FREE RADICAL
POLYMERIZATION OF STYRENE
UP TO
HIGH CONVERSION

FREE RADICAL POLYMERIZATION
OF STYRENE IN A BATCH REACTOR
UP TO HIGH CONVERSION

By

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SCOPE AND CONTENTS :

Polymerization of styrene was carried out experimentally using azobisisobutyronitrile (AZO) as catalyst and toluene as solvent in an isothermal batch stirred-tank reactor (BSTR). Conversion of monomer, molecular weight distribution (MWD) and viscosity were measured. The experimental results were used to develop viscosity correlations leading to polymerization kinetics applicable to high conversion. A model was developed based on the conventional kinetic scheme. Both conversion and MWD were solved and, the termination rate constant and catalyst efficiency were adjusted from the viscosity correlations at each time interval. Agreement was obtained between measured and predicted conversions and MWD's up to 70% conversion.

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1. ABSTRACT

The transient behaviour of a batch stirred-tank reactor (BSTR) for free radical polymerization of styrene in toluene has been studied experimentally and theoretically. A kinetic model applicable to high conversions was developed using data from measurements of monomer conversion and molecular weight distribution (MWD). Significant improvement over the conventional kinetic model is obtained when the viscosity or gel effect is accounted for. The termination rate constant and catalyst efficiency are allowed to vary with viscosity. The findings agree with the general theory of diffusion-controlled reaction which predicts that viscosity is the most important parameter.

2. INTRODUCTION

The present investigation is an extension of the study by Tebbens (1) on the free-radical polymerization of styrene in a BSTR at low conversions. Most industrial polymerization reactors operate at conversions of monomer near 100%. The need for kinetic models applicable at high conversions and viscosities is obvious. It is hoped that this investigation will shed some light on a most complex phenomenon.

It was reported by Tromsdorff (27) that autoacceleration was observed in the polymerization of methyl methacrylate using benzoyl peroxide as catalyst beyond a conversion of 20%. The conversion of monomer and molecular weights were found to be significantly higher than predicted by conventional kinetics. The autoacceleration of polymerization has been observed in viscous media and is referred to as "gel effect" or "viscosity effect".

Most of the kinetic studies of polymerization systems have been carried out at extremely low conversion and the data have been obtained from initial rate measurements. These data apply only at low conversions where the viscosity effect is unimportant. Kinetic models which account for the viscosity effect have not been developed prior to this study. The few investigations (30) (36) have been hampered by the unavailability of an instrument for the rapid analysis of MWD.

The objectives of the present investigation are to develop a kinetic model for the catalyst-initiated free radical polymerization of styrene in toluene in an isothermal BSTR. This model should predict conversion and MWD of sufficient accuracy over a range of operating conditions of temperature, solvent, monomer and catalyst levels and conversions. The definition of sufficient accuracy depends on the sensitivity of the polymer physical and chemical properties to MWD. The ultimate aim of this exercise on polymerization kinetics at high conversion is to develop kinetic models which may be used to control MWD and therefore the physical and chemical properties of the product polymer.

3. CONVENTIONAL KINETICS FOR FREE RADICAL POLYMERIZATION

3.1 Description

Conventional kinetics has been reported in detail (4) (9). In general, polymerization involves four basic steps, namely, initiation propagation, chain transfer and termination reactions. A brief description of these reaction steps is given below :

		Reaction Steps	Rate Constants
Initiation			
	(1)	Catalyst $\rightarrow 2R_c^o$	k_d
	(2)	$R_c^o + M \rightarrow R_1^o$	
Propagation			
	(3)	$R_1^o + M \rightarrow R_2^o$ $\vdots$ $R_r^o + M \rightarrow R_{r+1}^o$	k_p
Chain Transfer			
	(4)	$R_r^o + M \rightarrow P_r + M^o$	k_{fm}
	(5)	$R_r^o + S \rightarrow P_r + S^o$	k_{fs}
	(6)	$R_r^o + C \rightarrow P_r + C^o$	k_{fc}
	(7)	$R_r^o + P_q \rightarrow P_r + R_q^o$	k_{fp}

The transfer reaction involves transfer of activity from one radical to another species. It does not affect the total number of free radicals directly. However, the resulting radical may have different activity and it may affect the propagation and termination reaction in a slightly different manner.

Termination

(8) $$R_r^o + R_q^o \rightarrow P_{r+q} \qquad k_{tc}$$

(9) $$R_r^o + R_q^o \rightarrow P_r + P_q \qquad k_{td}$$

Reaction (8) is referred to as the termination reaction by combination and reaction (9) by disproportionation. For the polymerization of styrene, termination by disproportionation is neglected. The termination rate constant k_t or $(k_{tc} + k_{td})$ will be used to symbolize k_{tc}.

All reactions involved are relatively competitive, and the molecular weight distribution (MWD) of the polymer formed depends on the relative magnitudes of the rate constants k_d, k_p, k_{tc}, etc.

3.2 Assumptions

The previous description indicates the complexity of the kinetics involved. Calculation is usually simplified by making the following assumptions :-

(1) Chain length dependence

The reactivity of the radicals is assumed independent of chain length. This implies that the propagation, transfer and termination reaction rate constants do not depend on the size of the free radicals.

There is only one rate constant, e.g., k_p, k_{tc}, etc., for each type of reaction. The validity of this assumption is generally considered adequate for low conversions. Chain length may become important in viscous medium where the reaction becomes diffusion controlled.

(2) Chain transfer to catalyst and to dead polymer

It has been reported that chain transfer reaction to azo-catalyst is small and, for styrene polymerization transfer to polymer is insignificant (9). This leads to the elimination of reactions (6) and (7).

(3) Same activity of radicals resulting from chain transfer reactions

This assumption makes the radicals resulting from the chain transfer reactions (4) and (5) identical with other free radicals. Any reaction connected with the transferred radicals need not be considered separately.

(4) Primary radical terminations

The primary radical (R_c^o) can be terminated by

(10) $$R_c^o + R_c^o \rightarrow R_c - R_c$$

(11) $$R_c^o + R_r^o \rightarrow P_r$$

The recombination of primary radicals (R_c^o) in reaction (10) can be accounted for by the use of an efficiency factor (f) related to the decomposition of catalyst in reaction (1). The termination reaction (11) involving the primary radical (R_c^o) is usually ignored.

(5) Average chain length is large

The assumption is that consumption of monomer by initiation and chain transfer is very much smaller than by propagation.

This leads to a simplification in the calculation of the rate of polymerization and conversion.

(6) Steady-state hypothesis

It is assumed (9) that the concentration of free radicals are at a pseudo steady-state during the polymerization. Employing this assumption, the rate of change of concentration of free radicals with respect to time may be equated to zero, reducing a large set of differential equations to algebraic equations for the active polymer species.

3.3 Validity of Assumptions

The above mentioned kinetics and associated assumptions have been employed by Hamielec and Tebbens (4) (1) in the polymerization of styrene. Good agreement was obtained for MWD and conversions up to about 20% conversion of monomer. For polymerization in viscous media, the validity of these assumptions has to be re-examined.

The constancy of rate constants for polymerization in media with large viscosity variations is subject to question . In addition, an apparent solvent effect disproves the validity of the assumption of identifying the transferred radicals with all other free radicals.

4. SOLVENT EFFECT

4.1 Review of Literature

When styrene is polymerized in a solvent, the resulting polymer has a lower molecular weight than the product prepared in bulk. Mayo (13) investigated the chain transfer to solvent reaction with the objective of accounting for the deviation. It was found later, however, that the transfer to solvent alone could not account for all the change.

Bradbury and Melville (16) investigated the copolymerization of styrene and butyl acrylate in benzene solution using labelled azo catalyst. It was found that for each monomer, the quantity k_t/k_p^2 calculated from initial rates increased with increase of benzene concentration. One explanation was that there was preferential accumulation of monomer or solvent in the immediate neighbourhood of the growing radical. Such an effect could alter both the rates of propagation and termination. The observed variation of k_t/k_p^2 for styrene could therefore be explained in terms of accumulation of benzene on the radicals.

Another explanation involved the production of phenyl radicals (S^o) by the reaction of transfer to benzene. They could either attack a molecule of monomer to initiate a new chain or else react with another radical. Because of the high reactivity of the phenyl radical the rate constants for these types of termination are probably much greater than for the normal termination of growing chain. The apparent value of k_t/k_p^2 would become larger with increase of the amount of termination involving phenyl radicals, i.e., with increase of benzene concentration.

Burnett and Loan (19) reported on the solvent participation in radical chain reactions with reference to the polymerization of methyl methacrylate, methyl acrylate and vinyl acetate in benzene solution with 2.2 - azo - isobutyronitrile as catalyst. Experimental results indicated that the transfer radical from benzene had a decided chemical effect on the kinetics.

It was postulated that growing radicals could react with solvent molecules to produce a radical from the solvent with destruction of their own reactivity.

(5) $$R_r^o + S \rightarrow P_r + S^o$$

The solvent radical was capable of reacting with

(i) a reactant molecule to restart the chain,

(12) $$S^o + M \rightarrow S - M^o$$

(ii) another of its own kind

(13) $$S^o + S^o \rightarrow S_2$$

(iii) a chain carrier

(14) $$S^o + R_r^o \rightarrow S - P_r$$

Such a scheme was able to explain the effect of solvent on the activity of the solvent radical S^o relative to other radicals in the system.

Van Hook and Tobolsky (20) studied the polymerization of styrene in benzene and CCl_4 and showed that the value of k_t/k_p^2 again increased substantially upon dilution of the monomer. By using the equations of Burnett and Loan (19), and comparison of the data from Bradbury and Melville (16), it was possible to arrive at the conclusion that the apparent values of k_t/k_p^2 for styrene polymerization in benzene was a function of solvent concentration.

Bamford, Jenkins and Johnston (21) measured the rate of polymerization of styrene in N.N - dimethylformamide solution initiated with azo-bisisobutyronitrile. Significant departure from the conventional kinetic expression was observed for low monomer concentration and high rate of initiation. The discrepancy was explained by the primary radical termination reactions (10) and (11) (see section 3.2.4)

The existence of primary radical termination was also reported by Allen, Bevington (22) and Baldwin (23). The effect of primary radical termination on the rate of polymerization is twofold. Firstly, a radical that enters into a primary radical termination reaction (10) would otherwise have initiated a chain. Thus the effective initiation rate is lowered. Secondly, each primary radical entering into a termination reaction stops a chain. It thus functions as an added inhibitor, decreasing the rate of polymerization.

Henrici-Olive and Olive (24) (25) treated the problem with a different approach. The formation of electron-donor-aceptor complexes was postulated between polymer radicals and solvent molecules. The competitive reactions between these electron-donor-aceptor complexes were believed to be the cause of changes in the observed k_t/k_p^2. A general equation correcting for solvent effect was proposed. It follows :

$$\frac{[M]_{bulk}}{\phi_p [M]} = 1 + \frac{\tau_s}{\tau_M} \quad \frac{[S]}{[M]} \qquad (1)$$

or

$$\frac{1}{\phi_p} = \frac{[M]}{[M]_{bulk}} + \frac{\tau_s}{\tau_M} \frac{[S]}{[M]_{bulk}} \tag{2}$$

where

$$\phi_p = \frac{(k_t^{1/2}/k_p)_{bulk}}{(k_t^{1/2}/k_p)_{solution}} \tag{3}$$

τ_s/τ_M is called the tau ratio and is an indication for the magnitude of solvent effect. The postulation of electron complexes led to the variation of k_p with the concentration of solvent.

4.2 Correction for the Effects of Solvent

It seems obvious that the second assumption described in section 3.3 ignoring reactions connected with transferred radicals is not valid. The findings of Burnett (19) Van Hook (20) Bamford (21) and Olive (25) et al lead to essentially the same overall results as to compensate for the solvent effect by increasing the value of k_t/k_p^2, despite different proposed mechanisms and explanations. The true answer to the problem will probably remain unknown for some time.

Duerksen, Hamielec et al (3) (4) applied solvent corrections reported by Henrici-Olive and Olive (24) (25) in the solution polymerization of styrene in benzene carried out in a continuous stirred tank reactor (CSTR) and in a batch stirred tank reactor (BSTR). Good agreement was obtained by varying only k_t in k_t/k_p^2 rather than k_p proposed by Olive (25). There has not been any definite proof as to whether k_t, k_p or even both k_t and k_p should be corrected for. Correction for k_t favours the hypothesis proposed by most workers in this field. Duerksen and Hamielec et al (3) (4) justified the correction of k_t from the good agreements obtained for both conversion and molecular weight distribution (MWD).

The correction used here is to adjust k_t for solvent level. k_p is assumed constant and k_t adjusted for solvent as in equations (2) and (3). For styrene polymerization with toluene as solvent, a tau ratio (τ_s/τ_m) of 1.28 was used (25).

5. FREE RADICAL POLYMERIZATION IN VISCOUS MEDIA

The conventional kinetic scheme with assumptions as mentioned holds when applied to styrene polymerization in benzene for conversions less than about 20%. Further polymerization to higher conversion is more complicated. The polymerization of methyl methacrylate initiated by benzoyl peroxide was followed by Tromsdorff et al (27). It was observed that at conversion higher than about 20% the rate of polymerization started to increase rapidly and eventually reached a maximum in the region of 70% conversion. Further investigation indicated an increase in molecular weight along with the rate increase. These phenomena, generally referred to as "gel effect", can be explained in terms of the relative rates between the propagation and the termination reaction. Either a relative reduction of the termination rate constant or a relative increase of the propagation rate constant would account satisfactorily for the increase of both the rate and molecular weight.

5.1 Rabinowitch Equation

Rabinowitch (26) considered collisions between two molecules in a closely-packed medium. The colliding molecules were shown to be trapped by the surrounding molecules (e.g. solvent) and can escape from this "cage" only by a process of diffusion. Assuming that all liquids to possess a quasicrystalline structure, the velocity constant of a second-order reaction in which the two reactants A and B were of the same size and shape as the solvent molecules, was given by

$$k = \frac{C_1 \text{ Exp}(-E/RT)}{1 + \frac{C_2 \text{ Exp}(-E/RT)}{D_A + D_B}} \tag{4}$$

where C_1 and C_2 are constants, D_A and D_B the diffusion constants of the reactants A and B, and E is the activation energy of reaction.

5.2 Consideration of Diffusion Control in Polymerization

Vaughan (29) made use of the Rabinowitch equation and assumed that D_A, D_B vary directly as the absolute temperature T, and inversely as the bulk viscosity μ of the medium, as in the Stokes-Einstein equation,

$$\begin{aligned} D_A &= d_A T/\mu \\ D_B &= d_B T/\mu \end{aligned} \tag{5}$$

where d_A and d_B are proportionality constants. Equation (4) becomes

$$k = \frac{C_1 \text{ Exp}(-E/RT)}{1 + \frac{\mu C_2 \text{ Exp}(-E/RT)}{(d_A + d_B)\, T}} \tag{6}$$

If E is small and (or) viscosity is high (i.e. slow diffusion), the rate constant is given by

$$k = \frac{C_1 \,(d_A + d_B)\, T}{C_2 \mu} \tag{7}$$

Diffusion is the controlling step of the reaction.

If E is large and (or) viscosity is low (i.e. fast diffusion), the rate constant is

$$k = C_1 \text{ Exp}(-E/RT) \tag{8}$$

Chemical reaction is the controlling step.

For reactions occuring in a medium of increasing viscosity, the usually chemical activated reactions may become diffusion-controlled. In the transition period, there would be a gradual change over from one form to the other, and it would not seem correct to have a critical bulk viscosity for the onset of diffusion control, although a 100-fold range of $(D_A + D_B)$ may probably occur quickly under polymerization conditions.

Rabinowitch equation is not strictly applicable to polymerization systems where the polymer and solvent molecules are not of the same geometry. However, the error involved should not be so large as to offset the qualitative nature of the reactions.

Vaughan (29) applied this treatment to the thermal polymerization of styrene and concluded that the chain reaction involved should become diffusion controlled in the order, termination, propagation, transfer and initiation, i.e., in the order of increasing energies of activation as expected. By using an empirical relationship to calculate the bulk viscosity at different conversions, he was able to compare these with theoretical values and found reasonable agreement.

Robertson (30) furthered the work to the catalysed polymerization of methyl methacrylate and styrene. The bulk polymerization of styrene and methyl methacrylate was essentially the same both demonstrating three rather distinct periods of polymerization. At very low conversion, all the rate constants and the catalyst efficiency remained unchanged and independent of the reaction medium. The second period started from the onset of diffusion control of the termination reactions resulting in auto-acceleration phenomenon or the "gel-effect". The third period appeared when the rate of polymerization dropped sharply and stopped short before reaching 100% conversion. The sudden drop in the rate of polymerization was explained by the onset of diffusion control of propagation reaction. The decrease of k_p had a larger effect than k_t on the rate. Towards the end of the polymerization, the decrease of k_p dominated giving an apparently sudden retardation of polymerization. At this stage, interaction of radicals would have virtually ceased and all the radicals were said to be trapped due to the very high viscosity of the reaction medium.

5.3 Mechanism of Diffusion Controlled Bimolecular Reactions

It has been proposed by Benson and North (32) (33) that the bimolecular reaction between two molecular species present in low concentration in solution can be regarded as a successive three stage process. Firstly, two molecules must come into contact, a process dependent on the diffusion constants of the species in solution. Secondly, the reactive parts of the molecules must come within a certain distance of each other and possibly assume a certain configuration. Thirdly, after all positional factors are favorable, chemical reaction takes place. For most chemical reactions in normal solution, the third process requires large activation energy and is the slowest and rate-determining step of the three. But for many fast reactions such as the termination of free radicals, the first and second steps may be slow and the reaction is said to be "diffusion controlled".

The three stage reaction for free radicals R_A^o and R_B^o can be presented by

$$R_A^o + R_B^o \underset{k_2}{\overset{k_1}{\rightleftarrows}} (R_A^o --- R_B^o)$$

$$(R_A^o --- R_B^o) \underset{k_4}{\overset{k_3}{\rightleftarrows}} (R_A^o : R_B^o)$$

$$(R_A^o : R_B^o) \xrightarrow{k_5} \text{Dead Polymer } P_{AB}$$

For polymerization reactions between macro-molecules, the first stage is generally referred to as translational diffusion of the centre of gravity of the two species, the second stage as segmental diffusion of the radical chain ends.

Applying the stationary state assumption for the intermediate species $(R_A^o ---- R_B^o)$ and $(R_A^o : R_B^o)$, the rate of formation of product P_{AB} is given by

$$\frac{d\ P_{AB}}{dt} = k\ R_A^o\ R_B^o \tag{9}$$

where
$$k = \frac{k_1 k_3 [k_5/(k_4 + k_5)]}{k_2 + k_3 [k_5/(k_4 + k_5)]}$$

In the case of a very slow chemical reaction, i.e., $k_5 << k_4$ this reduces to

$$k = \frac{k_5\ K}{1 + k_5 K/k_1} \tag{10}$$

where $K = k_1 k_3 / k_2 k_4$ is the equilibrium constant for the formation of active pairs.

When the chemical reaction is very fast, $k_5 >> k_4$, the reaction rate constant becomes

$$k = \frac{k_1 k_3}{k_2 + k_3} \tag{11}$$

k here becomes the diffusion controlled reaction rate constant.

The above treatment is completely general for any bimolecular reactions. The kinetics can be solved provided all of the reaction rate constants are known.

Benson and North (39) carried the diffusion-controlled kinetic scheme further with the use of the Smoluchowsky equation and the ball and chain model. Theoretical calculations indicated that segmental diffusion was the controlling step.

Experimental investigation was also carried out with the simple dilatometric techniques (33). It was shown that for methyl methacrylate, k_p was independent of viscosity while k_t was inversely proportional to viscosity over the 1000-fold viscosity range. Polymerization of alkyl methacrylates with different alkyl groups signified that segmental diffusion of the radical chain end was the rate-determining step in the termination reaction.

The catalyst efficiency was also reported to be influenced by the viscosity of the reacting medium. De Schrijver and Smets (48) followed the decomposition of azobisisobutyronitrile (AZO) in viscous medium. It was found that increase of viscosity did not affect the rate of decomposition of the initiator, but increased the formation of waste product dimethyl-N-cyano-isopropylketenimine (DKI) showing appreciable decrease in catalyst efficiency.

At present, the theory of diffusion controlled polymerization reactions has not been well developed. Insufficient kinetic data are available rendering its application to real polymerization systems extremely difficult.

5.4 Present Interpretation

A simplified kinetic treatment is used here with the object of predicting both conversion and MWD up to high conversion. It accepts the conventional kinetics of free radical polymerization as described in Section Three. In addition, the termination constant k_t and catalyst efficiency f are assumed as functions of Newtonian viscosity.

The kinetic constants for various reactions in the kinetic scheme are selected from the literature (3). The complete set of Arrhenius equations is :

$$k_d = 1.58 \times 10^{15} \text{ Exp } (-15500/T)$$

$$k_p = 1.051 \times 10^{7} \text{ Exp } (-3557/T)$$

$$k_{fm} = 2.31 \times 10^{6} \text{ Exp } (-6377/T)$$

$$k_{fs} = 5.92 \times 10^{8} \text{ Exp } (-8660/T)$$

$$k_{tc} = 1.255 \times 10^{9} \text{ Exp } (-844/T)$$

$$k_{td} = 0.0$$

An initial catalyst efficiency of 0.6 is used throughout. Density has been assumed constant in the present investigations.

The complete derivation of kinetic equations can be found in literature (1) (9) and Appendix 1. The equation for conversion is

$$\frac{dX}{dt} = k_p\ (1-X)[2k_d f\ C_o\ \mathrm{Exp}(-k_d t)/k_t]^{1/2} \tag{13}$$

In general, $(f/k_t)^{1/2}$ is a function of time for each set of reactor conditions and equation (13) cannot be integrated. $(f/k_t)^{1/2}$ can be considered, however, as a constant over a small time interval. The analytical solution over a small time interval is

$$X_2 = 1 - \mathrm{Exp}\ \{\ell n(1-X_1) + 2k_p(\frac{2f\ C_o}{k_d\ k_t})^{1/2}[\mathrm{Exp}(-\ \frac{k_d t_2}{2}) - \mathrm{Exp}\ (-\ \frac{k_d t_1}{2}\ )\ ]\} \tag{14}$$

Alternatively, $\frac{f}{k_t}$ can be calculated if the conversion X_1, X_2 and time t_1, t_2 are known i.e.,

$$[\ \frac{f}{k_t}\ ]^{1/2} = \frac{-\ \ell n[(1-x_1)/(1-x_2)]\quad (k_d)^{1/2}}{2k_p(2\ C_o)^{1/2}[\mathrm{Exp}(-k_d t_2/2)-\mathrm{Exp}(-k_d t_1/2)]} \tag{14a}$$

Applying the steady-state hypothesis, the rate of formation of polymer of chain length r is

$$\frac{dP_r}{dt} = R^o(1-Z)(Z)^{r-1}\ [k_{fs}S+k_{fm}M_o(1-X) + R^o \{\ \frac{(r-1)k_{tc}(k_{fs}S+k_{fm}M_o(1-X)+I^{1/2}(k_t)^{1/2})}{2\ k_p M_o(1-X)} + k_{td}\}\ ] \tag{15}$$

where Z is the probability factor

$$Z = \frac{k_p M}{k_p M + k_{fs}S + k_{fm}\ M + I^{1/2}(k_t)^{1/2}} \tag{16}$$

Equation (14) along with conversion data may be used to find the variation of (f/k_t) with time, conversion and viscosity. The solution of dead polymer species P_r from equation (15) requires the knowledge of f and k_t individually as a function of viscosity. The molecular weight averages can be calculated once P_r's are known.

6. EXPERIMENTAL

6.1 General Description

Styrene polymerization initiated by azo-bisisobutyronitrile with toluene as solvent was studied. Experiments were set up to include catalyst concentration, solvent concentration and temperature as variables. The arrangement of experiments is given in Table 1.

TABLE 1 ARRANGEMENT OF EXPERIMENTS

Temperature ^{o}C		60		70		80	
Catalyst Conc. (C_o)		0.04	0.08	0.04	0.08	0.04	0.08
Toluene Conc. (S)	1.8	1	2	3	4	5	6
	3.6	7	8	9	10	11	12

Solvent level of 5.4 gm-mole/litre was also investigated. It was rejected, however, due to the low conversions obtained, and the difficulty of complete precipitation of the very low molecular weight polymer.

Conversion of monomer was determined gravimetrically. The weighed sample, diluted with dioxane if necessary, was poured slowly into about ten-fold excess of methanol precipitating all polymer, which was recovered after filtering and drying under vacuum at about 50^{o}C. The weight of polymer was used to calculate conversion, and the polymer obtained was used to determine molecular weight distribution by gel permeation chromatography (GPC) (3). Viscosity was measured at reaction temperature using a Brookfield viscometer. It was considered as Newtonian viscosity as the viscosity did not change significantly with shear rate within the range of measurements (46).

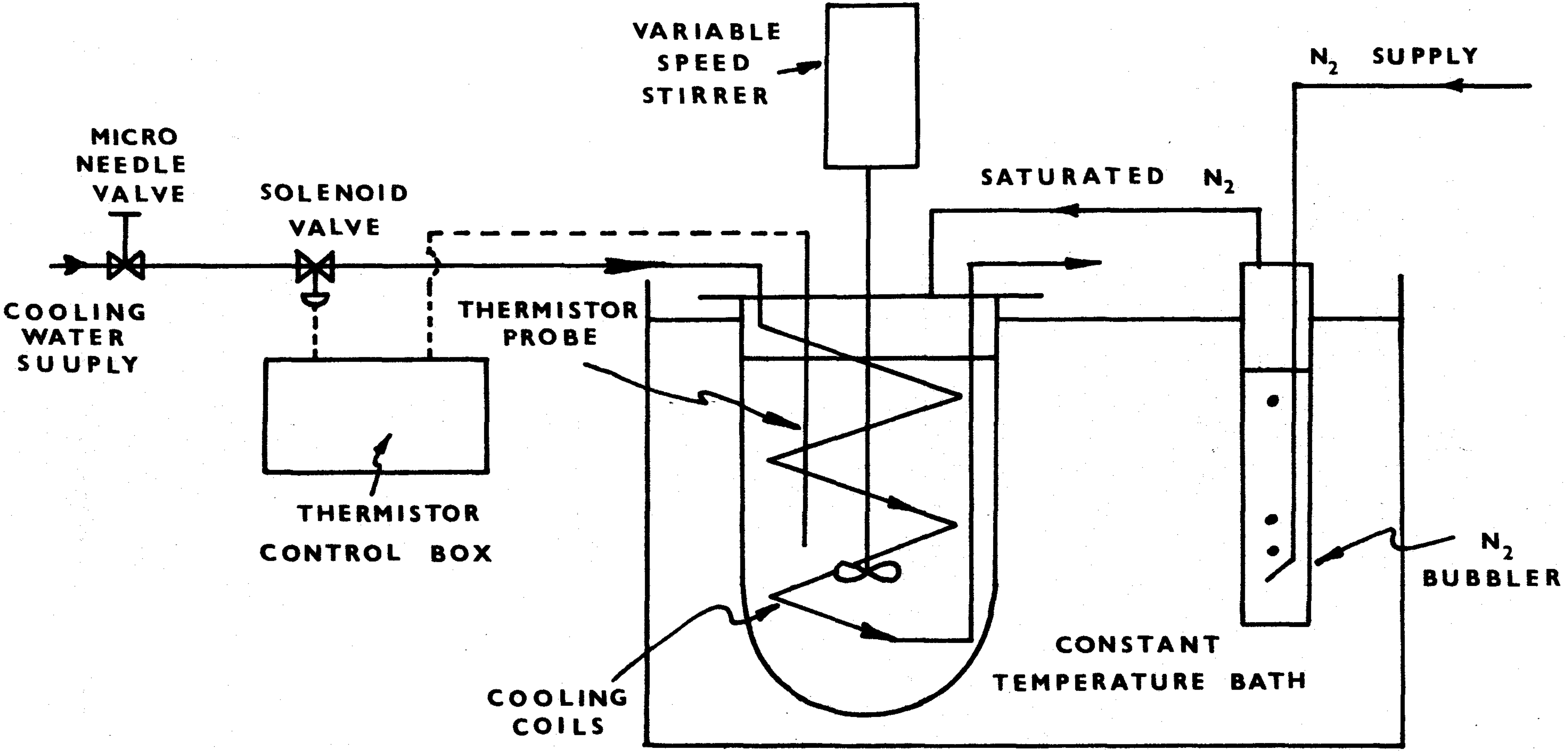
Azobisisobutyronitrile of Eastman Organic Chemicals was recrystallized once from methanol and certified grade toluene from Fisher Scientific Company was distilled once before used. Inhibitor-free styrene was provided by Polymer Corporation, Sarnia, Ontario, and was used directly without further purification.

6.2 Apparatus and Procedures

The batch reactor was an enclosed stainless steel vessel with 3 inches in diameter and 4 inches in cylindrical height having a volume of about 480 c.c. A variable speed stirrer was located centrally, approximately one third from the bottom of the vessel. The reactor was placed into a constant temperature bath operated at about 2 °C higher than the reaction temperature. The reaction mixture was cooled by means of a cooling coil through the reactor. Cold water was allowed through the coil and was controlled by the solenoid valve connected to a temperature control unit having a temperature sensing thermistor probe placed in the reactor. The temperature control was on-off type with an accuracy of ±0.2°C. Certified grade N_2 was saturated with a liquid in the gas bubbler, having the same monomer/solvent composition as the reaction mixture, before introducing into the reactor. Figure 1 gives a schematic view of the apparatus.

Catalyst, solvent and monomer were weighed separately to the predetermined feed composition. Catalyst being dissolved in solvent was introduced into the reactor and both the catalyst-solvent mixture

FIGURE 1. ISOTHERMAL BATCH STIRRED-TANK REACTOR



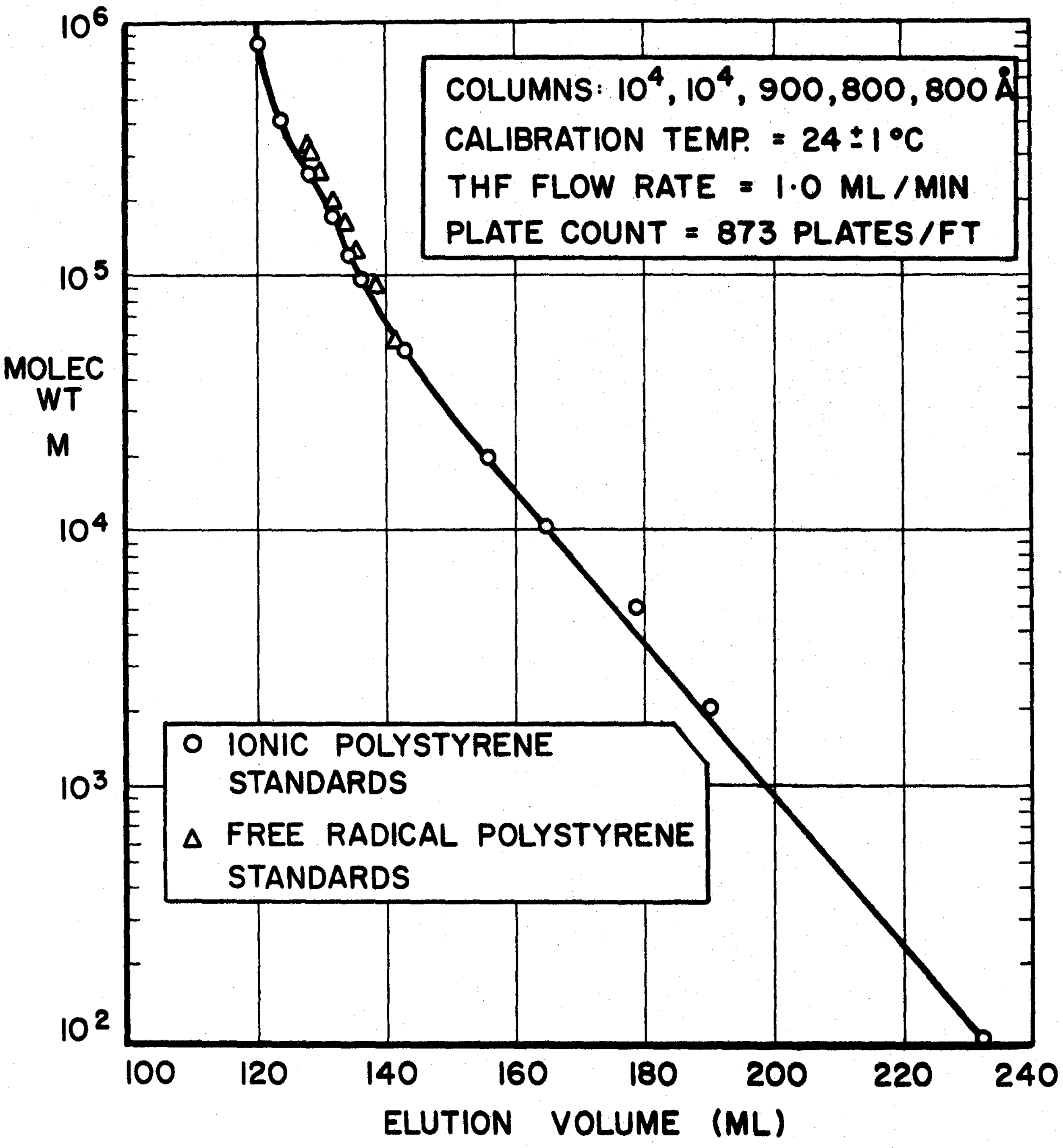
and monomer were heated separately to reaction temperature. Zero time was registered when monomer was introduced into the reactor with the complete mixture reaching the reaction temperature. Mixing was assisted by a constant speed stirrer turning at 300 r.p.m. The reaction mixture was under nitrogen atmosphere at all time. A liquid sample was forced out of the reactor under nitrogen pressure at the time of sampling.

6.3 Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a special type of elution chromatography in which the separation or fractionation is achieved according to the size of the solute molecules. It is the newest of the fractionation methods leading to the determination of molecular weight distribution of polymers and has already found widespread applications (2) (54).

Same techniques were used as reported by Duerksen et al (3). The gel permeation chromatograph (GPC) was supplied by Waters Associates. It consisted of 5 stainless steel columns of 3/8 inch diameter, 4 feet long, packed with porous cross-linked polystyrene beads. The maximum rated porosities of these columns were 10^4, 10^4, 900, 800 and 800 Angstroms in the direction of flow. Tetrahydrofuran (THF) was used as solvent eluting continuously at 1 ml./min. with temperature controlled to $(24 \pm 1)^{o}C$. The samples were prepared by dissolving the dry polymer in THF to give 0.5% by weight. The injection time was 60 seconds in all cases. The GPC was calibrated with polystyrene standards of known molecular weight averages. The calibration curve is shown in Figure 2.

FIGURE 2 GPC Calibration Curve



The sample was introduced onto the head of the column. Large molecules might be completely excluded from the gel, while intermediate ones were barred from entering the smaller pores thus causing separation. The separation was detected by means of a differential refractometer and was recorded on a Honeywell recorder. The GPC trace so obtained was corrected for imperfect resolution by Tung's Hermite polynomial method (55), (56) before the calculation of MWD.

There is a great deal of information available concerning gel permeation chromatography (2), (54). No further discussion will be reported here.

7. RESULTS AND DISCUSSIONS

The complete experimental and calculated results are given in Appendix 4. Results from the low conversion model (P_ℓ) developed by Tebbens (1) are also included for comparison. Viscosity correlations were developed relating the termination rate constant k_t and catalyst efficiency f as described in Appendix 3. Conversion X was obtained from the analytical solution equation (14) and the dead polymer species P_r's were obtained by solving equation (15) numerically using trapezoidal rule. A computer program was prepared to calculate both conversion and MWD incorporating changes in k_t and f via the viscosity correlations. A step size of ten minutes was used with k_t and f corrected for viscosity at each time increment. The logic diagram is shown in Figure 3. The results are given in Appendix 4 designated as P_h (high conversion model). The ratio of conversions (X_m / X_p) versus log (1+μ) is given in Figures 4 and 5 for the low conversion and high conversion kinetics, respectively. The data indicate that the high conversion model predicts conversion to within five percent for viscosities as large as 30 poises. Only high conversion experimental points are shown in Figures 4 and 5. The values of X_m and X_p are essentially equal for all experiments at low conversions. Another comparison is presented in Figure 6 where excellent agreement is found for the high conversion model up to 60% conversion or higher.

The ratios of (measured/predicted) values for the weight average chain length and the number average chain length versus log (1+μ) are shown in Figures 7 and 8, respectively. A comparison of a typical molecular weight distribution with and without viscosity correction is

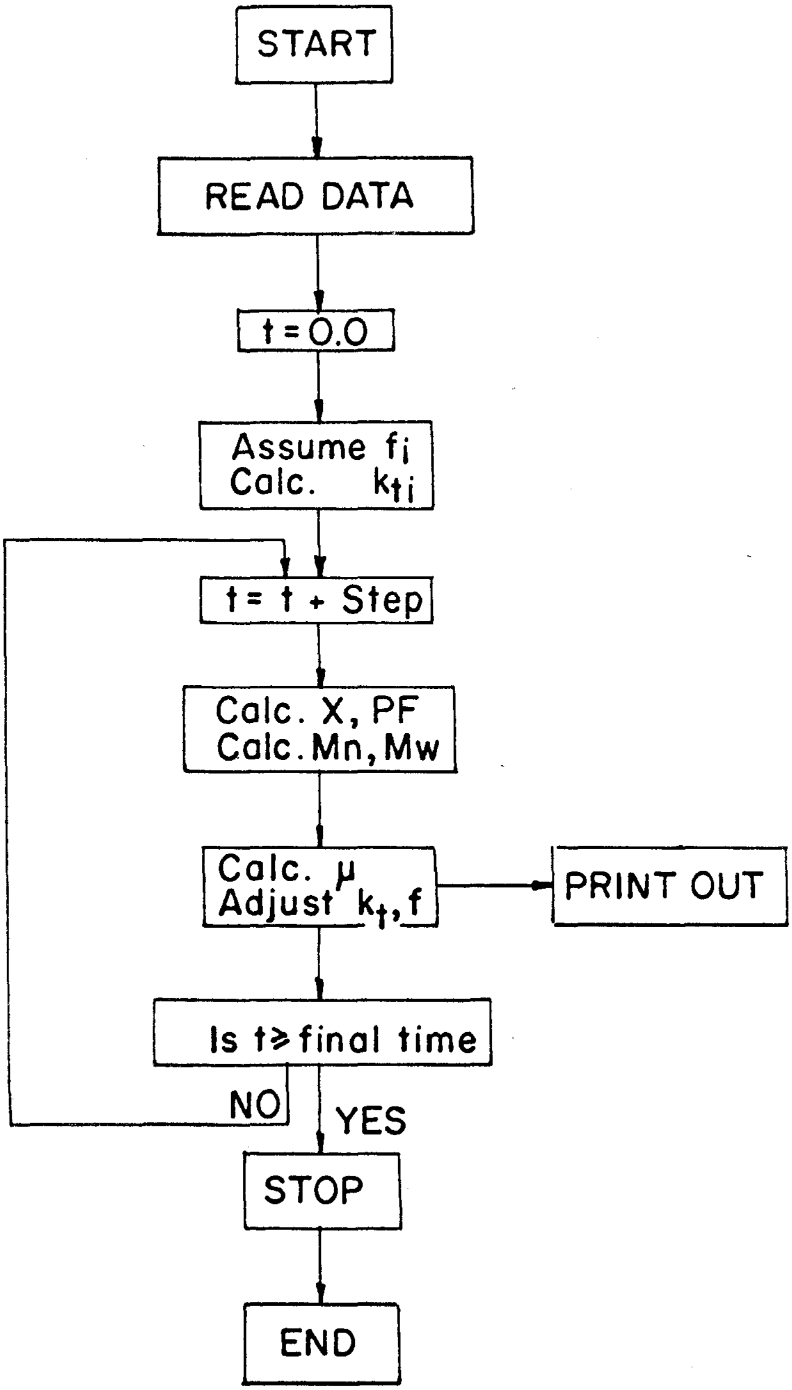


FIGURE 3 Logic Diagram of the BSTR Program

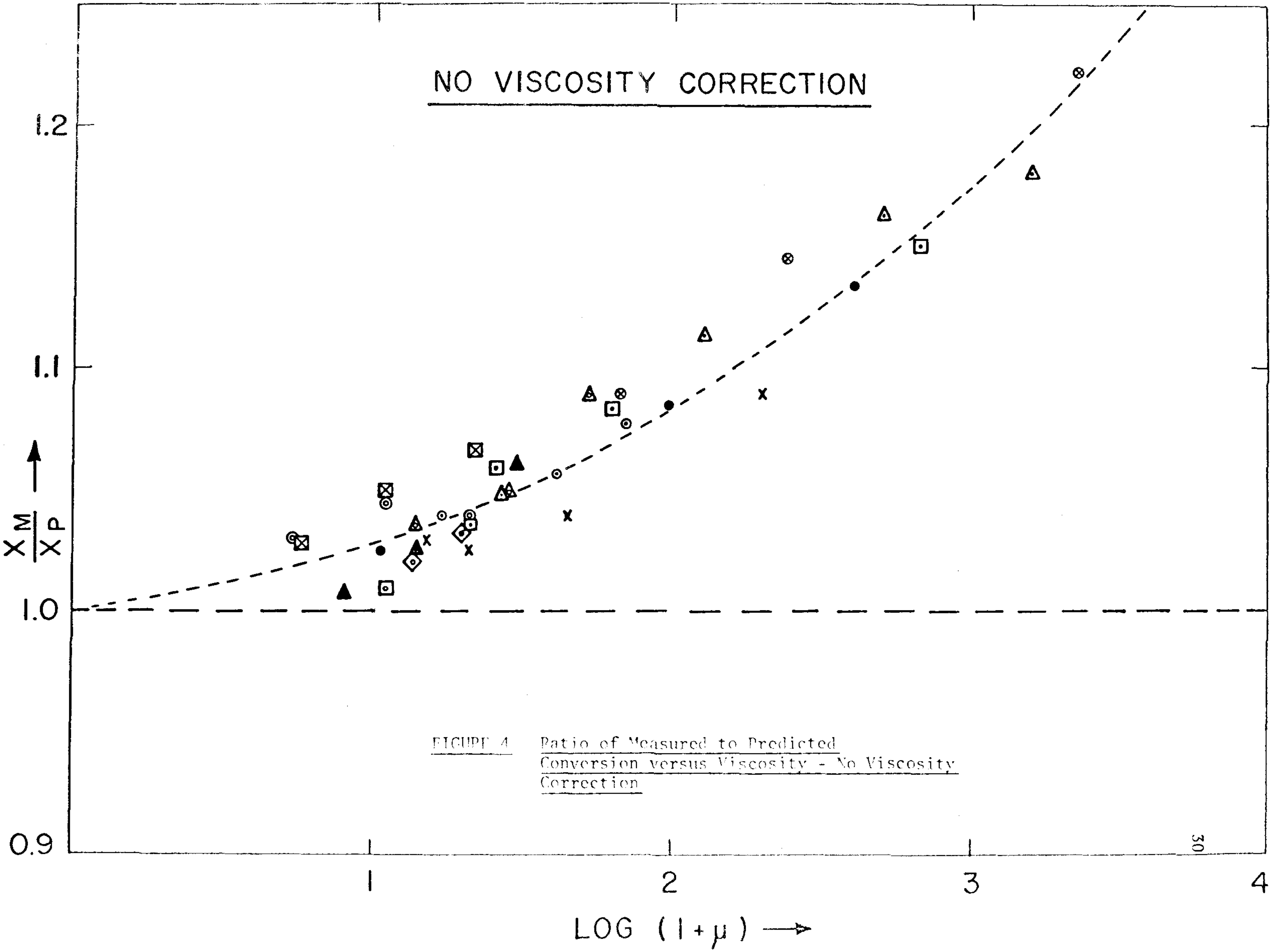


FIGURE 4 Ratio of Measured to Predicted Conversion versus Viscosity - No Viscosity Correction

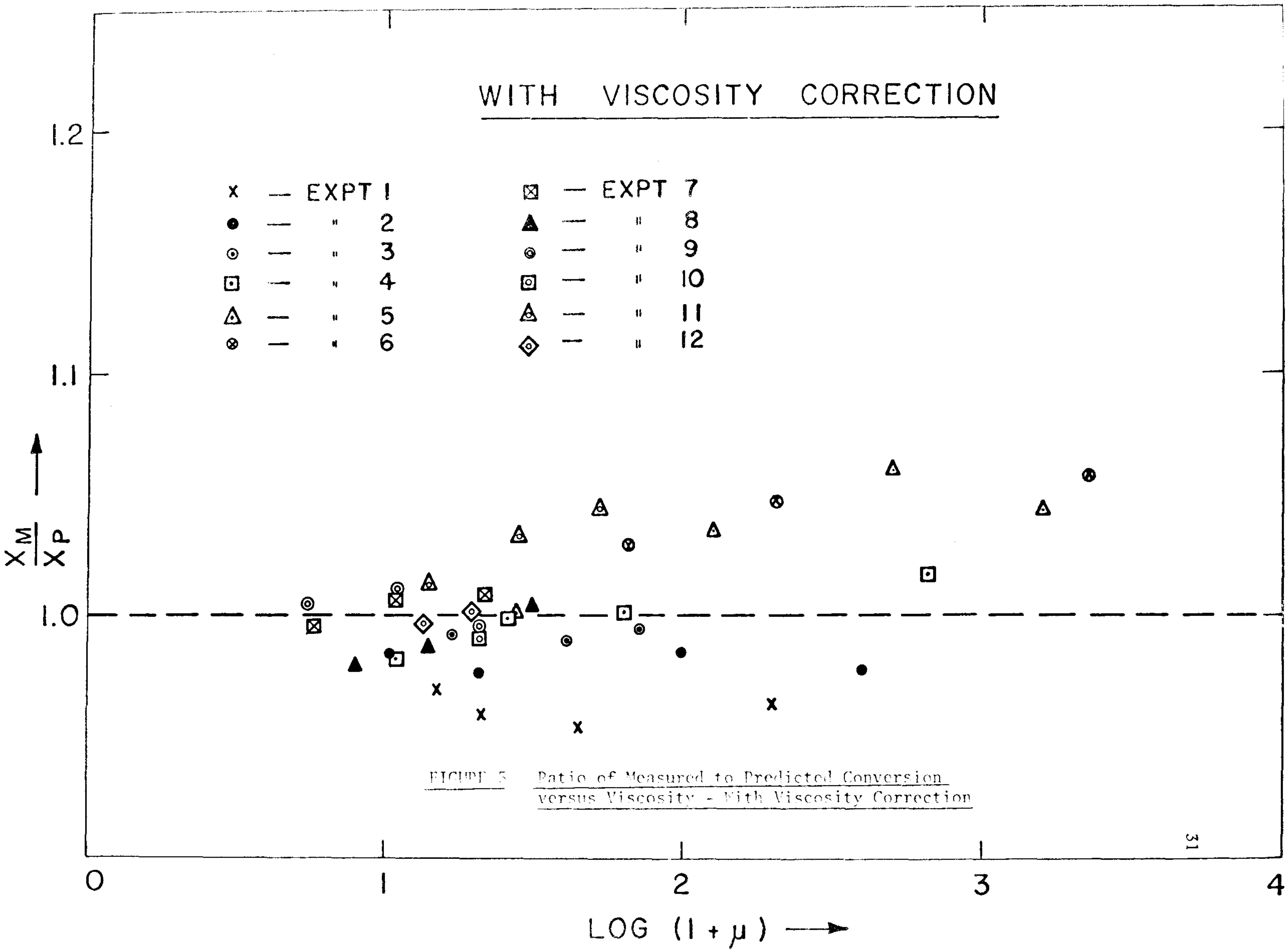


FIGURE 5 Ratio of Measured to Predicted Conversion versus Viscosity - With Viscosity Correction

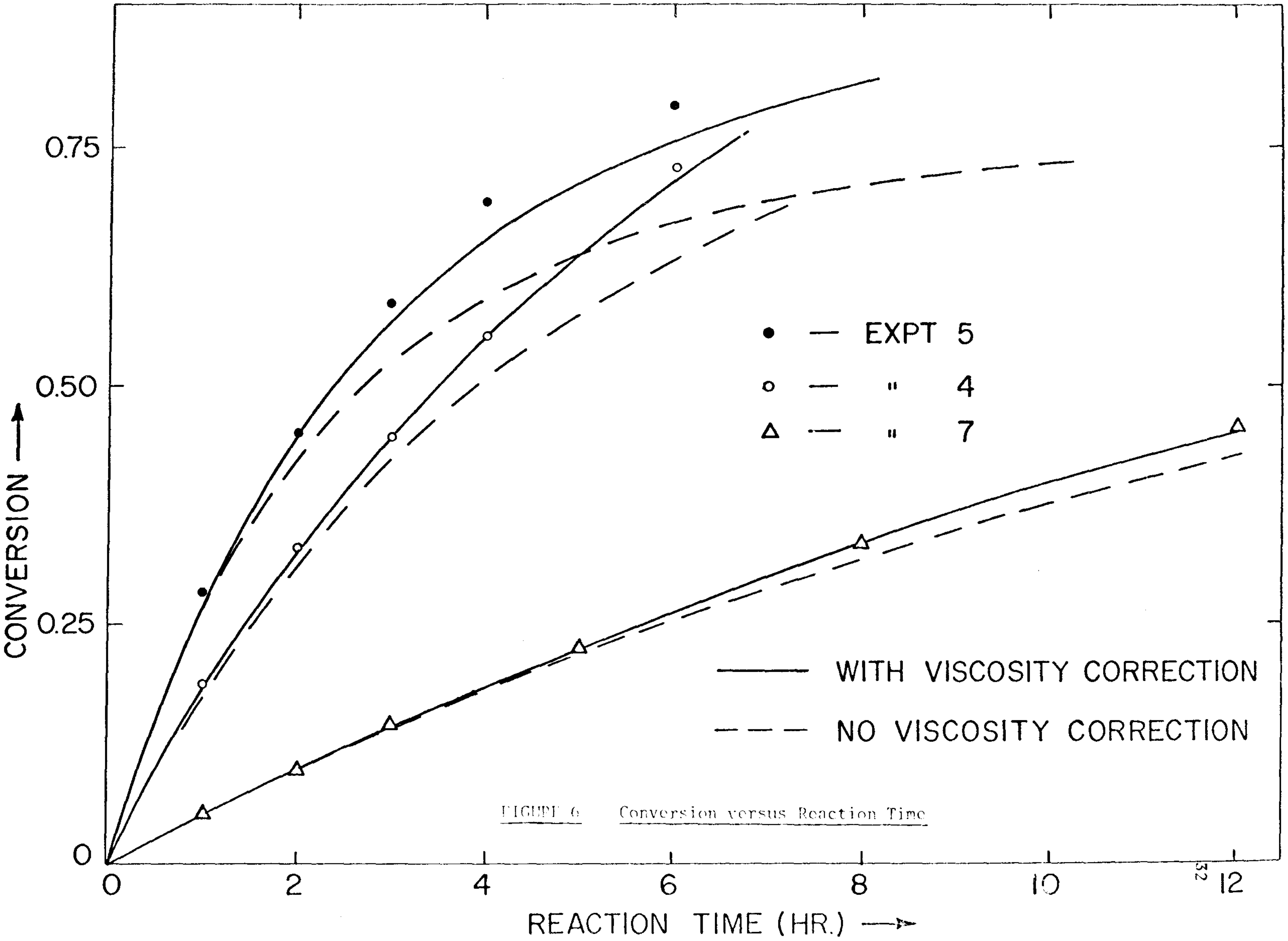


FIGURE 6 Conversion versus Reaction Time

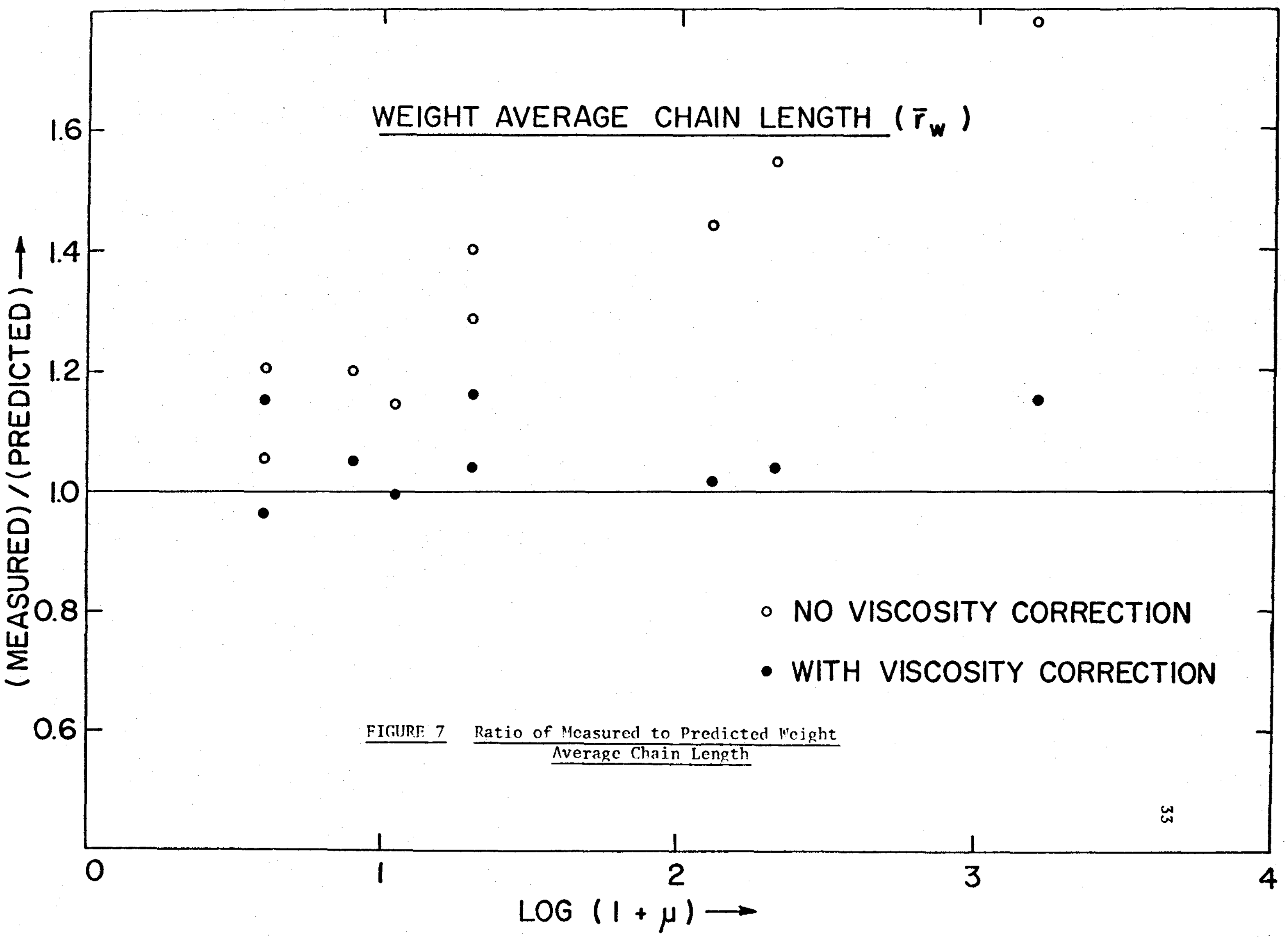


FIGURE 7 Ratio of Measured to Predicted Weight Average Chain Length

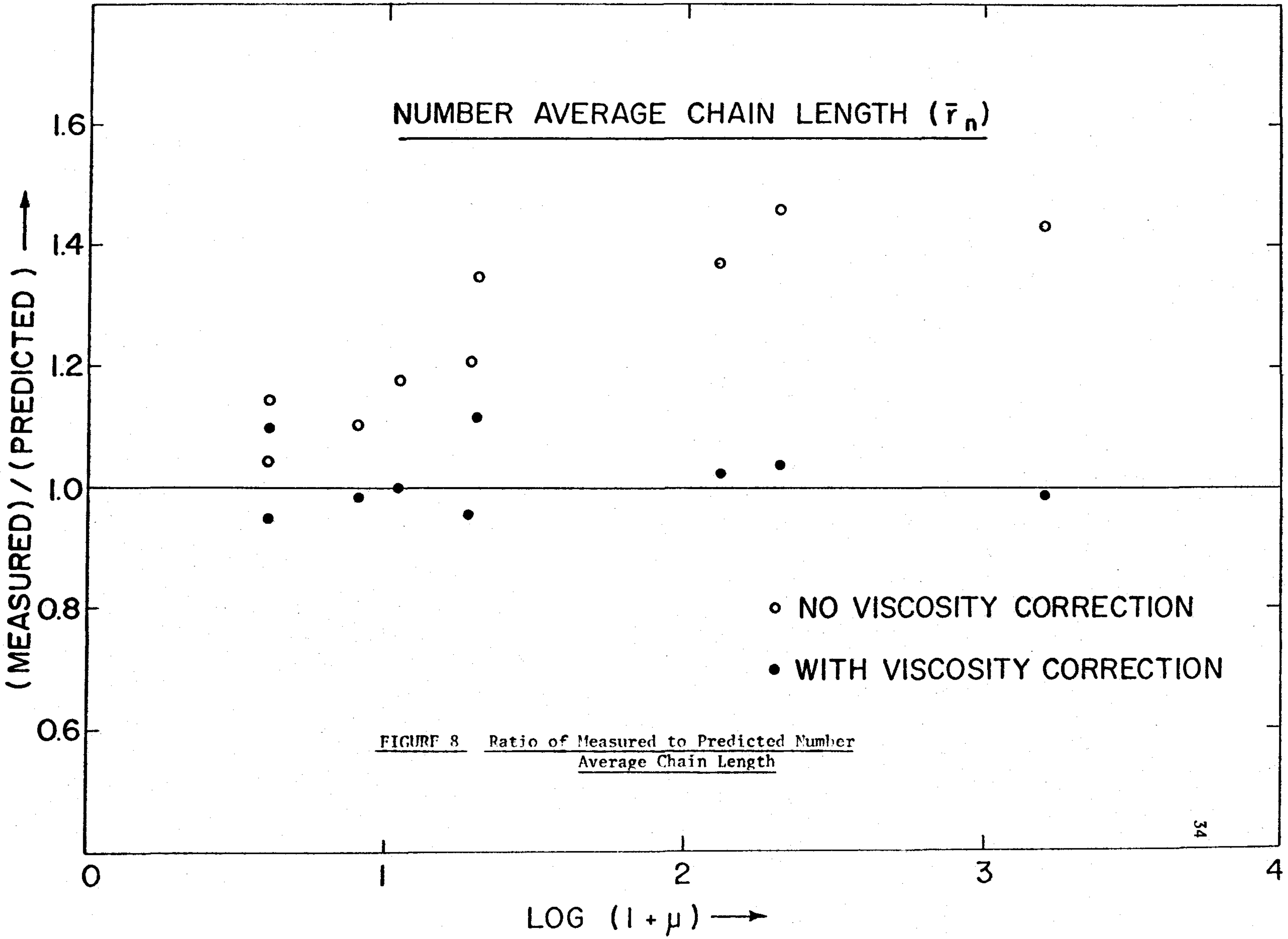
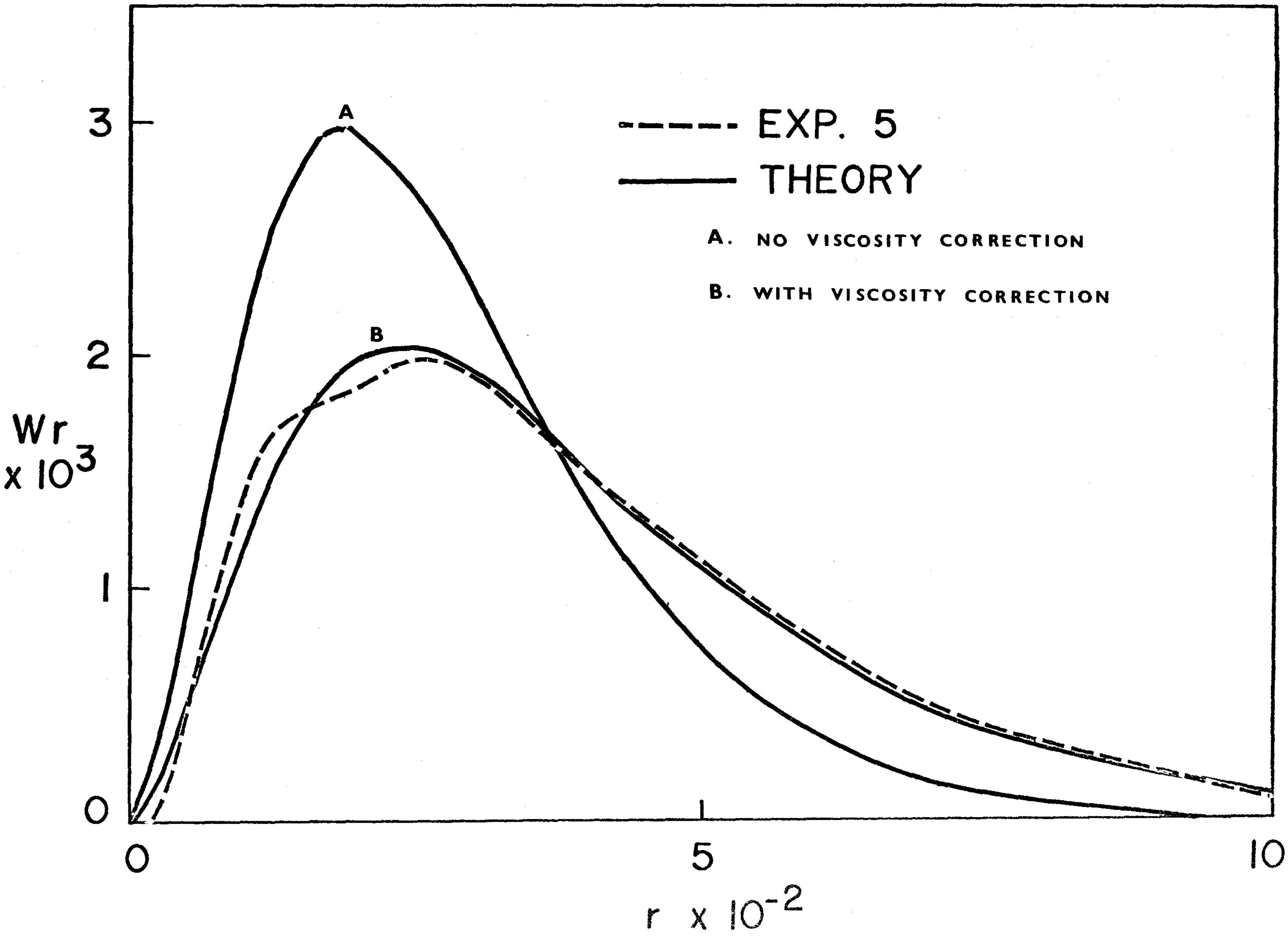


FIGURE 8 Ratio of Measured to Predicted Number Average Chain Length

FIGURE 9 Comparison of MWD's between Measured and Predicted Values With and Without Viscosity Correction



is shown in Figure 9.

The results as shown indicate a significant improvement in the predicted conversions and MWD values when viscosity correction is included. The predicted values for conversion and molecular weight averages are consistently too low when no viscosity correction is made. The viscosity correction involves the decreasing of f and k_t while keeping other factors constant. Decrease in f will lead to lower predicted conversions, but decrease in k_t while maintaining k_p constant will raise both conversion and molecular weight bringing them closer in line with the measured values. Decrease in k_t agrees with the theory of diffusion controlled kinetics.

There is only one exception which is evident in experiments 1 and 2 where the average chain lengths are over corrected. The overcorrection is believed due to the high molecular weights obtained in these two experiments as compared to those from all other experiments. The viscosity correlation tends to put more weight on the lower molecular weight polymers giving the higher molecular weight samples greater error. More experiments at much higher molecular weights would be required to elucidate this effect.

There is some scatters in the data. The experimental errors indicated in the study of reproducibility (Appendix 2) cannot account for all the variations. All the points in Figure 4 scatter about one line giving the equation

$$X_m/X_p = 1.0 + 0.0129 \log (1+\mu) + 0.0154 [\log((1+\mu)]^2 \qquad (17)$$

with a standard deviation estimate of 0.015 (or 1.5%) for X_m/X_p.

This is more than the experimental error which is about 1% (see Table 2 in Appendix 2). This suggests that viscosity alone accounts for most but not all of the variations in X_m/X_p. There appears to be some chain length dependence (see Table 6 in Appendix 4).

A comparison of Figure 4 and 5 indicates that the variation in Figure 5 is greater than 1.5%. It would appear that better correlation can be obtained based on equation (17). The viscosity dependence of k_t and f, however, does not permit the integration of equation (13). Knowing X_m/X_p does not yield the ratio of $k_t f_i/k_{ti} f$.

The increased variation of X_m/X_p in Figure 5 is due to the use of viscosity correlations. To determine the variations of f and k_t with viscosity individually requires the search of the right conversion-time equation for each experiment, essentially with concomitant introduction of errors. The regression equations are not perfect and the trial and error procedure in arriving at the k_t and f correlations does not guarantee the best possible correlating equations. On the other hand, the consideration of only f and k_t as functions of viscosity is an oversimplification. It has been reported (39) (41) that k_t is chain length dependent in viscous media. The deviation of MWD predictions for the high molecular weight polymers in experiments 1 and 2 indicates the inadequacy of the viscosity correlations in handling a large molecular weight range. The solvent and the viscosity corrections have opposite effects on k_t. The assumption of no interaction perhaps needs further justification.

The aim of the present study has been to develop a mathematical model to predict conversion and MWD up to high conversion. The model which was developed is the result of a preliminary study of the well-known "gel effect". The present treatment is perhaps a bit crude, but it achieves the aim of being able to predict both conversion and MWD up to 70% conversion within a tolerable limit in the range of experimental conditions.

Further work is required to improve and to extend the range of applicability with more data at higher viscosities and higher molecular weights. The improved version should consider the variation of k_p as well as k_t, and their dependence on chain length. Shear rate may be another variable affecting diffusion controlled reactions and should therefore be considered in any future investigation.

8. CONCLUSIONS AND RECOMMENDATIONS

A high conversion model for the solution polymerization of styrene has been developed by modifying conventional kinetics. Significant improvements over the low conversion model have been obtained with the inclusion of a solvent correction and the incorporation of changes in k_t and f with Newtonian viscosity.

The agreement reported here is another verification of the general theory of diffusion controlled polymerization reactions where viscosity is considered the major parameter. The present treatment will probably not be able to predict conversion and MWD to complete conversion where viscosity is extremely high and propagation and other reactions become diffusion controlled as well. Further work is required in this area to elucidate polymerization kinetics at extremely high viscosity (>10 poise).

A more sophisticated kinetic treatment including the variation of k_p with chain length and viscosity would probably be necessary. Controlling the rate of shear during polymerization should shed some light on the importance of this parameter with regard to molecular alignment and its effect on reaction rates.

9. NOMENCLATURE

BSTR - batch stirred-tank reactor

C - reactor catalyst concentration in gm-mole/litre

C_1 - constant in equation (4)

C_2 - constant in equation (4)

D_A, D_B - diffusion constants

E - activation energy in calories

Exp - exponential of (or e to the power)

f - catalyst efficiency

GPC - gel permeation chromatograph

I - initiation rate for free radical

I_c - initiation rate by catalyst decomposition

I_{th} - initiation rate by thermal energy

k - kinetic rate constant

m , M - measured values

M - monomer molecule or monomer concentration in gm-moles/litre

MWD - molecular weight distribution

PF - polymer weight fraction

P_h - predicted values by high conversion model

p_ℓ - predicted values by low conversion model

p_r - polymer species of chain length r

r - number of monomer units or chain length

$\bar{r}_n$ - number average chain length

$\bar{r}_w$ - weight average chain length

R - ideal gas law constant

R^o_r - free radical of chain length r gm-mole/litre

R^o - equals to $\sum_{r=1}^{\infty} R^o_r$, total concentration for all free radicals. gm-mole/litre

S - solvent molecule or solvent concentration in gm-mole /litre

t - reaction time in seconds

T - absolute temperature in degree Kelvin

μ - bulk viscosity in centipoises

W_r - weight fraction of polymer of chain length r

X - conversion of monomer

Z - probability factor

Subscripts for rate constant k

d - refers to decomposition of catalyst

fm - refers to transfer to monomer

fs - refers to transfer to solvent

p - refers to propagation reaction

tc - refers to termination by combination

td - refers to termination by disproportionation

t - $k_t = k_{tc} + k_{td}$

Other subscripts

h - refers to predicted values with viscosity correction

i - refers to initial value, e.g. k_{ti}, f_i

ℓ - refers to predicted values with no viscosity correction

m - refers to measured values

o - refers to initial concentration

p - refers to predicted values

r - refers to species of chain length r

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APPENDIX

1. SOLUTION OF POLYMERIZATION KINETICS

Rate equations can be derived based on reactions (1)-(5) and (8),(9) described in Section Three. Assuming S^o and M^o as R_1^o (Section 3.2.3) the rate of formation of R_1^o is

$$\frac{d\,R_1^o}{dt} = I - k_p M R_1^o + (k_{fs}S + k_{fm}M)\,R^o - (k_{fs}S + k_{fm}M)\,R_1^o - (k_{tc} + k_{td})\,R_1^o R^o \tag{18}$$

The rate of formation of R_2^o and higher is

$$\frac{d\,R_r^o}{dt} = k_p M R_{r-1}^o - k_p M R_r^o - (k_{fs}S + k_{fm}M)\,R_r^o - (k_{tc} + k_{td})\,R_r^o R^o \tag{19}$$

where $r \geqslant 2$

$$R^o = \sum_{r=1}^{\infty} R_r^o$$

and $I = 2\,k_d f\,C_o\,\mathrm{Exp}\,(-k_d t)$

There are altogether r ordinary differential equations one for each radical species. Addition of these r equations gives

$$\frac{d\,R^o}{dt} = I - (k_{tc} + k_{td})\,{R^o}^2 \tag{20}$$

The rate of monomer consumption is

$$-\frac{dM}{dt} = I + k_p MR^o + k_{fm} MR^o \tag{21}$$

The rate of formation of polymer of chain length r is

$$\frac{d\,P_r}{dt} = (k_{fs}S + k_{fm}M)\ R_r^o + k_{td}R_r^oR^o + \frac{1}{2}\,k_{tc}\sum_{n=1}^{r-1} R_n^o\ R_{r-n}^o \tag{22}$$

In general, equations (18) through (22) can be solved consecutively with increasing r to give conversion and MWD as a function of time. The consecutive nature of these equations should perhaps be given more emphasis as it is not generally appreciated that they are in fact consecutive. Equation (20) for the total free radical R^o can be solved independently and it is this solution of R^o that makes the solution of R_1, R_2 etc., uncoupled from the set of simultaneous equations. Liu and Amundson (57) did not realize that equation (20) could be used to make the set of equations consecutive and solved 201 equations simultaneously with the assumption that the propagation stopped at a chain length of 100. The numerical results of Liu and Amundson are therefore in error. In reality up to 4000 or more equations should be considered to obtain realistic answers. Had Liu and Amundson been aware of the consecutive nature of these equations they could have easily solved 4000 or more of these differential equations.

The solution may be simplified by making pseudo-steady-state assumption (Section 3.2.6) for free radicals. The validity of this assumption has been investigated $^{(4)}$, and is shown to be valid for styrene polymerization initiated with azo catalyst.

With the steady-state assumption for free radicals, equations (18), (19) and (20) becomes algebraic equations with solutions

$$R_1^o = \frac{I + (k_{fs}S + k_{fm}M)\ R^o}{k_pM + k_{fm}M + k_{fs}S + (k_{tc} + k_{td})\ R^o} \tag{23}$$

$$R_r^o = Z\ R_{r-1}^o = Z^{(r-1)}\ R_1^o \tag{24}$$

where

$$Z = \frac{k_pM}{k_pM + k_{fm}M + k_{fs}S + (k_{tc} + k_{td})\ R^o} \tag{16a}$$

$$R^o = [\ I\ /\ (k_{tc} + k_{td})\ ]^{1/2} \tag{25}$$

Equations (23), (24) and (25) can then be used in equations (21) (22) for numberical solutions. Notice again that the consective nature of equation (24) makes the solution of free radicals very easy.

Assuming that the chain length is large (Section 3.2.5), equation (21) becomes equation (13). Dead polymer species P_r in equation (22) can be solved with equation (23), (24), (25) to give equation (15) as described in Section 5.4.

Thermal polymerization has also been considered. Conversion was calculated assuming that the initiation rates due to thermal energy and catalyst decomposition are additive, i.e.,

$$I = I_{th} + I_c \tag{26}$$

The rate equation becomes

$$\frac{dX}{dt} = k_p \ (1-X) \ \left[\frac{I_{th} + I_c}{k_t} \right]^{1/2} \tag{27}$$

Apply the binomial theorem,

$$(I_{th} + I_c)^{1/2} = I_c^{1/2} \ \left[1 + \frac{1}{2} \ \frac{I_{th}}{I_c} - \frac{1}{2} \cdot \frac{1}{4} \left(\frac{I_{th}}{I_c}\right)^2 + \ldots \right]$$

$$= I_c^{1/2} \ [1 + I_{th}/2I_c] \tag{28}$$

as $I_c >> I_{th}$ Equation (27) then becomes

$$\frac{dX}{dt} = k_p \ (1-X) \ I_c^{1/2} [1 + I_{th}/2I_c] \ / \ k_t^{1/2} \tag{29}$$

Assuming constant I_{th}, integration of equation (29) gives

$$\ln \ (1-X) = k_p \ \left(\frac{2fC_o}{k_t k_d} \right)^{1/2} \{ \ 2 \ \mathrm{Exp}(-k_d t/2) - 2 \ - \ \frac{I_{th}}{2fC_o k_d} \ [\ \mathrm{Exp}(k_d t/2) \ - \ 1 \ ] \ \} \tag{30}$$

With the rate of thermal polymerization obtained from Boundy and Boyer (8), and making the steady-state assumption for the thermally initiated radicals alone, I_{th} can be solved as

$$\frac{dX}{dt} = k_p \ (1-X) \ [\ I_{th}/k_t \ ]^{1/2} \tag{31}$$

for small conversion, (1-X) → 1,

$$I_{th} = \left[\frac{(dX/dt)_{th}}{k_p} \right]^2 \ k_t \tag{32}$$

The conversion including the contribution from thermal polymerization and catalyst has been calculated by equations (30), (32). Results show no significant contribution from thermal polymerization.

The mechanism of thermal polymerization has not been well understood and the validity of the above mentioned treatment needs additional verification. In the present study, thermal polymerization is considered to be negligible.

The weight fraction of species r is given as

$$W_r = \frac{r\ P_r}{M_o X} \tag{33}$$

The number average chain length as

$$\bar{r}_n = \frac{\sum_{r=1}^{\infty} r\ P_r}{\sum_{r=1}^{\infty} P_r} \tag{34}$$

The weight average chain length as

$$\bar{r}_w = \frac{\sum_{r=1}^{\infty} r^2\ P_r}{\sum_{r=1}^{\infty} r\ P_r} \tag{35}$$

2. REPRODUCIBILITY OF EXPERIMENTAL DATA

The reproducibility of experimental techniques was investigated. Experiment 10 was repeated four times and the conversions, viscosities, molecular weight averages were measured. The results of the four levels of measurements are given in Table 2. The mean and standard deviation estimates are also given. They serve as an indicator for the errors involved within the range of measurements. The results show that the reproducibility is good and the experimental techniques are acceptable.

Attention is drawn to the standard deviation of viscosity shown in Table 2. The range of viscosities encountered here happens to be in the range recommended for the Brookfield viscometer used. The Brookfield has an operating speed of 6, 12, 30 and 60 R.P.M. The UL adaptor measures viscosity up to 100 c.p. while the co-axial adaptor 865 with the S-SP-865A spindle measures up to 500 c.p. The use of spindle 425A with the co-axial adaptor measures viscosity up to 80,000 c.p. The first two arrangements give best results, but spindle 425A is difficult to use and is more in error. UL adaptor has been used for the viscosity measurements given in Table 2, its standard deviation estimates do not represent the error beyond its range of measurement. Brookfield viscometer may not be the best instrument for the measurement of viscosity up to 30 poise. The search for a better method may be necessary especially for the measurement of viscosities >20 poise.

TABLE 2 REPRODUCIBILITY DATA

TIME (HR.)		Replicates				Mean	Est. Std. Deviation	$\frac{\text{STD.DEV.}}{\text{Mean}}$
		1	2	3	4			
1	X	16.40	16.43	16.38	16.65	16.47	0.125	0.76%
	μ	1.4	1.7	1.5	1.6	1.55	0.129	8.32%
	$\bar{r}_n$	142	142	142	141	141.75	0.50	0.35%
	$\bar{r}_w$	222	220	216	217	218.75	2.75	1.26%
	$\bar{r}_w/\bar{r}_n$	1.56	1.55	1.52	1.54	1.542	0.017	1.02%
2	X	30.65	28.86	29.32	29.53	29.59	0.76	2.57%
	μ	2.9	3.1	3.0	2.9	2.98	0.096	3.22%
	$\bar{r}_n$	147	141	140	143	142.75	3.10	2.17%
	$\bar{r}_w$	230	223	220	226	224.75	4.27	1.90%
	$\bar{r}_w/\bar{r}_n$	1.56	1.58	1.58	1.58	1.575	0.010	0.63%

TABLE 2 (Continued)

TIME (HR.)		Replicates				Mean	Est. Std Deviation	$\frac{\text{STD.DEV.}}{\text{MEAN}}$
		1	2	3	4			
3	X	39.87	39.54	39.80	39.99	39.80	0.19	0.48%
	μ	5.0	5.0	5.0	5.1	5.03	0.050	1.00%
	$\bar{r}_n$	135	136	134	148	138.25	6.55	4.74%
	$\bar{r}_w$	214	227	213	234	220.0	10.23	4.65%
	$\bar{r}_w/\bar{r}_n$	1.59	1.66	1.59	1.58	1.605	0.037	2.31%
4	X	48.48	47.93	48.78	49.17	48.59	0.523	1.08%
	μ	7.8	8.1	8.1	8.4	8.10	0.245	3.02%
	$\bar{r}_n$	142	143	140	136	140.25	3.10	2.21%
	$\bar{r}_w$	220	231	227	220	224.5	5.45	2.43%
	$\bar{r}_w/\bar{r}_n$	1.55	1.61	1.62	1.61	1.597	0.032	2.00%

TABLE 2 (Continued)

TIME (HR.)		Replicates				Mean	Est. Std. Deviation	STD.DEV. / MEAN
		1	2	3	4			
6	X	61.92	61.72	62.35	62.76	62.19	0.463	0.74%
	μ	17.5	17.5	17.4	18.7	17.78	0.618	3.48%
	$\bar{r}_n$	138	148	143	139	142.0	4.55	3.20%
	$\bar{r}_w$	222	222	222	224	222.5	1.0	0.45%
	$\bar{r}_w/\bar{r}_n$	1.61	1.50	1.55	1.61	1.567	0.053	3.38%

	X	μ	$\bar{r}_n$	$\bar{r}_w$	$\bar{r}_w/\bar{r}_n$
Pooled Estimate Std. Deviation	0.473	0.307	4.07	5.68	0.033

The difference in analytical techniques was also investigated with the collaboration of J.H. Duerksen. One sample (Expt. 10, 1 hour) was used to prepare the dry polymers. The dilution with dioxane was tested against no dilution before precipitation of polymer. The drying under ordinary oven was tested against drying under vacuum oven. Each of the resulting dry polymers was used to make up two 0.5% solution in THF, and each solution was analysed 5 times with gel permeation chromatography. The GPC results in this case were not corrected for imperfect resolution. The different methods were compared via the analysis of variance for two factors with replication$^{(58)}$. The combined analyses are shown in Table 3. Results of F-test show no <u>difference within 98% confidence limit between the different treatments</u>. Same indication is also obtained for the separate analyses testing separately the effect of oven drying versus vacuum drying and the effect of dilution with dioxane versus no dilution. Results for the separate analyses are similar and are not reported here.

The F-values at 98% confidence limit are

$$F_{1,24} = 7.82$$

$$F_{2,24} = 5.61$$

All the values of F-ratio in Tables 3 are less than the corresponding values in the F-table indicating that the variance estimates are not different. The analysis of variance is used here to compare several means in terms of the pooled variance of the measurements. The pooled estimate, $\bar{S}^2(n)$, is an estimate of the residual or error variance of the measurements, σ^2. It represents the variation of the duplicated measurements.

TABLE 3.1 VARIATIONS OF RW UPON TREATMENTS

INPUT DATA

	OVEN DRY	VACUUM DRY	
	NO DIOXANE	NO DIOXANE	WITH DIOXANE
SOLUTION 1	218.00	190.00	229.00
	230.00	219.00	222.00
	229.00	232.00	241.00
	221.00	214.00	236.00
	216.00	232.00	224.00
MEAN	222.80	217.40	230.40
STD DEV EST	6.38	17.26	8.02
SOLUTION 2	238.00	229.00	226.00
	219.00	221.00	229.00
	237.00	219.00	232.00
	216.00	221.00	230.00
	227.00	228.00	199.00
MEAN	227.40	223.60	223.20
STD DEV EST	10.06	4.56	13.70

POOLED EST. STD. DEVIATION = 0.1090E 02

TABLE 3.1 VARIATIONS OF RW UPON TREATMENTS

ANALYSIS OF VARIANCE FOR TWO FACTORS WITH REPLICATION

SOURCE	SUM OF SQUARES	D.F.	VARIANCES	F RATIO
C-FACTOR	0.2125E 03	2.	0.1062E 03	0.8945E 00
R-FACTOR	0.1080E 02	1.	0.1080E 02	0.9093E-01
C*R INTERACTION	0.2678E 03	2.	0.1339E 03	0.1127E 01
SUB-TOTAL	0.4911E 03			
ERROR	0.2850E 04	24.	0.1188E 03	
TOTAL	0.3341E 04			

TABLE 3.2 VARIATIONS OF RN UPON TREATMENTS

INPUT DATA

	OVEN DRY	VACUUM DRY	
	NO DIOXANE	NO DIOXANE	WITH DIOXANE
SOLUTION 1	125.00	116.00	134.00
	132.00	125.00	134.00
	131.00	133.00	135.00
	125.00	125.00	135.00
	130.00	133.00	137.00
MEAN	128.60	126.40	135.00
STD DEV EST	3.36	7.06	1.22
SOLUTION 2	132.00	126.00	129.00
	131.00	130.00	135.00
	135.00	131.00	137.00
	129.00	128.00	138.00
	133.00	134.00	121.00
MEAN	132.00	129.80	132.00
STD DEV EST	2.24	3.03	7.07

POOLED EST. STD. DEVIATION = 0.4597E 01

TABLE 3.2 VARIATIØNS ØF RN UPØN TREATMENTS

ANALYSIS ØF VARIANCE FØR TWØ FACTØRS WITH REPLICATIØN

SØURCE	SUM ØF SQUARES	D.F.	VARIANCES	F RATIØ
C-FACTØR	0.1475E 03	2.	0.7373E 02	0.3489E 01
R-FACTØR	0.1203E 02	1.	0.1203E 02	0.5694E 00
C*R INTERACTIØN	0.6827E 02	2.	0.3413E 02	0.1615E 01
SUB-TØTAL	0.2278E 03			
ERRØR	0.5072E 03	24.	0.2113E 02	
TØTAL	0.7350E 03			

TABLE 3.3 VARIATIONS OF RW/RN UPON TREATMENTS

INPUT DATA

	OVEN DRY	VACUUM DRY	
	NO DIOXANE	NO DIOXANE	WITH DIOXANE
SOLUTION 1	1.74	1.64	1.70
	1.74	1.75	1.66
	1.75	1.75	1.79
	1.78	1.72	1.74
	1.65	1.75	1.64
MEAN	1.73	1.72	1.71
STD DEV EST	0.05	0.05	0.06
SOLUTION 2	1.81	1.81	1.74
	1.68	1.70	1.69
	1.75	1.68	1.70
	1.67	1.73	1.67
	1.70	1.70	1.64
MEAN	1.72	1.72	1.69
STD DEV EST	0.06	0.05	0.04

POOLED EST. STD. DEVIATION = 0.5114E-01

```
TABLE 3.3  VARIATIØNS ØF RW/RN UPØN TREATMENTS


   ANALYSIS ØF VARIANCE FØR TWØ FACTØRS WITH REPLICATIØN
 ----------------------------------------------------------


-----------------------------------------------------------------------

     SØURCE      SUM ØF SQUARES   D.F.   VARIANCES      F RATIØ

-----------------------------------------------------------------------

    C-FACTØR      0.5307E-02      2.     0.2653E-02    0.1015E 01

    R-FACTØR      0.5633E-03      1.     0.5633E-03    0.2154E 00

C*R INTERACTIØN   0.5067E-03      2.     0.2533E-03    0.9688E-01

    SUB-TØTAL     0.6377E-02

      ERRØR       0.6276E-01     24.     0.2615E-02

-----------------------------------------------------------------------

      TØTAL       0.6914E-01

-----------------------------------------------------------------------



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3. VISCOSITY CORRELATIONS

Viscosity was assumed a function of temperature, solvent concentration, polymer weight fraction, number and weight average chain length of polymer. A regression analysis was carried out for all measurements giving the correlation equation

$$\begin{aligned}\log \mu = 17.66 &- 0.311 \log (1+S) - 7.72 \log (T) \\ &- 10.23 \log (1-PF) - 11.82 [\log (1-PF)]^2 \\ &- 11.22 [\log (1-PF)]^3 + 0.839 \log (\bar{r}_n)\end{aligned} \tag{36}$$

The measured and calculated viscosity is plotted in Figure 10. It is seen in this correlation that polymer weight fraction is the most important parameter affecting the bulk viscosity.

A best fit of conversion versus time data is first obtained for each experiment with k_{ti} corrected for solvent effect. The ratio of $(k_t f_i/k_{ti} f)$ calculated from equation (14) is correlated against measured viscosity. The correlation equation is

$$\log (k_t f_i/k_{ti} f) = -0.0777[\log(1+\mu)]^2 \tag{37}$$

and is shown in Figure 11.

The MWD calculation requires the knowledge of k_t and f individually. The problem here is to obtain data for k_t and f each as a function of viscosity obeying equation (37). A function related to viscosity is assumed for (f/f_i) and (k_t/k_{ti}) calculated. A good

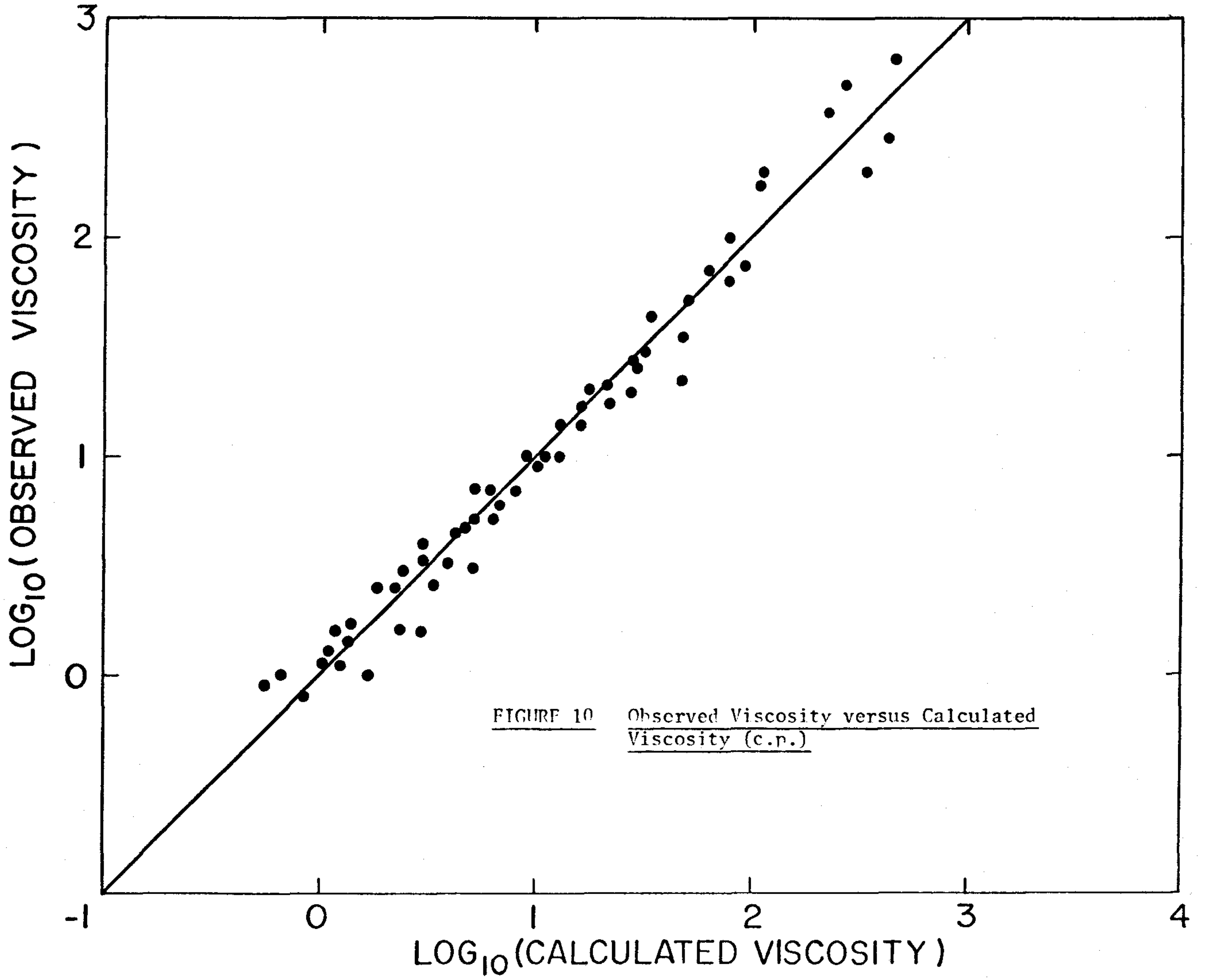
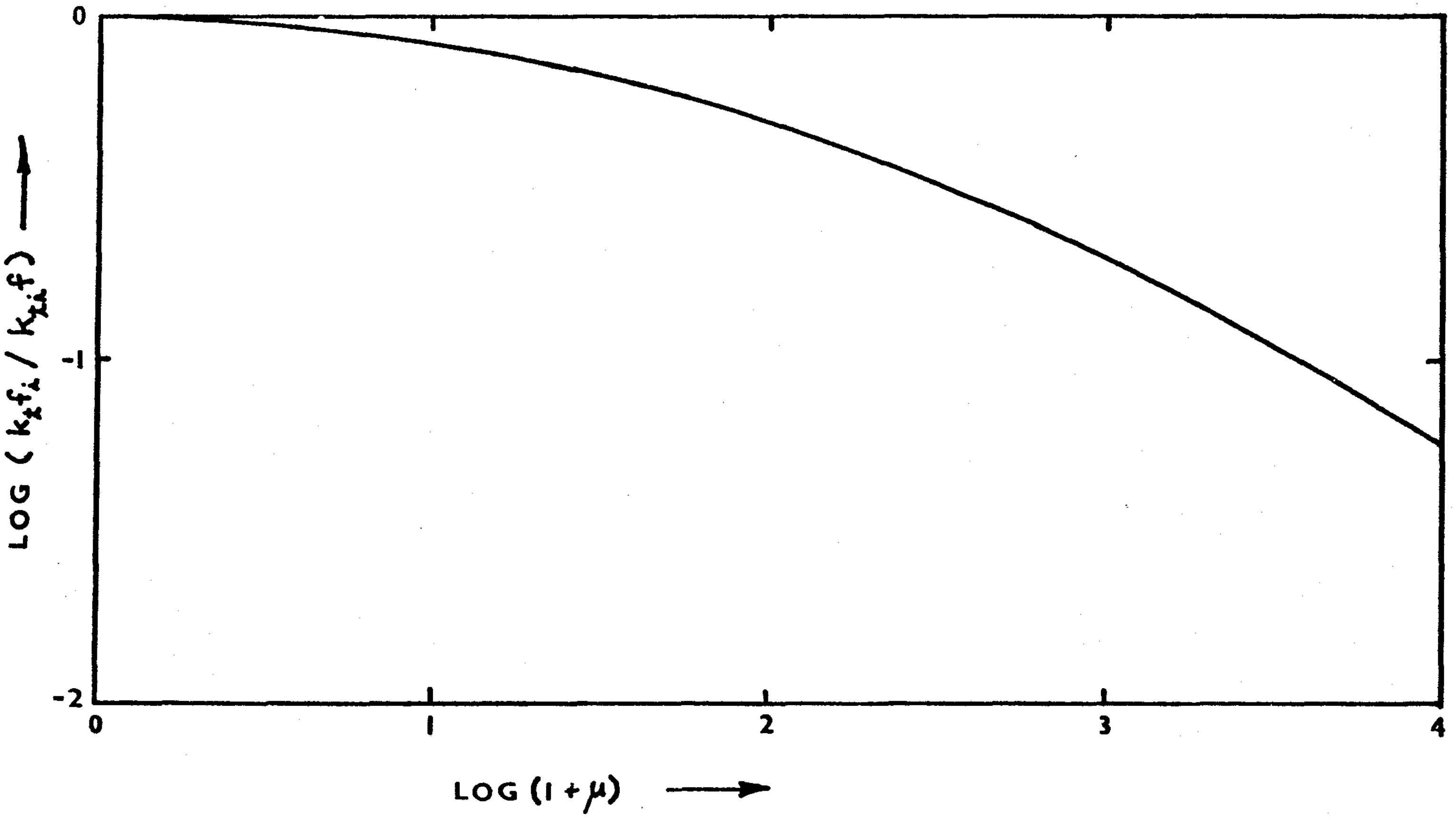


FIGURE 10 Observed Viscosity versus Calculated Viscosity (c.p.)

FIGURE 11 Correlation of $(k_t f_i / k_{ti} f)$ with Viscosity



fit is obtained after a few trials with

$$\log\ (f/f_i) = -o.133\ \log\ (1+\mu) \tag{38}$$

combining equations (37) & (38) gives

$$\log\ (k_t/k_{ti}) = -.0133\ \log(1+\mu) - 0.0777\ [\log(1+\mu)]^2 \tag{39}$$

Equation (38) and (39) are plotted in Figure 12. A better approach would be to search for (f/f_i) as a function of viscosity minimizing the square of the deviation for all experiments. An optimization search was not done here due to the excessive computer time that would have been required.

Equation (38) and (39) indicate a simple quadratic relationship in a log-log scale. Calculation shows that (f/f_i) and (k_t/k_{ti}) are relatively insensitive to the variations of viscosity as demonstrated in Table 4. This results in a large permissible tolerance in the viscosity correlation. The large standard deviation found with the regression equation for viscosity does not affect its ability when used with the kinetic model to predict accurate conversions and MWD's.

TABLE 4 VARIATION OF f/f_i & k_t/k_{ti} vs. μ

μ	f/f_i	k_t/k_{ti}
0.0	1.0	1.0
1.0	0.913	0.900
2.0	0.832	0.78
5.0	0.788	0.708
10.0	0.727	0.60
20.0	0.667	0.49
50.0	0.593	0.353
100.0	0.541	0.264
200	0.502	0.192
500	0.438	0.120
1000	0.400	0.080
2000	0.364	0.052

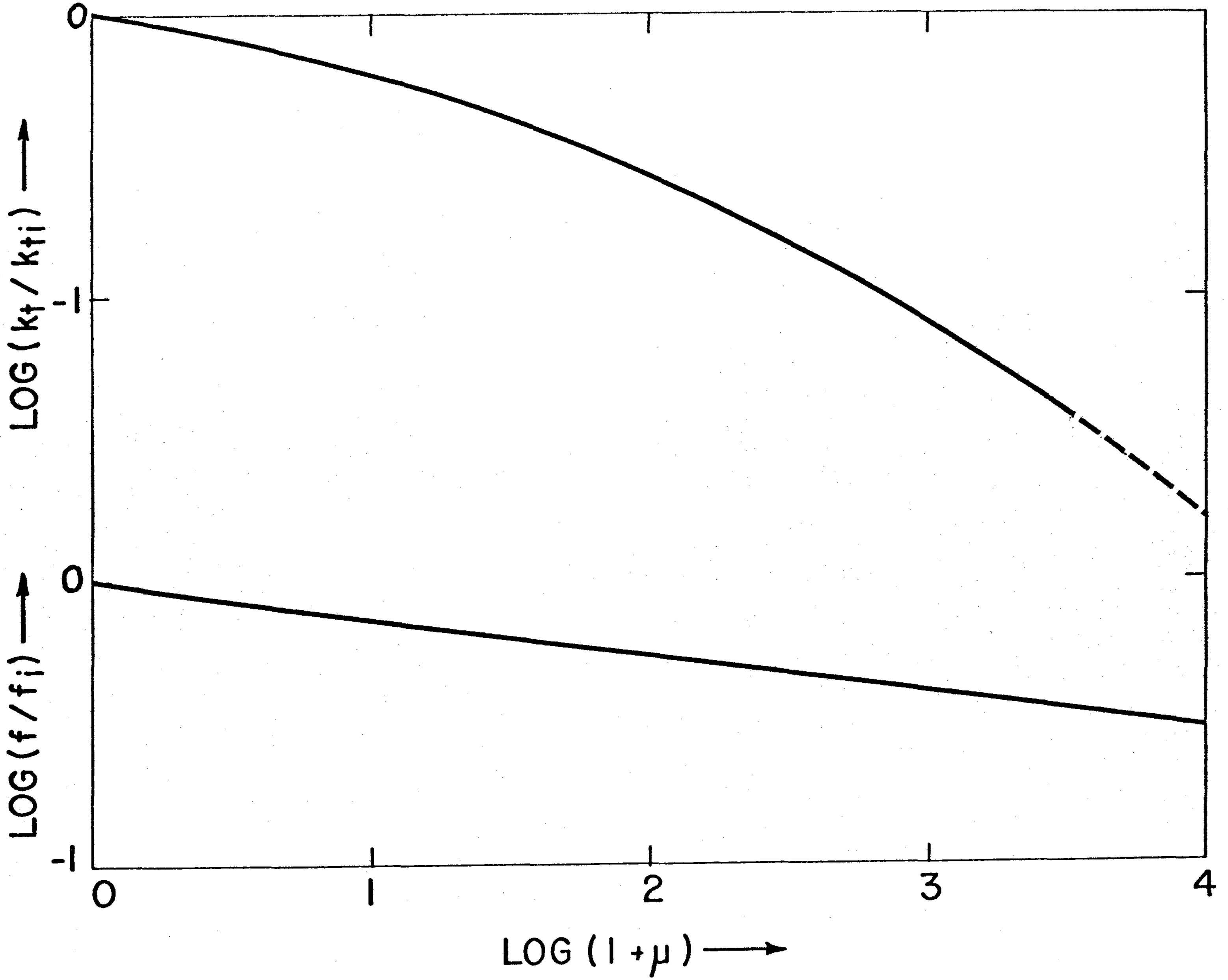


FIGURE 12 Correlation of (f_t/k_{ti}) and (f/f_i) with Viscosity

4. MEASURED AND PREDICTED CONVERSIONS, VISCOSITIES AND AVERAGE CHAIN LENGTH

TABLE 5.1A EXPERIMENT 1A

Time (Hr.)		1	2	3	6	12
X (%)	m	5.33	10.62	14.67	27.61	48.93
	p_ℓ^*	5.36	10.35	14.99	27.14	45.21
	p_h^{**}	5.47	10.67	15.59	29.06	51.83
$\bar{r}_w$	m	672	688	713	719	753
	p_ℓ	644	633	620	595	551
	p_h	744	765	779	821	921
$\bar{r}_n$	m	406	431	433	450	460
	p_ℓ	427	420	411	394	361
	p_h	491	505	515	541	597
$\bar{r}_w/\bar{r}_n$	m	1.65	1.60	1.65	1.60	1.64
	p_h	1.52	1.51	1.51	1.52	1.54
μ_m (c.p.)		1.6	3	5	20	160

Initial Conditions :-

Monomer Conc. = 6.69 gm mole/ℓ
Catalyst Conc. = 0.04 gm mole/ℓ
Solvent Conc. = 1.8 gm mole/ℓ
Temperature = 60°C

* P_ℓ predicted using low conversion model (conventional kinetics)

** P_h predicted using high conversion model (k_t and f corrected for viscosity)

TABLE 5.1B EXPERIMENT 1B

Time (Hr.)		1	3	5	8	12
X	m	5.54	15.26	23.84	35.10	49.05
	p_ℓ	5.36	14.99	23.37	33.97	45.21
	p_h	5.47	15.59	24.76	37.18	51.83
$\bar{r}_w$	m	700	660	680	708	696
	p_ℓ	644	623	602	577	551
	p_h	744	779	807	852	921
$\bar{r}_n$	m	468	431	450	460	454
	p_ℓ	427	413	398	381	361
	p_h	491	515	532	559	597
$\bar{r}_w/\bar{r}_n$	m	1.50	1.53	1.51	1.54	1.53
	p_h	1.52	1.51	1.52	1.52	1.54
μ_m (c.p.)		1.6	6	14	44	200

<u>Initial Conditions</u> :-

Monomer Conc. = 6.69		Solvent Conc. = 1.80	
Catalyst Conc. = 0.04		Temperature = 60°C	

TABLE 5.2 EXPERIMENT 2

Time (Hr.)		1	3	5	8	12
X	m	7.73	20.86	32.39	47.96	64.68
	p_ℓ	7.50	20.53	31.37	44.40	57.01
	p_h	7.62	21.29	33.36	49.30	67.45
$\bar{r}_w$	m	470	463	489	522	565
	p_ℓ	451	428	408	383	360
	p_h	512	532	550	584	635
$\bar{r}_n$	m	304	294	306	349	358
	p_ℓ	300	284	270	251	233
	p_h	339	352	364	383	411
$\bar{r}_w/\bar{r}_n$	m	1.55	1.58	1.60	1.50	1.58
	p_h	1.51	1.51	1.51	1.52	1.54
μ_m (c.p.)		5.0	10	20	100	400

Initial Conditions : -

Monomer Conc. = 6.69 Solvent Conc. = 1.80

Catalyst Conc. = 0.08 Temperature = 60°C

TABLE 5.3 EXPERIMENT 3

Time (Hr.)		1	2	3	4	5
X	m	14.17	24.72	33.45	41.62	49.02
	p_ℓ	12.89	23.43	32.13	39.37	45.44
	p_h	13.19	24.31	33.91	42.33	49.80
$\bar{r}_w$	m	470	508	509	476	515
	p_ℓ	418	406	397	388	382
	p_h	467	487	507	530	553
$\bar{r}_n$	m	301	302	316	310	301
	p_ℓ	278	270	263	257	252
	p_h	310	322	334	347	360
$\bar{r}_w/\bar{r}_n$	m	1.56	1.68	1.61	1.53	1.70
	p_h	1.51	1.52	1.51	1.53	1.54
μ_m (c.p.)		3	7	16	40	70

Initial Conditions :-

Monomer Conc. = 6.59 Solvent Conc. = 1.82

Catalyst Conc. = 0.04 Temperature = 70°C

TABLE 5.4 EXPERIMENT 4

Time (Hr.)		2	3	4	6
X	m	32.86	44.74	55.06	72.51
	p_ℓ	31.47	42.26	50.75	63.10
	p_h	32.72	44.93	55.37	72.20
$\bar{r}_w$	m	317	326	350	374
	p_ℓ	276	265	255	242
	p_h	332	344	359	391
$\bar{r}_n$	m	195	199	212	227
	p_ℓ	183	175	168	157
	p_h	220	228	236	253
$\bar{r}_w/\bar{r}_n$	m	1.62	1.64	1.66	1.64
	p_h	1.51	1.51	1.52	1.55
μ_m (c.p.)		9	25	62	670

Initial Conditions :-

Monomer Conc. = 6.60 Solvent Conc. = 1.80

Catalyst Conc. = 0.04 Temperature = 70°C

TABLE 5.5A EXPERIMENT 5A

Time (Hr.)		1	2	3	6
X	m	27.17	44.69	57.52	79.21
	p_ℓ	26.93	42.84	52.84	67.10
	p_h	27.39	44.83	56.91	76.65
$\bar{r}_w$	m	339	378	403	534
	p_ℓ	282	279	279	289
	p_h	321	355	397	536
$\bar{r}_n$	m	208	240	255	273
	p_ℓ	188	186	186	191
	p_h	211	230	250	294
$\bar{r}_w/\bar{r}_n$	m	1.63	1.57	1.58	1.96
	p_h	1.52	1.54	1.59	1.82
μ_m (c.p.)		7	27	74	1600

Initial Conditions :-

Monomer Conc. = 6.51 Solvent Conc. = 1.80

Catalyst Conc. = 0.04 Temperature = 80°C

TABLE 5.5B EXPERIMENT 5B

Time (Hr.)		1	3	4	8
X	m	29.36	59.81	68.93	86.12
	p_ℓ	26.93	52.84	59.42	71.06
	p_h	27.39	56.91	65.59	82.81
$\bar{r}_w$	m	302	387	435	566
	p_ℓ	282	279	281	300
	p_h	321	397	442	618
$\bar{r}_n$	m	184	243	240	304
	p_ℓ	188	186	187	195
	p_h	211	250	267	311
$\bar{r}_w/\bar{r}_n$	m	1.64	1.60	1.81	1.86
	p_h	1.52	1.59	1.65	1.99
μ_m (c.p.)		7	130	500	-

Initial Conditions :-

Monomer Conc. = 6.51 Solvent Conc. = 1.81

Catalyst Conc. = 0.04 Temperature = 80°C

TABLE 5.6 EXPERIMENT 6

Time (Hr.)		1	3	$4^{1}/_{3}$
X	m	37.07	73.94	87.76
	p_ℓ	35.81	65.41	72.20
	p_h	36.52	71.88	83.75
$\bar{r}_w$	m	219	273	307
	p_ℓ	190	176	173
	p_h	220	262	295
$\bar{r}_n$	m	142	171	181
	p_ℓ	126	117	115
	p_h	142	165	178
$\bar{r}_w/\bar{r}_n$	m	1.55	1.59	1.70
	p_h	1.55	1.59	1.66
μ_m (c.p.)		10	206	2300

Initial Conditions :-

Monomer Conc. = 6.52 Solvent Conc. = 1.80

Catalyst Conc. = 0.08 Temperature = 80°C

TABLE 5.7A EXPERIMENT 7A

Time (Hr.)		1	2	3	6
X	m	5.22	9.85	14.18	25.45
	p_ℓ	4.95	9.62	13.96	25.41
	p_h	5.07	9.85	14.34	26.37
$\bar{r}_w$	m	518	503	516	517
	p_ℓ	454	447	441	423
	p_h	501	507	508	513
$\bar{r}_n$	m	330	320	310	327
	p_ℓ	302	297	293	281
	p_h	332	336	337	340
$\bar{r}_w/\bar{r}_n$	m	1.57	1.57	1.67	1.58
	p_h	1.51	1.51	1.51	1.51
μ_m (c.p.)		1.0	1.6	2.3	5.0

Initial Conditions :-

Monomer Conc. = 5.02 Solvent Conc. = 3.60

Catalyst Conc. = 0.04 Temperature = 60°C

TABLE 5.7B EXPERIMENT 7B

Time (Hr.)		1	3	5	8	12
X	m	5.34	14.64	22.44	33.50	45.56
	p_ℓ	4.95	13.96	21.84	31.91	42.73
	p_h	5.07	14.34	22.58	33.36	45.37
$\bar{r}_w$	m	516	495	467	485	497
	p_ℓ	454	441	427	411	396
	p_h	501	508	511	516	523
$\bar{r}_n$	m	331	327	309	323	326
	p_ℓ	302	293	283	272	261
	p_h	332	337	339	342	346
$\bar{r}_w/\bar{r}_n$	m	1.56	1.51	1.51	1.50	1.53
	p_h	1.51	1.51	1.51	1.51	1.51
μ_m (c.p.)		1.7	3.3	5	10	21

Initial Conditions :-

Monomer Conc. = 5.02
Solvent Conc. = 3.60
Catalyst Conc. = 0.04
Temperature = 60°C

TABLE 5.8A EXPERIMENT 8A

Time (Hr.)		1	2	3	6
X	m	7.04	13.53	19.14	36.17
	p_ℓ	6.97	13.34	19.18	33.97
	p_h	7.08	13.61	19.63	35.20
$\bar{r}_w$	m	328	347	337	329
	p_ℓ	320	312	304	285
	p_h	346	347	346	343
$\bar{r}_n$	m	202	212	208	204
	p_ℓ	213	207	202	189
	p_h	230	231	230	229
$\bar{r}_w/\bar{r}_n$	m	1.62	1.64	1.60	1.61
	p_h	1.50	1.50	1.50	1.50
μ_m (c.p.)		1.0	1.7	2.5	6

Initial Conditions :-

Monomer Conc. = 5.01 Solvent Conc. = 3.60

Catalyst Conc. = 0.08 Temperature = 60°C

TABLE 5.8B EXPERIMENT 8B

Time (Hr.)		1	3	5	8	12
X	m	7.16	19.95	29.67	43.05	58.00
	p_ℓ	6.97	19.18	29.45	41.96	54.57
	p_h	7.08	19.63	30.38	43.87	58.10
$\bar{r}_w$	m	350	347	344	340	341
	p_ℓ	320	304	290	273	257
	p_h	346	346	344	343	342
$\bar{r}_n$	m	224	227	214	216	213
	p_ℓ	213	202	192	180	167
	p_h	230	230	229	228	228
$\bar{r}_w/\bar{r}_n$	m	1.57	1.53	1.61	1.58	1.60
	p_h	1.50	1.50	1.50	1.50	1.50
μ_m (c.p.)		1.7	4	7	13	30

Initial Conditions :-

Monomer Conc. = 5.01 Solvent Conc. = 3.60

Catalyst Conc. = 0.08 Temperature = 60°C

TABLE 5.9 EXPERIMENT 9

Time (Hr.)		1	2	3	5	7
X	m	12.89	22.79	31.29	45.24	54.59
	p_ℓ	12.11	22.10	30.41	43.25	52.52
	p_h	12.28	22.51	31.13	44.79	55.00
$\bar{r}_w$	m	311	314	320	329	324
	p_ℓ	295	287	281	272	286
	p_h	316	319	322	329	337
$\bar{r}_n$	m	193	193	197	206	197
	p_ℓ	196	191	187	180	176
	p_h	210	212	214	218	223
$\bar{r}_w/\bar{r}_n$	m	1.61	1.63	1.62	1.60	1.65
	p_h	1.50	1.50	1.50	1.51	1.51
μ_m (c.p.)		1.5	3	5	10	20

Initial Conditions :-

Monomer Comc. = 4.92

Solvent Conc. = 3.60

Catalyst Conc. = 0.04

Temperature = 70^{o}C

TABLE 5.10 EXPERIMENT 10

Time (Hr.)		2	3	4	6	9
X	m	30.36	40.17	48.91	62.61	74.34
	p_ℓ	29.75	40.10	48.40	60.60	72.22
	p_h	30.26	41.08	49.92	63.33	76.26
$\bar{r}_w$	m	206	220	213	223	226
	p_ℓ	195	188	182	173	164
	p_h	215	214	214	214	215
$\bar{r}_n$	m	136	138	131	137	141
	p_ℓ	130	125	120	113	106
	p_h	144	143	143	143	143
$\bar{r}_w/\bar{r}_n$	m	1.51	1.59	1.63	1.64	1.61
	p_h	1.50	1.50	1.50	1.50	1.50
μ_m (c.p.)		3	5	10	20	44

Initial Conditions :-

Monomer Conc.	= 4.92	Solvent Conc.	= 3.60
Catalyst Conc.	= 0.08	Temperature	= 70°C

TABLE 5.11 EXPERIMENT 11

Time (Hr.)		1	2	3	5	8
XX	m	26.09	41.18	52.12	65.45	74.69
	p_ℓ	25.24	40.50	50.26	61.30	68.57
	p_h	25.52	41.21	51.50	63.51	71.63
$\bar{r}_w$	m	227	227	248	276	284
	p_ℓ	198	197	198	204	216
	p_h	210	220	232	257	294
$\bar{r}_n$	m	144	148	154	169	178
	p_ℓ	132	131	132	135	140
	p_h	140	146	153	164	175
$\bar{r}_w/\bar{r}_n$	m	1.58	1.54	1.62	1.64	1.60
	p_h	1.50	1.51	1.52	1.57	1.68
μ_m (c.p.)		5	7	13	27	52

Initial Conditions :-

monomer Conc. = 4.82

Catalyst Conc. = 0.04

Solvent Conc. = 3.62

Temperature = 80°C

TABLE 5.12 EXPERIMENT 12

Time (Hr.)		1	2	3	4
X	m	32.78	52.00	64.26	71.86
	p_ℓ	33.74	52.03	62.77	69.48
	p_h	34.11	53.04	64.53	71.88
$\bar{r}_w$	m	162	163	168	175
	p_ℓ	134	129	126	125
	p_h	141	143	147	151
$\bar{r}_n$	m	103	107	110	112
	p_ℓ	90	86	84	83
	p_h	94	96	98	100
$\bar{r}_w/\bar{r}_n$	m	1.57	1.53	1.53	1.55
	p_h	1.49	1.50	1.50	1.51
μ_m (c.p.)		3	7	13	19

Initial Conditions :-

Monomer Conc. = 4.83 Solvent Conc. = 3.60

Catalyst Conc. = 0.08 Temperature = 80°C

Observation of Figure 4 for the ratio of X_m/X_p vs. log $(1+\mu)$ shows some indication of chain length dependence. A set of results at viscosity of 600 centipoise are given in the Table below.

TABLE 6 CHAIN LENGTH DEPENDENCE OF CONVERSION

Expt. No.	X_m/X_p	$\bar{r}_w$	$\bar{r}_n$
6	1.16	280	175
5	1.15	400	240
2	1.13	500	330
1	1.11	750	460

The deviation of conversion indicates a trend depending on molecular weight. However the large scatter of data does not permit a distinct verification of its existence. Table 6 only shows some possibility of chain length dependence. Further work is required to verify the dependence of polymerization reactions on chain length.

5. COMPUTER PROGRAMS

```
$IBFTC 2FWR1
C
C     ANALYSIS OF VARIANCE FOR TWO FACTORS WITH REPLICATION
C
      DIMENSION TITLE(10)
      DOUBLE PRECISION X(9,9,9),REPT(9,9),COLT(9),ROWT(9),MEAN(9,9)
      DOUBLE PRECISION REPT2(9,9),SUMRX2(9,9),RVARES(9,9),RSTDES(9,9)
      DOUBLE PRECISION SUMX,SUMX2,SREPT2,SCOLT2,SROWT2,CORR
      DOUBLE PRECISION SSCOL,SSROW,SSSUBT,SSTOT,SSCR,SSERR
      READ(5,1) I,J,K
      READ(5,1) NCASE
      DO 500 INCASE=1,NCASE
      READ(5,5) (TITLE(IT),IT=1,10)
      DO 90 N=1,K
      READ(5,2) ((X(L,M,N),L=1,I),M=1,J)
   90 CONTINUE
C
      COLN=I
      ROWN=J
      DUPL=K
      TOTN=I*J*K
      SREPT2=0.0
      SUMX=0.0
      SUMX2=0.0
      SCOLT2=0.0
      SROWT2=0.0
      DO 61 L=1,I
      COLT(L)=0.0
      DO 62 M=1,J
      SUMRX2(L,M)=0.0
      REPT(L,M)=0.0
   62 CONTINUE
   61 CONTINUE
      DO 63 M=1,J
      ROWT(M)=0.0
   63 CONTINUE
C
      DO 110 L=1,I
      DO 105 M=1,J
      DO 100 N=1,K
      REPT(L,M)=REPT(L,M)+X(L,M,N)
      SUMRX2(L,M)=SUMRX2(L,M)+X(L,M,N)*X(L,M,N)
  100 CONTINUE
      COLT(L)=COLT(L)+REPT(L,M)
      REPT2(L,M)=REPT(L,M)*REPT(L,M)
      SUMX2=SUMX2+SUMRX2(L,M)
      SREPT2=SREPT2+REPT2(L,M)
  105 CONTINUE
      SCOLT2=SCOLT2+COLT(L)*COLT(L)
  110 CONTINUE
      DO 120 M=1,J
      DO 115 L=1,I
      MEAN(L,M)=REPT(L,M)/DUPL
      ROWT(M)=ROWT(M)+REPT(L,M)
      RVARES(L,M)=(SUMRX2(L,M)-REPT2(L,M)/DUPL)/(DUPL-1.0)
      RSTDES(L,M)=SQRT(RVARES(L,M))
  115 CONTINUE
      SUMX=SUMX+ROWT(M)
      SROWT2=SROWT2+ROWT(M)*ROWT(M)
```

```
  120 CONTINUE
      PRINT 21, TITLE
      PRINT 22
C
      CORR=SUMX*(SUMX/TOTN)
      SSCOL=SCOLT2/(ROWN*DUPL)-CORR
      SSROW=SROWT2/(COLN*DUPL)-CORR
      SSSUBT=SREPT2/DUPL-CORR
      SSTOT=SUMX2-CORR
      SSCR=SSSUBT-(SSCOL+SSROW)
      SSERR=SSTOT-SSSUBT
      DFC=COLN-1.0
      DFR=ROWN-1.0
      DFCR=DFC*DFR
      DFERR=COLN*ROWN*(DUPL-1.0)
      VARC=SSCOL/DFC
      VARR=SSROW/DFR
      VARCR=SSCR/DFCR
      VARERR=SSERR/DFERR
      FC=VARC/VARERR
      FR=VARR/VARERR
      FCR=VARCR/VARERR
      STDDV=SQRT(VARERR)
C
      PRINT 23, ((X(L,1,N),L=1,I),N=1,K)
      PRINT 33, (MEAN(L,1),L=1,I)
      PRINT 34, (RSTDES(L,1),L=1,I)
      PRINT 24, ((X(L,2,N),L=1,I),N=1,K)
      PRINT 33, (MEAN(L,2),L=1,I)
      PRINT 34, (RSTDES(L,2),L=1,I)
      PRINT 19, STDDV
      PRINT 31
      PRINT 9, I,J,K
      PRINT 20, ((REPT(L,M),L=1,I),M=1,J)
      PRINT 20, (COLT(L),L=1,I)
      PRINT 20, (ROWT(M),M=1,J)
      PRINT 30
      PRINT 35, SUMX,SUMX2,SREPT2,SCOLT2,SROWT2
      PRINT 18, CORR,STDDV
      PRINT 50, ((MEAN(L,M),L=1,I),M=1,J)
      PRINT 50, ((RVARES(L,M),L=1,I),M=1,J)
      PRINT 50, ((RSTDES(L,M),L=1,I),M=1,J)
      PRINT 26, TITLE
      PRINT 11
      PRINT 40
      PRINT 12, SSCOL,DFC,VARC,FC
      PRINT 13, SSROW,DFR,VARR,FR
      PRINT 14, SSCR,DFCR,VARCR,FCR
      PRINT 15, SSSUBT
      PRINT 16, SSERR,DFERR,VARERR
      PRINT 40
      PRINT 17, SSTOT
  500 CONTINUE
    1 FORMAT (3I10)
    2 FORMAT (6F10.4)
    5 FORMAT (10A6)
    9 FORMAT (1X,12H COLUMN NO.=,I2,5X,9H ROW NO.=,I2,5X,
     2 15H NO. DUPLICATE=,I2//)
```

```
11 FORMAT ( 5X,54H ANALYSIS OF VARIANCE FOR TWO FACTORS WITH REPLICAT
  1ION/5X,55(1H-)//// 1H0,65(1H-) ///
  2              5X,7H SOURCE,4X,15H SUM OF SQUARES,2X,5H D.F.,2X
  3 10H VARIANCES,5X,8H F RATIO / )
12 FORMAT (4X,9H C-FACTOR,5X,E11.4,3X,F5.0,3X,E11.4,3X,E11.4 //)
13 FORMAT (4X,9H R-FACTOR,5X,E11.4,3X,F5.0,3X,E11.4,3X,E11.4 //)
14 FORMAT(16H C*R INTERACTION,2X,E11.4,3X,F5.0,3X,E11.4,3X,E11.4 //)
15 FORMAT (4X,10H SUB-TOTAL,4X,E11.4 //)
16 FORMAT (6X,6H ERROR,6X,E11.4,3X,F5.0,3X,E11.4/ )
17 FORMAT (6X,6H TOTAL,6X,E11.4 /// 1X, 65(1H-) ///////)
18 FORMAT (1H0,6H CORR=,D15.8,10X,20H STANDARD DEVIATION=,E15.8 //)
19 FORMAT (1H0, // 50X,28HPOOLED EST. STD. DEVIATION =, E11.4 //)
20 FORMAT (1H0,6D20.10//)
21 FORMAT (1H1 /// 40X,10A6 /////)
22 FORMAT ( 65X, 10HINPUT DATA / 65X, 10(1H-) //// 38X, 62(1H-) //
  2  58X, 8HOVEN DRY,12X, 12HVACUUM   DRY // 55X,45(1H-) // 57X,
  3 10HNO DIOXANE,5X, 10HNO DIOXANE,4X, 12HWITH DIOXANE // 38X,
  4 62(1H-) // )
23 FORMAT (40X, 10HSOLUTION 1,3F15.2, 4(/50X,3F15.2) // )
24 FORMAT (40X, 10HSOLUTION 2,3F15.2, 4(/50X,3F15.2) // )
26 FORMAT (1H1 ///  2X,10A6 /////)
30 FORMAT (1H0,131(1H*)//)
31 FORMAT (1H1,131(1H*) //)
33 FORMAT (43X,4HMEAN,3X,3F15.2 )
34 FORMAT (39X,11HSTD DEV EST, 3F15.2 /// 38X,62(1H-) //)
35 FORMAT (1H0,6H SUMX=,D15.8,4X,7H SUMX2=,D15.8,3X,8H SREPT2=,D15.8,
  2 3X,8H SCOLT2=,D15.8,3X,8H SROWT2=,D15.8///)
40 FORMAT (1H0,65(1H-)//)
50 FORMAT (1H0,6F20.6)
   STOP
   END

                                CD TOT   0148
```

```
$IBFTC
C
C     CALCULATION OF AKTC BASED ON EXPERIMENTAL CONVERSION
C
      READ(5,5) AKD1,AKP1,AKTC1,AKTD1,AKFM1,AKFS1
      READ(5,6) AKD2,AKP2,AKTC2,AKTD2,AKFM2,AKFS2
      READ(5,6) TAU
C
      READ(5,1) N
      DO 100 I=1,N
      READ(5,1) RUN,DATE
      READ(5,6)  TE,SMO,CO,S,F
      PRINT 12
      PRINT 2, RUN,DATE
      PRINT 11
      PRINT 47
      PRINT 48, TE,SMO,CO,S,F
      AKD=AKD1*EXP(-AKD2/TE)
      AKP=AKP1*EXP(-AKP2/TE)
      AKTC=AKTC1*EXP(-AKTC2/TE)
C
C     CORRECTION FOR EFFECTS OF DILUTION WITH SOLVENT
C           -- G.H.OLIVE N S.OLIVE (1966)
C
      BULKM=8.450-(TE-323.0)*0.0085
      TERM=(SMO+TAU*S)/BULKM
      COR=TERM*TERM
      AKTCN=AKTC*COR
      PRINT 90, TAU,BULKM,COR,TERM,AKTC
      X=0.0
      XT=0.0
      XCT=0.0
      T=0.0
      RATIO=1.0
      PRINT 20
      PRINT 21,T,X,XT,XCT,AKTCN,RATIO
C
C     ADJUSTING CONVERSION FOR THERMAL POLYMERISATION BASED ON
C     INITIAL MONOMER CONCENTRATION
C
      TEMP=TE-273.1
      IF (TEMP.LE.61.0) GO TO 31
      IF (TEMP.GE.79.0) GO TO 32
C
      RO=0.00205
      GO TO 35
   31 RO=0.00089
      GO TO 35
   32 RO=0.0046
C
   35 RTHML=RO/(TERM*3600.0)
   10 READ(5,6) T,X,CTER
      XT=RTHML*T
      XCT=X-XT
      C1=8.0*AKP*AKP*F*CO/AKD
      C2=(1.0-EXP(-AKD*T/2.0))/(-ALOG(1.0-XCT))
      AKTCEX=C1*C2*C2
      RATIO=AKTCEX/AKTCN
      PRINT 21,T,X,XT,XCT,AKTCEX,RATIO
```

```
      IF (CTER.LT.0.001) GO TO 10
  100 CONTINUE
C
    1 FORMAT (3I10)
    2 FORMAT (1H ,10X,4H RUN,I5,10X,5H DATE,I10   )
    5 FORMAT (6E10.4)
    6 FORMAT (6F10.4)
   11 FORMAT (1H0,131(1H*) //)
   12 FORMAT (1H1,131(1H*)// )
   20 FORMAT (1H0,6X,10H TIME(SEC),10X,2H X,12X,3H XT,11X,4H XCT,
     2 10X,5H AKTC,10X,5HRATIO //)
   21 FORMAT (1H ,5X,F10.1,3F15.5,E15.5,F15.5   )
   47 FORMAT(//6X,4HTEMP,4X,8HMON CONC,2X,8HCAT CONC,2X,8HSOL CONC,2X,
     1 8H CAT EFF  /)
   48 FORMAT (1H , 6F10.4///)
   90 FORMAT (1H0,5H TAU=,F10.4,5X,7H BULKM=,F10.4,5X,5H COR=,F10.4,
     2 5X,6H TERM=,F10.5,5X,6H AKTC=,E15.5 //)
C
      STOP
      END

                                         CD TOT    0079
```

```
$IBFTC
C
C     CALCULATION OF RATIO FROM CONVERSIONS
C
      READ(5,5) AKD1,AKP1,AKTC1,AKTD1,AKFM1,AKFS1
      READ(5,6) AKD2,AKP2,AKTC2,AKTD2,AKFM2,AKFS2
      READ(5,6) TAU,FI,H
      READ(5,5) B0,B1,B2,B3,B4,B5,B6,B7
      WRITE(6,8) B0,B1,B2,B3,B4,B5,B6,B7
      READ(5,1)  NCPP,NTP
      PRINT 50,  NCPP,NTP,H
C
      READ(5,1) N
      DO 100 IJ=1,N
      READ(5,1) RUN,DATE
      READ(5,6)  TE,SMO,CO,S
      READ(5,5) AX1,AX2
      PRINT 12
      PRINT 2, RUN,DATE
      PRINT 11
      PRINT 47
      PRINT 48, TE,SMO,CO,S,FI
      PRINT 8,  AX1,AX2
      AKD=AKD1*EXP(-AKD2/TE)
      AKP=AKP1*EXP(-AKP2/TE)
      AKTC=AKTC1*EXP(-AKTC2/TE)
C
      S1=S+1.0
      D1=ALOG10(S1)
      D2=ALOG10(TE)
      PRINT 30, AKP,AKD,AKDTH,AKTC
      PRINT 20
C
      I=0.0
      J=1
      T1=0.0
      X1=0.0
      E1=1.0
      RATIO=1.0
      C3=-AKD/2.0
      WRITE(6,31) T1,X1,AKTC   ,   RATIO,FT
  150 READ(5,6) T,X,CTER
      READ(5,9) PF,WN,WM,VIS
   10 I=I+1
      T2=T1+H
      X2=1.0-EXP(T2*(AX1+AX2*T2))
      C1=ALOG((1.0-X1)/(1.0-X2))
      C2=2.0*AKP*SQRT(2.0*CO/AKD)
      E2=EXP(C3*T2)
      FT12=C1/(C2*(E1-E2))
      FT=FT12*FT12
      T1=T2
      X1=X2
      E1=E2
      IF (ABS(T-T1).LE.100.0) GO TO 200
      IF (I.LT.NCPP) GO TO 10
      RATIO=FI/(AKTC *FT)
      AKTCEX=FI/FT
      WRITE(6,31) T1,X1,AKTCEX,   RATIO,FT
```

```
      I=0
      J=J+1
      IF (J.LT.NTP) GO TO 10
      IF (CTER.LT.0.001) GO TO 150
      GO TO 100
C
  200 D3=ALOG10(1.0-PF)
      D4=D3*D3
      D5=D4*D3
      D6=ALOG10(WN)
      D7=ALOG10(WM)
      VLG=B0+B1*D1+B2*D2+B3*D3+B4*D4+B5*D5+B6*D6+B7*D7
      VCAL=10.0**VLG
      V1=VCAL+1.0
      RATIO=FI/(AKTC *FT)
      AKTCEX=FI/FT
      PRINT 21, T,T1,X,X1,AKTCEX,RATIO,PF,WM,VIS,VCAL,FT
      IF (RATIO.GE.1.0) RATIO=1.0
      WRITE(7,7) V1,RATIO
      I=0
      J=J+1
      IF (CTER.LT.0.001) GO TO 150
  100 CONTINUE
C
    1 FORMAT (3I10)
    2 FORMAT (1H ,20X,4H RUN,I5,10X,5H DATE,I10   )
    5 FORMAT (8E10.4)
    6 FORMAT (6F10.4)
    7 FORMAT (F10.2,5F10.4 )
    8 FORMAT (1H0, 5E20.5/)
    9 FORMAT (20X,4F10.4)
   11 FORMAT (1H0,131(1H*) //)
   12 FORMAT (1H1,131(1H*)// )
   20 FORMAT (1H0,3X,2H T,6X,3H T1,10X,2H X, 11X,3H X1, 9X,5H AKTC,
     2  9X,5HRATIO, 8X,3H PF, 8X,3H MW,6X,11H V-MEASURED,3X,7H V-CALC,
     3 7X, 3H FT //)
   21 FORMAT (1H ,2F9.0,F11.4,F11.4,E14.4,2F12.4,3F12.2,E14.4 )
   30 FORMAT (1H0,5H AKP=,E15.5,5X,5H AKD=,E15.5,3X,7H AKDTH=,E15.5,
     2  4X,6H AKTC=,E15.5    //)
   31 FORMAT (1H , 9X,F9.0,11X,F11.4,E14.4,F12.4, 48X  ,E14.4 )
   47 FORMAT(//6X,4HTEMP,4X,8HMON CONC,2X,8HCAT CONC,2X,8HSOL CONC,2X,
     1 8H CAT EFF  /)
   48 FORMAT (1H , 6F10.4///)
   50 FORMAT (1H0, 27H CALCULATION / PRINT-OUT IS,I5,5X,
     2 17H NO. PRINT-OUT IS,I5,5X,13H STEP SIZE IS,F10.0,5H SEC. /)
   90 FORMAT (1H0,5H TAU=,F10.4,19X,6HBULKM=,F10.4,11X,4HCOR=,F10.4 //)
C
  500 STOP
      END

                                       CD TOT   0108
```

```
$IBFTC BATC10
C
C     ******************************************************************
C     BATCH STIRRED-TANK REACTOR MODEL - HIGH CONVERSIONS
C     CALCULATION FOR CONVERSIONS AND MOLECULAR WEIGHT DISTRIBUTIONS
C     STEADY-STATE FREE RADICAL CONCENTRATION ASSUMED
C     ******************************************************************
C
      DIMENSION PR(4000),PFRAC(200),MM(20),P(4000),Q(4000)
      DIMENSION X(200),T(200),U(200),Z(200),Z2(200),Z3(200),Z4(200)
      DIMENSION Z5(200),Z1(200),Z6(200)
C
      READ(5,5) AKD1,AKP1,AKTC1,AKTD1,AKFM1,AKFS1
      READ(5,6) AKD2,AKP2,AKTC2,AKTD2,AKFM2,AKFS2
      READ(5,5) AF0,AF1,AF2
      READ(5,5) AR0,AR1,AR2
      READ(5,5) AV0,AV1,AV2,AV3,AV4,AV5,AV6,AV7
C     AF1,AR1,AV1'S ARE CO-EFFICIENTS TO CALC. F/FI,RATIO,VIS
      PRINT 9,  AF0,AF1,AF2
      PRINT 9,  AR0,AR1,AR2
      PRINT 9,  AV0,AV1,AV2,AV3,AV4,AV5,AV6,AV7
      READ(5,1) NCASE
C
      DO 500 IJ=1,NCASE
      READ(5,1) NEXPT
      READ(5,6)  TE,SMO,CO,S
      READ(5,6) TAU,CL,FI,FN,DELT
C
      AKD=AKD1*EXP(-AKD2/TE)
      AKP=AKP1*EXP(-AKP2/TE)
      AKTC=AKTC1*EXP(-AKTC2/TE)
      AKTD=AKTD1*EXP(-AKTD2/TE)
      AKFM=AKFM1*EXP(-AKFM2/TE)
      AKFS=AKFS1*EXP(-AKFS2/TE)
C
C     CORRECTION FOR EFFECTS OF DILUTION WITH SOLVENT
C           -- G.H.OLIVE N S.OLIVE (1966)
C
      BULKM=8.450-(TE-323.0)*0.0085
      TERM=(SMO+TAU*S)/BULKM
      COR=TERM*TERM
      AKTC=AKTC*COR
      AKT=AKTC
C
      PRINT 73
      PRINT 2, NEXPT
      PRINT 72
      PRINT 47
      PRINT 48, TE,SMO,CO,S,FI,FN,DELT
      PRINT 90, TAU,BULKM,COR
      PRINT 49
      PRINT 50,AKD,AKTD,AKTC,AKFM,AKFS,AKP
C
      S1=S+1.0
      BV1=ALOG10(S1)
      BV2=ALOG10(TE)
      T1=0.0
      X1=0.0
      X(1) = 0.0
```

```
      T(1) = 0.0
      VCAL=0.0
      PFRAC(1)=0.0
      RATIO=1.0
      FFI=1.0
      F=FI
      FT=F/(AKTC+AKTD)
      INTI=DELT/60.0
      DO 30 J=1,4000
      PR(J)=0.0
   30 CONTINUE
      C1=SQRT(2.0*AKD*CO)
      C3=AKP*SMO
      C4=AKFM*SMO
      C5=AKFS*S
      D1=EXP(-AKD*DELT/2.0)
      D2=2.0*AKP*SQRT(2.0*CO/AKD)
      D4=1.0
      Z(1)=1.0
C
      READ(5,1) N
      READ(5,1) (MM(JL),JL=1,N)
C     MM(JL) MUST BE IN INCREASING TIME INTERVAL FROM 1 TO N
C
      JL=0
      I=1
  400 JL=JL+1
      LN=MM(JL)
      PRINT 70
      PRINT 71, LN,INTI
      PRINT 72
      PRINT 51
      PRINT 52,X(I),Z(I),T(I),PFRAC(I),AKTC,F,RATIO,FFI,VCAL
   10 I=I+1
C
C     CALCULATION OF CONVERSION BY ANALYTICAL SOLUTION
C
      D3=ALOG(1.0-X1)
      D5=D4*D1
      D6=SQRT(FT)
      X2=1.0-EXP(D3+D2*D6*(D5-D4))
      D4=D5
      X1=X2
      T1=T1+DELT
      X(I)=X1
      T(I)=T1
      PFRAC(I)=(SMO*X(I)*104.15)/(SMO*104.15+S*92.13)
C
C     CALCULATION OF PROPAGATION PROBABILITY
C
      C2=C1*SQRT(F*(AKTC+AKTD))
      Z1(I)=1.0-X(I)
      Z2(I)=D4
      Z3(I)=C5+C4*Z1(I)
      Z4(I)=C3*Z1(I)
      Z5(I)=C2*Z2(I)
      Z(I)=Z4(I)/(Z4(I)+Z3(I)+Z5(I))
      PRINT 52,X(I),Z(I),T(I),PFRAC(I),AKTC,F,RATIO,FFI,VCAL
```

```
      IF (X(I).GE.0.99) GO TO 500
      IF (I.GE.LN) GO TO 12
      GO TO 13
   12 PRINT 53
C
C     CALCULATION OF MOL WTS BY TRAP RULE
C
   13 SPR = 0.0
      SRPR = 0.0
      SRRPR = 0.0
      SRRRPR=0.0
      WR=0.0
      SWR=0.0
      RCL=0.0
      DO 15 L=1,4000
      R=L
      C6=R-1.0
      IF (I.GT.2) GO TO 25
      Z6(1)=C1*D6*Z2(1)
      P(L)=Z6(1)*(1.0-Z(1))*(Z(1)**C6)*(Z3(1)+Z6(1)*C6*AKTC*(Z3(1)+
     1 Z5(1))/(2.0*Z4(1)))
   25 Z6(I)=C1*D6*Z2(I)
      Q(L)=Z6(I)*(1.0-Z(I))*(Z(I)**C6)*(Z3(I)+Z6(I)*C6*AKTC*(Z3(I)+
     1 Z5(I))/(2.0*Z4(I)))
      D=DELT*(P(L)+Q(L))/2.0
      P(L)=Q(L)
      PR(L)=PR(L)+D
      SPR=SPR+PR(L)
      SRPR=SRPR+R*PR(L)
      SRRPR=SRRPR+R*R*PR(L)
      SRRRPR=SRRRPR+PR(L)*R*R*R
      APWR=R*PR(L)/(SMO*X(I))
      IF (APWR.LE.1.0E-09 .AND. L.GE. 1500 ) GO TO 22
   15 CONTINUE
   22 IF (I.LT.LN) GO TO 250
      DO 20 L=1,4000
      R=L
      WR=R*PR(L)/SRPR
      SWR=SWR+WR
      IF (WR.LE.1.0E-08 .AND. L.GE.1500 ) GO TO 250
      IF (R-RCL) 20,16,16
   16 PRINT 54, SWR,WR,R
      RCL=RCL+CL
   20 CONTINUE
C
  250 RAV = SRPR/SPR
      RAVMW=RAV*104.15
      WAV = SRRPR/SRPR
      WAVMW=WAV*104.15
      ZAV=SRRRPR/SRRPR
      ZAVMW=ZAV*104.15
      RAT=WAV/RAV
C
C     NOW , AKTC IS ADJUSTED BASED ON CALCULATED VISCOSITY
C
      PF1=1.0-PFRAC(I)
      BV3=ALOG10(PF1)
      BV4=BV3*BV3
```

```
      BV5=BV4*BV3
      BV6=ALOG10(RAV)
      BV7=ALOG10(WAV)
      VLG=AV0+AV1*BV1+AV2*BV2+AV3*BV3+AV4*BV4+AV5*BV5+AV6*BV6+AV7*BV7
      VCAL=10.0**VLG
      VN1=VCAL+1.0
      CV1=ALOG10(VN1)
      CV2=CV1*CV1
      RLG=AR0+AR1*CV1+AR2*CV2
      FLG=AF0+AF1*CV1+AF2*CV2
      RATIO=10.0**RLG
      FFI=10.0**FLG
      F=FFI*FI
      IF (F.GE.FN) GO TO 225
      F=FN
      FFI=FN/FI
  225 AKTC=AKT*RATIO*FFI
      IF (AKTC.GE.AKT) AKTC=AKT
      FT=F/AKTC
      IF (I.LT.LN) GO TO 10
C
  200 PRINT 54, SWR, WR, R
      PRINT 55
      PRINT 56,SPR,SRPR,SRRPR,RAV,WAV,ZAV
      PRINT 57, RAV
      PRINT 58, RAVMW
      PRINT 59, WAV
      PRINT 60, WAVMW
      PRINT 61, ZAVMW
      PRINT 62,ZAV
      PRINT 63, RAT
      IF (JL.GE.N) GO TO 500
      GO TO 400
  500 CONTINUE
C
    1 FORMAT (8I10)
    2 FORMAT (30X,12H EXPT NUMBER, I5 / )
    5 FORMAT (8E10.4)
    6 FORMAT (8F10.4)
    7 FORMAT (3F20.8)
    8 FORMAT (5F10.4,I10)
    9 FORMAT (1H0,9E14.5 /)
   47 FORMAT(//1H , 8X,5H TEMP,6X,9H MON CONC,6X,9H CAT CONC,6X,
     29H SOL CONC,10X,3H FI,12X,3H FN,10X,5H DELT  /)
   48 FORMAT (1H , 7F15.5 ///)
   49 FORMAT(9X,3HAKD,11X,4HAKTD,11X,4HAKTC,11X,4HAKFM,11X,4HAKFS,12X,
     1 3HAKP/)
   50 FORMAT(1H 6E15.5///)
   51 FORMAT(6X,10HCONVERSION,4X,11HPROBABILITY,6X,9HTIME(SEC),
     2 2X,14H POLY FRACTION, 6X,5H AKTC,10X,4H EFF, 8X,6H RATIO, 9X,
     3 5H F/FI, 9X,5H VCAL //)
   52 FORMAT(1H 2F15.9,2F14.4, E14.4,3F14.5,F14.1 )
   53 FORMAT (///1X,19HCUM WEIGHT FRACTION,8X,15HWEIGHT FRACTION,6X,
     1 12HCHAIN LENGTH/  )
   54 FORMAT (1H 1F16.9,1F23.9,1F18.2   )
   55 FORMAT(////13X,3HSPR,15X,4HSRPR,13X,5HSRRPR,14X,3HRAV,14X,3HWAV,
     1 14X,3HZAV/)
   56 FORMAT(1H 6F18.6// )
```

```
57 FORMAT (35H THE NUMBER AVERAGE CHAIN LENGTH IS, F10.2,2X,
  1 14H MONOMER UNITS//)
58 FORMAT (39H THE NUMBER AVERAGE MOLECULAR WEIGHT IS,F10.2//)
59 FORMAT (35H THE WEIGHT AVERAGE CHAIN LENGTH IS, F10.2,2X,
  1 14H MONOMER UNITS//)
60 FORMAT (39H THE WEIGHT AVERAGE MOLECULAR WEIGHT IS,F10.2//)
61 FORMAT (34H THE Z AVERAGE MOLECULAR WEIGHT IS,F10.2,2X,
  1 14H MONOMER UNITS//)
62 FORMAT (32H THE ZEE AVERAGE CHAIN LENGTH IS, F8.2,2X,
  1 14H MONOMER UNITS//)
63 FORMAT (46H THE WEIGHT AVERAGE TO NUMBER AVERAGE RATIO IS,F5.2///)
70 FORMAT (1H1,131(1H*)//)
71 FORMAT (36H CALCULATION FOR REACTION TIME OF  (,1I4, 8H - 1 ) *,
  2 I5,8H MINUTES/)
72 FORMAT (1H0,131(1H*)//)
73 FORMAT (1H1,131(1H*)//)
80 FORMAT (F10.4)
85 FORMAT (1H0,10X,5E20.5 //)
90 FORMAT (1H0,5H TAU=,F10.4,5X,7H BULKM=,F10.4,5X,5H COR=,F10.4//)
C
   STOP
   END

                            CD TOT   0255
```

```
$IBFTC BATC2A
C
C     ******************************************************************
C     BATCH STIRRED-TANK REACTOR MODEL - LOW  CONVERSIONS
C     CALCULATION FOR CONVERSIONS AND MOLECULAR WEIGHT DISTRIBUTIONS
C     STEADY-STATE FREE RADICAL CONCENTRATION ASSUMED
C     REFERENCE - K. TEBBENS M.ENG. THESIS(1966)
C     ******************************************************************
C
      DIMENSION PR(4000),PFRAC(200),MM(20),P(4000),Q(4000)
      DIMENSION X(200),T(200),      Z(200),Z2(200),Z3(200),Z4(200)
      DIMENSION Z5(200),Z1(200),Z6(200)
C
      READ(5,5) AKD1,AKP1,AKTC1,AKTD1,AKFM1,AKFS1
      READ(5,6) AKD2,AKP2,AKTC2,AKTD2,AKFM2,AKFS2
      READ(5,1) NCASE
C
      DO 500 IJ=1,NCASE
      READ(5,1) NEXPT,N,NPNT
      READ(5,6)  TE,SMO,CO,S
      READ(5,6) TAU,CL,F,DELT
C
      AKD=AKD1*EXP(-AKD2/TE)
      AKP=AKP1*EXP(-AKP2/TE)
      AKTC=AKTC1*EXP(-AKTC2/TE)
      AKTD=AKTD1*EXP(-AKTD2/TE)
      AKFM=AKFM1*EXP(-AKFM2/TE)
      AKFS=AKFS1*EXP(-AKFS2/TE)
C
C     CORRECTION FOR EFFECTS OF DILUTION WITH SOLVENT
C           -- G.H.OLIVE N S.OLIVE (1966)
C
      BULKM=8.450-(TE-323.0)*0.0085
      TERM=(SMO+TAU*S)/BULKM
      COR=TERM*TERM
      AKTC=AKTC*COR
      AKT=AKTC
C
      PRINT 73
      PRINT 2, NEXPT
      PRINT 72
      PRINT 47
      PRINT 48, TE,SMO,CO,S,F,DELT,N
      PRINT 90, TAU,BULKM,COR
      PRINT 49
      PRINT 50,AKD,AKTD,AKTC,AKFM,AKFS,AKP
C
      X(1)=0.0
      T(1)=0.0
      PFRAC(1)=0.0
      NPI=1800.0/DELT
      INTI=DELT/60.0
      DO 30 J=1,4000
      PR(J)=0.0
   30 CONTINUE
      C1=2.0*F*AKD*CO*(AKTC+AKTD)
      C2=2.0*F*AKD*CO/(AKTC+AKTD)
      C3=AKP*SMO
      C4=AKFM*SMO
```

```
      C5=AKFS*S
      D1=SQRT(C1)
      D2=SQRT(C2)
      D3=2.0*AKP*D2/AKD
      D4=EXP(-AKD*DELT/2.0)
      Z1(1)=1.0
      Z2(1)=1.0
      Z3(1)=C5+C4
      Z4(1)=C3
      Z5(1)=D1
      Z(1)=C3/(C3+C5+C4+D1)
      PRINT 51
C
C     CALCULATION OF CONVERSION BY ANALYTICAL SOLUTION
C
      DO 10 I=2,N
      Z2(I)=Z2(I-1)*D4
      X(I)=1.0-EXP(D3*(Z2(I)-1.0))
      T(I)=T(I-1)+DELT
      PFRAC(I)=(SMO*X(I)*104.15)/(SMO*104.15+S*92.13)
C
C     CALCULATION OF PROPAGATION PROBABILITY
C
      Z1(I)=1.0-X(I)
      Z3(I)=C5+C4*Z1(I)
      Z4(I)=C3*Z1(I)
      Z5(I)=D1*Z2(I)
      Z(I)=Z4(I)/(Z4(I)+Z3(I)+Z5(I))
      IF (X(I).GE.0.99) GO TO 11
   10 CONTINUE
   11 DO 12 I=1,N,NPI
      PRINT 52,X(I),Z(I),T(I),PFRAC(I)
   12 CONTINUE
C
      READ(5,1) (MM(JL),JL=1,NPNT )
C     MM(JL) MUST BE IN INCREASING TIME INTERVAL FROM 1 TO N
C
      JL=0
      I=1
  400 JL=JL+1
      LN=MM(JL)
      PRINT 70
      PRINT 71, LN,INTI
      PRINT 72
C
C     CALCULATION OF MOL WTS BY TRAP RULE
C
      SPR = 0.0
      SRPR = 0.0
      SRRPR = 0.0
      SRRRPR=0.0
      WR=0.0
      SWR=0.0
      RCL=0.0
   35 I=I+1
      DO 15 L=1,4000
      R=L
      C6=R-1.0
```

```
      IF (I.GT.2) GO TO 25
      Z6(1)=D2*Z2(1)
      P(L)=Z6(1)*(1.0-Z(1))*(Z(1)**C6)*(Z3(1)+Z6(1)*C6*AKTC*(Z3(1)+
     1 Z5(1))/(2.0*Z4(1)))
   25 Z6(I)=D2*Z2(I)
      Q(L)=Z6(I)*(1.0-Z(I))*(Z(I)**C6)*(Z3(I)+Z6(I)*C6*AKTC*(Z3(I
     1 Z5(I))/(2.0*Z4(I)))
      D=DELT*(P(L)+Q(L))/2.0
      P(L)=Q(L)
      PR(L)=PR(L)+D
      IF (L .LT. 1500) GO TO 14
      APWR=R*PR(L)/(SMO*X(I))
      IF (APWR .LE. 1.0E-09) GO TO 22
   14 IF (I.LT.LN) GO TO 15
      SPR=SPR+PR(L)
      SRPR=SRPR+R*PR(L)
      SRRPR=SRRPR+R*R*PR(L)
      SRRRPR=SRRRPR+PR(L)*R*R*R
   15 CONTINUE
   22 IF (I.LT.LN) GO TO 35
C
      DO 20 L=1,4000
      R=L
      WR=R*PR(L)/SRPR
      SWR=SWR+WR
      IF (WR.LE.1.0E-08 .AND. L.GE.1500 ) GO TO 250
      IF (R-RCL) 20,16,16
   16 PRINT 54, SWR,WR,R
      RCL=RCL+CL
   20 CONTINUE
  250 RAV = SRPR/SPR
      RAVMW=RAV*104.15
      WAV = SRRPR/SRPR
      WAVMW=WAV*104.15
      ZAV=SRRRPR/SRRPR
      ZAVMW=ZAV*104.15
      RAT=WAV/RAV
C
  200 PRINT 54, SWR, WR, R
      PRINT 55
      PRINT 56,SPR,SRPR,SRRPR,RAV,WAV,ZAV
      PRINT 57, RAV
      PRINT 58, RAVMW
      PRINT 59, WAV
      PRINT 60, WAVMW
      PRINT 61, ZAVMW
      PRINT 62,ZAV
      PRINT 63, RAT
      IF (JL.GE.NPNT) GO TO 500
      GO TO 400
  500 CONTINUE
C
    1 FORMAT (8I10)
    2 FORMAT (30X,12H EXPT NUMBER, I5 / )
    5 FORMAT (8E10.4)
    6 FORMAT (8F10.4)
    7 FORMAT (3F20.8)
    8 FORMAT (5F10.4,I10)
```

```
    9 FORMAT (1H0,9E14.5 /)
   47 FORMAT(//1H , 8X,5H TEMP,8X,9H MON CONC,6X,9H CAT CONC,6X,
     29H SOL CONC,10X,3H F ,10X,5H DELT,6X, 9HTOTAL INC /)
   48 FORMAT (1H , 6F15.4 , I12 ///)
   49 FORMAT(9X,3HAKD,11X,4HAKTD,11X,4HAKTC,11X,4HAKFM,11X,4HAKFS,12X,
     1 3HAKP/)
   50 FORMAT(1H 6E15.5///)
   51 FORMAT(6X,10HCONVERSION,4X,11HPROBABILITY,6X,9HTIME(SEC),
     2 3X,14H POLY FRACTION/)
   52 FORMAT(1H 2F15.9,2F15.4    )
   53 FORMAT (///1X,19HCUM WEIGHT FRACTION,8X,15HWEIGHT FRACTION,6X,
     1 12HCHAIN LENGTH/   )
   54 FORMAT (1H 1F16.9,1F23.9,1F18.2   )
   55 FORMAT(////13X,3HSPR,15X,4HSRPR,13X,5HSRRPR,14X,3HRAV,14X,3HWAV,
     1 14X,3HZAV/)
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     1 14H MONOMER UNITS//)
   62 FORMAT (32H THE ZEE AVERAGE CHAIN LENGTH IS, F8.2,2X,
     1 14H MONOMER UNITS//)
   63 FORMAT (46H THE WEIGHT AVERAGE TO NUMBER AVERAGE RATIO IS,F5.2///)
   70 FORMAT (1H1,131(1H*)//)
   71 FORMAT (36H CALCULATION FOR REACTION TIME OF  (,1I4, 8H - 1 ) *,
     2 I5,8H MINUTES/)
   72 FORMAT (1H0,131(1H*)//)
   73 FORMAT (1H1,131(1H*)//)
   80 FORMAT (F10.4)
   85 FORMAT (1H0,10X,5E20.5 //)
   90 FORMAT (1H0,5H TAU=,F10.4,5X,7H BULKM=,F10.4,5X,5H COR=,F10.4//)
C
      STOP
      END

                                 CD TOT   0213
```