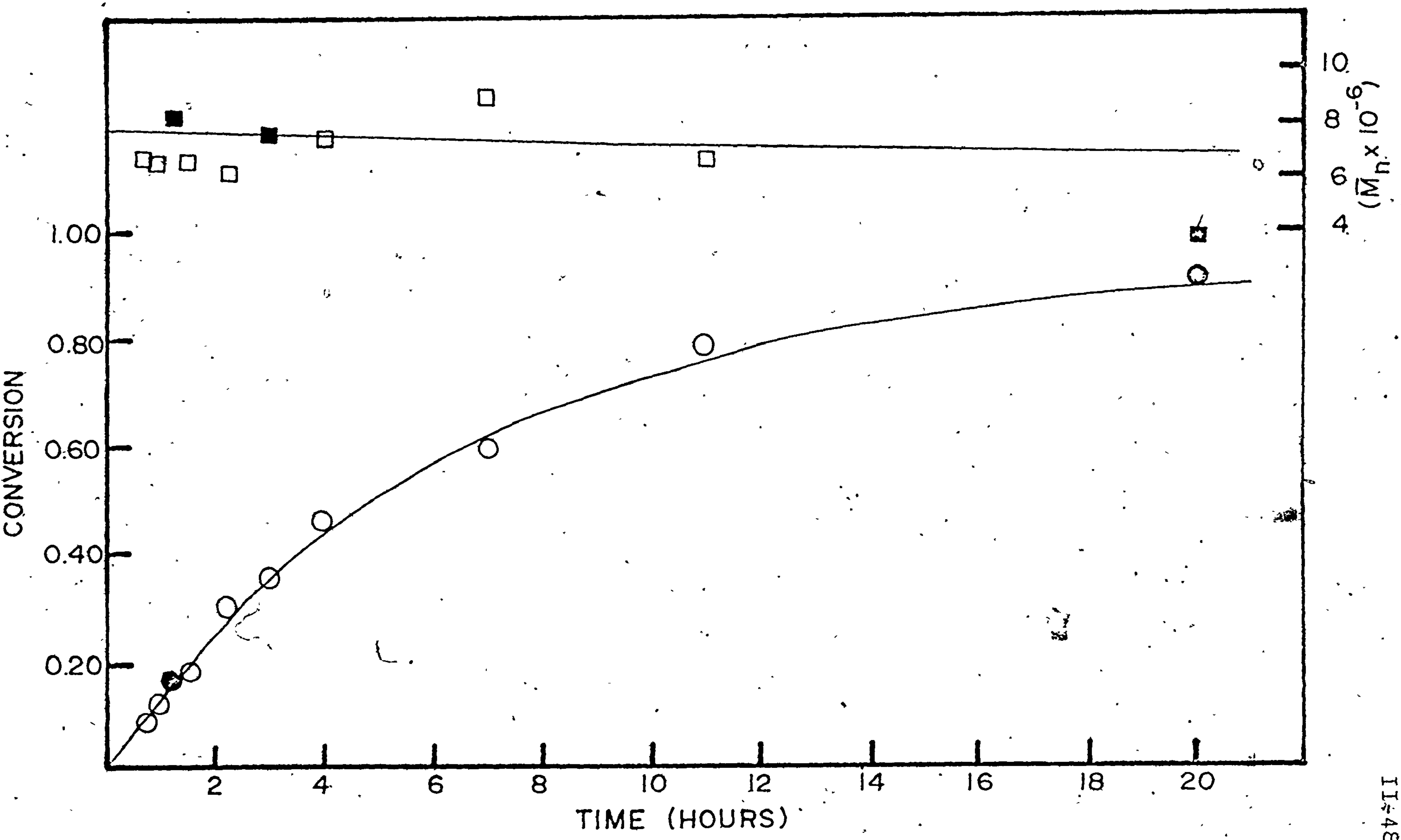
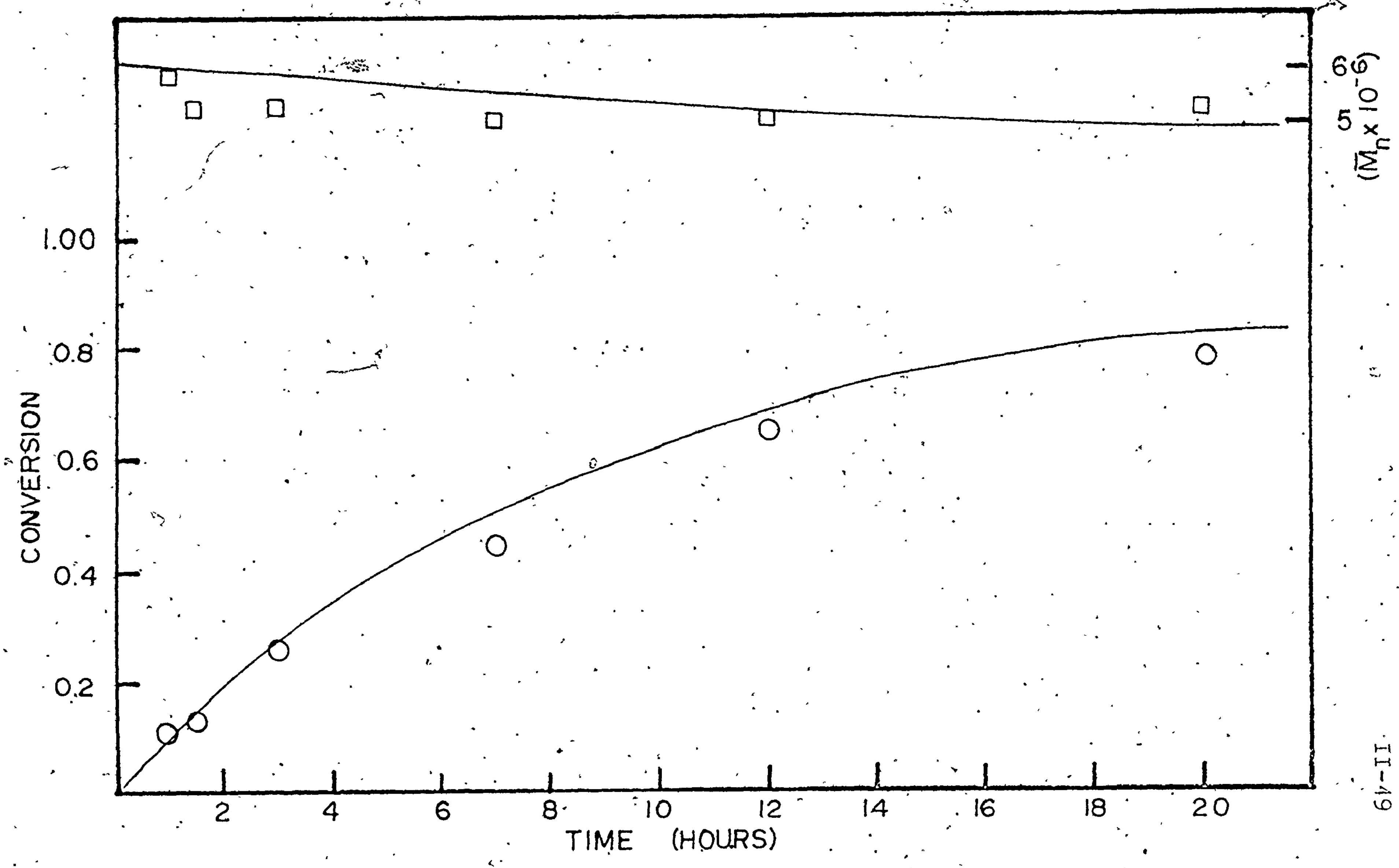


Fig. (II-4) - Run (25-20-10)

Fig. (II-5) - Run (25-05-10)



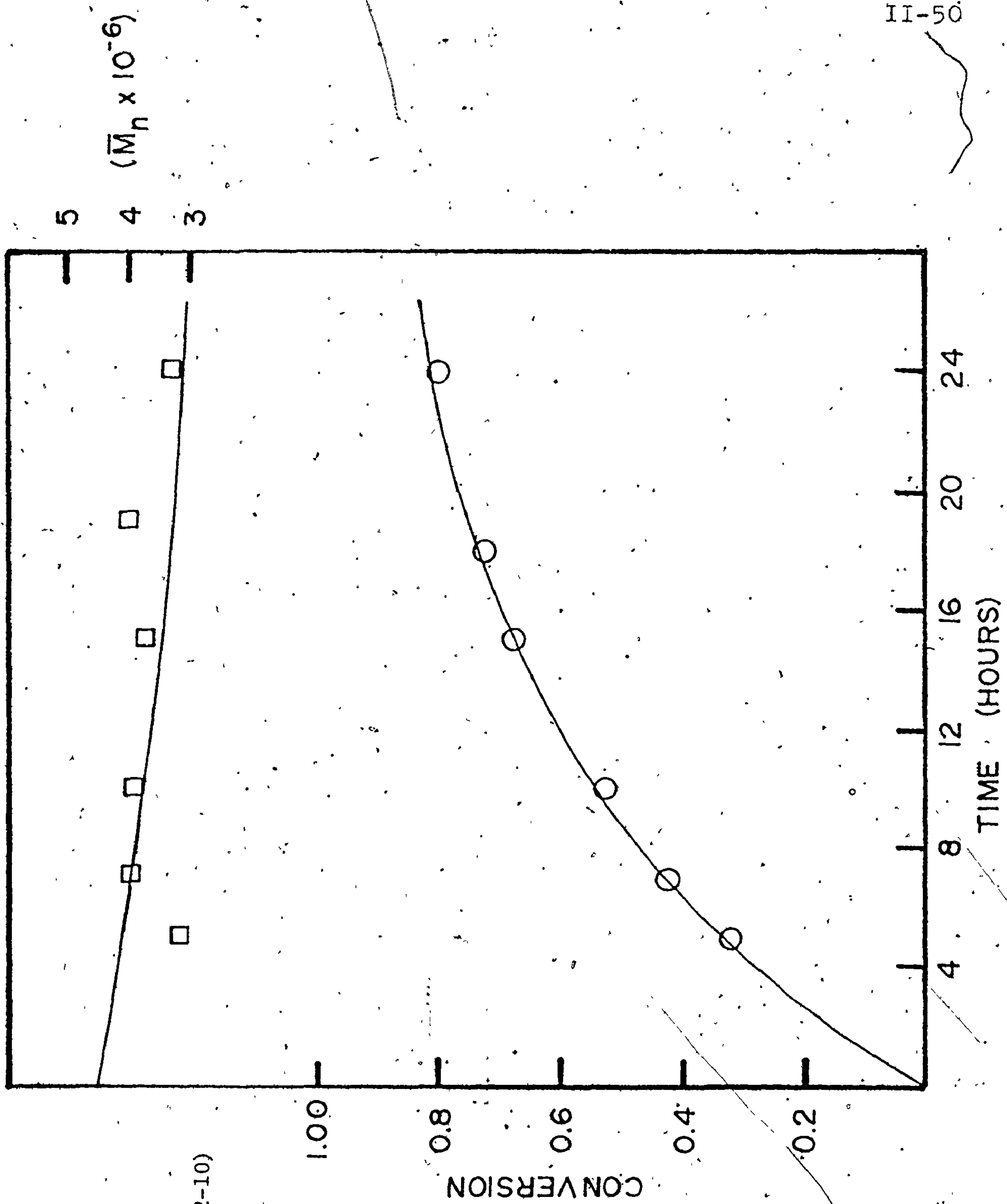


Fig. (II-6) - Run (25-02-10)

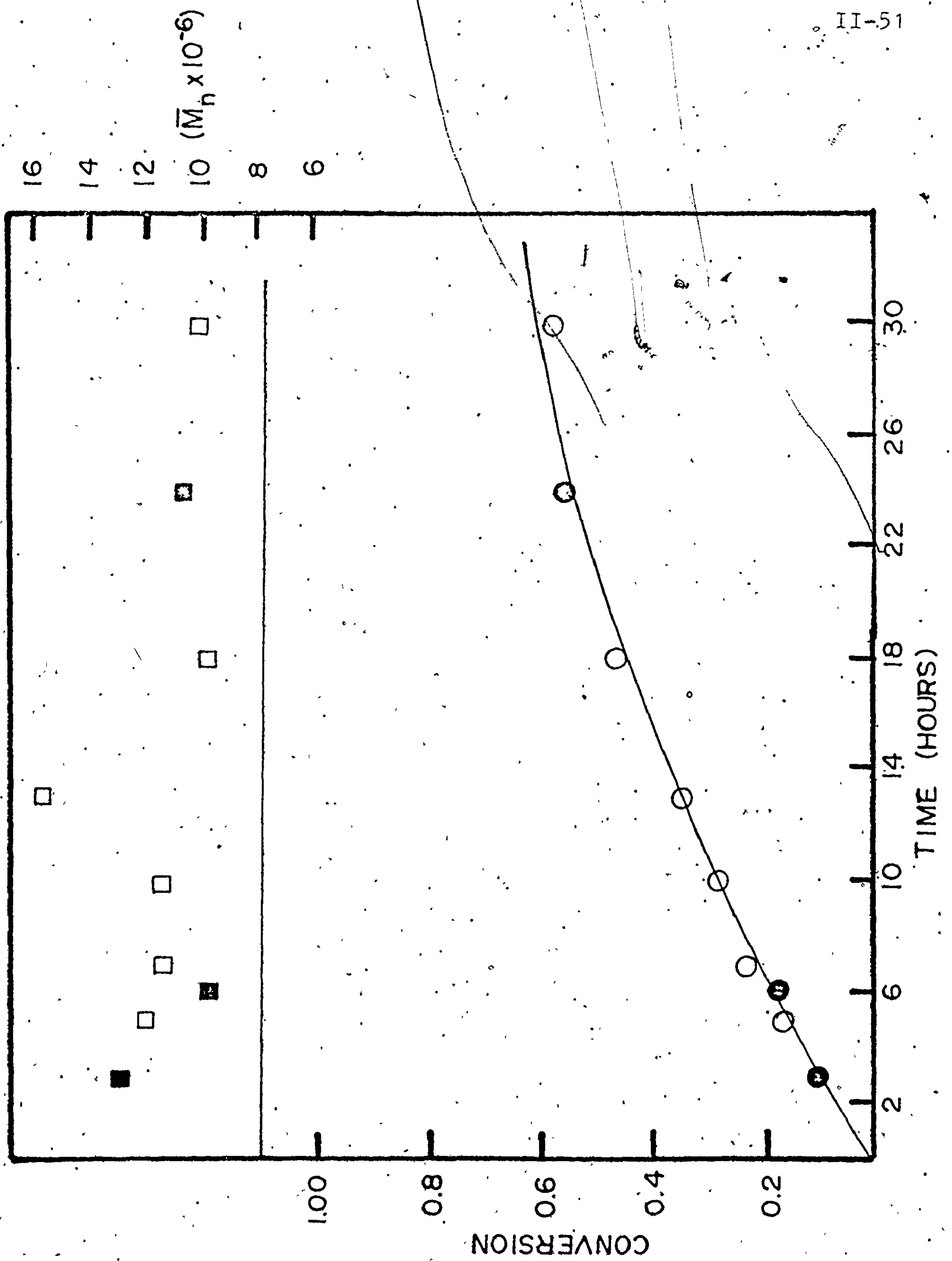


Fig. (II-7).-

Run (25-05-01)

Fig. (II-9) - Run (25-05-25)

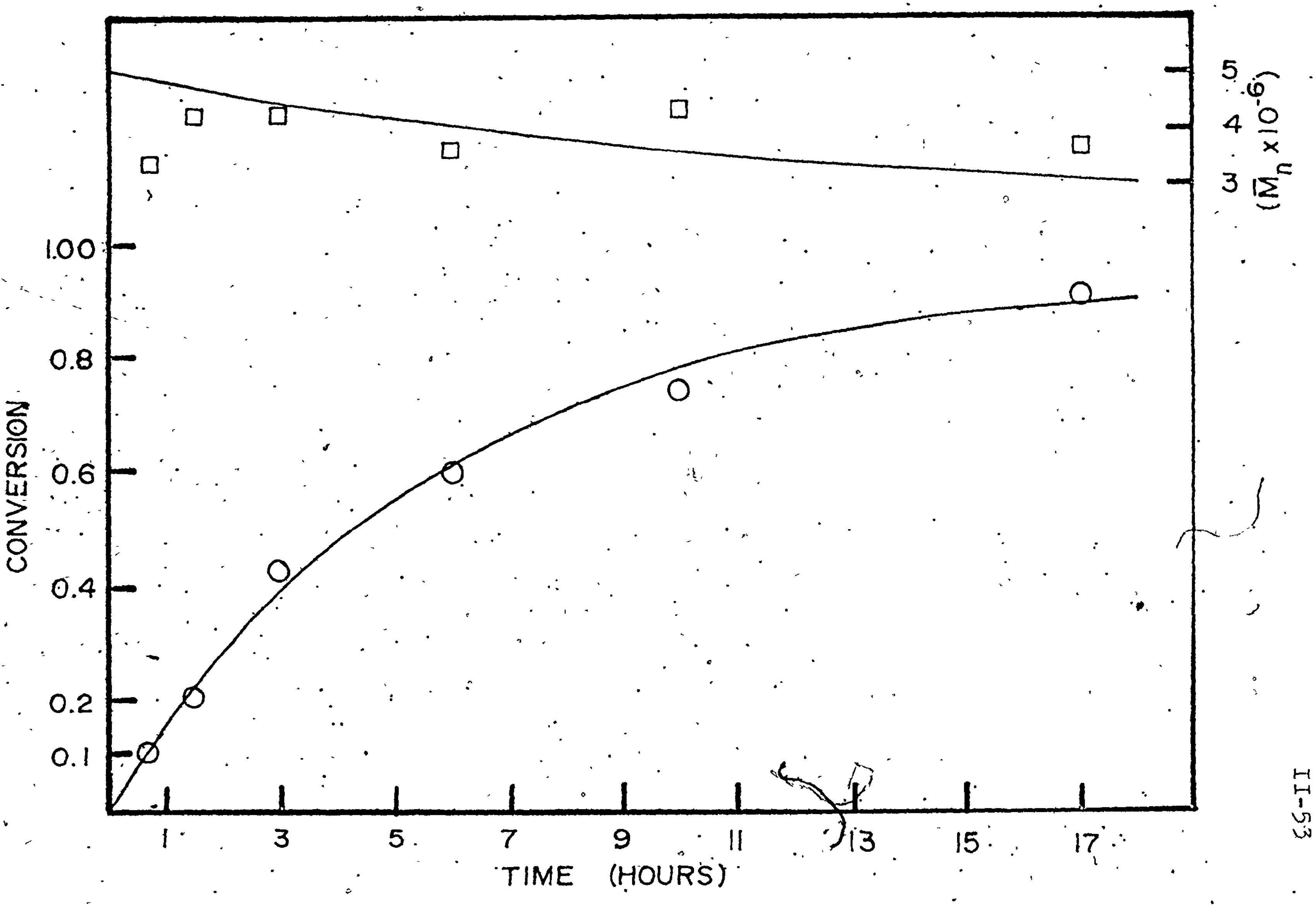


Fig. (II-9) - Run (25-05-25)

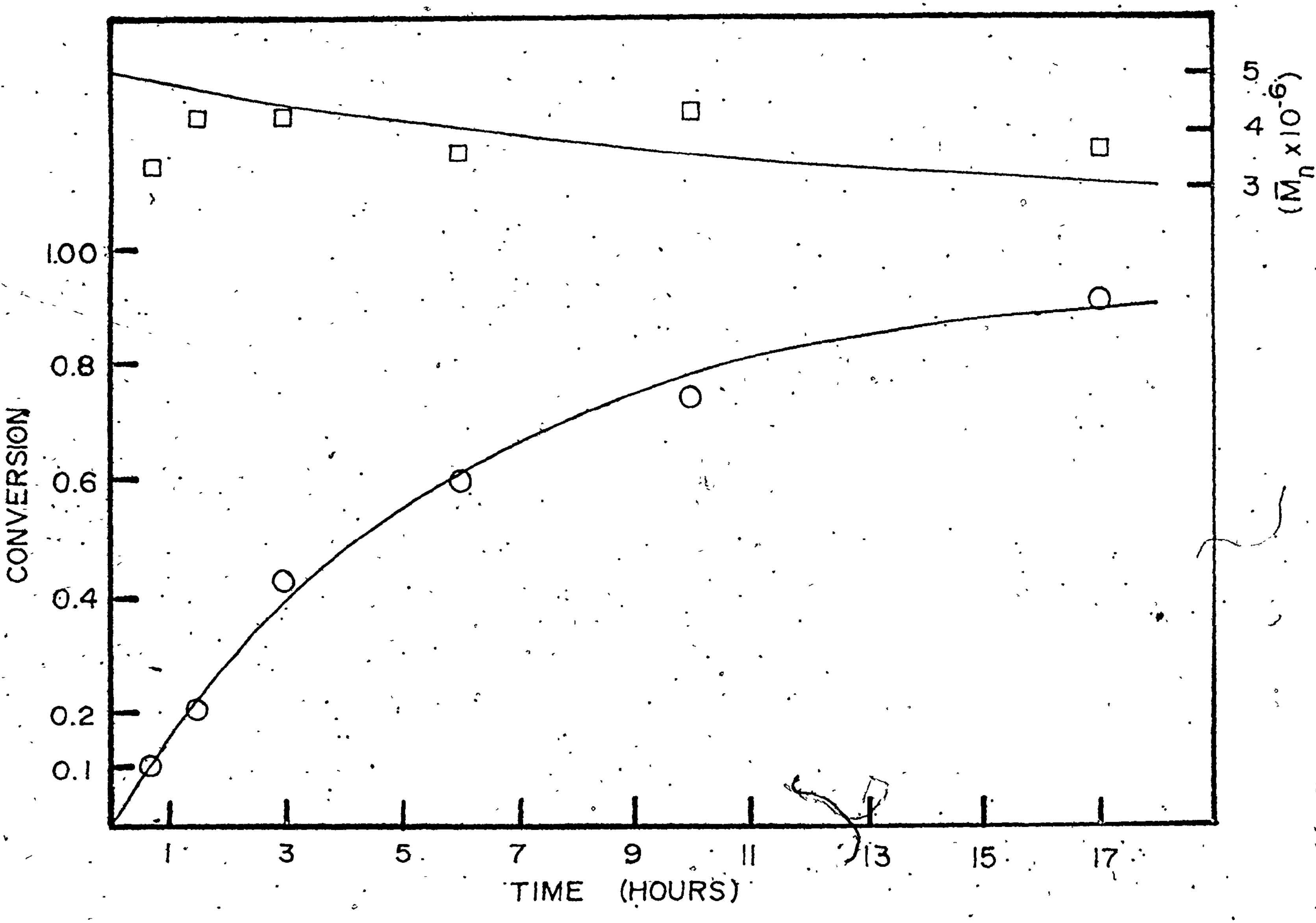


Fig. (II-10) - Run (40-20-05)

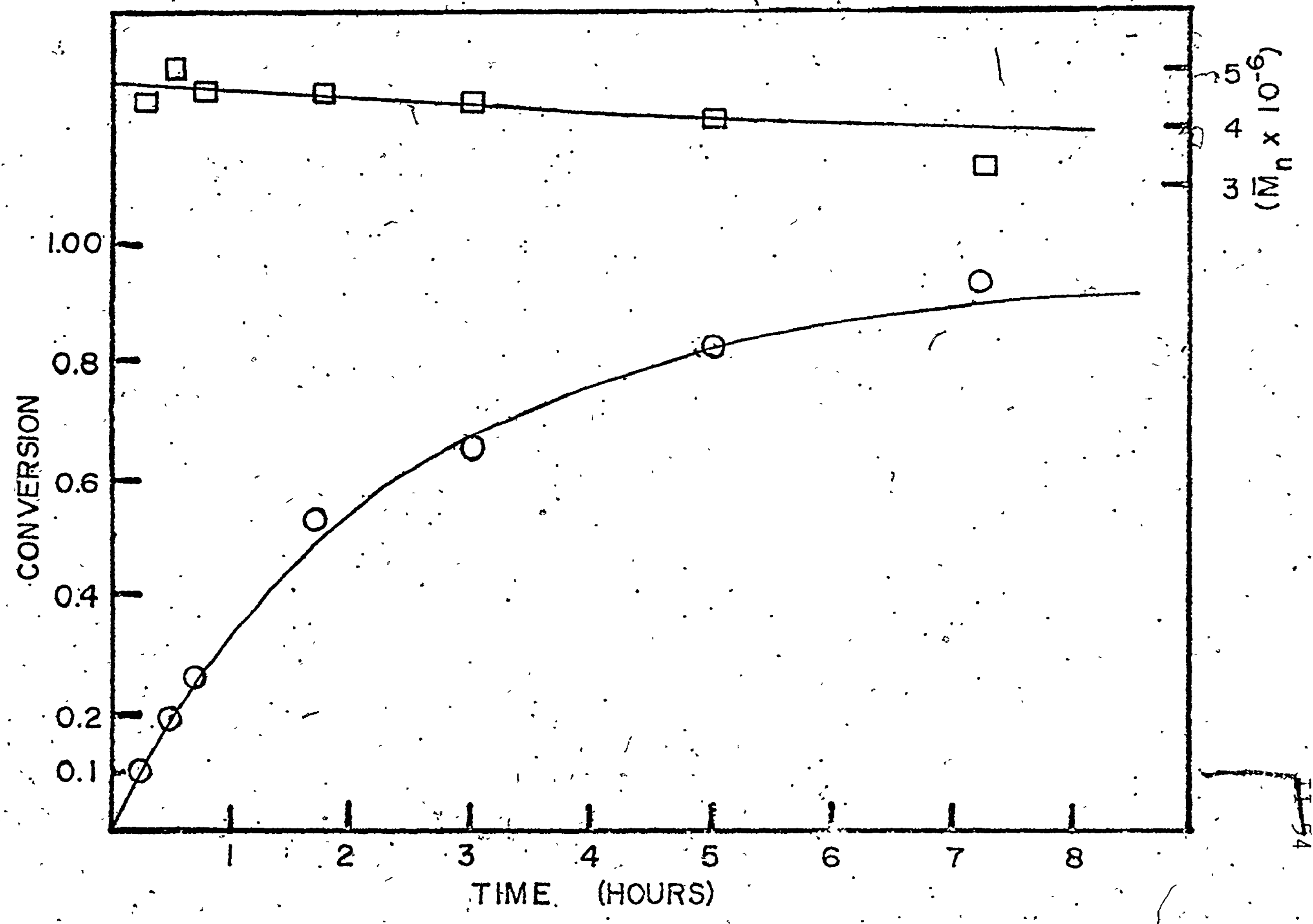


Fig. (II-11) - Run (40-05-059)

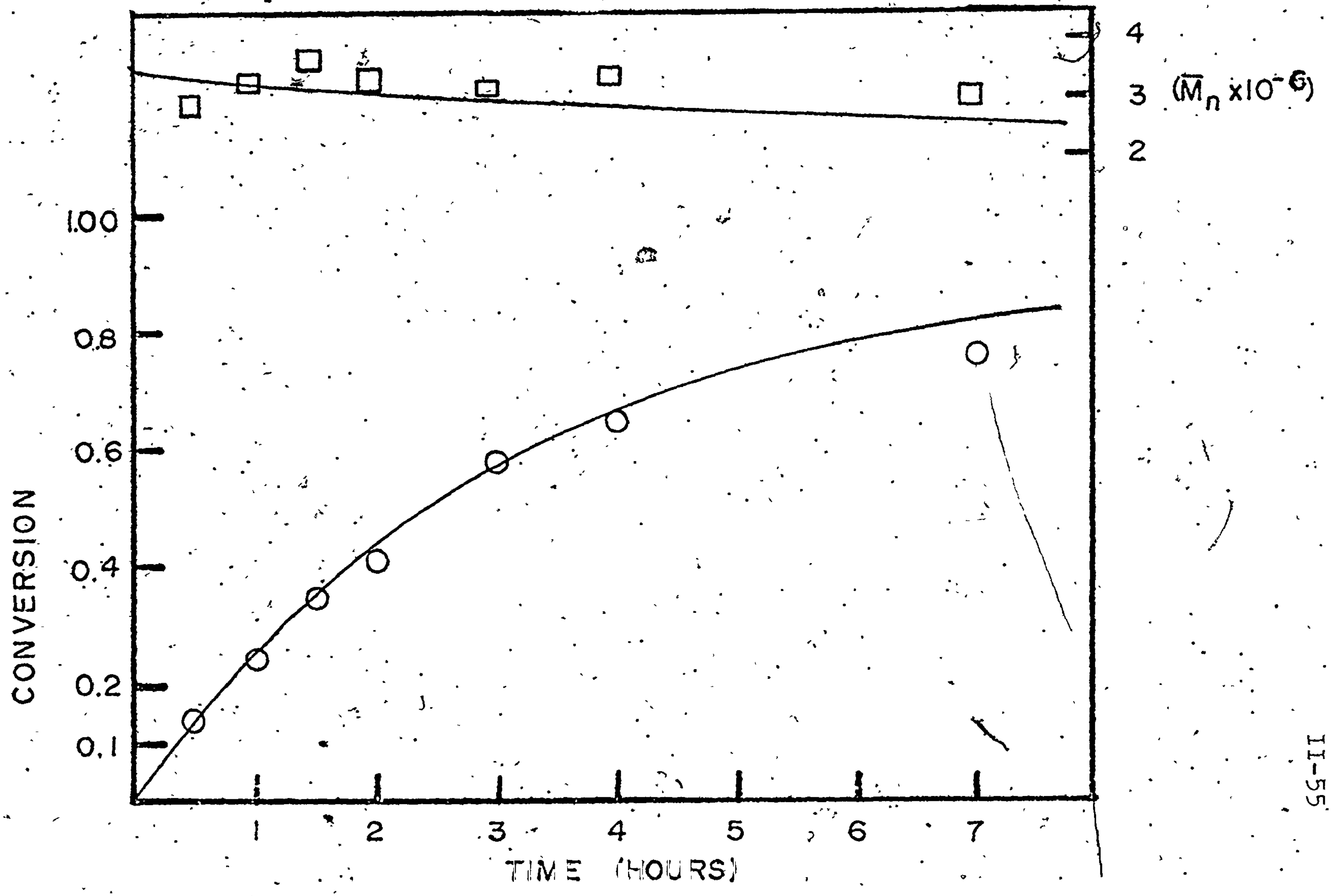


Fig. (II-12) - Run (40-02-05)

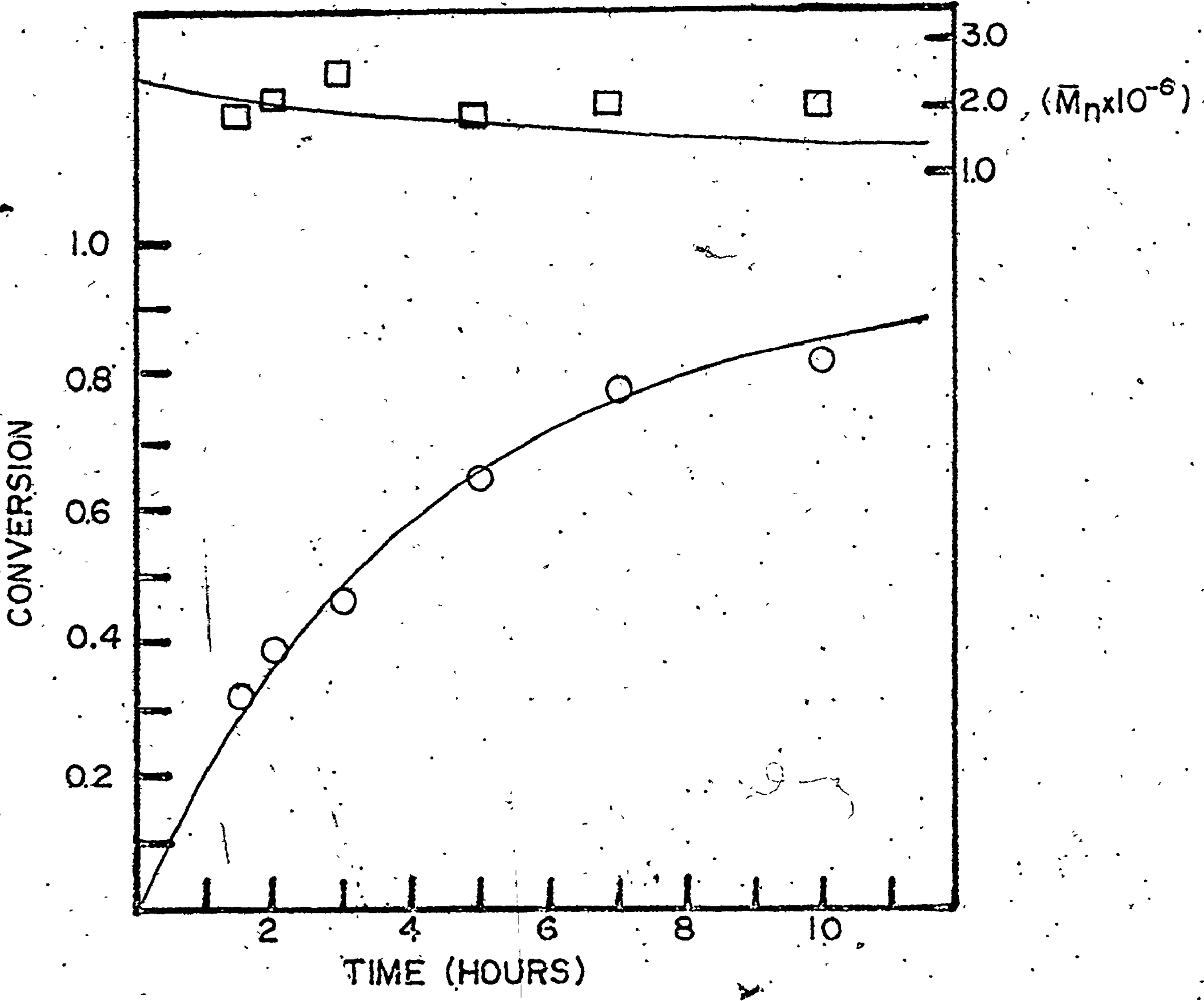
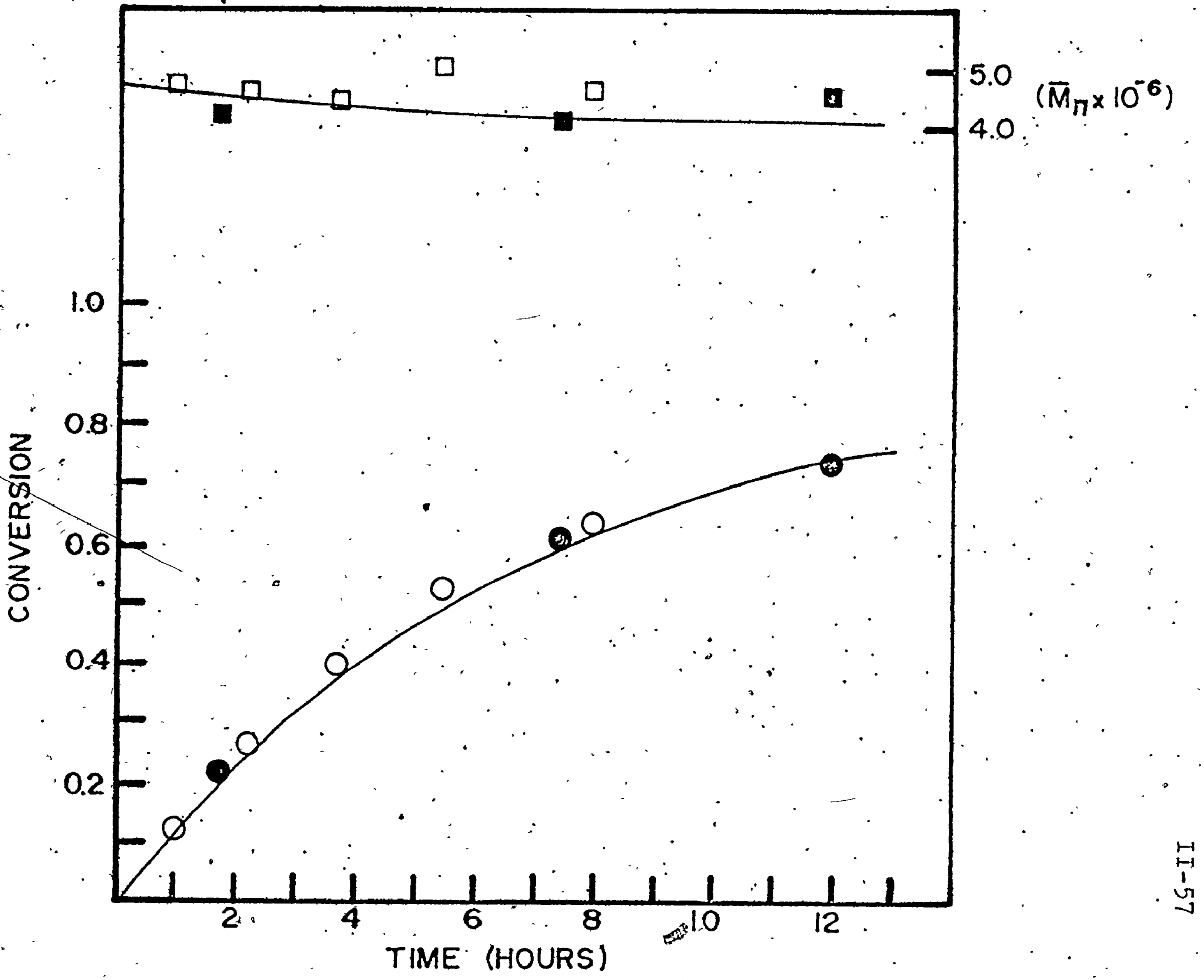


Fig. (II-13) - Run (40-05-01)



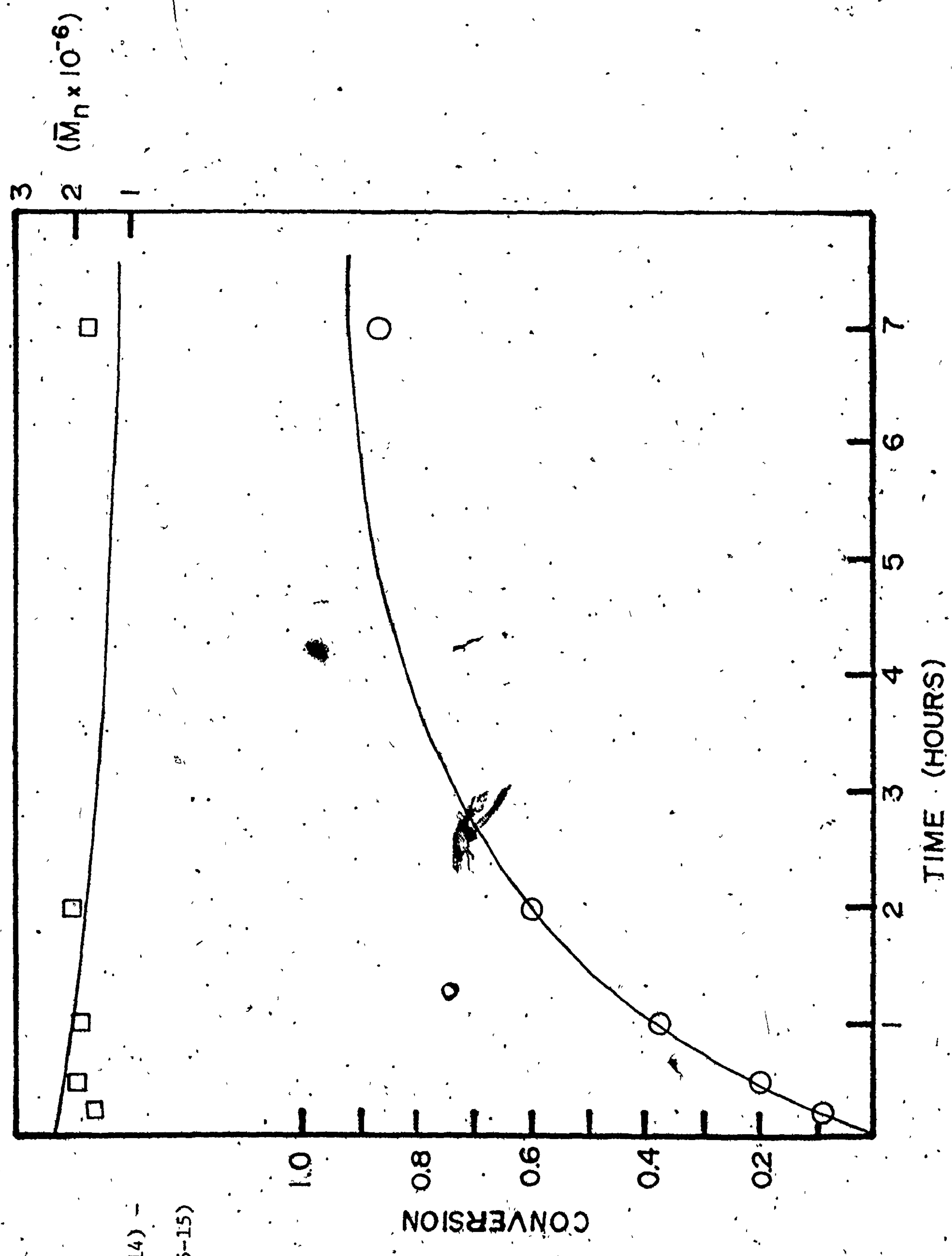
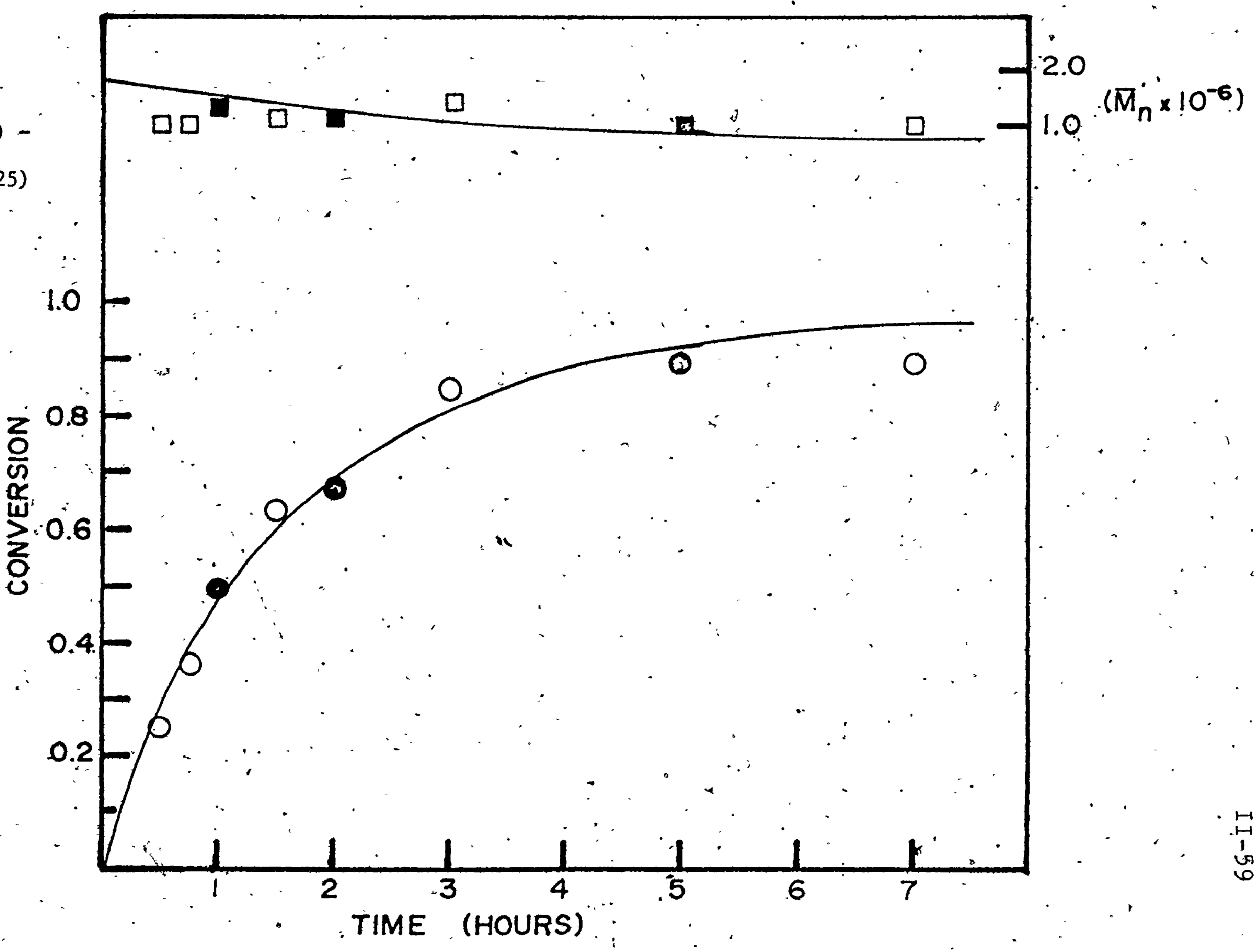


Fig. (II-14) -

Run (40-05-15)

Fig. (II-15) -

Run (40-05-25)



Hence, an accurate expression for R_p is essential for the estimation of the transfer parameters C_M and C_I.

Examination of the rate data in Figures (II-4) to (II-15) leads to the following conclusions :

1. There is excellent reproducibility of the rate data as evident from comparing the points obtained in the "reproducibility tests" to those obtained from the original runs.

2. ~~There is~~ an excellent agreement between the present data and the empirical rate expression proposed by Riggs and Rodriguez(43), viz. Eq. (II-33). It may be noted that the lowest temperature investigated by Riggs and Rodriguez was 30°C and the highest $[M]_o$ was 0.40 (g moles/l). The present data validates their rate expression extrapolated to T = 25°C and $[M]_o = 2.0$ (g moles/l).

3. Hence, no effort was done here to fit a general rate expression of the form $R_p = k\ [M]^{\alpha}\ [I]^{\beta}$. Normally, separate plots of log (R_p) versus log $[M]$ at constant $[I]$ and of log (R_p) versus log $[I]$ at constant $[M]$ would be constructed to estimate α and β, respectively. Then the value of k would be calculated that would give the best fit. But, due to the excellent agreement with the results of Riggs and Rodriguez, hereinafter the values for R_p will be calculated from Eq. (II-26) and the values for the empirical constant $k_{1.25}$ will be calculated from Eq. (II-27).

4. It may be noted that it is the integrated rate

expression, Eq. (II-33), that was found to fit the rate data very closely. This has the further implication that the assumption made in obtaining Eq. (II-33), viz. that $[I]$ remains substantially constant at its initial value $[I]_0$ throughout the polymerization reaction, is valid. This, of course, was to be expected due to the extremely long life of $K_2S_2O_8$ compared to the reaction times involved here.

5. It follows from the above that the integrated expression for the cumulative number average chain length, Eq. (II-37), is necessarily valid, as the only assumptions made in obtaining this equation, by integrating Eq. (II-12), are the validity of the rate expression, Eq. (II-26), and that the initiator concentration $[I]$ remains constant, both of which were proved true. Hence, Eq. (II-37) may be used to estimate the values of the transfer constants C_M and C_I from the molecular weight data of the polymers obtained.

II.4.3 The Transfer Constants

The next step in our kinetic investigation was to use the molecular weight data collected to estimate the rest of the kinetic parameters in Eq. (II-37).

Examination of the molecular weight data in Appendix (II-2) and Figures (II-4) to (II-15) reveals the following characteristics :

1. The data tend to confirm both the observation made by Riggs and Rodriguez(43) that the degree of polymeri-

zation decreased with increasing $[I]_o$ and with decreasing $[M]_o$ and the apparently contradictory observation made by Kwangfu$^{(42)}$ that the degree of polymerization remained virtually constant with increasing conversion. Both these papers dealt with an identical system as the one investigated here, viz. the aqueous polymerization of acrylamide with potassium persulfate initiator.

The only exceptions in the present data to the second of the above observations, are the polymers recovered in the runs where the highest initial monomer concentration was used (2.0 g moles/l), viz. polymers (25-20-10-J) and (40-20-05-G). The molecular weight averages of these two polymers were found to be significantly lower than the polymers recovered at lower conversion levels in their respective runs. But, as pointed out in Section (II.3.6), the step where the contents of the ampoules were diluted with water required, for these two polymers, about two weeks of constant stirring. Hence it was impossible to know whether the drop in the viscosity of these polymers' solutions was due to a drop in molecular weight with increasing conversion, or to the degradation of the polymer molecules in solution due to the prolonged mechanical stirring.

An explanation of the apparent contradiction in the molecular weight data referred to above will be advanced below, after the estimation of the values of the parameters in Eq. (II-37) is complete.

2. The reproducibility of the intrinsic viscosities, hence of the molecular weight averages, of the polymers produced under the same experimental conditions but at different runs - the "reproducibility tests" - is satisfactory. This can be verified by examining these points on Figures (II-4), (II-7), (II-13) and (II-15).

We now proceed to estimate the kinetic parameters in Eq. (II-37). As mentioned before, the ratio $\frac{k_p}{k_t^{1/2}}$ has been found by Dainton and his coworkers$^{(28)}$ to be expressed by Eq. (II-25) from data at 25°C and 40°C. Also, values for individual constants k_p and k_t were estimated at 25°C by the rotating sector technique, and the result was found to conform to Eq. (II-25). Furthermore, the ratio $\frac{k_p}{k_t^{1/2}}$ was estimated at 25°C and at pH values from 1 to 13$^{(32)}$. This ratio was found to be almost constant throughout this range, and to agree with Eq. (II-25). Subsequent investigators have accepted this result, and those who independently estimated values for the ratio $\frac{k_p}{k_t^{1/2}}$ confirmed it$^{(20)}$. Therefore it was decided in the present instance to use Eq. (II-25) as given to compute values for the ratio $\frac{k_p}{k_t^{1/2}}$.

The following table summarizes the values, at 25°C and 40°C, of the constants $\frac{k_t}{k_p^2}$, computed from Eq. (II-25), $k_{1.25}$, computed from Eq. (II-27) and of constant k' of Eq. (II-37) which is the product of the previous two constants.

	25°C	40°C	Units
$\frac{k_t}{k_p^2}$	4.73×10^{-2}	3.71×10^{-2}	$\left(\frac{\text{mole sec.}}{\text{l}}\right)$
$k_{1.25}$	1.16×10^{-3}	4.54×10^{-3}	$\left(\frac{\text{l}}{\text{mole}}\right)^{0.75} \left(\frac{1}{\text{sec.}}\right)$
k'	5.49×10^{-5}	1.68×10^{-4}	$\left(\frac{\text{mole}}{\text{l}}\right)^{0.25}$

Inspection of Eq.(II-37) reveals that the value of the first term on the right side of the equation can be calculated at any temperature and conversion. Hence, rearranging the equation to read

$$\text{Cum}\left(\frac{1}{\bar{r}_n}\right) - 4\,k'\,\frac{[I]_o^{0.50}}{[M]_o^{0.75}}\,\frac{(1-(1-X)^{0.25})}{X} = C_M + C_I\,\frac{[I]_o}{[M]_o}\,\frac{\ln\left(\frac{1}{1-X}\right)}{X} \qquad \text{(II-37-a)}$$

Which may be written as

$$Y = C_M + C_I\,Z \qquad \text{(II-37-b)}$$

where,

$$Y = \text{Cum}\left(\frac{1}{\bar{r}_n}\right) - 4\,k'\,\frac{[I]_o^{0.50}}{[M]_o^{0.75}}\,\frac{(1-(1-X)^{0.25})}{X} \qquad \text{(II-38)}$$

and

$$Z = \frac{[I]_o}{[M]_o}\,\frac{\ln\left(\frac{1}{1-X}\right)}{X} \qquad \text{(II-39)}$$

Evidently, the free radical polymerization model predicts, for this particular case, a linear relationship between the variables Y and Z, defined by Eq. (II-38) and Eq. (II-39), respectively. The slope of this straight line is the ratio $\frac{k_{fi}}{k_p}$ and the intercept is $\frac{k_{fm}}{k_p}$. All the data necessary for calculating the values of Y and Z, viz. Cum $(\frac{1}{\bar{r}_n})$, k', $[I]_o$, $[M]_o$ and X are either known or have been measured. Now remains the task of quantitatively estimating the values of C_M and C_I at the two temperatures used.

Appendix (II-3) is a detailed presentation of the linear regression methods used below for the estimation of C_M and C_I. The primary references are the book on statistical methods by Himmelblau(46) and the one on regression analysis by Draper and Smith(47).

The estimators for the parameters C_M and C_I presented below are those obtained by least squares. The assumptions made to justify the use of the least squares method for parameter estimation are listed in Appendix (II-3). Of all these assumptions, the one most deserving of scrutiny here is the one that stipulates that the independent variable Z in Eq. (II-38), takes known and fixed values, whereas all the experimental errors are in the values of the dependent variable Y. However, as is clear from Eq. (II-39), Z is a function of the conversion X, which is measured experimentally, and is subject to some experimental error. However, in the present situation, the least squares approach is still justified mainly because the error inherent in measuring the conversion X, hence in calculating Z, is much smaller than the error inherent in calculating Y. This is shown by the scatter of the rate data— the conversion versus time curves— which is much smaller than the scatter of the molecular weight data. It must be remembered that whereas the conversion is measured directly, the calculations of the cumulative average chain length involves the following steps :

1. Measuring the viscosity of the polymer solution at different concentrations and shear rates.

2. Extrapolating the data to high shear rates , then to zero concentration.

3. Using Eq. (I-37) and the intrinsic viscosity at high shear rates to calculate the number average molecular weight.

Each of these steps introduces an error, and the errors accumulate. It is felt that step 3 introduces the largest relative error in the values of the computed molecular weights due to the extremely wide range of molecular weights over which Eq. (I-37) is used. Therefore it is reasonable to assume that the error inherent in the determination of Y in Eq.(II-38) is significantly larger than the one associated with measuring Z. This validates the least squares approach, and the quantitative results that ensue.

The first step was to apply the least squares method to Eq. (II-37-a). The following table summarizes the results thus obtained. The equations used to obtain these results and their derivation are detailed in Appendix (II-3).

Least Squares Estimates of	T = 25°C	T = 40°C
C_M	$7.86\times10^{-6} \pm 1.07\times10^{-6}$	$1.20\times10^{-5} \pm 3.28\times10^{-6}$
C_I	$4.12\times10^{-4} \pm 2.38\times10^{-4}$	$2.63\times10^{-3} \pm 7.08\times10^{-4}$
Sum of Squares of Residuals	2.62×10^{-10}	2.23×10^{-9}
Residual Variance, s^2	6.55×10^{-12}	5.71×10^{-11}
Correlation Coefficient	-0.670	-0.686

The confidence intervals of the parameters C_M and C_I were calculated at 95% confidence level as detailed in Appendix (II-3). The individual confidence interval for each parameter was calculated instead of the more accurate joint confidence region because of the moderate value of the correlation coefficient at each temperature.

The next step was to ascertain that each of the terms on the right-hand side of Eq. (II-37-a), accounting for the transfer reaction to the monomer and the initiator molecules respectively, is statistically significant. In other words, it was necessary to find whether the addition of each of these terms to the kinetic model resulted in a significant improvement in the fit of the experimental data to the model equation, or does any of the two terms simply fit some of the random errors inherent in the measurements and therefore can be ignored.

For this purpose, truncated forms of Eq. (II-37-b) were fitted to the experimental data, and an analysis of variance was carried out between the complete model Eq. (II-37-b) and the truncated one. Details of this type of analysis of variance as applied to linear regression, sometimes referred to as the "extra sum of squares principle", are detailed in Appendix (II-3).

First, to test the significance of the transfer reaction to the initiator, the following equation was fitted to the experimental data

$$Y = C_M \qquad \text{(II-40)}$$

where Y has been defined by Eq. (II-38). Following the procedure outlined in Appendix (II-3), the least squares estimator for C_M was found, at 95% confidence level, to be

Least Squares Estimate of	T = 25°C	T = 40°C
C_M	$9.10\times10^{-6} \pm 9.00\times10^{-7}$	$2.04\times10^{-5} \pm 3.68\times10^{-6}$
Sum of Squares of Residuals	3.42×10^{-10}	5.43×10^{-9}
Residual Variance	8.34×10^{-12}	1.36×10^{-10}

To perform the analysis of variance, a null hypothesis may be constructed, viz. that Y is unrelated to Z, i.e.

$$H_o : C_I = 0$$

To be able to reject this hypothesis at 95% confidence level, the following inequality must prove true

$$\frac{(N-2)\,(SSR1 - SSR2)}{SSR2} > F_{.95}\,(1\ ,\ N-2) \qquad \text{(II-41)}$$

where N is the number of observations, SSR1 is the sum of squares of the residuals for the truncated model, SSR2 is the sum of squares of the residuals for the complete model, and $F_{.95}$ (1 , N-2) is the critical value of the F-distribution that leaves 5% of the distribution in the right-hand tail, with 1 and N-2 degrees of freedom.

As N=42 at 25°C and N=41 at 40°C, we find that for both cases $F_{.95}$ (1 , N-2) is equal to 4.08. Computing the left-hand side of the inequality, Eq. (II-41) at each temperature, we find it to be

at 25°C

$$\frac{40(3.42 \times 10^{-10} - 2.62 \times 10^{-10})}{2.62 \times 10^{-10}} = 12.2 > 4.08$$

at 40°C

$$\frac{39(5.43 \times 10^{-9} - 2.23 \times 10^{-9})}{2.23 \times 10^{-9}} = 56.0 > 4.08$$

Therefore the null hypothesis is rejected in each case, hence it can be stated at 95% confidence level that the transfer reaction to initiator molecules is significant. It may also be noted that the critical values of the F-distribution are equal to 7.31 and 8.83 at 99% and 99.5%

confidence levels, respectively. Therefore the transfer reaction to $K_2S_2O_8$ cannot be ignored even at these higher confidence levels. However, at 99.9% confidence level, the critical value for the F-distribution becomes 12.6. Comparing this value to the result obtained at 25 °C, we find that this is the highest possible confidence level at which the null hypothesis of $C_I = 0$ may be rejected. At 40 °C however, the null hypothesis may be rejected at even higher confidence levels than 99.9%.

Repeating the above analysis of variance to test the significance of the transfer to monomer term, the following truncated model was fitted to the experimental data -

$$Y = C_I Z \qquad \text{(II-42)}$$

As detailed in Appendix(II-3), the least squares estimate of C_I and its 95% confidence interval were found to be

	T = 25 °C	T = 40 °C
C_I	$1.58\times10^{-3} \pm 2.2\times10^{-4}$	$4.41\times10^{-3} \pm 3.91\times10^{-4}$
Sum of Squares of residuals	4.12×10^{-11}	1.34×10^{-10}
Residual Variance	1.69×10^{-9}	5.37×10^{-9}

Now the null hypothesis becomes

$$H_o : C_M = 0$$

The same inequality expressed in Eq.(II-41) must hold true to reject the null hypothesis. Computing the left side of this inequality as before, it was found to equal 218 at 25 °C and 55 at 40 °C. Comparing these values with the critical values of the F-distribution listed before, it is clear that the transfer to monomer reaction is statistically significant up to, and above, a confidence level of 99.9% at both temperatures investigated.

Therefore it has been established that both the transfer reaction to the acrylamide monomer and the one to the potassium persulfate initiator are significant at both temperatures investigated. Hence it is the complete form of the model, expressed by Eq.(II-37), that should be used to predict the cumulative molecular weight averages of the polymer molecules. Using this equation with the kinetic parameters associated with it, it was possible to calculate the predicted number average molecular weight as it changes with conversion for all the experimental conditions used in the present investigation. These predicted values are listed in the tables of Appendix (II-2). Also, the predicted $\overline{M}_n$ versus conversion (hence, time) curves have been drawn as solid lines in the upper portions of figures (II-4) to (II-15). Comparing these predicted values to the experimentally determined number average molecular weights as illustrated in these figures, it is clear that the agreement is satisfactory for all the experimental runs except for run No. (25-05-01). In this run, the predicted molecular weight averages are uniformly smaller in magnitude than the measured ones. These experimental values for $\overline{M}_n$ are reproducible as evidenced by the corresponding "reproducibility test".

A possible explanation for this discrepancy between predicted and experimental molecular weights lies in the fact that the polymers formed during these experimental conditions had the highest intrinsic viscosities of all the polymers formed throughout this investigation. As the empirical relationship used to calculate the molecular weight averages from the corresponding intrinsic viscosities was developed using polymers having molecular weight averages less than 10^6 (29), it would be expected that the error introduced by using this relationship to calculate $\overline{M}_n$ from the intrinsic viscosity will be the largest for the high molecular weight polymers formed during run (25-05-01). In addition, due to the extreme curvature of the viscosity-shear rate data of these high molecular weight polymers, as made clear in Fig.(I-2) for polymer (25-05-01-G), the error introduced by extrapolating the flow data to high shear rates will be larger for these polymers. This would explain the considerable scatter exhibited by the molecular weight averages during this run. It has also been observed by several investigators studying the flow properties of high polymers(48-50) that the logarithmic dependence of the apparent viscosity of a polymer solution on the molecular weight of the polymers, at a fixed concentration, was linear up to a critical molecular weight above which the straight line showed a sudden break and increased in slope. This is generally attributed to the onset of polymer chain "entanglements". If the line describing the viscosity-molecular weight relationship below the critical molecular weight was extrapolated to the region above the critical molecular weight, it will predict, for any particular viscosity, a molecular weight that is larger in value than the true molecular weight. Such a phenomenon would explain the fact that all the experimental $\overline{M}_n$ calculated from viscosity data for the high molecular weight polymers formed during run (25-05-01) were higher than predicted by the model. However, additional data is clearly needed to confirm this argument.

On the other hand, an explanation can be given now for the apparent insensitivity of the measured molecular weights of the polymers to the conversion at which these polymers were recovered. It is clear from the curves depicting the predicted $\overline{M}_n$ versus conversion relationship that the drop of $\overline{M}_n$ with increasing conversion is moderate. This is due to the relatively large effect of the transfer to monomer constant, C_M. This is especially true for runs of high $[M]_o$ and low $[I]_o$. Due to the fact that the measured $\overline{M}_n$ is subject to a relatively large experimental error, for reasons detailed before in this section, the moderate drop in $\overline{M}_n$ values with increasing conversion apparently cannot be detected by viscometry. It may also be argued that viscometry is relatively insensitive to the low molecular weight tail of a wide molecular weight distribution.

As mentioned before, the values for the transfer constant $C_I = \frac{k_{fi}}{k_p}$ to potassium persulfate during the polymerization of acrylamide are being reported here for the first time. The value for this constant presently estimated at 4.12×10^{-4} at 25 °C may be compared to the corresponding value for the transfer reaction to H_2O_2 at 25 °C reported as 5×10^{-4} by Dainton and Tordoff(30).

On the other hand, different values for the transfer to monomer constant $C_M = \frac{k_{fm}}{k_p}$ have previously been reported in the literature. These values were listed in Section (II.2.3). Comparing these reported values at different temperatures to the ones found in this investigation, the following observations were made :

1. The value for C_M at 40 °C reported by Kwangfu(39) is 5.8×10^{-4}, which is almost 50 times greater than the one presently found at the same temperature ($1.20 \times 10^{-5} \pm 3.28 \times 10^{-6}$). This implies that the molecular weight averages measured by Kwangfu were several orders of magnitude lower than those measured in the present investigation under the same conditions. This is shown by the fact that when Kwangfu used $K_2S_2O_8$ as initiator at 40 °C(42), he reported values for $\overline{M}_n$ ranging from about 1.8×10^5 to

3.4×10^5 when $[M]_0$ and $[I]_0$ were equal to 1.41 and 10^{-4} (g moles/l), respectively. The values of $\overline{M}_n$ predicted by the present model and parameter values are of the order of 5×10^6. Furthermore, with $[M]_0$ equal to 0.704 and $[I]_0$ to 9.7×10^{-5}, Kwangfu's measured $\overline{M}_n$ values ranged from 10^5 to 2.3×10^5 whereas the present model predicts values of about 4.8×10^6.

The only plausible explanation for this wide discrepancy in molecular weights is that a transfer reaction to the buffering material used by Kwangfu to control the pH of the aqueous polymerization medium occurred, but was not accounted for in his analysis. In other words, the last term on the right-hand side of Eq. (II-12) was not to be neglected. On the other hand, Kwangfu's observation that in alkaline solutions the degree of polymerization increased with conversion can only be explained by assuming that long chain branching becomes significant at pH > 7.

2. Using the values for C_M at 25°C and 40°C obtained from the present data, the overall activation energy for the ratio $\frac{k_{fm}}{k_p}$ was found to be 5.24 (KCal./mole). Extrapolating to 50°C and to 60°C, the value of C_M is estimated to be 1.56×10^{-5} and 2.0×10^{-5}, respectively. This is in excellent agreement with the value of C_M reported at 50°C by Ishige(20) of 1.45×10^{-5}. On the other hand, the value of C_M at 60°C reported by Fadner and Morawetz(33) of 6.0×10^{-5}

is three times larger than the one predicted by the present data.

It is extremely important to observe that the value of C_M predicted by the present data at 50°C agrees quite closely with the value reported by Ishige(20) at the same temperature. It has been shown in Part I of this thesis that due to the dimensions of the viscometers used by Ishige for measuring the intrinsic viscosities of his polymer solutions, the conditions were such that his calculated intrinsic viscosities fortuitously approximated those obtained by extrapolating the flow data to high shear rates. This latter method was used in the present investigation to calculate $\overline{M}_n$. Therefore for the only investigator for whom it was possible to ascertain that the shear conditions employed were close to those used here, the estimated C_M was almost identical to the one presently found. This demonstrates the influence of the shear conditions at which the intrinsic viscosities are calculated on the ultimate kinetic results. Unfortunately, the information necessary to determine the shear rate conditions under which the other investigators measured their viscosities was not available to us.

3. Finally, at 25°C the present experimental data indicate a value for C_M equal to $7.86 \times 10^{-6} \pm 1.07 \times 10^{-6}$. Dainton et al.(28) found this parameter to be less than 10^{-6}, whereas four other investigations(30,33,34,35) reported values for C_M ranging from 1.2×10^{-5} up to 2.0×10^{-5}.

None of these values lie within the 95% confidence interval found here. Apart from the possible effect of shear rate on their viscosity data, two more observations can be made to account for these discrepancies.

First, the procedure followed by all the above-mentioned investigators was to use one measurement of the average molecular weight at each set of experimental conditions, either at very low conversions or at very high ones, and this data was fitted to the expression for the instantaneous number average chain length, Eq.(II-12), with R_p, $[M]$ and $[I]$ taken at their original values at zero conversion. Therefore each experimental run yielded one molecular weight observation and consequently the number of data points used to fit the equation was very limited. For example, Dainton and Tordoff$^{(30)}$ used five data points to estimate the two parameters C_M and C_I (to H_2O_2). Similarly, the number of points used by Ishige$^{(20)}$, Cavell and Gilson$^{(35)}$ and Kwang-fu$^{(39)}$ were eight, seven and six, respectively. On the other hand, in the present investigation, the integrated expression for the cumulative average chain length, Eq.(II-37), where conversion appears explicitly, was used for the first time to fit the data. This permitted the utilization of all the molecular weight information gathered at different conversions within every run to estimate C_M and C_I. Therefore the data was much more extensive, as 42 points were used to estimate the parameters at 25°C and 41 points were used at 40°C.

Although the previous reports did not provide the necessary information whereby the confidence intervals of their estimated parameters may be calculated, one would expect that with such a limited amount of data, these confidence intervals would be rather wide. This means that the confidence intervals of their estimated C_M and the present ones may overlap, which would eliminate some of the discrepancy between their results and the present ones.

The second observation to be made is that a number of these investigators$^{(30,34,35)}$ chose to use Eq.(I-38) to calculate the weight average molecular weight from the measured intrinsic viscosity, then they divided the resulting $\overline{M}_w$ by 2.0 to estimate a value for the number average molecular weight $\overline{M}_n$. In the present investigation, as in several previous ones$^{(20,39,42,43)}$, $\overline{M}_n$ was calculated directly from Eq.(I-37). The discrepancy between the values of $\overline{M}_n$ estimated by these two methods increases with increasing intrinsic viscosity, with Eq.(I-38) giving the smaller estimate of $\overline{M}_n$, in the molecular weight range investigated here. Smaller values for $\overline{M}_n$ lead to a larger value for C_M, as is evident from Eq.(II-34). This is actually the case for most C_M values reported in the literature.

II.5 Conclusions

An experimental investigation was carried out on the polymerization of acrylamide in water with potassium persulfate initiator in such conditions that the polymers produced had a number average molecular weight in excess of one million.

Conversion was measured by gravimetry and molecular weight by viscometry. For the first time, shear rate effects were accounted for by extrapolation to high shear rates where the polymer solutions approximated Newtonian behaviour.

The present experimental rate data was found to agree quite well with the empirical rate expression proposed by Riggs and Rodriguez(43), Eq.(II-26) and Eq.(II-27).

Using this rate expression to calculate R_p , together with the values of $\frac{k_p}{k_t^{1/2}}$ reported by Collinson, Dainton and McNaughton(28), Eq.(II-25), values for the transfer constants to the acrylamide monomer and to the potassium persulfate molecules were estimated at 25 °C and 40 °C. By assuming that the initiator concentration remained constant throughout the course of the polymerization reaction, the integrated form of the cumulative molecular weight expression Eq.(II-37), was used for the first time to fit the molecular weight data. Hence all the molecular weight measurements obtained at all levels of conversion were used to fit the data and to obtain values for C_M and C_I. Both transfer reactions were found to be statistically significant up to a confidence level of 99.9%.

The values for the transfer constant to $K_2S_2O_8$ are reported here for the first time. However, the value of this parameter at 25 °C was found to be very close to that reported by Dainton and Tordoff$^{(30)}$ for the transfer to H_2O_2 molecules at the same temperature.

The values presently found for the transfer constant to monomer molecules were found to be generally smaller than the values reported in the literature at the same temperatures. However, the present value for C_M extrapolated to 50 °C was found to be in excellent agreement with that reported by Ishige$^{(20)}$ at that temperature. The reason advanced for the above observations is that Ishige's viscometers closely approximated the shear conditions employed in the present investigation to calculate $\overline{M}_n$, whereas the flow conditions used by the other investigators were not reported and hence could not be evaluated. In addition, the empirical expression by which the number average molecular weights were calculated from the measured intrinsic viscosities were not the same for all investigators, which must account for some of these discrepancies.

The above observations clearly point to the need for a uniform and standard method whereby non-Newtonian aspects of the polymer solution viscosities are accounted for. Such a method has been proposed in Part I of the present thesis and was used, for the first time, in Part II to evaluate C_M and C_I.

Furthermore, it was observed that in comparing the values for the transfer constants reported by different investigators, the difference in the expressions used by these investigators to compute the molecular weight averages from the intrinsic viscosities must be taken into account.

Finally, it was concluded that the use, whenever possible, of integrated expressions such as Eq.(II-33) and Eq.(II-37), wherein conversion appears explicitly, makes possible the utilization of data obtained at all conversion levels to estimate the kinetic parameters. Hence this constitutes an improvement on the current practice of using differential-type expressions, such as Eq.(II-12) and Eq.(II-26), where only one experimental data point is obtained for each run. Furthermore, the present method does not require data collected at extremely low conversion levels, where the relative error introduced by the presence of small amounts of impurities in the reaction mixture and by the uncertainties inherent in the measurements of conversions and intrinsic viscosities would be maximum.

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Appendix II.1

Development of the Kinetic Expressions for the Free-Radical Polymerization Model

The following reaction scheme will be considered in the present analysis of the free-radical homopolymerization

Initiation

The initiation rate of primary radicals R_1^* in g mole/(litre x second) will be represented by R_I. Keeping R_I unspecified renders the analysis as general as possible. R_I is an instantaneous rate and will depend on temperature, concentration and time.

Propagation

$$R_r^* + M \xrightarrow{k_p} R_{r+1}^* , \quad r = 1,2,\ldots,\infty$$

Transfer

$$R_r^* + M \xrightarrow{k_{fm}} P_r + R_1^* \qquad \text{(monomer)}$$

$$R_r^* + I \xrightarrow{k_{fi}} P_r + R_1^* \qquad \text{(initiator)}$$

$$R_r^* + S \xrightarrow{k_{fs}} P_r + R_1^* \qquad \text{(solvent or chain transfer agent)}$$

With transfer to small molecules, it is assumed that the transfer radical R_1^* reacts with monomer instantaneously.

Termination

$$R_r^* + R_s^* \xrightarrow{k_{tc}} P_{r+s} \qquad \text{(combination)}$$

$$R_r^* + R_s^* \xrightarrow{k_{td}} P_r + P_s \qquad \text{(disproportionation)}$$

All the assumptions listed in Section II.2.2 of the present thesis are assumed valid, viz. the reactions are elementary, the steady-state hypothesis (SSH) is valid for all free-radical species, the long-chain approximation (LCA) is valid and volume contraction may be neglected.

Polymer Production Rate for a Batch Reactor

The differential equations describing the time variation of polymer-radicals concentrations are as follows

$\underline{r = 1}$

$$\frac{d[R_1^*]}{dt} = R_I + (k_{fm}[M] + k_{fi}[I] + k_{fs}[S]) \sum_{r=2}^{r=\infty} [R_r^*] - (k_p[M][R_1^*])$$

$$- (k_{tc} + k_{td})[R_1^*] \sum_{r=1}^{r=\infty} [R_r^*] \qquad \text{(II-A1-1)}$$

$\underline{r \geqslant 2}$

$$\frac{d[R_r^*]}{dt} = k_p[M][R_{r-1}^*] - k_p[M][R_r^*] - (k_{fm}[M] + k_{fi}[I] + k_{fs}[S])[R_r^*]$$

$$-(k_{tc} + k_{td})[R_r^*] \sum_{r=1}^{r=\infty} [R_r^*] \qquad \text{(II-A1-2)}$$

Summing the above equations with respect to r for r = 1,2, ...,∞ we get

$$\frac{d[R^*]}{dt} = R_I - (k_{tc} + k_{td}) [R^*]^2 \qquad \text{(II-A1-3)}$$

where $[R^*]$ is the total polymer-radical concentration

$$[R^*] = \sum_{r=1}^{r=\infty} [R_r^*] \qquad \text{(II-A1-4)}$$

The SSH applied to Eq.(II-A1-3) yields

$$R_I \doteq (k_{tc} + k_{td}) \left[R^*\right]^2 \gg \frac{d\left[R^*\right]}{dt} \qquad \text{(II-A1-5)}$$

Therefore, the total radical concentration is given by

$$\left[R^*\right] = \left(\frac{R_I}{k_{tc} + k_{td}}\right)^{\frac{1}{2}} \qquad \text{(II-A1-6)}$$

The rate of the propagation step may now be expressed as

$$R_P = k_p \left[M\right]\left(\frac{R_I}{k_{tc} + k_{td}}\right)^{\frac{1}{2}} \qquad \text{(II-A1-7)}$$

Application of the LCA permits the use of the above expression to calculate the total monomer consumption or polymer production

$$-\frac{d\left[M\right]}{dt} = k_p \left[M\right] \left(\frac{R_I}{k_{tc} + k_{td}}\right)^{\frac{1}{2}} \qquad \text{(II-A1-8)}$$

And in terms of monomer conversion X,

$$\ln (1-X) = -\int_0^t k_p \left(\frac{R_I}{k_{tc} + k_{td}}\right)^{\frac{1}{2}} dt \qquad \text{(II-A1-9)}$$

where, $X = \dfrac{\left[M\right]_o - \left[M\right]}{\left[M\right]_o}$

Eq.(II-A1-9) can be integrated given the expression for R_I, and the variation – if any – of k_p, k_{tc} and k_{td} with conversion (gel effect, non-isothermal effects, etc.)

Molecular Weight Distributions from the Kinetic Model

Rearranging Eq.(II-A1-7) we obtain

$$R_I = \frac{(k_{tc} + k_{td})\, R_P^2}{k_p^2\, [M]^2} \qquad \text{(II-A1-10)}$$

Define the following two dimensionless groups

$$\alpha \equiv \frac{k_{td}\, R_P}{k_p^2\, [M]^2} \qquad \text{(II-A1-11)}$$

$$\beta \equiv \frac{k_{tc}\, R_P}{k_p^2\, [M]^2} \qquad \text{(II-A1-12)}$$

Therefore Eq.(II-A1-10) becomes

$$R_I = (\alpha + \beta)\, R_P \qquad \text{(II-A1-13)}$$

Now define two more dimensionless groups

$$T = \frac{k_{fm}}{k_p} + \frac{k_{fi}}{k_p}\frac{[I]}{[M]} + \frac{k_{fs}}{k_p}\frac{[S]}{[M]} \qquad \text{(II-A1-14)}$$

$$\Phi = \frac{1}{1 + T + \alpha + \beta} \qquad \text{(II-A1-15)}$$

Applying the SSH to Eq.(II-A1-1) and Eq.(II-A1-2), solving for the concentrations of the radicals and substituting for R_I from Eq.(II-A1-13) we obtain

$$[R_1^*] = \frac{R_P}{k_p [M]} \cdot \frac{T + \alpha + \beta}{1 + T + \alpha + \beta} \qquad \text{(II-A1-16)}$$

And $[R_r^*] = [R_{r-1}^*]$ (II-A1-17)

The last equation is a recurrence formula leading to the result

$$R_r^* = \phi^{r-1}\left[R_1^*\right] \quad , \qquad \text{(II-A1-18)}$$

Now we develop the rate expression for dead polymers according to the kinetic scheme outlined before

$$\frac{d\left[P_r\right]}{dt} = \left(k_{fm}\left[M\right] + k_{fi}\left[I\right] + k_{fs}\left[S\right]\right)\left[R_r^*\right] + k_{td}\left[R^*\right]\left[R_r^*\right] + \frac{1}{2}k_{tc}\sum_{j=1}^{j=r-1}\left[R_j^*\right]\left[R_{r-j}^*\right] \qquad \text{(II-A1-19)}$$

Substituting from equations (II-A1-16) and (II-A1-18) into Eq.(II-A1-19) to eliminate the radical concentrations we obtain

$$\frac{d\left[P_r\right]}{dt} = R_p\left[\mathcal{T}\,(\mathcal{T}+\beta) + \frac{1}{2}\,\beta\,(\mathcal{T}+\beta)^2(r-1)\right]\phi^r \qquad \text{(II-A1-20)}$$

where the new dimensionless quantity $\mathcal{T}$ is defined as

$$\mathcal{T} \equiv \alpha + \mathrm{T}$$

or

$$\mathcal{T} \equiv \frac{k_{td}\,R_p}{k_p^2\left[M\right]^2} + \frac{k_{fm}}{k_p} + \frac{k_{fi}}{k_p}\frac{\left[I\right]}{\left[M\right]} + \frac{k_{fs}}{k_p}\frac{\left[S\right]}{\left[M\right]} \qquad \text{(II-A1-21)}$$

In Eq.(II-A1-20), $(r - 1)$ may be approximated by r, which is consistent with the LCA. Again, arguing that we are dealing with high polymers, $(\mathcal{T}+\beta)\sim 10^{-4}$, and the approximation $\left[\frac{1}{1+\mathcal{T}+\beta}\right]^r \doteq \exp(-(\mathcal{T}+\beta)\,r)$ is valid, therefore Eq.(II-A1-20) becomes

$$\frac{d\left[P_r\right]}{dt} = R_p\,(\mathcal{T}+\beta)\left[\mathcal{T} + \frac{1}{2}\,\beta\,(\mathcal{T}+\beta)\,r\right]\exp\left[-(\mathcal{T}+\beta)r\right] \qquad \text{(II-A1-22)}$$

The instantaneous differential molecular weight distribution w(r,t) is defined as the weight fraction of polymer of chain length r produced instantaneously at time t.

$$w(r,t) \equiv \frac{d(r\,[P_r])}{R_p\ dt} \qquad \text{(II-A1-23)}$$

Substituting from Eq.(II-A1-22) for $\frac{d[P_r]}{dt}$ we obtain

$$w(r,t) = (\tau + \beta)\,r\left[\tau + \tfrac{1}{2}\beta(\tau + \beta)r\right]\exp\left[-(\tau + \beta)r\right] \qquad \text{(II-A1-24)}$$

The instantaneous number and weight-average chain lengths of the total polymer produced at any instant may be found by direct integration of Eq.(II-A1-24) according to the definitions of these averages as follows

$$\bar{r}_n \equiv \frac{1}{\sum_{r=1}^{r=\infty} \frac{w(r,t)}{r}} = \frac{1}{\tau + \frac{\beta}{2}} \qquad \text{(II-A1-25)}$$

$$\bar{r}_w \equiv \sum_{r=1}^{r=\infty} r\ w(r,t) = \frac{2\left(\tau + \frac{3\beta}{2}\right)}{(\tau + \beta)^2} \qquad \text{(II-A1-26)}$$

Similarly, an expression for the instantaneous intrinsic viscosity of the whole polymer produced at any instant may be expressed as

$$[\eta] \equiv K\ M_m^a \sum_{r=1}^{r=\infty} r^a\ w(r,t) \qquad \text{(II-A1-27)}$$

where, K and a are the Mark-Houwink constants
and M_m is the molecular weight of the monomer

It must be emphasized that $w(r,t)$, $\bar{r}_n$, $\bar{r}_w$ and $[\eta]$ thus derived are instantaneous values, corresponding to the polymers being produced at a particular time t. Therefore, in a batch reactor system, they must be integrated over the reaction time to obtain the corresponding values for the final polymer produced. These are called the cumulative values and are given by the following integrations:

$$\mathrm{Cum}\left[w(r,X)\right] = \frac{1}{X}\int_0^X w(r,X)\,dX \qquad \text{(II-A1-28)}$$

$$\mathrm{Cum}\left[\frac{1}{\bar{r}_n}\right] = \frac{1}{X}\int_0^X \frac{1}{\bar{r}_n}\,dX = \frac{1}{X}\int_0^X \left(\tau + \frac{\beta}{2}\right) dX \qquad \text{(II-A1-29)}$$

$$\mathrm{Cum}\left(\bar{r}_w\right) = \frac{1}{X}\int_0^X \bar{r}_w\,dX = \frac{2}{X}\int_0^X \frac{\left(\tau + \frac{3\beta}{2}\right)}{(\tau + \beta)^2}\,dX \qquad \text{(II-A1-30)}$$

$$\mathrm{Cum}\left[\eta\right] = \frac{1}{X}\int_0^X \left[\eta\right] dX \qquad \text{(II-A1-31)}$$

where X is the fractional conversion.

The integration of the above equations requires the knowledge of the dependence of τ and β on conversion. These equations apply to non-isothermal as well as isothermal batch polymerizations. The instantaneous equations could be applied directly to flow reactors.

A Special Case : Termination by Combination is Negligible

This case is of particular importance for polyacrylamide, where k_{tc} was found to be negligible. From Eq.(II-A1-12) it is clear that $\beta = 0$, and the instantaneous values of the molecular weight distribution, molecular weight averages and intrinsic viscosity are expressed as follows

$$W(r,t) = \tau^2 r \exp(-\tau r) \qquad \text{(II-A1-32)}$$

$$\bar{r}_n = \frac{1}{\tau} \qquad \text{(II-A1-33)}$$

$$\bar{r}_w = \frac{2}{\tau} \qquad \text{(II-A1-34)}$$

$$[\eta] = K\ M_m^a\ \frac{\Gamma(2+a)}{\tau^a} \qquad \text{(II-A1-35)}$$

where $\Gamma(2+a)$ is the Gamma function of $(2+a)$.

The distribution described by Eq.(II-A1-32) often occurs in polymer systems and is referred to as "the most probable distribution". It may be noted that in this special case where $k_{tc} = 0$, the free-radical polymerization mechanism yields a one parameter model, viz. τ defined by Eq.(II-A1-21)

It has been shown that acrylamide polymerization falls into this special case of $k_{tc} = 0$. Furthermore, in the aqueous solution polymerization of acrylamide with potassium persulfate initiator, the rate of polymerization may be expressed as $R_p = k_{1.25} [I]^{0.5} [M]^{1.25}$, and the tranfer reaction to water may be neglected. Therefore Eq.(II-A1-21) reduces to

$$\mathcal{T} = \frac{k_{td}}{k_p^2} k_{1.25} \frac{[I]^{0.50}}{[M]^{0.75}} + \frac{k_{fm}}{k_p} + \frac{k_{fi}}{k_p} \frac{[I]}{[M]} \qquad \text{(II-A1-36)}$$

It has also been shown that $K_2S_2O_8$ has a very long half-life compared to the polymerization times at the relatively high monomer concentrations used in the present study. Therefore $[I]$ may be considered to remain constant at its original value $[I]_o$ without introducing a serious error in the calculations. In this case, Eq.(II-A1-36) reduces to

$$\mathcal{T} = k' \frac{[I]_o^{0.50}}{[M]_o^{0.75}} \frac{1}{(1 - X)^{0.75}} + C_M + C_I \frac{[I]_o}{[M]_o} \frac{1}{(1 - X)} \qquad \text{(II-A1-37)}$$

with

$$k' = \frac{k_{td}}{k_p^2} k_{1.25}$$

$$C_M = \frac{k_{fm}}{k_p}$$

$$C_I = \frac{k_{fi}}{k_p}$$

Hence, the cumulative number-average chain length for all the polymer molecules produced up to conversion X may be found by substituting for $\mathcal{T}$, Eq.(II-A1-37), into Eq.(II-A1-29), with $\beta = 0$, and integrating analytically to get

$$\mathrm{Cum}\left[\frac{1}{\bar{r}_n}\right] = 4\ k' \frac{[I]_o^{0.50}}{[M]_o^{0.75}} \frac{(1 - (1 - X)^{0.25})}{X} + C_M + C_I \frac{[I]_o}{[M]_o} \frac{\ln\left(\frac{1}{1 - X}\right)}{X} \qquad \text{(II-A1-38)}$$

In the case wherethe assumption of constant $[I]$ does not hold, the integration of Eq.(II-A1-29) has to be performed numerically.

Appendix (II-2) Conversion and Molecular Weight Data for Acrylamide Polymerization

Run No. 25-20-10

Polymer	Reaction Time (hr.)	Measured Conversion	Predicted Conversion	$[\eta]_o$ (dl/g)	$[\eta]_\infty$ (dl/g)	Measured ($\overline{M}_n \times 10^{-6}$)	Predicted ($\overline{M}_n \times 10^{-6}$)
A	0.75	.088	.109	36.0	21.7	6.77	7.78
B	1.00	.124	.142	33.0	21.5	6.68	7.76
C	1.50	.184	.204	33.0	21.5	6.68	7.72
D	2.25	.304	.287	28.0	20.5	6.21	7.66
E	4.00	.463	.441	32.0	23.2	7.50	7.55
F	7.00	.597	.620	55.0	26.2	9.01	7.42
G	11.00	.783	.761	26.8	21.5	6.68	7.16
			Reproducibility Test				
H	1.25	.168	.174	42.0	25.0	8.40	7.74
I	3.00	.351	.359	41.0	23.6	7.69	7.63
J	20.00	.915	.901	21.4	15.0	3.86	6.78

Run No. 25-05-10

Polymer	Reaction Time (hr.)	Measured Conversion	Predicted Conversion	$[\eta]_o$ (dl/g)	$[\eta]_\infty$ (dl/g)	Measured ($\overline{M}_n \times 10^{-6}$)	Predicted ($\overline{M}_n \times 10^{-6}$)
A	1.00	.106	.103	30.0	19.8	5.89	6.04
B	1.50	.127	.150	26.3	18.5	5.31	6.02
C	3.00	.266	.273	26.3	18.5	5.31	5.89
D	7.00	.447	.508	25.5	18.0	5.10	5.67
E	12.00	.643	.682	25.5	18.0	5.10	5.34
F	20.00	.778	.828	26.5	18.4	5.27	5.02

Run No. 25-02-10

Polymer	Reaction Time (hr.)	Measured Conversion	Predicted Conversion	$[\eta]_o$ (dl/g)	$[\eta]_\infty$ (dl/g)	Measured ($\overline{M}_n \times 10^{-6}$)	Predicted ($\overline{M}_n \times 10^{-6}$)
A	5.00	.325	.341	19.6	13.5	3.29	4.16
B	7.00	.430	.436	23.3	15.5	4.09	4.02
C	10.00	.530	.549	21.0	15.4	4.02	3.88
D	15.00	.676	.681	21.5	14.9	3.82	3.60
E	18.00	.723	.737	24.0	15.6	4.10	3.50
F	24.00	.803	.817	22.0	13.75	3.39	3.28

Run No. 25-05-01

Polymer	Reaction Time (hr.)	Measured Conversion	Predicted Conversion	$[\eta]_o$ (dl/g)	$[\eta]_\infty$ (dl/g)	Measured ($\bar{M}_n \times 10^{-6}$)	Measured ($\bar{M}_n \times 10^{-6}$)
A	5.00	.169	.158	50.0	32.0	12.2	7.95
B	7.00	.232	.212	53.0	31.0	11.6	7.93
C	10.00	.281	.285	48.0	31.0	11.6	7.91
D	13.00	.350	.350	56.0	38.0	15.9	7.87
E	18.00	.469	.443	55.0	28.0	9.98	7.79
F	30.00	.575	.607	52.5	28.5	10.20	7.71
Reproducibility Test							
G	3.00	.103	.098	58.0	33.5	13.10	7.98
H	6.00	.179	.185	54.0	28.0	9.98	7.95
I	24.00	.554	.534	55.0	29.5	10.80	7.73

Run No. 25-05-05

Polymer	Reaction Time (hr.)	Measured Conversion	Predicted Conversion	$[\eta]_o$ (dl/g)	$[\eta]_\infty$ (dl/g)	Measured ($\overline{M}_n \times 10^{-6}$)	Predicted ($\overline{M}_n \times 10^{-6}$)
A	2.00	.167	.142	29.0	20.7	6.30	6.76
B	4.00	.299	.260	30.6	21.0	6.44	6.64
C	8.00	.499	.441	26.0	18.5	5.31	6.43
D	13.00	.658	.596	29.3	19.0	5.53	6.19
E	17.50	.703	.692	29.5	20.4	6.07	6.10

Run No. 25-05-25

Polymer	Reaction Time (hr.)	Measured Conversion	Predicted Conversion	$[\eta]_o$ (dl/g)	$[\eta]_\infty$ (dl/g)	Measured ($\overline{M}_n \times 10^{-6}$)	Predicted ($\overline{M}_n \times 10^{-6}$)
A	0.75	.104	.121	20.8	13.8	3.40	4.80
B	1.50	.201	.225	22.5	16.0	4.26	4.67
C	3.00	.421	.390	22.5	16.0	4.26	4.41
D	6.00	.597	.607	18.6	14.5	3.67	4.11
E	10.00	.742	.766	23.8	16.3	4.38	3.79
F	17.00	.903	.892	20.5	14.6	3.71	3.20

Run No. 40-20-05

Polymer	Reaction Time (hr.)	Measured Conversion	Predicted Conversion	$[\eta]_o$ (dl/g)	$[\eta]_\infty$ (dl/g)	Measured ($\bar{M}_n$ x 10^{-6})	Predicted ($\bar{M}_n$ x 10^{-6})
A	0.25	.100	.102	21.3	16.5	4.47	4.73
B	0.50	.189	.190	26.0	17.8	5.01	4.67
C	0.75	.261	.269	25.0	17.0	4.67	4.65
D	1.75	.522	.501	22.8	17.0	4.67	4.47
E	3.00	.652	.676	23.5	16.5	4.47	4.37
F	5.00	.827	.823	21.2	15.7	4.14	4.12
G	7.25	.948	.902	20.2	13.6	3.33	3.74
			Run No.	40-05-05			
A	0.50	.136	.140	15.8	12.3	2.86	3.31
B	1.00	.245	.256	18.0	13.5	3.29	3.22
C	1.50	.346	.353	18.0	14.5	3.67	3.14
D	2.00	.409	.435	16.8	13.5	3.29	3.09
E	3.00	.572	.563	16.5	13.0	3.11	2.92
F	4.00	.651	.657	18.5	13.8	3.36	2.81
G	7.00	.759	.821	17.0	12.8	3.04	2.65

Polymer	Reaction Time (hr.)	Measured Conversion	Predicted Conversion	$[\eta]_o$ (dl/g)	$[\eta]_\infty$ (dl/g)	Measured ($\overline{M}_n \times 10^{-6}$)	Predicted ($\overline{M}_n \times 10^{-6}$)
Run No. 40-02-05							
A	1.50	.312	.296	11.7	9.4	1.90	2.07
B	2.00	.383	.369	11.8	10.2	2.15	2.02
C	3.00	.452	.489	13.6	11.3	2.51	1.96
D	5.00	.641	.655	11.7	9.4	1.90	1.77
E	7.00	.779	.759	12.1	10.0	2.09	1.58
F	10.00	.815	.851	11.1	9.8	2.02	1.52
Run No. 40-05-01							
A	1.00	.129	.126	25.5	17.3	4.80	4.56
B	2.25	.268	.257	24.0	17.0	4.67	4.51
C	3.75	.409	.384	21.5	16.5	4.47	4.41
D	5.50	.532	.499	25.0	18.0	5.10	4.31
E	8.00	.642	.621	24.0	17.0	4.67	4.21
Reproducibility Test							
F	1.75	.221	.208	21.5	16.0	4.26	4.53
G	7.50	.614	.600	20.8	15.8	4.18	4.26
H	12.00	.739	.748	26.2	16.7	4.55	4.09

Polymer	Reaction Time (hr.)	Measured Conversion	Predicted Conversion	$[\eta]_o$ (dl/g)	$[\eta]_\infty$ (dl/g)	Measured ($\overline{M}_n$ x 10^{-6})	Predicted ($\overline{M}_n$ x 10^{-6})
			Run No. 40-05-15				
A	0.25	.092	.123	9.9	8.6	1.66	2.25
B	0.50	.201	.227	10.7	9.7	1.99	2.18
C	1.00	.277	.392	10.8	9.6	1.96	2.04
D	2.00	.600	.610	12.3	9.9	2.05	1.82
E	7.00	.867	.928	11.1	9.0	1.78	1.41
			Run No. 40-05-25				
A	0.50	.247	.281	7.4	6.4	1.06	1.66
B	0.75	.353	.384	7.0	6.4	1.06	1.59
C	1.50	.628	.600	7.5	6.8	1.16	1.36
D	3.00	.839	.810	8.3	7.8	1.43	1.09
E	7.00	.881	.957	7.0	6.4	1.06	1.01
			Reproducibility Test				
F	1.00	.491	.469	8.3	7.4	1.32	1.48
G	2.00	.671	.693	7.2	6.7	1.13	1.31
H	5.00	.883	.916	6.6	6.4	1.06	1.01

Appendix II.3 Linear Regression Analysis

The General Linear Model

Consider a mathematical model of the following form with one dependent variable

$$\eta_i = f(\underline{\beta}, \underline{\zeta}_i) \qquad \text{(II-A3-1)}$$

where η_i is the dependent variable

$\underline{\beta}$ is a vector of the model's parameters

$\underline{\zeta}_i$ is a vector of the independent variables

When the model expressed by the above equation is linear in the parameters $\underline{\beta}$, it can be expressed by the following matrix equation

$$\underline{\eta} = \underline{\underline{X}}\,\underline{\beta} \qquad \text{(II-A3-2)}$$

where $\underline{\eta}$ is an (N x 1) vector of the dependent variable where N is the number of observations

$\underline{\beta}$ is a (P x 1) vector of the parameters, where P is the number of parameters in the model

$\underline{\underline{X}}$ is an (N x P) matrix that is independent of the parameters $\underline{\beta}$ in a linear model and is defined by the following equation

$$\underline{\underline{X}} = \left[\frac{\partial \eta_u}{\partial \beta_i} \right] \quad \begin{array}{l} u = 1,2,\ldots,N \\ i = 1,2,\ldots,P \end{array} \qquad \text{(II-A3-3)}$$

Estimation of the Parameters by the Method of Least Squares

Suppose that N experiments were carried out to collect a vector of observations $\underline{Y}$ on the predicted response $\underline{\eta}$ at different values of $\underline{\zeta}$. For any observation u,

$$y_u = \eta_u + \epsilon_u \quad , \quad u = 1,2,\ldots,N \qquad \text{(II-A3-4)}$$

where ϵ_u is the error inherent in the observation.

In calculating the "best" estimates of the parameters in the model, a criterion has to be chosen that these estimates must fulfill. The "least squares estimates" of the parameters $\underline{\beta}$, say $\hat{\underline{\beta}}$, are chosen so as to minimize the sum of the squares of the error terms, or residuals, ϵ_u for all the observations. This sum of squares of the residuals will be a function of the parameters $\underline{\beta}$ and is defined by

$$S(\underline{\beta}) = \sum_{u=1}^{u=N} (y_u - \eta_u)^2 \qquad \text{(II-A3-5)}$$

$$= \sum_{u=1}^{u=N} (y_u - f(\underline{\beta}, \underline{\zeta}_u))^2$$

The least squares estimates $\hat{\underline{\beta}}$ that will minimize $S(\underline{\beta})$ can be obtained directly for a linear model by differentiating Eq.(II-A3-5) with respect to each parameter β_i and equating the differentials to zero,

$$\frac{\partial S(\underline{\beta})}{\partial \beta_i} = 0 \quad , \quad i = 1,2,\ldots,P \qquad \text{(II-A3-6)}$$

The set of P equations expressed by Eq.(II-A3-6) are called the "Normal Equations", and their solution yields the least squares estimates $\hat{\underline{\beta}}$ of the parameters $\underline{\beta}$.

Statistical Justification of the Least Squares Method

First we make two assumptions regarding the errors ϵ_u inherent in the observations :

1. The errors ϵ_u , hence the uncertainty, are confined to the values of the observations y_u , whereas the independent variables ζ_u take fixed and known values. This assumption is usually justified on the basis that the variance of y_u is large in comparison to that of ζ_u .

2. The expected value of the errors is zero. This is equivalent to the assumption that there is no systematic bias in the observations, and that the model expressed by Eq.(II-A3-1) is correct. It follows from Eq.(II-A3-4) that the expected value of any observation y_u is η_u predicted by the model.

Granted that these two assumptions hold, it is possible to prove that the expected value of the vector of the least squares estimators $\hat{\underline{\beta}}$, is the vector of parameters $\underline{\beta}$ i.e.

$$E(\hat{\underline{\beta}}) = \underline{\beta} \qquad \text{(II-A3-7)}$$

In other words, assumptions (1) and (2) ensure that the least squares estimators are unbiased.

Now we make two more assumptions about the error terms ϵ_u, viz.

3. The errors ϵ_u are independent random variables which implies that the observations y_u are also independent.

4. For all observations, the errors have a constant variance σ^2 from the same probability distribution.

Granted that assumptions (1) through (4) hold, a theorem attributed to Gauss yields that of all estimates of the parameters $\underline{\beta}$ that are linear combinations of the observations $\underline{Y}$, the least squares estimates $\hat{\underline{\beta}}$ obtained from solving the set of normal equations have, component by component, the smallest variance. In other words, the least squares estimators in this case are the linear unbiased minimum variance estimators. It may be noted that this conclusion required no assumptions about the shape of the distribution of the error terms.

Now we make one more assumption about ϵ_u, viz.

5. The probability distribution of the errors is the normal (Gaussian) distribution. This assumption, together with assumptions (2) and (4) may be expressed as follows

$$\epsilon_u \sim N(0, \sigma^2) \qquad \text{(II-A3-8)}$$

With the complete set of five assumptions granted as true, then the least squares estimators also become the maximum likelihood estimators of the parameters $\underline{\beta}$. Furthermore, assumption (5) also implies that the likelihood function of the parameters $\underline{\beta}$ given a set of observations $\underline{Y}$ and the probability density functions of the responses $\underline{\eta}$ given a set of parameters $\underline{\beta}$, are normal with a variance equal to σ^2. This allows some statistical inferences to be made about $\underline{\beta}$ and $\underline{\eta}$ (e.g.,t and F tests, confidence intervals, etc.).

It may be noted that assumption (5) is not as restrictive as it may appear. If the errors can be regarded as being the sum of many independent errors, the "central-limit theorem" indicates that, in many cases, the errors in the observations will be approximately normally distributed.

The Least Squares Equations for the General Linear Model

By combining Eq.(II-A3-2) and Eq.(II-A3-4), the general linear model may be expressed by the following equation

$$\underline{Y} = \underline{\underline{X}}\,\underline{\beta} + \underline{\epsilon} \qquad \text{(II-A3-9)}$$

And the sum of squares of the residuals, $S(\underline{\beta})$, defined by Eq.(II-A3-5), may be expressed as

$$S(\underline{\beta}) = \underline{\epsilon}'\,\underline{\epsilon} \qquad \text{(II-A3-10)}$$

where $\underline{\epsilon}'$ is the transpose of the vector $\underline{\epsilon}$. The above two equations may be combined to yield

$$S(\underline{\beta}) = (\underline{Y} - \underline{\underline{X}}\,\underline{\beta})'\,(\underline{Y} - \underline{\underline{X}}\,\underline{\beta}) \qquad \text{(II-A3-11)}$$

Differentiating the above expression with respect to the vector of the parameters $\underline{\beta}$ we obtain

$$\frac{\partial S(\underline{\beta})}{\partial \underline{\beta}} = -2\,\underline{\underline{X}}'\,(\underline{Y} - \underline{\underline{X}}\,\underline{\beta}) \qquad \text{(II-A3-12)}$$

Equating the result of the above differential to zero we obtain the set of normal equations whose solution yields the least squares estimators $\hat{\underline{\beta}}$ as

$$\hat{\underline{\beta}} = (\underline{\underline{X}}'\underline{\underline{X}})^{-1} \underline{\underline{X}}' \underline{Y} \qquad \text{(II-A3-13)}$$

provided that $(\underline{\underline{X}}' \underline{\underline{X}})$ is non-singular.

These estimators have an expected value of

$$E(\hat{\underline{\beta}}) = \underline{\beta} \qquad \text{(II-A3-14)}$$

and the following variance-covariance matrix,

$$\mathrm{Var}(\hat{\underline{\beta}}) = (\underline{\underline{X}}' \underline{\underline{X}})^{-1} \sigma^2 \qquad \text{(II-A3-15)}$$

Each diagonal element of this matrix, $C_{ii}\,\sigma^2$ say, represents the variance of the estimator $\hat{\beta}_i$, whereas each non-diagonal element, $C_{ij}\,\sigma^2$, represents the covariance between the estimators $\hat{\underline{\beta}}_i$ and $\hat{\underline{\beta}}_j$. The "correlation coefficient" between each pair of estimators is defind by

$$\rho_{ij} = \frac{\mathrm{Cov}(\hat{\beta}_i, \hat{\beta}_j)}{(\mathrm{Var}(\hat{\beta}_i)\ \mathrm{Var}(\hat{\beta}_j))^{\frac{1}{2}}}$$

$$= \frac{C_{ij}}{(C_{ii}\ C_{jj})^{\frac{1}{2}}} \qquad \text{(II-A3-16)}$$

The assumption that the errors are normally distributed leads to the conclusion that the parameters are also normally distributed as

$$\hat{\underline{\beta}} \sim N(\underline{\beta}, (\underline{\underline{X}}' \underline{\underline{X}})^{-1} \sigma^2) \qquad \text{(II-A3-17)}$$

And each individual parameter estimator will be distributed as

$$\hat{\beta}_i \sim N(\beta_i\ ,\ C_{ii}\ \sigma^2) \qquad \text{(II-A3-18)}$$

which allows the following statistical inference to be made about the value of each individual parameter

$$\frac{\hat{\beta}_i - \beta_i}{(C_{ii}\ \sigma^2)^{\frac{1}{2}}} \sim N(0\ ,\ 1) \equiv Z \qquad \text{(II-A3-19)}$$

As the variance σ^2 is not usually known, its unbiased estimator s^2 (the error-mean square or the residual variance) is used in its place. s^2 is defined by

$$s^2 = \frac{S(\underline{\beta})}{N - P} \qquad \text{(II-A3-20)}$$

After substituting s^2 for σ^2, the standardized $\hat{\beta}_i$ will no longer be normal, but instead will have the slightly more spread t-distribution with (N-P) degrees of freedom.

$$\frac{\hat{\beta}_i - \beta_i}{(C_{ii}\ s^2)^{\frac{1}{2}}} \doteq t_{(N-P)} \qquad \text{(II-A3-21)}$$

Therefore, at a $100(1 - \alpha)\%$ confidence level, the confidence interval of each of the individual parameters will be

$$\hat{\beta}_i \pm t_{\frac{\alpha}{2}}\ (N-P)\quad (C_{ii}\ s^2)^{\frac{1}{2}} \qquad \text{(II-A3-22)}$$

The following is the application of the above general equations to the specific models employed in Part II of this thesis.

1. Model : $\eta = \beta_1 + \beta_2 x$

In this case, matrix $\underline{\underline{X}}$ defined by Eq.(II-A3-3) takes the following form, where N is the number of observations

$$\underline{\underline{X}} = \begin{pmatrix} 1 & x_1 \\ 1 & x_2 \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \\ 1 & x_N \end{pmatrix} \qquad \text{(II-A3-23)}$$

Therefore,

$$\underline{\underline{X}}' \underline{\underline{X}} = \begin{pmatrix} N & \sum x_i \\ \sum x_i & \sum x_i^2 \end{pmatrix} \qquad \text{(II-A3-24)}$$

where all summations are from $i = 1$ to $i = N$.

Therefore

$$(\underline{\underline{X}}' \underline{\underline{X}})^{-1} = \frac{\begin{pmatrix} \sum x_i^2 & -\sum x_i \\ -\sum x_i & N \end{pmatrix}}{N \sum x_i^2 - (\sum x_i)^2} \qquad \text{(II-A3-25)}$$

Substituting from the above into Eq.(II-A3-13) we obtain the least squares estimates of the parameters as

$$\hat{\beta}_2 = \frac{N(\sum x_i y_i) - (\sum x_i)(\sum y_i)}{N(\sum x_i^2) - (\sum x_i)^2} \qquad \text{(II-A3-26)}$$

and

$$\hat{\beta}_1 = \frac{(\sum y_i) - \hat{\beta}_2 (\sum x_i)}{N} \qquad \text{(II-A3-27)}$$

And, from Eq.(II-A3-15), after substituting s^2 for σ^2, we obtain

$$\mathrm{Var}(\hat{\beta}_1) = \left(\frac{\sum x_i^2}{N \sum x_i^2 - (\sum x_i)^2} \right) s^2 \qquad \text{(II-A3-28)}$$

$$\mathrm{Var}(\hat{\beta}_2) = \left(\frac{N}{N \sum x_i^2 - (\sum x_i)^2} \right) s^2 \qquad \text{(II-A3-29)}$$

Where s^2 is defined by

$$s^2 = \frac{\sum (y_i - \hat{\beta}_1 - \hat{\beta}_2 x_i)^2}{N - 2} \qquad \text{(II-A3-30)}$$

And the covariance between the two parameters is expressed by

$$\mathrm{Cov}(\hat{\beta}_1 , \hat{\beta}_2) = \frac{- \sum x_i}{N \sum x_i^2 - (\sum x_i)^2} \qquad \text{(II-A3-31)}$$

Now the variances may be substituted into Eq.(II-A3-22) to obtain the individual confidence intervals for the parameters β_1 and β_2, and into Eq.(II-A3-16) together with the covariance to obtain the correlation coefficient.

2. Model : $\eta = \beta_1$

In this case, the general equations lead to the following results

$$\hat{\beta}_1 = \frac{\sum y_i}{N} \qquad \text{(II-A3-32)}$$

$$s^2 = \frac{\sum (y_i - \hat{\beta}_1)^2}{(N - 1)} \qquad \text{(II-A3-33)}$$

And at a 95 % confidence level,

$$\beta_1 = \hat{\beta}_1 \pm t_{.975}(N-1)\left(\frac{s^2}{N}\right)^{\frac{1}{2}} \qquad \text{(II-A3-34)}$$

3. Model : $\eta = \beta_2 x$

For this model we obtain,

$$\hat{\beta}_2 = \frac{\sum (x_i\ y_i)}{\sum x_i^2} \qquad \text{(II-A3-35)}$$

$$s^2 = \frac{\sum (y_i - \hat{\beta}_2 x_i)^2}{N-1} \qquad \text{(II-A3-36)}$$

And at 95% confidence level,

$$\beta_2 = \hat{\beta}_2 \pm t_{.975}(N-1)\left(\frac{s^2}{\sum x_i^2}\right)^{\frac{1}{2}} \qquad \text{(II-A3-37)}$$

The Analysis of Variance in Linear Regression - The Extra Sum of Squares Principle.

Suppose that to a set of N experimental observations, a general linear regression model of the following form has been fitted

$$y = \beta_1 x_1 + \beta_2 x_2 + \dots + \beta_q x_q + \beta_{q+1} x_{q+1} + \dots$$
$$\dots + \beta_p x_p + \epsilon_p \qquad \text{(II-A3-38)}$$

The sum of squares of the residuals for this model is $(\sum \epsilon_p^2)$ with (N-P) degrees of freedom. Therefore, an unbiased measure of the variance σ^2 is $s^2 = (\sum \epsilon_p^2)/(N-P)$.

Now assume that it is desired to carry out an analysis of variance to determine whether the experimental data warrant the inclusion of any number of the independent variables, say x_{q+1} , x_{q+2} , ... , x_p , in the model. For this purpose, the following truncated model is also fitted to the data

$$y = \beta_1 x_1 + \beta_2 x_2 + \ldots + \beta_q x_q + \epsilon_q \qquad \text{(II-A3-39)}$$

The sum of squares of the residuals for the truncated model will be $(\sum \epsilon_q^2)$ with $(N-q)$ degrees of freedom.

Therefore, the improvement in the fit of the model to the data due to the inclusion of the variables x_{q+1} , x_{q+2} , ... , x_p may be represented by the increment in the sum of squares of the residuals due to the deletion of these variables. This "extra sum of squares" is equal to $(\sum \epsilon_q^2 - \sum \epsilon_p^2)$ with $(p-q)$ degrees of freedom.

If the response y is independent of the variables deleted in Eq.(II-A3-39), then these terms should only fit some of the random errors in the observations and the reduction of the sum of squares of the residuals should reflect this fact. This implies that the quantity $(\sum \epsilon_q^2 - \sum \epsilon_p^2)/(p-q)$ will, in this case, also be a measure of the variance σ^2 of the errors inherent in the observations.

Therefore an F-test may be performed on these two measures of the variance to test the null hypothesis that the variables deleted were not significant, i.e.

$$H_o : \beta_{q+1} = \beta_{q+2} = \ldots = \beta_p = 0$$

The ratio of the two measures of the variance will have the F-distribution as follows

$$\frac{(\sum \epsilon_q^2 - \sum \epsilon_p^2)/(p - q)}{(\sum \epsilon_q^2)/(N - q)} \sim F(p-q \ , \ N-q)$$

If the variance ratio exceeds the value of $F_{(1-\alpha)}$ for the selected significance level, then the group of variables x_{q+1}, x_{q+2}, ..., x_p makes a significant contribution to the complete model, Eq.(II-A3-38), and the null hypothesis can be rejected at this confidence level.

Appendix II.4 The Termination Rate Constant in Free-Radical Polymerization.

It has been suggested that the termination rate constant k_t in free-radical polymerization is diffusion controlled at all conversions. The following is a review of the experimental evidence supporting this claim.

1. Hayden and Melville(51) investigated the variation of the rate of polymerization of methyl methacrylate (MMA) with conversion. In the initial stages of polymerization (up to 10% conversion), they observed a decrease in the reaction rate with conversion, greater than can be expected on the basis of monomer and initiator consumption. At higher conversions, gel effect predominated resulting in an increase in the reaction rate.

2. By varying η_0, the viscosity of the solvent in which MMA polymerization was conducted, North and Reed(52) and Benson and North(53) observed that k_t decreased almost linearly with increasing η_0.

3. In some polymerization systems, k_t was found to decrease somewhat with increasing molecular weight. This has been observed in the bulk polymerization of MMA and the solution polymerization of polystyrene in toluene and of polyoxyethylene in water(54).

The following is a review of the models that have been proposed in the literature to account for the above observations.

Cardenas and O'Driscoli(55) applied the concept of polymer entanglements in conjunction with free-radical polymerization kinetics to predict the rapid increase in rate and molecular weight with conversion associated with the gel effect. They found that their model yielded results in good agreement with published data for MMA. The authors then showed that chain transfer to monomer can greatly affect the rate of polymerization and the molecular weight averages when polymerization is subjected to autoacceleration due to gel effect(56). Finally, the same authors collected experimental data for the polymerization of ethyl methacrylate and showed that they conformed to the results predicted by their model(57).

Turner(58) proposed a different model to account for autoacceleration in the rate of polymerization of MMA. In it, he treated the macromolecules as equivalent to uniform rigid spheres with a radius that can be calculated from their unperturbed dimensions. The gel effect is assumed to occur when the concentration of polymer reaches a critical value corresponding to close packing of the discrete molecular spheres. Lee and Turner(59,60) followed the polymerization of MMA by dilatometry and found the data to conform to the macromolecular close packing theory. It is interesting to note that in their experimental results, Lee and Turner did not observe the rate deceleration at low conversions reported by Hayden and Melville(51).

The first attempt to model for this deceleration at low conversions was done by North and Reed(61). They experimentally showed that this decrease in rate was a direct consequence of an increase in k_t for the MMA polymerization system. They proposed a model that predicted a linear relationship of the form

$$\frac{k_t}{k_{to}} = 1 + \delta C \qquad \text{(II-A4-1)}$$

Where k_t is the termination rate constant at any conversion where the polymer concentration is C and k_{to} is the corresponding value at zero conversion. The estimation of the parameter δ allows the prediction of rate deceleration during the initial stages of polymerization of MMA.

Mahabadi and O'Driscoll(62) proposed a different model to simulate the same rate data for MMA dealt with in the previous paper. They improved on the model by taking into account the concentration dependence of the linear expansion factor α and the effect of that on the conversion dependence of k_t. This model also predicted a linear increase in k_t with conversion at low conversions, in an expression identical to Eq.(II-A4-1). However, a more complicated expression was used to estimate the parameter δ. The reacting molecules were assumed monodispersed, having a number of monomer units N_A and N_B, respectively, with $N_A = 2 N_B$.

In another publication, Mahabadi and O'Driscoll(54) proposed a model to account for the variation of k_t with the solvent viscosity η_o and the molecular weight of the polymer molecules. Again they assumed two monodispersed polymer molecules reacting, with $N_A = 2N_B$. They obtained an expression of the form

$$k_t = F_1 \cdot F_2 \qquad \text{(II-A4-2)}$$

Where, F_1 is a function representing the effect of frictional properties and has η_o in its denominator.

And F_2 represents the effect of excluded volume and molecular weight.

The model was found to predict reasonably well the change in k_t with molecular weight observed experimentally in bulk polymerization of MMA and solution polymerization of polystyrene in toluene and of polyoxyethylene in water.

Applicability to acrylamide polymerization.

The polymerization of acrylamide does not exhibit any of the phenomena associated with MMA polymerization, viz. retardation at low conversions, acceleration due to gel effect and a k_t that varies with η_o and molecular weight. Extensive rate data have been gathered for acrylamide polymerization by several investigators, mainly by dilatometry, using different initiation systems and over wide ranges of conditions. However, neither an initial deceleration nor a later acceleration in rate has been observed. Furthermore, values for the parameter (k_p^2 / k_t) have been estimated over wide ranges of initial monomer concen~~tra~~tions, hence η_o , and molecular weights of the resulting polymers. Consistent results were always obtained, indicating that k_t is not affected by these variables, e.g.

Reference No.	$[M]_o$ (moles/l)	$\bar{M}_n \times 10^{-6}$	$\frac{k_p^2}{k_t}$ at 50°C (l/mole.sec)
28	0.1 - 2.0	0.7 - 6.0	31
63	0.3 - 1.1	0.35 - 0.77	30
5	0.28 - 2.25	2.4 - 4.8	28

Therefore it is not necessary, indeed it is impossible, to apply the previously mentioned models to the kinetic data collected for acrylamide polymerization. This is due to the fact that the trends that these models were specifically developed to predict, are not exhibited in this polymerization system. It may also be noted that one of these models predicts that the initial decrease in rate is more pronounced when the molecular weight of the polymers produced is high(62). Therefore, with the extremely large molecular weights encountered in acrylamide polymerization, one would expect that this rate decrease would be most pronounced. But this has never been observed in practice.

The above observations indicate the validity of the approach adopted in the present investigation for acrylamide polymerization, viz. to consider k_t to be independent of conversion, viscosity and molecular weight, and to fit the data to the equations predicted by the classical free-radical kinetics. The reasonably good fit between model and data over a wide range of molecular weights further validates this approach.

III. The Copolymerization of Acrylamide and Acrylic Acid

III.1 Introduction

It has been observed that introduction of ionic groups into acrylamide polymer chains renders these polymers more effective in certain industrial applications(1). Of these groups, acrylic acid and its salts are the most common. These groups may be introduced by either alkali or acid hydrolysis of the acrylamide polymer in aqueous solution. Hydrolysis by alkali occurs in two steps, a rapid reaction up to 40 - 50% conversion, and a slow second stage, continuing to complete conversion(2). Acid hydrolysis is complicated by the fact that an amide group adjacent to a carboxylic group hydrolyses much more rapidly than other amide groups(3).

However, these ionic derivatives are often produced more conveniently by copolymerization of acrylamide with other monomers. The copolymers with acrylic acid $CH_2 = CH{-}COOH$, with methacrylic acid $CH_2 = C(CH_3){-}COOH$ and their salts are the most common.

Acrylic acid monomer is a clear colorless liquid at room temperature which is miscible with water and several organic solvents. It is a weak acid ($K_a = 4.25 \times 10^{-5}$) and exhibits chemical properties similar to those of acetic acid. In addition, it takes part in reactions that are characteristic of a reactive activated double bond.

Linear polymers of polyacrylic acid may be prepared by the general methods used with other vinyl monomers. The physical and chemical properties of acrylic acid monomer and its polymers as well as the rheological behaviour of these polymers in aqueous solutions have been comprehensively reviewed by Miller(4).

Acrylic acid polymers are weaker acids than their monomeric counterparts. They are hard to titrate precisely when dissolved in water alone. However, if titrations are carried out in 0.01 - 1 N solutions of neutral salts, end points are sharp and titrations are precise. Neutral salts cause the increase in acid strength by decreasing the thickness of the ionic double layer around the ionized carboxyl groups and thereby decreasing their effect on the ionization of neighbouring carboxyls(4).

The applications of these copolymers are substantially the same as those listed in Section (II.2) for the acrylamide homopolymers. These applications are discussed in detail by Miller(4) and by Glavis(5). In these applications hydrolysed polyacrylamides act differently than copolymerized material. This is probably due to a nonrandom hydrolysis mechanism.

The techniques for the chemical analysis of these copolymers have been detailed by Norris(6). The number of acrylamide molecules in a copolymer sample may be estimated by the Kjeldahl method for the determination of total nitrogen, while the carboxyl content may be determined by titration with alkali in a neutral salt solution.

III.2 Theoretical Background and Literature Review

III.2.1 The Chain Copolymerization Model - The Copolymer Composition(7)

The following model has been developed to predict the composition of a copolymer by assuming the chemical reactivity of the propagating chain in copolymerization to be dependent only on the monomer unit on the growing end and independent of the chain composition preceding the last monomer unit(8-10).

Consider the case for the copolymerization of the two monomers A and B. This copolymerization will lead to two types of propagating species, one with A at the propagating end and the other with B. These will be represented by $A^{*}_{m,n}$ and $B^{*}_{m,n}$, respectively, where m and n are the number of units of A and of B on these chains, respectively, and where the superscript * represents, in the present case, a radical, but may also represent a carbonium ion or a carbanion, depending on the type of polymerization taking place.

The assumption that the reactivity of the propagating species is dependent only on the monomer unit at the end of the chain leads to the conclusion that four propagating reactions are possible, viz.

$$A^*_{m,n} + A \xrightarrow{k_{p_{aa}}} A^*_{m+1,n} \qquad \text{(III-1)}$$

$$A^*_{m,n} + B \xrightarrow{k_{p_{ab}}} B^*_{m,n+1} \qquad \text{(III-2)}$$

$$B^*_{m,n} + A \xrightarrow{k_{p_{ba}}} A^*_{m+1,n} \qquad \text{(III-3)}$$

$$B^*_{m,n} + B \xrightarrow{k_{p_{bb}}} B^*_{m,n+1} \qquad \text{(III-4)}$$

It is these propagation reactions that determine the chains composition, independently from the initiation, transfer and termination steps. In the general case of N monomers copolymerizing, a total of N^2 reactions and rate constants are needed.

There is some evidence which suggests that in copolymerizations involving highly polar or sterically hindered monomers, the four propagation reactions given above are not sufficient to describe the development of the microstructure of a growing chain. Apparently the rate of addition of a monomer will then depend not only upon the type of the monomer unit at the growing end, but also upon the monomer type in the penultimate position. This greatly complicates any analysis. However, the simple copolymer equations based on equations (III-1) to (III-4) have found wide use and have been experimentally verified in innumerable comonomer systems. Hence, assuming the penultimate effects can be neglected, the rates of disappearance of the two monomers are given by

$$-\frac{d[A]}{dt} = k_{p_{aa}}[A^*][A] + k_{p_{ba}}[B^*][A] \qquad \text{(III-5)}$$

$$-\frac{d[B]}{dt} = k_{p_{bb}}[B^*][B] + k_{p_{ab}}[A^*][B] \qquad \text{(III-6)}$$

Dividing Eq.(III-5) by Eq.(III-6) yields the ratios of the rates at which the two monomers enter the copolymer, i.e. the copolymer composition,

$$\frac{d[A]}{d[B]} = \frac{k_{p_{aa}}[A^*][A] + k_{p_{ba}}[B^*][A]}{k_{p_{bb}}[B^*][B] + k_{p_{ab}}[A^*][B]} \qquad \text{(III-7)}$$

To remove the concentration terms in A^* and B^*, from Eq.(III-7), the steady state hypothesis is assumed to hold for each of the reactive species A^* and B^* separately. This implies,

$$k_{p_{ab}}[A^*][B] = k_{p_{ba}}[B^*][A] \qquad \text{(III-8)}$$

Equation (III-8) may also be obtained by a statistical method without resorting to any steady-state assumptions(11,12).

Substituting for the concentration of one of the reactive species from Eq.(III-8) into Eq.(III-7) and rearranging we obtain

$$\frac{d[A]}{d[B]} = \frac{[A]\,(r_1[A] + [B])}{[B]\,([A] + r_2[B])} \qquad \text{(III-9)}$$

Where parameters r_1 and r_2 are defined by

$$r_1 = \frac{k_{p_{aa}}}{k_{p_{ab}}} \quad \text{and} \quad r_2 = \frac{k_{p_{bb}}}{k_{p_{ba}}} \qquad \text{(III-10)}$$

Eq.(III-9) is known as the "copolymerization equation" or the "copolymer composition equation". The parameters r_1 and r_2 are termed the "monomer reactivity ratios". Each reactivity ratio is defined as the ratio of the rate constant for a reactive propagating species adding its own type of monomer to the rate constant for its addition of the other monomer.

The copolymer equation can also be expressed in terms of mole fractions instead of concentrations. If f_1 and f_2 are the mole fractions of monomers A and B in the feed, and F_1 and F_2 are the mole fractions of A and B in the copolymer formed, then

$$f_1 = 1 - f_2 = \frac{[A]}{[A] + [B]} \qquad \text{(III-11)}$$

And

$$F_1 = 1 - F_2 = \frac{d[A]}{d[A] + d[B]} \qquad \text{(III-12)}$$

Combining equations (III-11) and (III-12) with Eq.(III-9) yields

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad \text{(III-13)}$$

Equations (III-9) and (III-13) give the instantaneous composition of the copolymer formed as a function of the monomer mixture composition. In a batch reactor, the monomer mixture changes in composition towards the less reactive monomer as the degree of conversion increases. This results in a similar variation of the copolymer composition as a function of conversion. To express the cumulative composition of all the polymer chains formed from the beginning of the reaction to any conversion X, one must resort to an integrated form of the copolymerization equation.

It can be shown that the following material balance equation holds for any infinitesimal increment in conversion

$$M f_1 - (M - dM)(f_1 - df_1) = F_1 \, dM \qquad \text{(III-14)}$$

Where, M is the number of moles of the two monomers

dM is the number of moles of monomers that have been copolymerized

df_1 is the change in the monomer composition due to the polymerization of dM monomer molecules.

Eq.(III-14) may be rearranged, neglecting the (df_1 dM) term, to give

$$\int_{M_0}^{M} \frac{dM}{M} = \int_{f_{10}}^{f_1} \frac{df_1}{F_1 - f_1} \qquad \text{(III-15)}$$

Where M_0 and f_{10} are the initial values of M and f at zero conversion, respectively. The left side of the above equation may be integrated, and substituting the definition of the fractional conversion $X = 1 - \frac{M}{M_0}$, to obtain

$$\ln(1 - X) = \int_{f_{10}}^{f_1} \frac{df_1}{F_1 - f_1} \qquad \text{(III-16)}$$

For isothermal copolymerization, Meyer and Lowry(13) substituted Eq.(III-13) into Eq.(III-16) to eliminate F_1 and integrated the latter equation analytically to obtain the following closed form expression

$$X = 1 - \left(\frac{f_1}{f_{10}}\right)^{\alpha} \left(\frac{f_2}{f_{20}}\right)^{\beta} \left(\frac{f_{10} - \delta}{f_1 - \delta}\right)^{\gamma} \qquad \text{(III-17)}$$

Where, $\alpha = \frac{r_2}{1 - r_2}$, $\beta = \frac{r_1}{1 - r_1}$

$$\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)}$$

$$\delta = \frac{1 - r_1}{2 - r_1 - r_2}$$

Eq.(III-17) may be used to calculate the drift in the cumulative copolymer composition with conversion. In this equation, f_1 refers to the mole fraction of A in the monomer molecules remaining unreacted at conversion X.

III.2.2 Experimental Evaluation of the Copolymerization Reactivity Ratios

✓ All procedures for the evaluation of the reactivity ratios involve the experimental determination of the composition of the copolymers formed from several different comonomer feed compositions(7). These procedures may be divided into two major categories : those dealing with data collected at extremely low conversion levels and those dealing with data collected at higher conversion levels.

III.2.2.1 Data Obtained at Low Conversion Levels

The older, more established procedures involve copolymerizations carried out to low degrees of conversion (approximately $< 5\%$). In this case the assumption may be made that the monomer concentrations do not change appreciably during the reaction. Therefore the differential equations relating the instantaneous monomer compositions and copolymer compositions (Eq. (III-9) and Eq. (III-13)) may be used in the estimation of the reactivity ratios.

The "curve fitting method" involves plotting the instantaneous copolymer composition versus the comonomer feed composition, and then determining which theoretical curve would best fit the data by trial and error selections of r_1 and r_2 (14). However, this is a very tedious procedure that requires extensive calculations and provides only a qualitative measure of the precision of the estimates of the reactivity ratios. Furthermore, the observer is required to weight the data subjectively, so that different observers may obtain different values for the estimates of r_1 and r_2 from the same body of experimental data.

The "intersection method" was proposed by Mayo and Lewis$^{(9)}$. They rearranged Eq.(III-9) to read

$$r_2 = \frac{[A]}{[B]}\left\{\frac{d[A]}{d[B]}\left(1 + \frac{r_1\,[A]}{[B]}\right) - 1\right\} \qquad \text{(III-18)}$$

Data for the monomer feed and copolymer compositions from each experiment are substituted in the above equation and r_2 is plotted as a function of various assumed values of r_1. Each experiment yields a straight line and the intersection of the lines from all the experiments gives the best estimates of the reactivity ratios. Any variation observed in the points of intersection of the various lines is a measure of the experimental errors in the composition data. This method has the same limitations as the curve fitting method, viz. that the "best" values obtained for r_1 and r_2 from the same set of experimental data may vary with the observer, and that only a qualitative measure of the precision of the estimates of r_1 and r_2 are provided.

The "linearization method" was advanced by Fineman and Ross$^{(15)}$. They rearranged Eq.(III-13) in the following form

$$\frac{f_1\ (1 - 2F_1)}{F_1\ (1 - f_1)} = r_2 + \left[\frac{f_1^2\ (F_1 - 1)}{F_1\ (1 - f_1)^2}\right] r_1 \qquad \text{(III-19)}$$

The left side of the above equation when plotted against the coefficient of r_1 yields a straight line with slope r_1 and intercept r_2. The linear least squares procedures have been applied to fit Eq.(III-19). However, Tidwell and Mortimer(16,17) have pointed out that these procedures are inappropriate in this case because Eq.(III-19) violates some of the assumptions made to justify the use of the linear least squares method for parameter estimation. These assumptions are listed in Appendix(II-3) in Part II of the present thesis. Tidwell and Mortimer showed that the use of the linear least squares method for Eq.(III-19) results in improper weights being applied to the observations. Furthermore, they showed that no valid expression for the precision with which the estimates are known can be obtained from this method since the "dependent variable" in Eq.(III-19) clearly does not have a constant variance given some reasonable and rational assumptions about the distribution of the errors in the observed polymer composition. Furthermore, the "independent variable" in the equation, which in the least squares method is assumed to be exact, contains a variable which has a stochastic element.

More recently, Tudos and Kelen(18) proposed a new improved linear graphic method for determining the reactivity ratios which overcomes one of the disadvantages of the Fineman-Ross method, viz. the unequal weighting of the data. However, the other objections raised against the Fineman-Ross method are still valid here, viz. that no quantitative statistical inferences can be made about r_1 and r_2 because the "independent" and the "dependent" variables in the equation do not conform to the assumptions made in the linear least squares method. In a later paper(19) Tudos et al. extended their method to apply to data obtained at higher conversion levels by assigning an average monomer composition to the corresponding experimental average copolymer composition, then using the linearization technique previously developed for low conversions.

The best method to date proposed to calculate the reactivity ratios from data obtained at low conversion levels is the one developed by Behnken(20) and by Tidwell and Mortimer(16). In this method Eq. (III-13) is used in conjunction with a non-linear least squares method to estimate r_1 and r_2. This method is based on the Gauss linearization technique, to be explained below in Section (III.2.4). This is the only method that does not violate the least squares assumptions, hence it has the following desirable characteristics :

1. It gives unbiased estimates of the reactivity ratios.
2. The values of the parameters calculated by this method do not depend upon arbitrary factors such as which

monomer is subscripted 1.

3. The values obtained for the reactivity ratios are unique since, for a given body of data, any person will arrive at the same values of r_1 and r_2.

4. Because Eq. (III-13) conforms to the assumptions made about independent and dependent variables in the least squares method, this method is unique among all the previously mentioned ones, in that it provides a means of evaluating how well the reactivity ratios have been estimated as well as a means of determining if the data are consistent with the assumption that the copolymerization equation describes the relationship between monomer and copolymer composition through an analysis of variance procedure.

III.2.2.2 Data Obtained at High Conversion Levels

As pointed out by Montgomery and Fry(21), the requirement of low conversions in many cases would involve extraordinary experimental conditions to satisfy. The first few per cent of polymer made may not be as nearly representative of the theoretical copolymer composition as the polymer made at higher conversion. This is due to the fact that any impurities present will have a larger percentage effect upon observed composition at low conversions than at higher ones. Moreover, the assumption that no significant change in monomer composition occurs due to the polymer formed when the polymerization is stopped at low conversions may be a major source of error when the reactivity ratios are greatly different and when the more reactive monomer is present in small amounts. The above arguments lead to the conclusion that numerous advantages may accrue from using an integrated form of the copolymerization equation and thereby correcting for the drift in composition of monomers and polymers with conversion.

Two more reasons may be advanced to show the importance of using an integrated form of the copolymerization equation in evaluating the reactivity ratios. First, even when one of the differential forms of the copolymerization equation is used to estimate r_1 and r_2, the conversion levels are still usually measured and reported by the investigators to ascertain that these conversions were low enough to validate the use of such differential equations. Therefore, these conversions may be regarded as pieces of information that are not used in the actual estimation of the parameters. But, as Tidwell and Mortimer(17) have pointed out, a good estimation method should utilise all the information resident in the data with regard to the parameters to be estimated, thus providing precise estimates. Secondly, with the availability of high speed computing facilities that facilitate the numerical solution of the integrated form of the equations, there is little justification for using the approximate differential model when the more exact integral equations are available.

The first attempt to evaluate the reactivity ratios from the integrated form of the copolymerization equation was made by Mayo and Lewis(9). They integrated Eq. (III-9) to obtain

$$r_2 = \frac{\log \frac{[B_0]}{[B]} - \frac{1}{p}\log\left\{\frac{1-p\frac{[A]}{[B]}}{1-p\frac{[A_0]}{[B_0]}}\right\}}{\log \frac{[A_0]}{[A]} + \log\left\{\frac{1-p\frac{[A]}{[B]}}{1-p\frac{[A_0]}{[B_0]}}\right\}} \qquad \text{(III-20)}$$

Where,

$$p = \frac{1 - r_1}{1 - r_2} \qquad \text{(III-21)}$$

$[A_0]$ and $[B_0]$ are the concentrations of the monomers at the start of the reaction, whereas $[A]$ and $[B]$ are the corresponding concentrations experimentally measured at the point when the reaction is stopped. Mayo and Lewis then proposed a graphical procedure whereby r_1 and r_2 may be evaluated. They chose arbitrary values for the parameter p and substituted them in Eq.(III-20) to get the corresponding values of r_2; r_1 was then calculated from Eq.(III-21) for each pair of values of r_1 and p. Then the corresponding values of r_1 and r_2 were plotted against each other. The plot corresponding to a single experiment was found to be practically a straight line. The intercepts of the lines obtained from all the experimental runs were used to estimate the reactivity ratios. Later, Montgomery and Fry$^{(20)}$ presented a computer program capable of performing all the calculations necessary for this method.

The above method suffers some of the shortcomings mentioned before in connection with the graphical methods of obtaining the reactivity ratios from the differential copolymerization equation, viz. that different investigators may obtain different values for the reactivity ratios from the same data and that no quantitative measures of the precision of these values are provided, although the area of intersection of the lines may be used as a qualitative measure of this precision.

A somewhat similar method has been suggested by Meyer$^{(22)}$. In this method, Meyer used the closed form of the integrated copolymerization equation, Eq.(III-17). For fixed values of r_2 the right side of this equation was calculated for increments of r_1 to find the value of r_1 that satisfies the equation. For each data point, the r_1 vs. r_2 curve was found to be approximately a straight line, and the intersections of these lines were used to estimate the reactivity ratios. Obviously, this method is almost identical to the one proposed by Mayo and Lewis twenty years earlier, and hence has the same weaknesses inherent in such graphical procedures that were detailed above.

The only method found in the literature that circumvents these drawbacks is the one proposed by Behnken$^{(20)}$. Unfortunately this method has not received as much attention in the copolymerization literature as it deserves. Behnken suggested the use of a non-linear least squares technique on the integrated expression of the form developed by Mayo and Lewis, viz. Eq.(III-20) and Eq.(III-21). But since in these equations the dependent variables $[A]$ and $[B]$ cannot be solved for explicitly as a function of the independent variables $[A_0]$ and $[B_0]$ and the parameters r_1 and r_2, Behnken had to work with the implicit function in the response variable. Given first guesses for the values of the parameters and the measured values of the dependent variables, he used the Newton-Raphson method to solve for the value of the response variable, the residual monomer composition, that satisfies the equations. The experimentally observed values of the copolymer composition were used to calculate first guesses for the Newton's iterations. The residuals were obtained by subtracting the experimentally observed values of the copolymer composition from the corresponding values yielded by Newton's algorithm for all the experimental runs, and their sum of squares was minimized by the Gauss linearization procedure to produce the least squares estimates of r_1 and r_2. Behnken applied this method to several sets of experiments where the reaction was terminated at low conversions and obtained estimates of the reactivity ratios in good agreement with the values obtained from the non-linear least squares procedure as applied to the differential form of the copolymer composition equation, Eq. (III-13), as was detailed in the previous section.

The advantages of this method are similar to those mentioned in Section (III.2.2.1) in connection with the non-linear least squares method applied for data obtained at low conversions, and may be summarized as follows :

1. From a body of data, the method yields unique estimates for the values of the parameters that do not depend on the observer.

2. Under a given set of assumptions, to be detailed below in Section (III.2.4), the estimates of the parameter values obtained by this method can be proved mathematically to be the best estimates obtainable from this set of data.

3. Under the additional assumption that the errors are normally distributed, the method supplies objective and quantitative measures of the accuracy of the resulting parameter estimators, in the form of individual confidence limits, joint confidence regions, etc.

4. The method provides a means of determining if the data are consistent with the assumption that the copolymer composition equation adequately describes the relationship between monomer and polymer composition, i.e. the validity of the copolymerization model with all its inherent assumptions. This is achieved through an analysis of variance procedure.

In addition, this method has the further advantage over the corresponding non-linear least squares method applied to the differential form of the copolymer composition equation, in that it utilizes all the information available, including the measured conversion levels, in computing the parameters' estimates. Moreover, when using the present method, the experimenter does not have to employ extraordinary experimental techniques to ensure extremely low conversion levels, thus avoiding all the difficulties and pitfalls associated with such techniques and which were detailed at the beginning of the present section.

III.2.3 The Literature Values for the Reactivity Ratios of Acrylic Acid-Acrylamide System in Aqueous Polymerization

Jacques Bourdais was the first to report the reactivity ratios for the copolymerization of acrylic acid and acrylamide in aqueous solution(23). Referring to acrylic acid by the subscript 1 and to acrylamide by the subscript 2, he reported the following values for the reactivity ratios at 25 °C,

$$r_1 = 1.43 \pm 0.03$$
$$r_2 = 0.60 \pm 0.02$$

Bourdais stopped all his reactions at very low conversion levels and fitted a differential form of the copolymer composition equation, Eq. (III-13). He used the "curve-fitting method" described in Section (III.2.2.1) to fit his data through successive approximations. He did not indicate, however, how he had obtained the confidence intervals reported in conjunction with the values of r_1 and r_2 above.

It is useful to summarize the experimental data reported by Bourdais as these data will be examined in detail later in this report. As before, f_{10} refers to the mole fraction of acrylic acid in the starting monomer mixture and F_1 is the measured mole fraction of acrylic acid in the resulting polymer. X is the fractional conversion.

f_1	F_1	X
.125	.183	.07
.250	.327	.10
.375	.466	.06
.500	.607	.06
.625	.712	.05
.750	.817	.02
.875	.901	.02

The acrylic acid content in the polymer was determined by potentiometric titration against sodium hydroxide in 0.05N aqueous solution of NaCl. Under these conditions, Bourdais reported sharp inflection points in the titration curves. The acrylamide content in the polymers was determined by elemental analysis of nitrogen by the micro-Kjeldahl method. The sum of the results of these two analyses for each of the polymers was reported to be within three per cent of the exact value.

Cabaness, Lin and Parkanyi(24) studied the same system at 60 °C and reported the following reactivity ratios :

$$r_1 = 1.73 \pm 0.21$$
$$r_2 = 0.48 \pm 0.06$$

They stopped the reactions at low conversion levels and fitted the differential copolymer composition equation, as was rearranged by Fineman and Ross, Eq. (III-19), using the graphical "linearization method" proposed by these authors to obtain their estimates for r_1 and r_2. As was the case with Bourdais, Cabaness et al. did not report how they have obtained the confidence intervals cited above.

The following table summarizes the experimental results obtained by Cabaness and his coworkers :

f_1	F_1	X
.800	.8749	.0392
.667	.7688	.0254
.500	.6451	.0430
.351	.4997	.1070
.200	.3346	.0446

The composition of the copolymers was determined from their nitrogen content using the semi-micro Kjeldahl method.

It becomes clear from the above that the values reported in the literature for the reactivity ratios of this important copolymerization system were obtained by the graphical methods that were severely criticized by Tidwell and Mortimer(16,17) as rendering estimates for r_1 and r_2 that are arbitrary in that they depend on the observer. And as these methods cannot give a quantitative measure of the accuracy of the parameters' estimates obtained, therefore the confidence intervals of r_1 and r_2 reported cannot be accepted at face value, especially that no confidence level was reported in connection with these confidence intervals.

Therefore the present investigation was undertaken with the following objectives :

1. To use the experimental data reported by Bourdais(23) and by Cabaness et al.(24) to obtain estimates of the reactivity ratios through more objective non-linear regression methods, and to compare these estimates with the ones reported by these previous investigators.

2. To develop computer programs to fit these data, by the non-linear least squares method, to the differential form of the equation, as suggested by Behnken(20) and by Tidwell and Mortimer(16), and to an integrated form of the copolymer composition equation, as suggested by Behnken(20). If the estimates of r_1 and r_2 obtained from these two methods agreed closely, it would validate the use of the integrated expression in parameter estimation and hence make the stopping of the polymerization reactions at very low conversions superfluous.

3. To estimate the confidence intervals and confidence

regions for the values of the parameters and compare them with those reported by the previous investigators. This would make it possible to ascertain whether the values for r_1 and r_2 reported at 25 °C by Bourdais and at 60 °C by Cabaness et al. are significantly different at a particular confidence level, 95% say.

4. An experimental part of the investigation was designed to obtain conversion-composition data for the acrylamide-acrylic acid copolymerization system at intermediate conversion levels (20 - 70%) and to estimate the reactivity ratios through the non-linear least squares algorithm developed to analyse the data from the previous investigations. From the size and shape of the confidence regions of the reactivity ratios obtained, the reliability of this method would be estimated.

5. One further aspect of the estimation of the reactivity ratios was to be studied. In several copolymer systems, only a limited range of the copolymer compositions is of importance industrially, e.g. it is known that the range of compositions of the acrylamide-acrylic acid copolymers most useful as flocculating agents in the water treatment processes is from zero to about ten per cent acrylic acid content, whereas the compositions of the copolymers used in the paper industry as filler-retention aids and as dry-strength agents range from about five to fifteen per cent acrylic acid(4). Therefore the manufacturers of copolymers

for these applications would be interested in the range of compositions low in acrylic acid content. Also sometimes practical difficulties occur at certain ranges of copolymer composition, and the investigator may want to avoid these difficulties in his analysis, e.g. Bourdais(23) found that copolymers with acrylic acid content exceeding 30 - 50 % became insoluble when dried even at room temperature. Hence it was impossible to redissolve them for the purpose of titration.

For the above reasons, it was decided to limit the composition range to be studied to about zero to thirty per cent acrylic acid content. This would eliminate the difficulties encountered by Bourdais, but, more importantly, it would give an indication of the possibilities and limitations of trying to estimate the reactivity ratios from a set of experimental data confined to a limited range of compositions.

III.2.4. The Non-Linear Estimation of Parameters by Least Squares.

Parameter estimation for a model that is linear in the parameters by the least squares method has been detailed in Appendix (II-3). When the model is non-linear in the parameters, exact results, such as the expression for the linear least squares parameters' estimators expressed by Eq.(II-A3-13), are not available and the estimators have to be approached through an iterative technique. Moreover, the justification of the least squares procedure on theoretical grounds is not so straightforward. On this latter point, it may be stated that as long as the random experimental errors can be assumed normally distributed, the least squares estimators may be regarded as maximum likelihood estimators, even for a non-linear model. And while the assumption of normality is rarely completely realistic, most of the useful statistical theory based upon it is not too sensitive to the small departures from exact normality to be expected as a result of the central limit theorem (20). Another problem in the non-linear case is that the least squares estimators are not unique because the sum of squares of the residuals, as a function of the parameters, may have multiple minima.

The general non-linear model with one dependent variable may be expressed as follows

$$\eta = f(\underline{\beta}, \underline{\zeta}) \qquad \text{(III-22)}$$

Where, η is the dependent variable

$\underline{\beta}$ is the vector of the model's parameters

$\underline{\zeta}$ is the vector of independent variables

and where the function $f(\underline{\beta}, \underline{\zeta})$ is non-linear in the parameters $\underline{\beta}$.

Suppose that N experiments were carried out to collect a vector of observations $\underline{Y}$ on the predicted responses $\underline{\eta}$ at different values of $\underline{\zeta}$, then for any one observation,

$$y_u = \eta_u + \epsilon_u \quad , \quad u = 1,2,\ldots,N \qquad \text{(III-23)}$$

where ϵ_u is the experimental error inherent in the observation. The sum of squares of all the error terms for all the observations will be a function of the parameters $\underline{\beta}$ and may be defined by

$$\begin{aligned} S(\underline{\beta}) &= \sum_{u=1}^{u=N} (y_u - \eta_u)^2 \\ &= \sum_{u=1}^{u=N} (y_u - f(\underline{\beta}, \underline{\zeta}_u))^2 \end{aligned} \qquad \text{(III-24)}$$

Differentiation of the residual sum of squares function, Eq.(III-24), with respect to the parameters in the case of non-linear models does not usually produce simultaneous equations of a tractable nature.

It was shown by Gauss(25) that the solution can be approached in most cases by a series of linear approximations which will converge on the solution values. The procedure basically consists of expanding the function in a Taylor's series about a set of first guesses for the parameters $\underline{\beta}$, to be designated by $\underline{\beta}^{\circ}$, dropping all but the linear terms to obtain

$$f(\underline{\beta}, \underline{\zeta}_u) \doteq f(\underline{\beta}^{\circ}, \underline{\zeta}_u) + \sum_{i=1}^{i=p} (\beta_i - \beta_i^{\circ}) \left. \frac{\partial f(\underline{\beta}, \underline{\zeta}_u)}{\partial \beta_i} \right|_{\underline{\beta}=\underline{\beta}^{\circ}}$$

$$u = 1,2,\ldots,N \qquad \text{(III-25)}$$

where p is the number of parameters in the model.

Eq.(III-25) may be written more compactly as follows

$$\underline{\eta}(\underline{\beta}) \doteq \underline{\eta}^{\circ} + \underline{\underline{X}}\,\underline{\delta} \qquad \text{(III-26)}$$

where, $\underline{\eta}(\underline{\beta})$ is the (N x 1) vector $f(\underline{\beta}, \underline{\zeta}_1), \ldots, f(\underline{\beta}, \underline{\zeta}_N)$

η° is the (N x 1) vector $\underline{\eta}(\underline{\beta}^{\circ})$

$\underline{\delta}$ is the correction vector defined by

$$\underline{\delta} = \underline{\beta} - \underline{\beta}^{\circ} \qquad \text{(III-27)}$$

and $\underline{\underline{X}}$ is the (N x p) matrix defined by

$$\underline{\underline{X}} = \left[\frac{\partial f(\underline{\beta}, \underline{\zeta}_u)}{\partial \beta_i} \right]_{\substack{u = 1,2,\ldots,N \\ i = 1,2,\ldots,p}} \qquad \text{(III-28)}$$

Now the expression on the right side of Eq.(III-26) is linear in the parameters. From this equation, an approximation for the residual sum of squares function may be obtained as

$$\dot{S}(\underline{\beta}) = (\underline{Y} - \underline{\eta}^{o} - \underline{\underline{X}}\,\underline{\delta})'(\underline{Y} - \underline{\eta}^{o} - \underline{\underline{X}}\,\underline{\delta}) \qquad \text{(III-29)}$$

And, corresponding to Eq.(II-A3-13) in Appendix(II-3) for the linear model, the value of the parameter $\underline{\delta}$ which minimizes $\dot{S}(\underline{\beta})$ is

$$\hat{\underline{\delta}} = (\underline{\underline{X}}'\,\underline{\underline{X}})^{-1}\,\underline{\underline{X}}'\,\underline{r} \qquad \text{(III-30)}$$

where,

$$\underline{r} = \underline{Y} - \underline{\eta}^{o} \qquad \text{(III-31)}$$

Then, from the definition of $\underline{\delta}$ in Eq.(III-27), the new improved guesses of the parameters' values are

$$\underline{\beta}^{(1)} = \hat{\underline{\delta}} + \underline{\beta}^{o} \qquad \text{(III-32)}$$

And the next iteration can be started by expanding about $\underline{\beta}^{(1)}$. The sequence is repeated until the minimum of $S(\underline{\beta})$ is reached.

Another way to minimize the sum of squares of the deviations is to linearize the objective function, $S(\underline{\beta})$, itself. Such methods include the well-known steepest descent method(26). The gradient of S, i.e. grad S, is a vector perpendicular to the surface S in parameter space which extends in the direction of the maximum increase in S at a given point. Therefore the negative of the gradient extends in the direction of steepest descent. Suppose S is expanded in a truncated Taylor's series about $\underline{\beta}^{o}$,

$$S \doteq S^{o} + \sum_{i=1}^{i=p} (\beta_i - \beta_i^{o}) \left.\frac{\partial S(\underline{\beta})}{\partial \beta_i}\right|_{\underline{\beta} = \underline{\beta}^{o}} \qquad \text{(III-33)}$$

The partial derivatives appearing in this first order expression are identical to the magnitudes of the components of the vector (- grad S) in the $\underline{\beta}$ space, evaluated at $\underline{\beta}^o$, and these components are used to establish the direction of search in the method of steepest descent.

A method suggested by Marquardt(27) combines the Gauss method and the method of steepest descent. The idea behind the algorithm is based on the following observations. The method of steepest descent often works well on the initial iterations, but the approach to the minimum grows progressively slower because the direction of steepest descent proves to be nearly perpendicular to the direction that will minimize $S(\underline{\beta})$. The negative of grad S points in the direction that minimizes S only in a local region and not in the direction of the global minimum of S, the minimum desired, unless the contours of constant S are arcs of circles, with S_{min} as a center. On the other hand, the method of Gauss works well when the minimum of $S(\underline{\beta})$ is near, but may not converge on the initial iterations, especially if the initial guesses of the parameters' values are not close enough to their best estimates.

Marquardt observed in practice that the method of steepest descent and the method of Gauss give directions of search nearly orthogonal to each other. He suggested a method where the actual search will proceed on a composite of the two directions of search indicated by the preceding two methods. In Marquardt's compromise, the correction vector is computed by using the following formula instead of Eq.(III-30)

$$\underline{\delta}_m = (\underline{\underline{X}}' \, \underline{\underline{X}} + \lambda \, \underline{\underline{I}})^{-1} \, \underline{\underline{X}}' \, \underline{r} \tag{III-34}$$

where λ is a non-negative number and $\underline{\underline{I}}$ is the identity matrix.

It can be shown that the method of steepest descent and the method of Gauss are represented by the above equation when $\lambda \longrightarrow \infty$ and $\lambda \longrightarrow 0$, respectively. Intermediate values of λ result in a correction vector $\underline{\delta}_m$ which is effectively an interpolation between the vectors produced by the above two methods. Thus, in the Marquardt's algorithm, initially a relatively large value of λ is used, and then is decreased as the iterations progress. Of course, λ is decreased, and the region of linear approximation is enlarged, only if the progress is satisfactory, i.e. only if the sum of squares $S(\underline{\beta})$ at the new estimates of the parameters is smaller than that at the previous ones.

Marquardt's method is quite effective and is definitely superior to either the Gauss method or the method of steepest descent$^{(26)}$. It has been implemented in the computer program GAUSHAUS prepared by D.A. Meeter at the University of Wisconsin Computing Center, Madison, Wis. and dated December 1965. A version of this program adapted to the CDC 6400 computer by J.F. MacGregor at McMaster University

Hamilton, Ontario was used in the present study.

The confidence regions for the values of the parameters estimated by non-linear least squares can be given approximately by using the linear theory if the errors can ~~be~~ assumed to be normally distributed$^{(28)}$. The most satisfactory method for estimating such a region is to find the locus of all parameter sets $\underline{\beta}$ that yield a residual sum of squares $S(\underline{\beta})$ related to the minimum residual sum of squares at the best estimates of the parameters $S(\hat{\underline{\beta}})$ by the following expression

$$S(\underline{\beta})_{\alpha} = S(\hat{\underline{\beta}}) + p\, s^2\, F_{\alpha}(p\,,\, N-p) \qquad \text{(III-35)}$$

Where α is the approximate probability content, or confidence level, chosen to calculate the confidence region, $F_{\alpha}(p\,,\, N-p)$ is the critical value of the F-distribution that leaves $(1-\alpha)$ per cent of the distribution in the right-hand tail with the bracketed degrees of freedom, and s^2 is the residual variance in regression defined by

$$s^2 = \frac{S(\hat{\underline{\beta}})}{N-p} \qquad \text{(III-36)}$$

The use of the residual sum of squares $S(\hat{\underline{\beta}})$, and indeed this whole procedure of estimating the confidence region, is justified by the assumption that the function $f(\underline{\beta}, \underline{\zeta})$ is sufficiently close to being linear in $\underline{\beta}$ near the best estimates of the parameters$^{(20)}$. It must be emphasized that although the contours defined by Eq.(III-35) for the confidence regions are exact, their probability content, or confidence level, is only approximate in the case of non-linear functions.

Approximate individual confidence limits on the predicted values of each of the parameters, based on a linear approximation to the model in the neighbourhood of $\hat{\underline{\beta}}$, can be obtained at a $(1 - \alpha)$ confidence level from the following expression

$$(\beta_i)_\alpha = \beta_i \pm t_{\frac{\alpha}{2}, (N-p)} (C_{ii} s^2)^{\frac{1}{2}} \qquad \text{(III-37)}$$

Where $t_{\frac{\alpha}{2}, (N-p)}$ is the α percentage point of the two-tailed tabulation of the t-distribution with $(N - p)$ degrees of freedom, and C_{ii} is the ith diagonal element of the $(\underline{\underline{X}}' \underline{\underline{X}})^{-1}$ matrix evaluated at $\hat{\underline{\beta}}$ and where matrix $\underline{\underline{X}}$ has been defined by Eq.(III-28).

However, it must be pointed out that the confidence intervals on the individual parameters frequently do not clearly convey the message of which set of values of the parameters are consistent with the data, especially when there is a high degree of correlation between the different parameters. Tidwell and Mortimer$^{(16)}$ show examples where this is particularly evident. In such cases, joint confidence regions, as computed from Eq.(III-35), must be used.

The matrix $(\underline{\underline{X}}' \underline{\underline{X}})^{-1}$ is, apart from a factor σ^2, the variance-covariance matrix of $\underline{\hat{\beta}}$ in the linear case. Then, according to the linear approximation near $\underline{\hat{\beta}}$, the correlation coefficient between parameters β_i and β_j is expressed by

$$\rho_{ij} = \frac{C_{ij}}{(C_{ii}\ C_{jj})^{\frac{1}{2}}} \qquad \text{(III-38)}$$

Where C_{ij} is a non-diagonal element of the matrix $(\underline{\underline{X}}' \underline{\underline{X}})^{-1}$. The values of the correlation coefficients lie between +1 and -1. An absolute value of ρ_{ij} near one is evidence that parameters β_i and β_j are highly dependent.

III.3 Application of the Non-Linear Regression Methods on the Previously Published Experimental Data

The objective of this part of the investigation is to apply the principles of non-linear least squares, as detailed in Section (III.2.4) to the experimental data for the copolymerization of acrylamide with acrylic acid previously published in the literature. Details of these data were tabulated in Section (III.2.3).

These data were first fitted to the differential form of the copolymer composition equation, Eq. (III-13), using the GAUSHAUS program as detailed in the previous section. The differential equation contains one dependent variable, the copolymer composition F_1 whose measurements may be assumed to be subject to random errors that are independent and have a constant variance from the same probability distribution. Furthermore, this distribution may be assumed to be normal by the central-limit theorem. Also, Eq. (III-13) contains one independent variable, the mole fraction of monomer A in the monomer mixture, and this composition may be assumed to be known exactly and to remain constant at its original value f_{10}. Hence all the assumptions necessary to validate the use of the least squares method for parameter estimation, as detailed in Appendix (II-3), are justified. And Eq. (III-13), being explicit in the dependent variable F_1, was very easy to fit with the least squares procedure, as the residuals are simple to calculate. Therefore, this part of the regression analysis was straightforward, and the results will be detailed below.

The next step was to fit an integrated form of the copolymer composition equation to the same data, this time incorporating the conversion measurements made and reported by the original investigators. Our first approach was to try to fit the data to the closed form of the integrated copolymer composition equation, Eq. (III-17), developed by Meyer and Lowry(13).

In this equation, there are two variables that are experimentally measured and hence are subject to error, viz. the conversion X and the residual monomer composition f_1 at this conversion; f_1 is obtained from the measured value of the average cumulative copolymer composition $\overline{F}_1$ through the simple material balance equation

$$f_1 = \frac{f_{10} - \overline{F}_1 X}{1-X} \qquad \text{(III-39)}$$

For the purpose of maintaining the error structure in the least squares method simple, all the experimental errors were assumed to be inherent in the measured copolymer composition $\overline{F}_1$, whereas the conversion X was considered to be an independent variable, hence, according to the assumptions of the least squares method, to be known exactly. This assumption is justified on the basis that the error inherent in measuring the conversion X is much smaller than that inherent in measuring the copolymer composition $\overline{F}_1$. This is similar to the assumption made in Part II of the present thesis where, to estimate the transfer constants, all the experimental errors were assumed to reside in the measured molecular weights, whereas conversions were assumed to be known exactly. From the experimental data in Part II, the conversion measurements were found to be fairly accurate and reproducible with very little scatter, even between different investigators, which is not always the case with molecular weight and composition measurements. It may be pointed out that the alternative to making such an assumption will be the use of a weighted least squares method for the estimation of the parameters which greatly complicates the procedure.

Another difficulty associated with fitting Eq. (III-17) with the least squares method becomes evident if we compare this equation with the general form of the non-linear model, Eq. (III-22). An important difference is that the copolymerization equation is implicit in the dependent variable f_1. Hence, the non-linear regression program has to be coupled with a subroutine capable of solving this equation for f_1 at any given values of f_{10}, X, r_1 and r_2. Following Behnken's suggestion(20), a Newton-Raphson algorithm was chosen to perform this task. In the present investigation no difficulties such as multiple roots were accrued from the incorporation of this search routine provided that the original estimates of the parameters were close to their best estimates, and the Newton-Raphson method always converged.

However, these difficulties did occur when the confidence regions of the parameters were to be calculated. As pointed out by Eq.(III-35), the estimation of such a confidence region entails the calculation of the residual sum of squares $S(\underline{\beta})$ at a network of values of r_1 and r_2, and the confidence region will be bounded by the pairs of values of the reactivity ratios that satisfy Eq.(III-35). As some of the values of r_1 and r_2 used in these calculations have to be fairly removed from their best estimates, convergence problems often occured in the Newton-Raphson algorithm. These problems were compounded by the fact that the best estimates of r_1 and r_2 for the data provided by Bourdais$^{(23)}$ are very close to one of the singularities inherent in Eq.(III-17), viz. that at ($r_1 + r_2 = 2.0$). Similar problems will occur in other systems whenever the best estimates of r_1 and r_2 were close to any of the other singular points, viz. $r_1 = 1.0$, $r_2 = 1.0$, and $f_1 \in \delta$. Hence it was felt that a computer program designed to fit Eq.(III-17) can never be of such generality as to be usable for any copolymerization system without exercising particular care about which pairs of values of r_1 and r_2 are used, and convergence problems are always to be expected in conjunction with the estimation of the confidence regions. Similar difficulties will also be encountered when using equations (III-20) and (III-21) to estimate r_1 and r_2 as suggested by Behnken$^{(20)}$. Hence, an alternative approach had to be found.

A procedure was developed that overcame the above difficulties. This procedure entailed the use of the integral form of the copolymerization equation, Eq. (III-16), in conjunction with Eq. (III-13) relating the instantaneous monomer mixture composition with that of the copolymer formed at that instant. The procedure is as follows :

1. Given the measured value for conversion X, the left hand side of Eq. (III-16), viz. ln (1-X), was calculated. Then a value for f_1, the upper limit of integration on the right hand side of Eq. (III-16), that would satisfy this equation had to be found.

2. This was accomplished by successively applying a stepwise numerical integration algorithm, viz. the Simpson's rule, to the right hand side of the equation while incrementing the upper limit of the integration f_1 "in the right direction", i.e. starting from f_{10}, f_1 was progressively decreased if monomer 1 was the more reactive component and f_1 was progressively increased otherwise. At each point, the value of the function to be integrated, viz. $(\frac{1}{F_1 - f_1})$, was computed using Eq. (III-13) that expresses the instantaneous composition of the polymer formed, F_1, in terms of the monomer composition at that particular instant, [illegible]. The step-size for incrementing f_1 was chosen as (2×10^{-5}).

3. The mid-point of the last interval of the variable f_1 that made the right hand side of Eq. (III-16) just exceed in absolute value the left hand side of the equation, was taken as the solution of Eq. (III-16). Hence the corresponding value of the average cumulative copolymer composition $\overline{F}_1$ was calculated from the material balance equation, Eq. (III-39). The residual, or error, in each run will be the difference between the value of $\overline{F}_1$ thus calculated and that measured experimentally.

Using this technique, no convergence problems were encountered either in the estimation of the values of the parameters nor in the calculation of the confidence regions. The resulting computer programs are general enough to be used for any set of experimental data in any copolymerization system. The only situation where this approach will fail is in the case of azeotropic copolymerization, with $f_1 = F_1$, where Eq. (III-16) has a singularity. However, azeotropic copolymerizations are of little interest in research as the copolymer composition always corresponds to the monomer composition.

Table (III-1) and Figure (III-1) summarize the results obtained when analysing the experimental data reported by Bourdais [(23)] and by Cabaness et al.[(24)] by the above-mentioned computer programs. These experimental data were detailed in Section (III.2.3). In the first column of Table (III-1) are the values of the reactivity ratios and their respective

Table (III-1) Reactivity Ratios for the Acrylic Acid (1) - Acrylamide (2) Copoymerization System from Previously Published Data.

Reference		Values Given by Original Authors	Obtained by Fitting Differential Eq.(13)	Obtained by Fitting Integral Eq.(16)
Bourdais(23)	r_1	1.43 ± 0.03	1.46 ± 0.16	1.44 ± 0.17
	r_2	0.60 ± 0.02	0.66 ± 0.08	0.63 ± 0.07
	$S(\hat{\underline{\beta}})$	—	3.1×10^{-4}	3.0×10^{-4}
	s^2	—	6.2×10^{-5}	6.0×10^{-5}
	ρ_{12}	—	0.75	0.75
Cabaness(24)	r_1	1.73 ± 0.21	1.60 ± 0.17	1.62 ± 0.13
	r_2	0.48 ± 0.06	0.45 ± 0.06	0.44 ± 0.05
	$S(\hat{\underline{\beta}})$	—	9.5×10^{-5}	8.1×10^{-5}
	s^2	—	3.2×10^{-5}	2.7×10^{-5}
	ρ_{12}	—	0.75	0.61

confidence intervals as reported by the original investigators. In the second column of the table are the results presently obtained by fitting the differential form of the copolymer composition equation, Eq.(III-13), assuming f_1 to remain constant at its original value f_{10}, by using the non-linear least squares method (Marquardt's compromise) as detailed in Section(III.2.4). In the third column of Table(III-1) are the results obtained by using the same non-linear regression method to fit the experimental data, including conversion levels, to the integral form of the copolymer composition equation, Eq.(III-16), as was detailed above. In each of the last two columns, first the reactivity ratios are given together with their respective individual 95 % confidence intervals calculated from Eq.(III-37). Then, the residual sum of squares at the best estimates of the parameters $S(\hat{\underline{\beta}})$ are given, as computed from Eq.(III-24). Then the residual variance s^2 is reported, as obtained from Eq.(III-36). Finally, the correlation coefficient ρ_{12} between the two estimators of the reactivity ratios is reported as calculated from Eq.(III-38).

In Fig.(III-1), the best estimates of the values of r_1 and r_2 as given by the original investigators and those obtained presently are shown. Also shown on this figure are the joint confidence regions on the values of the parameters at a 95 % confidence level, as computed from Eq.(III-35) for both cases investigated here, viz.

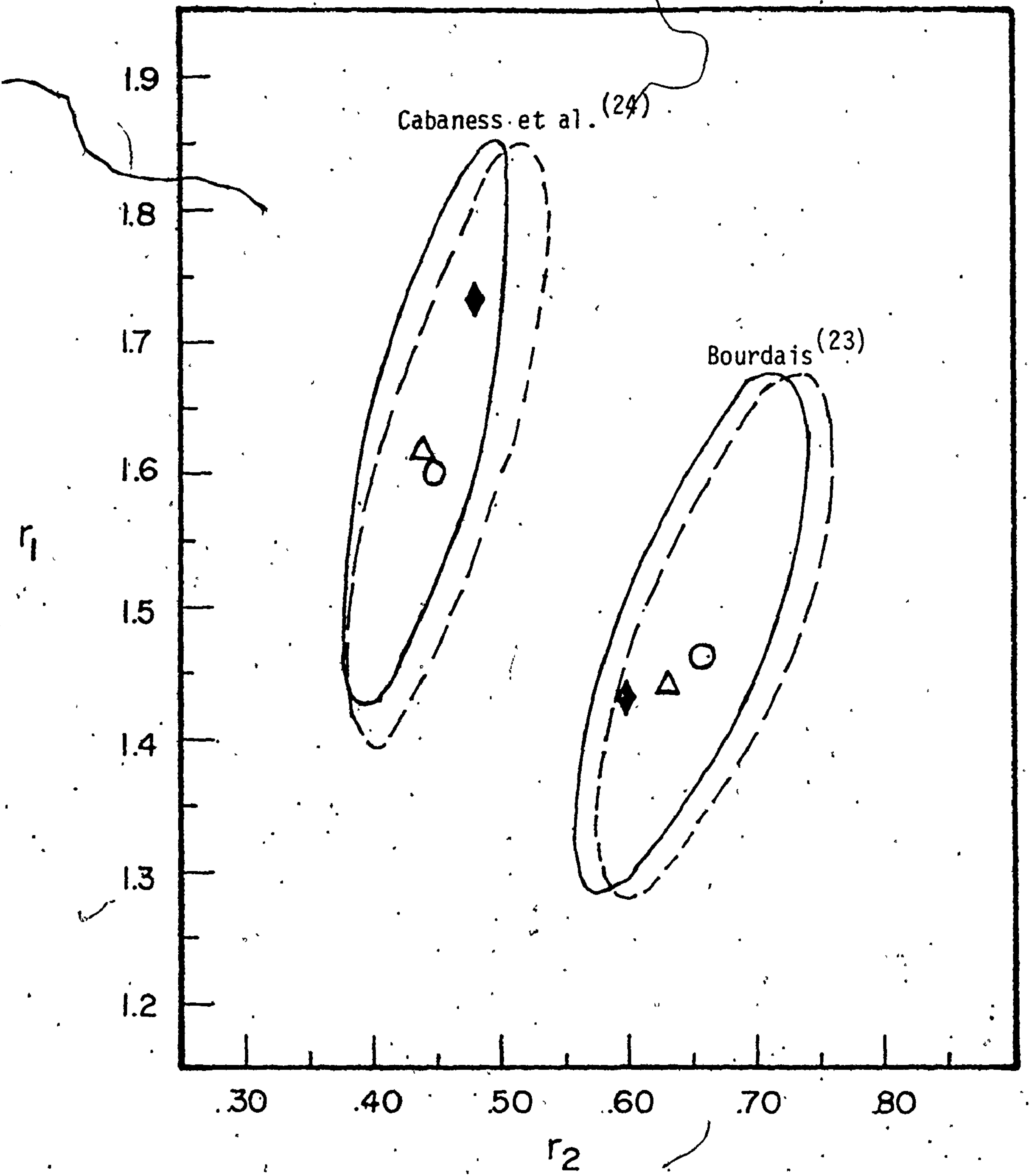

Fig.(III-1) Joint Confidence Regions for the Reactivity Ratios from Previously Published Experimental Data

◆ Best estimates of r_1 and r_2 according to original author
○ Best estimates of r_1 and r_2 obtained by fitting differential equation
△ Best estimates of r_1 and r_2 obtained by fitting integral equation
—— Confidence region from integral equation
- - - - Confidence region from differential equation

fitting the differential form of the copolymerization equation and fitting the integral one.

Examination of the results shown in Table (III-1) and in Fig.(III-1) reveals the following :

1. Due to the approximate graphical methods used by the previous investigators to obtain their estimates of r_1 and r_2, it is clear that the values they obtained do not correspond to those that minimize the squares of the residuals or errors. In fact, Fig(III-1) shows that the pair of values of r_1 and r_2 chosen by each investigator lies almost on the edge or border of their respective 95 % confidence region. This clearly shows the superiority of the non-linear regression method presently used as it provides unique estimates of the values of the parameters that do not require subjective judgement from the part of the investigator.

2. The above observations equally apply to the individual confidence limits on the values of r_1 and r_2 given by the previous investigators. From the values in Table(III-1) it is clear that Bourdais underestimated these confidence intervals by several orders of magnitude, whereas Cabaness slightly overestimated them. Here again, the non-linear least squares method yields unique values for these intervals for each specific confidence level.

3. The non-linear regression method makes possible the estimation of joint confidence regions as illustrated

in Fig.(III-1). No other method can provide this information. These regions are better representatives of which pairs of values of r_1 and r_2 may be used at a certain confidence level than the individual confidence intervals on each parameter.

4. Comparing the results obtained when the experimental data were fitted to the differential form of the copolymerization equation to those obtained from fitting the data to the integral form of the equation, it is clear that the values of the parameters' estimators as well as the confidence intervals and confidence regions agree closely. It is also clear that for both sets of data, the integral equation fitted the data better than the differential equation, as evidenced by the fact that the residual sum of squares was less in the case of fitting the integral equation. This observation tends to validate the statement made in Section(III.2.2.2) to the effect that the integral form of the equation was expected to provide better estimates for the values of the reactivity ratios, because all the available information, including the conversion data, are used. Also the integral model is a more exact model than the differential one, being free from the assumption that no significant drift in composition occurs during the reaction. Another important implication of the above observations is that, having proven the validity of fitting the integral copolymerization equation, the conventional experi-

mental technique of stopping the reactions at very low conversions becomes superfluous. Hence the experimental difficulties associated with such procedures can be avoided.

5. It is clear from Fig.(III-1) that the experimental data reported by Bourdais at 25°C and those reported by Cabaness et al. at 60°C result in mutually exclusive confidence regions with no overlap at 95 % confidence level. Therefore one can state, at this confidence level, that the two pairs of values of r_1 and r_2 indicated by these two sets of data are significantly different from each other. This difference has to be attributed to the different temperatures at which the experiments were conducted.

III.4 Experimental Part

III.4.1 Experimental Conditions

The objective of this part of the study was to obtain experimental data for the acrylic acid-acrylamide system at intermediate levels of conversion (about 20 - 70 %). The range of compositions of the resulting copolymers was to be limited to less than about 30 - 50 % acrylic acid content. The reasons for these choices were previously given in Section(III.2.3). These experimental data were to be used to estimate values for the reactivity ratios through the statistical methods employed in the foregoing Section (III.3) to analyse the results of the previous investigators. The shape and size of the confidence intervals and confidence regions for r_1 and r_2 obtained, as well as the amount of correlation between the values of the parameters, will provide a measure of the inherent possibilities and limitations of trying to estimate r_1 and r_2 from data obtained at intermediate conversion levels and limited composition range.

The temperature at which the present experiments were conducted is 40 °C. The reason for this choice is the two previous investigators reported two significantly pairs of values for the reactivity ratios at 25 °C and at 60 °C. Therefore it was hoped that by obtaining values for r_1 and r_2 at the intermediate temperature of 40 °C, the set of three values for each reactivity ratio may fit an Arrhenius type expression and the activation energy for each one may be estimated.

The original potassium persulfate concentration was 10^{-3} (g moles/l) in all experiments, whereas the total original monomer concentration was 1.0 (g mole/l).

Four different runs were conducted and six polymers were recovered in each run at different levels of conversion. The mole fractions of acrylic acid f_{10} in the original monomer mixtures for the four runs were 0.08, 0.15, 0.20 and 0.25, respectively.

III.4.2 Reagents

Acrylamide monomer, potassium persulfate initiator and the water used as reaction medium were all purified as was indicated in Section (II.3.1) in the homopolymerization study of acrylamide.

The acrylic acid monomer was purchased from the Eastman Kodak Co., Rochester, New York. It was inhibited with 200 ppm p-methoxyphenol. It was purified by distillation under a reduced pressure of about 10 mm Hg (bp 39 °C) in an all-Pyrex apparatus. The purified monomer was stored in the frozen state inside a refrigerator.

III.4.3 Apparatus and Procedure

At first, several copolymerization runs were conducted in ampoules deaerated in the N_2-vacuum line previously shown in Figures (II-1) through (II-3) in a procedure identical to that described in Section (II.3.5) and used in the homopolymerization runs of acrylamide. However, the measured compositions of the copolymers obtained at the same conditions were not reproducible. It also became evident that the measured mole fraction of acrylic acid in the recovered polymer was higher if the ampoule in which it was synthesized was deaerated early in the polymerization run than a polymer recovered under the same conditions but whose ampoule was deaerated late in the run. The only explanation for this phenomenon was that some of the acrylic acid monomer present in solution in burette A in Figure (II-2) was lost as the deaeration procedure was in progress due to its greater volatility. This was confirmed by the strong smell of acrylic acid monomer present inside the trap just preceding the vacuum pump at the end of these runs.

To avoid this serious source of error, the deaeration procedure used by both Bourdais(23) and Cabaness et al.(24) in their investigation of the same copolymerization system was applied in the present case. The reaction vessels presently used for copolymerization were Kimax brand test tubes with screw-caps equipped with pressure-fit inert rubber liners. The dimensions of these tubes were O.D. = 20 mm and L = 150 mm. The deaeration procedure consisted of bubbling nitrogen gas into the reaction mixture inside the tubes for 15 minutes while the tubes were immersed in an ice bath. Then the caps were secured tightly to the tubes which were then transferred to the constant temperature bath. After the required time had elasped, the reaction was quenched by thrusting the tube into liquid nitrogen. Then the tube was cut and the frozen reaction mixture was transferred into a volume of water to which the inhibitor hydroquinone was added. This mixture was stirred on a magnetic stirrer till dilution was complete. The polymers were then precipitated out by adding this solution dropwise to ten times its volume of acetone acidified with a few drops of concentrated hydrochloric acid. The copolymers were then filtered out, washed and then dried under vacuum to constant weight just as described in Section (II.3.2.1) for the homopolymers.

III.4.4 Analytical Techniques

Conversion measurements were done gravimetrically as was described in the case of homopolymerization of acrylamide in Section (II.3.2.1).

Composition measurements were done by potentiometric titration of the acrylic acid groups against alkali in a dilute aqueous solution of the copolymer together with an electrolyte to suppress the double layer. The procedure was as follows :

1. Samples of the copolymer of about 0.05 - 0.10 grams were weighed and transferred to a screw-cap glass bottle. To this, about 100 ml of a 0.1-N solution of NaCl in water was added. The polymer was dissolved by stirring over a magnetic stirrer.

2. The polymer solution was titrated against a 0.05 - N solution of NaOH. A Model-230 Fisher Accumet pH meter with an expanded millivolt range and an accuracy of ± 1.4 mV on the expanded mode was used in the potentiometric titration in conjunction with a Fisher combination electrode where the indicating and reference elements are enclosed in the same glass/ceramic body at a short, fixed distance apart.

3. The polymer solution was stirred vigorously during the titration procedure by means of a magnetic bar and a magnetic stirrer. It was also found that, in order to obtain sharp end points, nitrogen gas had to be bubbled into the solution throughout the course of titration. Otherwise, the solution absorbed CO_2 from the surrounding air, and the end points became quite diffuse.

4. The calculations used to estimate the precise location of the end point were done as described by Vogel(29). The alkali was added in small volumetric increments ΔV and the change in the reading on the expanded mV span of

the pH meter corresponding to each of these additions, ΔE, was recorded. Then a plot was prepared of the quantity $(\Delta E/\Delta V)$ as ordinate versus V, where V is the total volume of alkali added to that point. The point where $(\Delta E/\Delta V)$ reaches a maximum corresponds to the inflection point on the E vs. V curve, hence to the end point. As will be seen in the following section, the end points were quite sharp, provided nitrogen was bubbled continuously into the solution.

III.4.5 The Reliability of the Titration Procedure

It was important to establish that the procedure followed for titrating the copolymers, together with the instruments and standard solutions used, yielded reliable and reproducible results. This could be accomplished by titrating some copolymer "standards" whose compositions are accurately known. As no such standards are available commercially, they had to be manufactured. This was accomplished by allowing a monomer mixture of known composition to polymerize virtually to complete conversion. Therefore the composition of the resulting copolymer must correspond closely to that of the starting monomer mixture. These polymers were recovered and titrated by the same methods used throughout the study. The following table summarizes the results obtained with these standards. All conversions were between .95 and 1.0 .

All compositions are in (mole fraction acrylic acid).

Standard	Original Monomer Composition, f_{10}	Measured Polymer Composition, $\bar{F}_1$
C-1	.220	.216
C-2	.200	.195
C-3	.150	.153
C-4	.140	.141
C-5	.110	.115

Table (III-2) and Figure (III-2) are the detailed readings and calculations associated with copolymer standard C-1. From Figure (III-2) it is clear that the end point of titration is quite sharp. The total mass of this particular sample of polymer was 0.0436 grams. From the above results, it is clear that the present titration method is within ± 5% of the expected composition values.

It may also be noted that some trial titrations were performed with phenolphthalein indicator, and the results agreed closely to those obtained by potentiometric titration. However, in the present study, potentiometric titration was used throughout because it provided a more accurate and objective method of determining the end points.

Table (III-2) Potentiometric Titration of Standard S-1

V (ml)	E (mV)	$\left(\frac{\Delta E}{\Delta V}\right)$
0.	+198	
		75
0.20	+183	
		20
0.35	+180	
		67
0.50	+170	
		40
0.70	+162	
		35
0.90	+155	
		60
1.10	+143	
		55
1.20	+137.5	
		45
1.30	+133	
		49
1.40	+128.1	
		56
1.50	+122.5	
		55
1.60	+117	
		50
1.70	+112	
		59
1.80	+106.1	
		59
1.90	+100.2	
		57
2.00	+94.5	

Table (III-2) (Continued)

V (ml)	E (mV)	$\left(\frac{\Delta E}{\Delta V}\right)$
2.00	+94.5	
		75
2.10	+87	
		80
2.20	+79	
		184
2.25	+69.8	
		136
2.35	+56.2	
		164
2.40	+48	
		222
2.50	+25.8	
		320
2.55	+9.8	
		482
2.60	-14.3	
		754
2.65	-5[illegible]	
		740
2.70	-89	
		378
2.75	-107.9	
		242
2.80	-120	
		180
2.90	-138	
		120
3.0	-150	
		100
3.1	-160	
		50
3.3	-170	
		90
	-179	

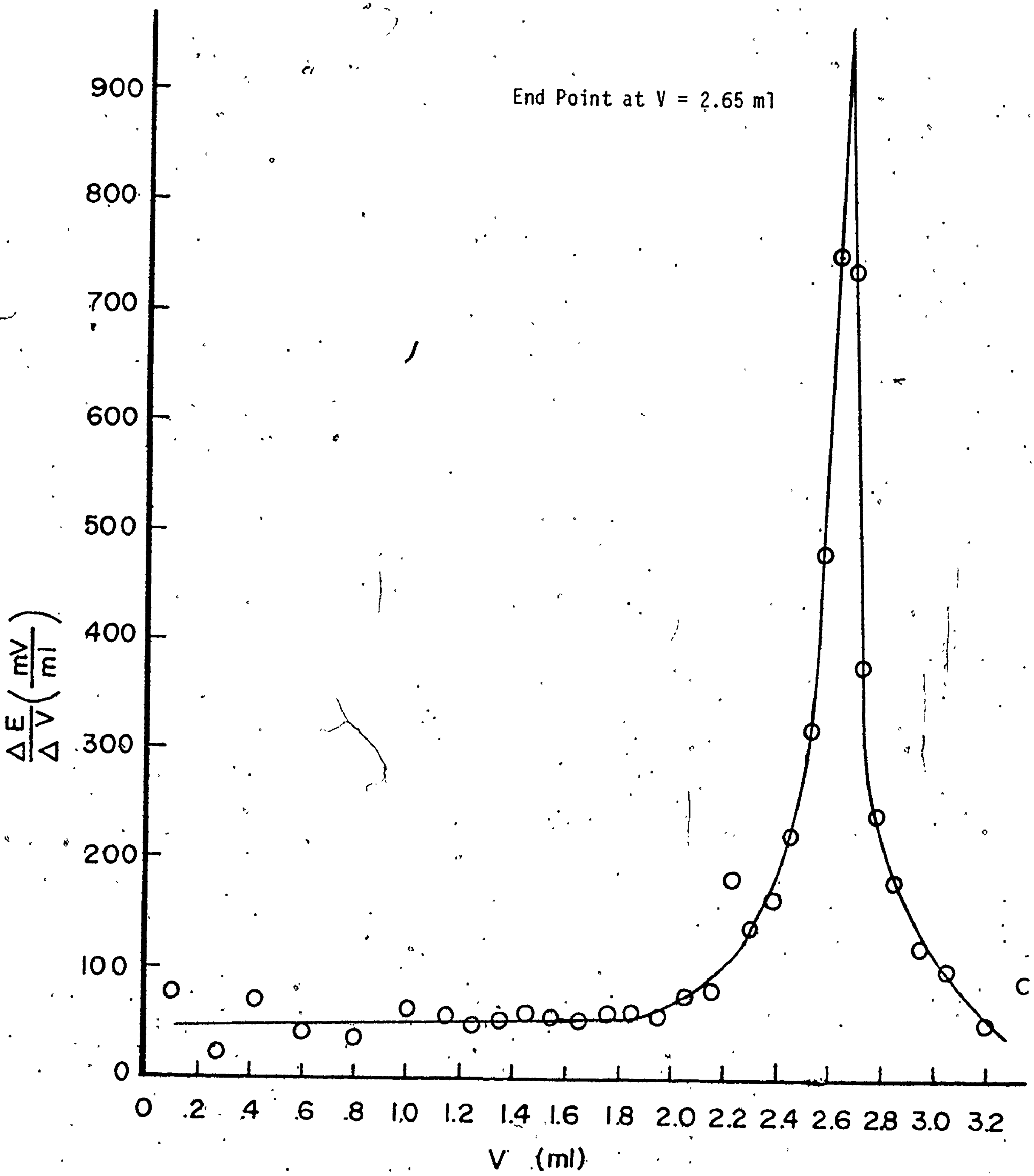

Fig. (III-2) Titration Curve for Copolymer Standard S-1

III.5 Results and Discussion

Table (III-3) summarizes the results obtained from the four copolymerization runs conducted under the conditions detailed in Section (III.4.1). As before, subscript 1 refers to acrylic acid.

Using the previously described non-linear regression technique to fit these data to the integral copolymer composition equation, Eq. (III-16), the following estimates of the reactivity ratios were obtained, together with the other statistical parameters calculated in the same way as the corresponding ones in Table (III-1). The calculation procedure was described in detail in Section (III.3).

$r_1 = 1.45 \pm 0.33$

$r_2 = 0.57 \pm 0.04$

Residual Sum of Squares $S(\hat{\underline{\beta}}) = 5.4 \times 10^{-4}$

Residual Variance $s^2 = 2.5 \times 10^{-5}$

Correlation Coefficient $\rho_{12} = 0.95$

Figure (III-3) represents the 95% joint confidence region for r_1 and r_2 based on the present experimental results, whereas the dotted line in the figure is part of the corresponding confidence region based on the experimental data obtained by Bourdais$^{(23)}$, and previously shown in full in Figure (III-1).

Figures (III-4) and (III-5) represent the change of the average cumulative copolymer composition with conversion for the four initial monomer compositions examined in the present study. The solid lines in these figures are the

Table (III-3) Experimental Results of Copolymerization Runs

Mole Fraction Acrylic Acid in Original Monomer Mixture f_{10}	Conversion X	Cumulative Average Mole Fraction Acrylic Acid in Copolymer $\bar{F}_1$
0.08	.164	.128
	.241	.115
	.380	.117
	.509	.111
	.583	.103
	.689	.096
0.15	.234	.217
	.318	.204
	.472	.210
	.521	.194
	.602	.186
	.711	.180
0.20	.197	.288
	.276	.273
	.381	.264
	.490	.266
	.583	.256
	.621	.239
0.25	.228	.335
	.340	.334
	.449	.323
	.512	.313
	.638	.309
	.661	.297

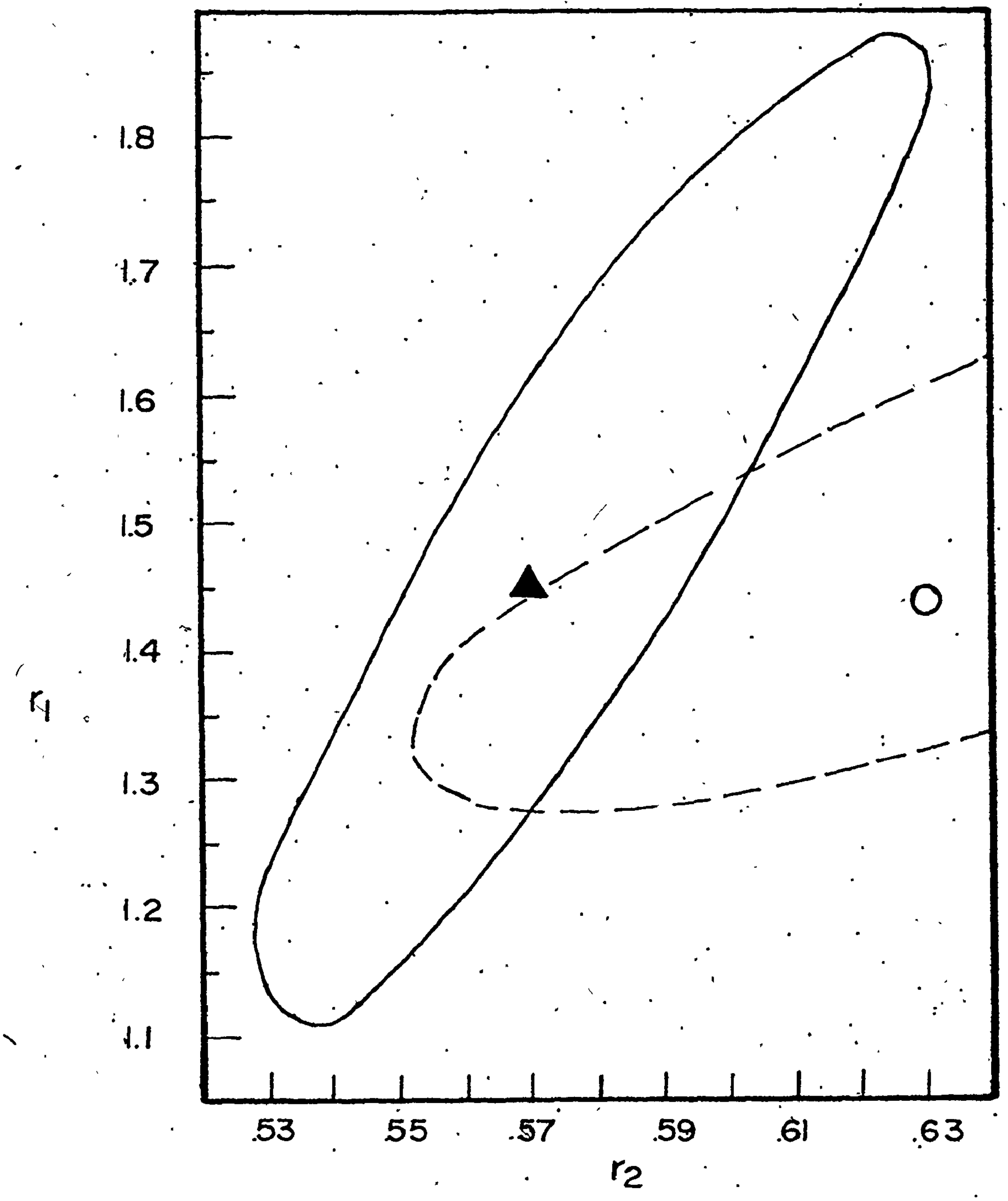

Fig. (III-3) Joint Confidence Region from Present Data

▲ Best estimates of r_1 and r_2 from present data

○ Best estimates of r_1 and r_2 from data by Bourdais(23)

—— 95% confidence region from present data

---- 95% confidence region from data by Bourdais(23)

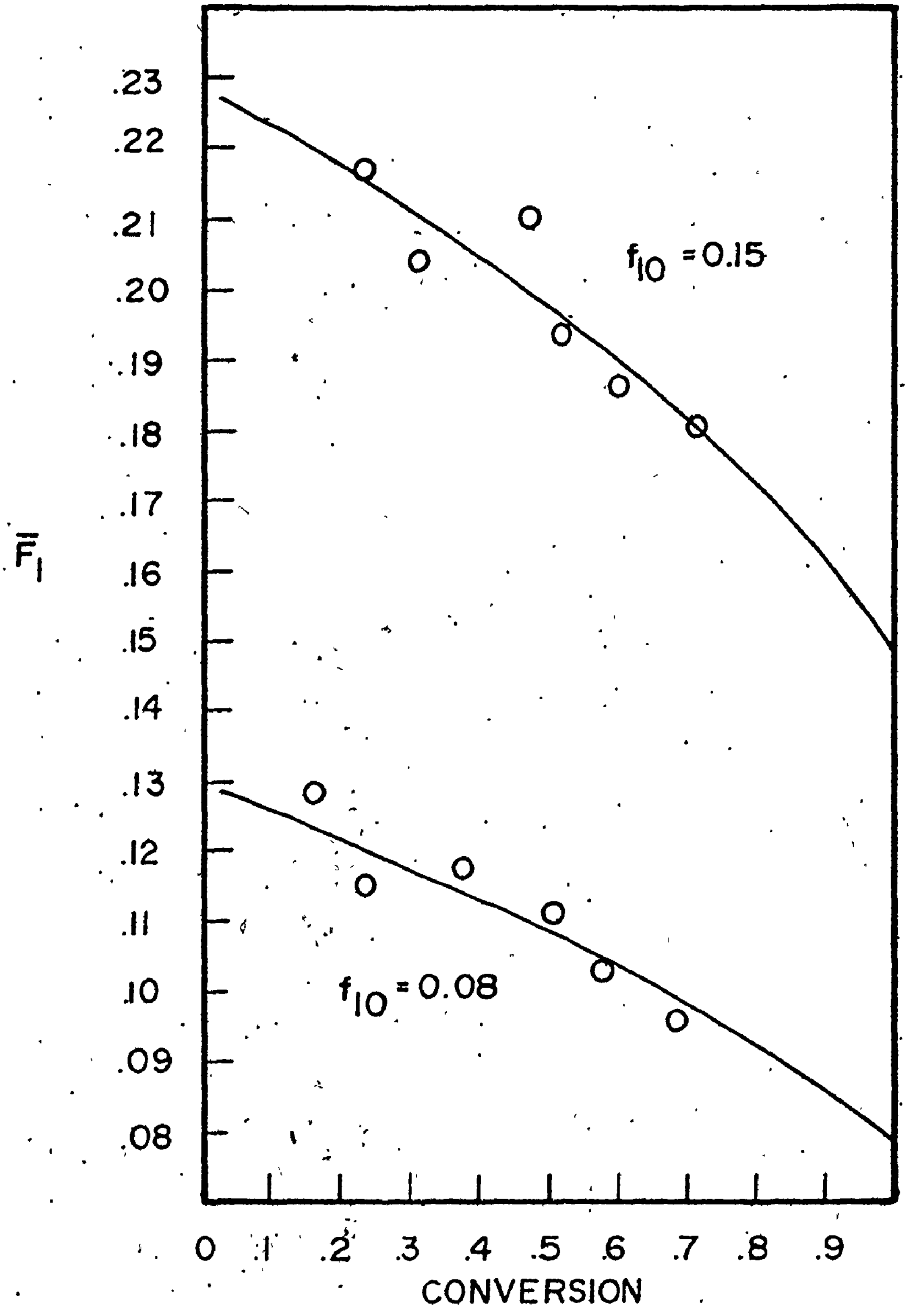

Fig. (III-4) Predicted and Measured Drift in the Cumulative Average Copolymer Composition with Conversion $r_1 = 1.45$, $r_2 = 0.57$

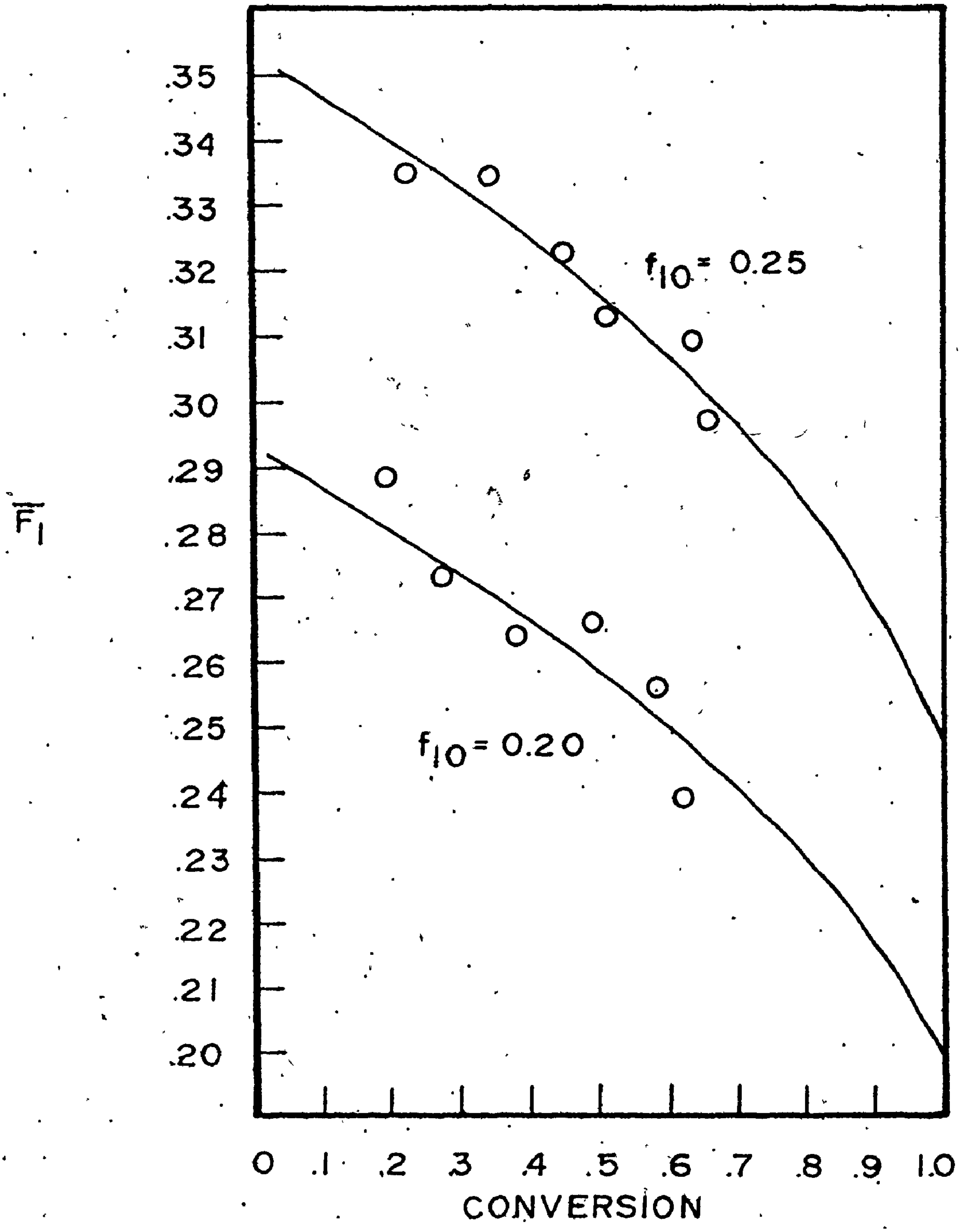

Fig. (III-5) Predicted and Measured Drift in the Cumulative Average Copolymer Composition with Conversion $r_1 = 1.45$, $r_2 = 0.57$

results predicted by the copolymerization model, Eq. (III-17), using the values of r_1 and r_2 obtained by the non-linear regression analysis, viz. $r_1 = 1.45$ and $r_2 = 0.57$. The circles on these figures are the experimental results obtained in the present investigation.

From the above tables and figures, the following observations can be made.

1. From Figure (III-4) and Figure (III-5), the agreement between the predicted composition drift with conversion and the measured copolymer composition is satisfactory. This leads to the conclusion that the various assumptions made in the development of the copolymerization model in Section (III.2.1) are valid for the acrylic acid-acrylamide system. A further implication of this good agreement between model and observations is that the estimates of r_1 and r_2 obtained by the non-linear regression analysis as developed in the present investigation are consistent with the experimental observations, which validates the whole procedure of estimating the reactivity ratios from composition data obtained at intermediate conversion levels by the present non-linear regression algorithm.

2. Although the variance of the present experimental results ($s^2 = 2.5 \times 10^{-5}$) compares favourably with those obtained by the previous investigators ($s^2 = 6.0 \times 10^{-5}$ and $s^2 = 2.7 \times 10^{-5}$, respectively), the correlation coefficient between the values of the two parameters in the present case

(ρ_{12} = 0.95) is much larger than those associated with the previous data (ρ_{12} = 0.75 and ρ_{12} = 0.61). The reason for this observation is that whereas the previous investigators collected data over the whole spectrum of compositions, this investigation restricted the present polymers to less than 35% acrylic acid. This undesirable aspect, viz. the high correlation between r_1 and r_2, will always be characteristic of reactivity ratios computed from a limited range of compositions. In other words, obtaining more experimental data in the same composition range as before will not decrease the correlation between r_1 and r_2. The only method to achieve this in the present case is to obtain data for copolymers with higher acrylic acid content.

3. There is some overlap between the confidence region of r_1 and r_2 obtained at 40°C from the present data and that obtained from the data reported by Bourdais$^{(23)}$ at 25°C, as evident from Figure (III-3). Although this observation would indicate that the reactivity ratios are not significantly affected by temperature, this is contradicted by the fact that there is no overlap with the confidence region obtained from the data reported by Cabaness et al.$^{(24)}$ at 60°C. Moreover, the attempt to fit the variation of each reactivity ratio with temperature to an Arrhenius type expression, using their respective set of three values each, was not successful. It is likely that the accuracy of the experimental data and hence of the estimated parameters, do

not warrant such a fit. It may also be pointed out that r_1 and r_2 are the ratios of propagation rate constants, each of the latter having an activation energy of the order of 5 KCal/mole, or less. Hence the reactivity ratios would be expected to have a very small activation energy, rendering them insensitive to changes in temperature.

III.6 Conclusions and Recommendations for Further Study

In Part III of the thesis, a computer program was developed to apply the principles of non-linear regression analysis to the integral form of the copolymer composition equation. It was shown that the non-linear least squares algorithm is best applied to the integral equation in the form of Eq. (III-16), together with a numerical integration algorithm, to ensure convergence.

This procedure was shown to have numerous advantages over all the preceding methods reported in the literature. It is superior to the differential methods in that it does not require the reactions to be stopped at very low conversions and does not assume constant compositions throughout the course of the reaction. The present method is also clearly superior to all graphical methods that have been widely used in the past for the estimation of r_1 and r_2 in that it yields unique and objective estimates of the reactivity ratios, independent of the observer, and provides individual and joint confidence limits and a measure of the degree of correlation between the values of the two parameters.

The above algorithm was used to analyse the previously published data for the acrylic acid-acrylamide copolymerization system(23,24). The results thus obtained were compared with those reported by the original investigators using graphical methods. The differences between the estimates of the parameters were not significant at a 95% confidence level. However, the confidence limits reported by these investigators were considerably different from those obtained by the least squares method at a 95% confidence level. Moreover, the joint confidence regions for r_1 and r_2 and the amount of correlation between them, based on the above-mentioned data, were reported here for the first time.

Finally, an attempt was made to use the presently developed algorithm to estimate the reactivity ratios of the acrylic acid - acrylamide copolymerization system, from a set of composition-conversion measurements where the conversion levels were intermediate (20 - 70%) and where the range of copolymer compositions was limited to less than about 35% acrylic acid content in moles. Although the resulting estimates of the parameters r_1 and r_2 were consistent with the previous ones, it was found that the practice of limiting the compositions to a narrow range resulted in a high degree of correlation between the two parameters r_1 and r_2. This is tantamount to bad experimental design, and should be avoided whenever possible.

For future study, a further refinement of the above parameter estimation procedure may be accomplished by eliminating the assumption that the degree of conversion X is an independent variable, hence exactly known. If X is considered to be a second dependent variable, besides the copolymer composition, subject to a significant measurement error, the copolymerization equation becomes a multiresponse problem. In this case, one of the basic assumptions necessary for a valid application of the least squares techniques, viz. that for all observations the errors have a constant variance, cannot be assumed to hold. Therefore duplicate measurements are required to estimate the individual variances in the measurements of the copolymer compositions and of conversions. Then a weighted estimate of an overall variance (or pooled variance) for each observation may be obtained from the individual variances, these latter being assumed constant for all observations. Then the quantity to be minimized becomes the sum over all the observations of the square of the ratio of each error divided by its corresponding pooled variance. Such a weighted least squares method has been outlined by Himmelblau(26) in connection with linear models, but may be readily extended to non-linear models.

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