FREE-RADICAL
POLYMERIZATION OF STYRENE
IN A
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By

KLAAS TEBBENS, B.Sc. Chem. Eng.

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AUTHOR: Klaas Tebbens, B. Sc. Chem. Eng. (University of Saskatchewan)

SUPERVISORS: Dean J. W. Hodgins and Dr. A. E. Hamielec

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SCOPE AND CONTENTS: Several concentrations of styrene in benzene were polymerized at various temperatures and catalyst (Azo) concentrations in a small, isothermal, stirred batch reactor. Using the steady-state assumption, the differential rate equations predicting conversion of the monomer and the molecular-weight distribution of the resulting polymer were solved on the IBM 7040 digital computer. Experimental batches were prepared, and conversion and molecular weight distribution determined; for the latter analysis, the Gel Permeation Chromatograph was employed.

Good agreement between theoretically predicted and experimentally measured conversion can be obtained, provided the catalyst efficiency is adjusted according to the monomer concentration. Agreement for molecular-weight distributions also is good except for bulk polymerization and the results suggest that the rate constants rather than the catalyst efficiency are monomer-concentration dependent.

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NOMENCLATURE

C	Catalyst concentration - gm. moles/l
C_o	Initial catalyst concentration
DP	Degree of polymerization
f	Catalyst initiation efficiency (See Appendix 1.1)
I	Rate of initiation or rate of formation of R_1^o
k_p	Rate of propagation constant - l./gm.mole-second
k_t	Rate of termination constant - l./gm.mole-second
k_{tc}	Rate constant for termination by combination
k_{td}	Rate constant for termination by disproportionation
k_{fs}	Rate constant for chain transfer to solvent - l./gm.mole-second
k_{fm}	Rate constant for chain transfer to monomer - l./gm.mole-second
k_d	Rate of catalyst decomposition constant - seconds $^{-1}$
k_R	Rate constant for catalyst wastage reaction within a cage - seconds $^{-1}$
k_X	Rate constant for monomer initiation - l./gm.moles-seconds
k_D	Rate of diffusion constant - seconds $^{-1}$
k_R'	Rate constant for catalyst wastage reaction between catalyst radicals outside a cage - l./gm.mole-seconds
M	Monomer (styrene) concentration - gm.moles/l.
M_o	Initial monomer concentration
M^o	Monomer free radical concentration - gm.moles/l.
ΔM	Total amount of monomer consumed

$\bar{M}_n$	Number average molecular-weight
$\bar{M}_w$	Weight average molecular-weight
N	Number of monomer-polymer particles per cm^3 of reaction mixture
PG	Polyglycol standard
P_r	Concentration of dead polymer molecules containing r monomer units - gm.moles/l.
PS	Polystyrene standard
Q	Wastage product in recombination of catalyst fragments within a cage
R_c^o	Catalyst free radical fragment or concentration - gm.moles/l.
R_1^o	Polymer free radical or concentration containing one monomer unit - gm.moles/l.
R_r^o	Polymer free radical or concentration containing r monomer units
R^o	Total free radical concentration - gm.moles/l.
S	Solvent concentration - gm.moles/l.
S^o	Solvent free radical concentration - gm.moles/l.
R_p	Rate of polymerization - gm.moles/l.-second
R_t	Rate of termination - gm.moles/l.-second
R_i	Rate of initiation - gm.moles/l.-second
$\bar{r}$	Number average chain length
$\bar{r}_w$	Weight average chain length
$\bar{r}_z$	Z average chain length
$\bar{W}_r$	Weight fraction of polymer having chain length r
X	Fractional conversion or catalyst wastage product
ζ	Probability factor

ρ Rate of free radical generation from catalyst

APPENDIX

1. ABSTRACT

The free radical polymerization of styrene in benzene using azo-bisisobutyronitrile as a catalyst has been studied both theoretically and experimentally. The molecular-weight distribution and conversion are predicted on the basis of a simplified kinetic mechanism, neglecting a number of minor side reactions. The steady-state assumption is investigated and is shown to be applicable in the case of styrene polymerization, a pseudo-steady-state being reached in less than one second. Using the steady-state approach a relatively simple kinetic model is obtained, suitable for computer simulation. The prime variables consist of the ordinary reaction conditions such as monomer concentration, solvent concentration, catalyst concentration, reaction temperature and reaction time.

The polymerization was carried out isothermally in a stirred batch reactor from which samples were abstracted at various time intervals. Conversion was determined by precipitating the polymer with methanol, filtering, and weighing, and the molecular-weight distribution has been obtained by gel-permeation chromatography. A computer program was written to interpret the variation of refractive index with respect to the elution volume trace from the chromatograph, giving a readout of molecular chain length in monomer units versus weight fraction.

The experimentally obtained conversion and distribution curves are compared with those obtained from the mathematical model. Except for bulk polymerization agreement between the two is good. Good agreement for conversion is obtained for all cases if the catalyst initiation efficiency is adjusted according to the monomer or solvent concentration. However, the same considerations do not give good agreement for molecular-weight distribution. Rather it appears that the rate constants instead of the catalyst efficiency are monomer or solvent concentration dependent, which would explain the discrepancies.

2. INTRODUCTION

Polymer chemistry became of major importance at the beginning of the second world war with the enormous demand for synthetic rubbers. During the 1950's a large amount of polymer research was done, especially on kinetic mechanisms and average-molecular-weight studies with the polymerization of styrene being of particular interest. Styrene kinetics are now fairly well established and for this reason styrene was selected as a suitable monomer for the present exploratory study.

The statistics relating molecular-weight distributions in vinyl polymers to the reaction mechanism have been well worked out, especially for solution polymerization. However, the solution of the resulting differential equations in many cases has proved to be very complex. The introduction of high-speed digital computers has made it possible though to solve a number of these equations which in part justifies this re-examination.

Another reason for undertaking this study was the recent development of gel-permeation chromatography as a means of measuring molecular-weight distributions of polymers. It is a relatively simple and fast method making a study of the field more attractive than older methods did.

Both the conversion and molecular-weight distribution are of particular interest to the chemical engineer because they are greatly affected by the reactor design and such variables as hold-up time, reactant concentrations, and temperature. The molecular-weight and its distribution in turn may affect the physical characteristics of the final product, making it a prime variable that should be controlled.

In the present study the solution and bulk polymerization of styrene is carried out isothermally in a batch reactor and conversion and molecular-weight distribution of the resulting high polymers are determined and compared with theoretically calculated values. Reasonable agreement between the two is obtained and any deviation is shown to be likely due to variations in rate constants rather than the selection of an inadequate or wrong mathematical model.

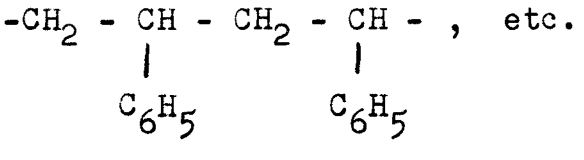
3. HISTORICAL BACKGROUND

High polymers consist of long chains of monomer molecules held together by covalent bonds. Yet this picture was not accepted until about 1930 and even then some contrary viewpoints still existed. The modern concept of high polymers required that appropriate means had to be provided for elucidating their macromolecular structures, and for establishing relationships between the structures so evaluated and their physical and chemical properties.

The term colloid meaning "gluelike" was first coined by Thomas Graham[1] in 1861, who called attention to the very slow rates of diffusion of certain polymers in solution. The concept of a colloidal state of matter was introduced later and in particular by W. Ostwald[2]. The early concept of a colloid was that virtually any substance may be rendered into a colloidal state, a colloidal solution being defined as one in which the dispersed particle comprises many molecules. However, the implied converse, that a colloid always reverts back to a crystalloid structure without chemical change is not true. Cellulose and polystyrene are typical colloids according to the early definition but cannot be disaggregated by any process corresponding to a physical change of state. Thus the colloidal concept of polymers is inadequate, yet for many years investigators were unaware of the distinction.

The first means of determining molecular weight of polymeric substances became available because of the work of van't Hoff[3] in the formulation of solution laws and Raoult[4] who developed the cryoscopic method for determining the molecular weight of dissolved substances. In 1881 Musculus and Meyer[5] measured the rate of diffusion of starch and dextrin to determine whether they were isomeric or polymeric forms of simple sugars and concluded that dextrin molecules must be much larger than those of sugars. However, in 1881 Brown and Morris[6] used Raoult's method to answer the same questions. Similar experiments were made with cellulose and natural rubbers and although the molecular weight thus obtained was considerably in error compared with that obtained by modern techniques, it did suggest the concept of a molecule containing hundreds of repeat units. Nevertheless, the mechanism as to how these large molecules were held together was not understood, the most popular concept being that basic simple molecules were loosely held together by association forces. This viewpoint was strenthened by the elucidation of Van der Waal's forces, and the subsequent interest in this subject.

Not until 1920 was the above concept seriously challenged in a paper by Staudinger[7]. He proposed the first chain formula for polystyrene,



$$-CH_2 - \underset{\underset{C_6H_5}{|}}{CH} - CH_2 - \underset{\underset{C_6H_5}{|}}{CH} - \text{ , etc.}$$

which is accepted today. Yet his views were not widely accepted until about 1929 after the work of Carothers[8]. The object of his research was to prepare polymeric molecules of definite structures through the use of established reactions and to investigate how the properties of these substances depend on their constitution.

As soon as the covalent chain concept took hold the first application of statistical methods to a polymer problem was published by Kuhn[9], who derived formulas expressing the molecular-weight distribution in degraded cellulose on the assumption that splitting of bonds between repeat units occurs at random. The statistical approach to molecular composition now plays a major role in the assessment of molecular-weight distributions and the physical properties of polymers.

The quantitative evaluation of a polymer's constitution is a necessary counterpart of the theoretical approach, and could not take place until methods for quantitative characterization of polymer structures had been established. In particular, measurement of correct molecular weights played an important part. Associated with this is the related problem of measuring molecular-weight distributions. Staudinger[10] in particular must be credited for having developed a relationship between polymer molecular weight and its viscosity in dilute solutions.

The idea that polymers are heterogeneous and therefore that two different polymers could have the same molecular weight led to a number of fractionation methods. Fractional precipitation was first used for the purpose of purification of rubber by Caspari[11] in 1913 and it was quickly adopted with respect to cellulose and various synthetic polymers by Staudinger and co-workers. Fractional solution was first introduced by Craik and Miles[12] in 1931 and it is at present the most widely used.

Sedimentation methods also have become of prime importance, particularly since the development of the ultracentrifuge. Much of the early work in developing this technique was done by Kraemer[13] who applied it to linear high polymers. Today the ultracentrifuge is considered to provide one of the best techniques available for molecular-weight distribution measurements.

Chromatographic adsorbtion was first studied by Mark and Saito[14] in 1936, however, without much success. Not until the commercialization of ion-exchange processes did new interest in this field develop. In their work on ion-exclusion (in the early fifties), Wheaton and Bauman[58] found that many nonionic substances of low molecular weight were separated through elution with water through a packed bed of ion-exchange resin particles. Lathe and Ruthven[59] showed that the separating range could be greatly extended by using swollen starch particles as a column packing, allowing differentiation between globulin and hemoglobulin having molecular-weights of 150,000 and 67,000 respectively. Moore[60] further extended this work to the separation of polymers in organic solvents by elution through columns packed with crosslinked polystyrene beads.

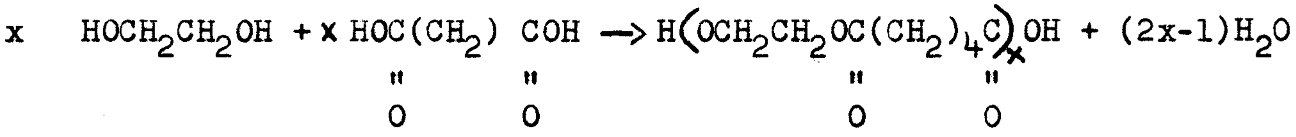
He showed that good separations of anionically prepared polystyrenes having molecular weights ranging from 13,850 to 3,500,000 could be obtained. Moore and Hendrickson[61] further applied this technique to measuring molecular weight distributions and this led to the manufacture of the gel-permeation chromatograph in 1964 which is now available commercially. Its principle of operation is based on the work by Moore and is discussed in detail in Section 6.3 and Appendix 4.

The gel-permeation chromatograph has a number of advantages over other methods, being easy to operate and subject to very few operating errors. A complete sample characterization can be obtained in about two hours and a number of samples can in part be run simultaneously further shortening the average time to about one half to one hour, depending on the type of impurities in the sample and the number of columns used. This compares very favorably with solution methods which may take as much as 24 hours per fraction. No great time savings is obtained compared with the ultracentufuge, however the latter is considered to be inadequate at molecular-weights lower than 100,000 whereas the gel-permeation chromatograph has its best performance in this region. The major disadvantage of the gel-permeation method is that it requires polymer standards having a very narrow molecular weight distribution of the material being investigated. Nevertheless, it has found widespread use largely, it is believed, because it is reasonable in cost and very useful as a qualitative tool.

4. THEORY OF POLYMERIZATION AND MOLECULAR-WEIGHT DISTRIBUTION

Polymerization in its broadest definition may be described as the addition of a random number of monomer units to one another to form a molecule of higher molecular-weight. The monomer units may add to form a continuous "straight" chain or they may form branches. Furthermore, there is no restriction as to the number of monomers uniting to form a macromolecule. Two, three or more different types of monomers may react together forming copolymers; thus a terpolymer is formed by the polymerization of three different monomers.

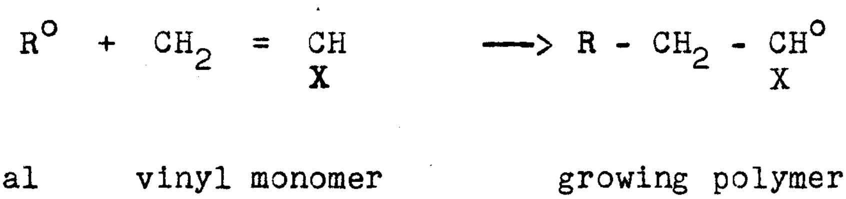
There are two basic types of polymerizations. These are known as condensation and addition polymerization. Condensation polymerization, which is also called step-reaction polymerization is analogous to the classical condensation reaction of low molecular weight compounds. The formation of polyethylene adipate is an example of condensation polymerization



$$x\ \ HOCH_2CH_2OH + x\ HO\underset{\overset{\|}{O}}{C}(CH_2)\ \underset{\overset{\|}{O}}{C}OH \rightarrow H\left(OCH_2CH_2O\underset{\overset{\|}{O}}{C}(CH_2)_4\underset{\overset{\|}{O}}{C}\right)_x OH + (2x-1)H_2O$$

ethylene glycol   adipic acid   polyethylene adipate

Addition or chain-reaction polymerization involves chain reactions with a chain carrier, called a free radical, consisting of an ion or other reactive intermediate having one unpaired electron. Free radicals are capable of adding to double bonds with one electron remaining unpaired:



$$R^{o} + CH_2 = \underset{X}{CH} \longrightarrow R - CH_2 - \underset{X}{CH^{o}}$$

In a very short time, usually a few seconds or less, numerous monomer units add to the growing chain and finally two growing radicals combine to stop each others growth, with the formation of a covalent bond from the two previously unpaired electrons.

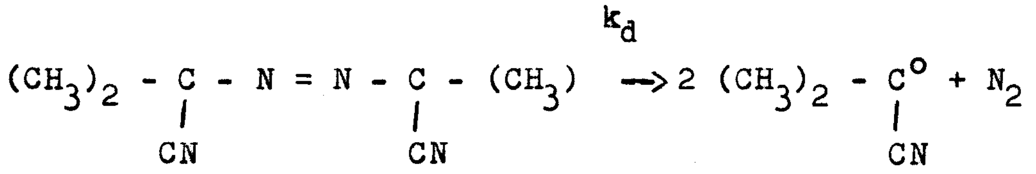
In the present treatise, the latter type of polymerization will be considered, using azobisiso butyronitrile as a free radical source and styrene as a monomer. Azo catalyst was chosen, because it exhibits no chain transfer (15). Styrene reactions have been extensively investigated thus allowing a fair degree of reliance on the literature for rate constants as well as comparison with other workers data.

4.1 Discussion of Reaction Mechanisms

In its most elementary form polymerization can be envisaged as consisting of three basic steps, initiation, propagation and termination. Usually, a fourth step, chain transfer, is considered but it may be looked upon as a termination step. Initiation involves the "slow" formation of free radicals, followed by a "rapid" growth process called propagation and finally a number of reactions causing cessation of growth, called termination.

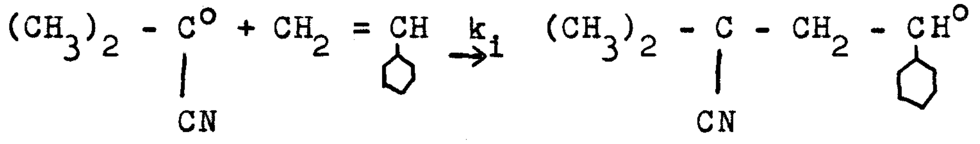
4.1.1 Initiation

Azobisisobutyronitrile decomposes into two free radical fragments with the elimination of nitrogen as follows (16)



$$(CH_3)_2 - \underset{CN}{C} - N = N - \underset{CN}{C} - (CH_3) \xrightarrow{k_d} 2\ (CH_3)_2 - \underset{CN}{C^{o}} + N_2$$

The rate of nitrogen elimination has been used as a quantitative measure of the rate of catalyst decomposition by various workers and compared with other methods (16). The free radical catalyst then reacts with monomer to form a growing polymer chain:



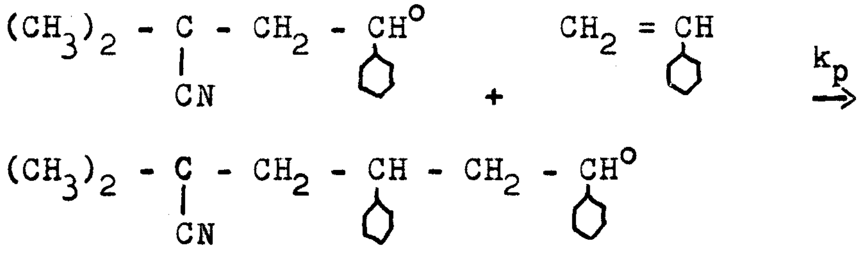
catalyst
radical monomer growing polymer radical

Usually k_d is very small compared with k_i and the normal procedure is to consider the catalyst decompostion as the initiation rate controlling step.

Often only a fraction of the catalyst free radicals succeeds in initiating a polymer chain, a phenomena which has been the subject of extensive investigation (17, 18).

4.1.2 Propagation

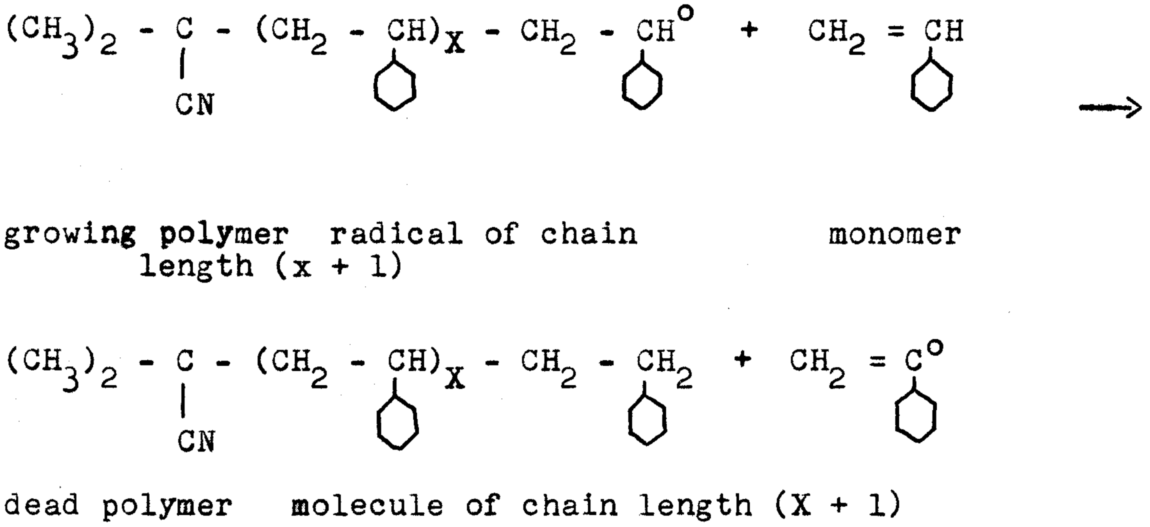
Propagation consists of the growing process of polymer free radicals through the addition of monomer units. In the case of styrene this can be shown as follows:



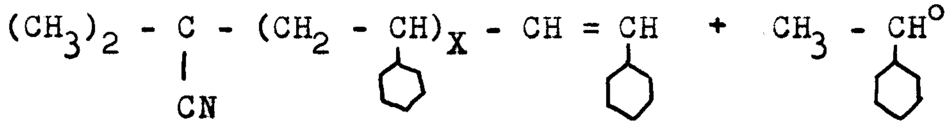
This process continues until no more monomer is available or until two growing chains react with one another.

4.1.3 Chain transfer

In the chain transfer process, the growing polymer chain acquires a hydrogen atom from some other source such as a monomer, solvent or catalyst molecules and then loses its free-radical property which is transferred to the other reacting substance. In the case of styrene and polystyrene radicals:



In the case of unsaturated molecules instead of transfer to a polymer molecule, it is possible to have transfer of a hydrogen from the polymer molecules leaving it with a double bond at one end, giving



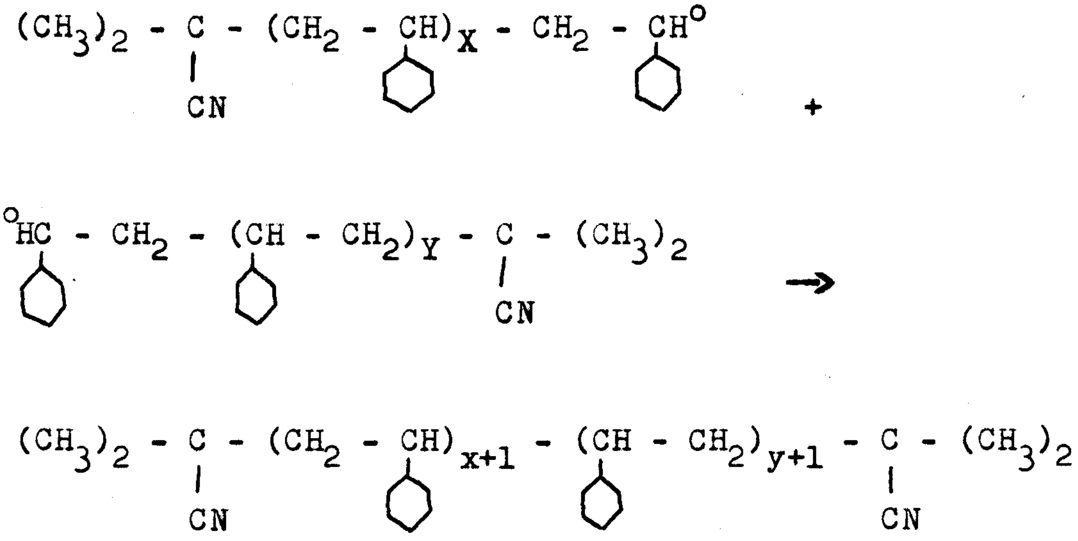
In this case it is conceivable that the double bond in the dead polymer chain will be subject to further attack from free radicals, re-initiating the chain. Then the transfer process can be considered as a terminating reaction without changing the free radical concentration.

4.1.4 Termination

Free radical reactions can be terminated in a number of ways. There are two termination mechanisms which are as follows:

A. Combination

Two free radicals combine to form one dead polymer molecule whose chain length is the sum of the chain lengths of the two free radicals.

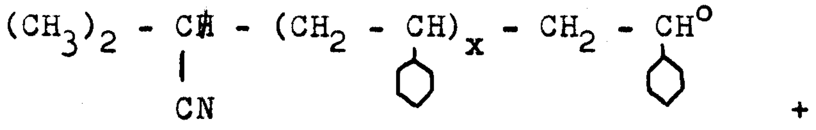


dead polymer of chain length (x + y + 2)

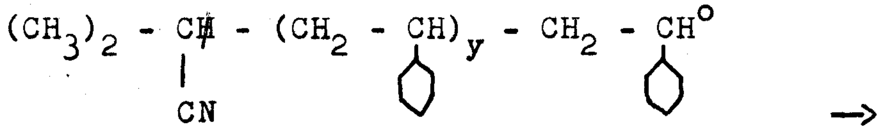
It is interesting to note that the structure of this polymer molecule is different for different combinations of x and y although their sum may be the same. The degree of combination as compared with other forms of termination may be determined chemically by analyzing the polymer for the amount of incorporated catalyst fragments. Sometimes the same analysis can be used to determine the degree of polymerization, provided the termination mechanism is known.

B. Disproportionation

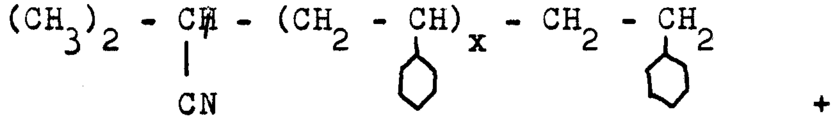
Disproportionation involves the transfer of a hydrogen atom from one growing polymer chain to another, terminating both but leaving one of them with a double bond. The polymer molecules thus formed are indistinguishable from those formed by chain transfer processes.



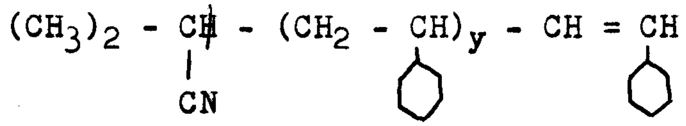
radical of chain length (x + 1)



radical of chain length (y + 1)



dead polymer



dead polymer

The difference with an ordinary chain transfer process is that no new free radicals are created but rather two free radicals disappear. In the case of styrene disproportionation is very small (19).

4.2 Development of the Rate Equations

The principles discussed in Section 4.1 may be illustrated in a simple mathematical manner. In the following equations R_c^o represents one of two similar free-radical fragments formed in the decomposition of the catalyst; R_r^o represents a polymer radical comprising r monomer units, S is a solvent and M a monomer molecule, while P_r represents a dead polymer molecule containing r monomer units.

Initiation

$$\text{Cat} \longrightarrow 2R_c^o \qquad \text{rate constant } k_d$$

$$R_c^o + M \longrightarrow R_1^o \qquad \text{rate of formation of } R_1^o \text{ is } I$$

Propagation

$$R_1^o + M \longrightarrow R_2^o \qquad \text{rate constant } k_{p1}$$

$$R_2^o + M \longrightarrow R_3^o \qquad \text{rate constant } k_{p2}$$

$$R_r^o + M \longrightarrow R_{r+1}^o \qquad \text{rate constant } k_{pr}$$

Transfer

$$R_r^o + S \longrightarrow P_r + S^o \qquad \text{rate constant } k_{fs}$$

$$R_r^o + M \longrightarrow P_r + M^o \qquad \text{rate constant } k_{fm}$$

Termination

$$R_r^{o} + R_s^{o} \longrightarrow P_{r+s} \qquad \text{rate constant } k_{tc}$$

$$R_r^{o} + R_s^{o} \longrightarrow P_r + P_s \qquad \text{rate constant } k_{td}$$

In the development of the rate equations used in this investigation it is assumed that only the foregoing reactions take place. Furthermore, it is assumed that the solvent and monomer radicals formed in the chain-transfer process have the same reactivity as any other radicals; this implies that S^{o} is not a retarder or inhibitor. Finally, the rate of propagation is assumed to be independent of the polymer radical size. Numerous other reactions can and do take place and there is substantial literature on the subject; see for example, Bamford, Barb, Jenkins and Onyon. For the present study, the simplest reaction mechanism has been chosen which closely approximates the experimental results, using molecular-weight distribution of the resulting polymer as the measured criterion. On the basis of the foregoing set of reactions, the rate of formation of R_1^{o} is

$$\frac{dR_1^{o}}{dt} = I - k_p M R_1^{o} + (k_{fs} S + k_{fm} M) R^{o} - (k_{fs} S + k_{fm} M) R_1^{o} - (k_{tc} + k_{td}) R_1^{o} R^{o} \qquad (1)$$

where R^{o} is the total free-radical concentration,

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

The rate of formation of R_2^{o} and longer chains is:

$$\frac{dR_r^o}{dt} = k_p MR_{r-1}^o - k_p MR_r^o - (k_{fs}S + k_{fm}M)R_r^o - (k_{tc} + k_{td})R^oR_r^o \qquad (2)$$

The rate of monomer consumption is:

$$-\frac{dM}{dt} = I + k_p MR^o + k_{fm}MR^o \qquad (3)$$

For long chains the first and third terms of equation (3) become insignificant and the equation simplifies to

$$\frac{dM}{dt} = -k_p MR^o \qquad (4)$$

The rate of formation of polymer of chain length r is:

$$\frac{dP_r}{dt} = (k_{fs}S + k_{fm}M)R_r^o + k_{td}R^oR_r^o + \tfrac{1}{2}k_{tc}\sum_{n=1}^{r-1} R_n^oR_{r-n}^o \qquad (5)$$

Rigorous simultaneous solution of equations(1) through (5) would give the total monomer consumption and polymer production of species 1 to r. However, this would involve the solution of a very large number of simultaneous differential equations. An attempt to solve the equations simultaneously by Runge Kutta has been published, where r was taken to vary from 2 to 100 (23). In real polymerization system, however, r often becomes as large as 5,000 or more, making the techniques impractical. Several mathematical techniques for obtaining analytical solutions of the equations also have been developed, specifically transform methods (20, 21). Still another method consists of using a so-called continuous variable technique, which has been applied to a backmix reactor (22). In the latter case an infinite set of algebraic equations is reduced to a finite set of differential equations. However, in all of these methods the resulting mathematical equations become extremely complex, limiting their usefulness.

There is, however, a further major assumption that is often made in free radical polymerizations, namely that the free radical concentration reaches a "steady state". This involves the assumption that the rate of growth of intermediate live polymer molecules reaches a steady state also. As a result equation (2) is eliminated and (R_r^o) is expressed in terms of (R_1^o) as shown in equation (19). Liu and Amundsen showed that serious errors can be introduced if the steady state is not reached quickly. However, most polymerization reactions take place very rapidly and are complete within the order of seconds or micro-seconds. For styrene polymerization this is shown to be so making the assumption quite justifiable.

4.3 The Stationary-State Method

The stationary or steady-state concept involves the assumption that the concentration of radical intermediates remains constant during the course of the reaction. It is clear though that this is never really the case. At the very beginning there will be a period during which the free radical concentration increases rapidly to a certain value and from then on it gradually declines, as the catalyst source becomes depleted. This can be shown more clearly by the following equations. The rate at which polymer free radicals appear has been defined as I and the only manner in which they disappear is by termination. Thus in general:

$$\frac{dR^{o}}{dt} = I - k_t(R^{o})^2 \qquad (6)$$

at steady state $\frac{dR^{o}}{dt} = 0$ and $(R^{o}) = (I/k_t)^{\frac{1}{2}}$ $\qquad$ (7)

or the rate of initiation equals the rate of termination. The concentration of R^{o} can of course only remain constant if I remains constant, which in turn is dependent upon the catalyst concentration. However, the rate of catalyst decomposition and therefore the rate of initiation is very slow. Thus to a very good approximation equation (7) holds true. To prove this, equation (6) and equation (3) were slightly transformed as follows and then solved. The solution showed that a steady state is reached in less than one second. Normal polymerization times are of the order of several hours.

The rate of catalyst decomposition, is a first order process (18) and may be written as

$$-\frac{dC}{dt} = k_d C \qquad (8)$$

where C is the catalyst concentration.

Integration gives

$$C = C_o \exp(-k_d t) \qquad (9)$$

Since the rate of catalyst decomposition, given by equation (8) is the rate controlling step, the rate of initiation I may be set equal to the rate of catalyst decomposition.

$$I = 2f\left(-\frac{dC}{dt}\right) = 2f\ k_dC \tag{10}$$

Here f is an efficiency factor, usually considered to be independent of the catalyst concentration. This factor f must be included because not all catalyst free radical fragments are captured by the monomer molecules and some combine to form waste products.

Substituting equation (9) into equation (10) gives

$$I = 2f\ k_dC_o\ \exp(-k_dt) \tag{11}$$

Substituting equation (11) into equation (6) gives

$$\frac{dR^o}{dt} = 2f\ k_dC_o\ \exp(-k_dt) - k_t(R^o)^2 \tag{12}$$

Substituting equation (11) into equation (3) and defining the conversion X as

$$M = M_o(1 - X) \tag{13}$$

one obtains:

$$\frac{dX}{dt} = \frac{2f\ k_dC_o}{M_o}\ \exp(-k_dt) + k_p(1-X)R^o + k_{fm}(1-X)R^o \tag{14}$$

Equations (12) and (14) were solved simultaneously by a fourth-order Runge-Kutta method to determine the time required to reach steady state and the degree of conversion that had taken place. At 75°C. this is about 0.75 seconds while the conversion is only about $1.5 \times 10^{-5}\%$. Since the overall reaction times considered range from 2 to 15 hours the steady state concept is justified. See Table 1 in Section 6.2.

4.4 Conversion and Molecular Weight Distribution

Assuming a steady state exists, equations (4) and(5) may now be solved. From equation (7) and (11) one gets:

$$R^{o} = \left[\frac{2f\ k_d\ C_o\ \exp(-k_d t)}{k_{td} + k_{tc}}\right]^{\frac{1}{2}} \tag{15}$$

and substituting this into equation (4), making the proper transformation to conversion gives

$$\frac{dX}{dt} = k_p(1-X)\left[\frac{2f\ k_d\ C_o\ \exp(-k_d t)}{k_{td} + k_{tc}}\right]^{\frac{1}{2}} \tag{16}$$

which allows the calculation of conversion as a function of time and initial catalyst concentration. Equation (16) was solved numerically using a fourth-order Runge-Kutta process, but may be solved analytically as well. To obtain the molecular-weight distribution equation (5) has to be solved. However, before this can be done an expression giving R_r^{o} must be developed. This may be obtained from equation (2). For an overall stationary-state to exist each radical polymer species must have come to steady-state. Setting equation (1) equal to zero and substituting for R^{o} gives:

$$R_1^{o} = \left[\frac{I}{k_{tc} + k_{td}}\right]^{\frac{1}{2}} \left\{\frac{k_{fs}S + k_{fm}M + \left[I(k_{tc} + k_{td})\right]^{\frac{1}{2}}}{k_pM + k_{fs}S + k_{fm}M + \left[I(k_{tc} + k_{td})\right]^{\frac{1}{2}}}\right\} \tag{17}$$

Similarly from equation (2) one obtains

$$R_r^o = R_{r-1}^o \left\{ \frac{k_p M}{k_p M + k_{fs} S + k_{fm} M + \left[I(k_{tc} + k_{td}) \right]^{\frac{1}{2}}} \right\} \tag{18}$$

which holds for $r \geq 2$.

This equation may be written as

$$R_r^o = R_{r-1}^o \xi \tag{18a}$$

where the term ξ is often referred to as the probability factor. It gives the statistical probability that a certain polymer free radical will propagate rather than enter into a termination reaction of some sort. Equation (18) relates R_r^o and R_{r-1}^o. Equation (17) may be written in a similar form as equation (18a).

$$R_1^o = \left[\frac{I}{k_{tc} + k_{td}} \right]^{\frac{1}{2}} (1 - \xi) \tag{17a}$$

Combining (17a) and (18a) gives

$$R_r^o = R_1^o \xi^{(r-1)} = \left[\frac{I}{k_{tc} + k_{td}} \right]^{\frac{1}{2}} (1 - \xi) \xi^{r-1} \tag{19}$$

Equation (19) although here derived from the rate equations rather than statistically shows immediately why ξ is called the probability of propagation. For example, the probability that a radical will propagate r consecutive times is ξ^{r-1}, while the probability of termination is always $(1 - \xi)$. Thus the probability that an r-mer free radical is formed followed by termination, is $\zeta^{r-1}(1 - \zeta)$. With

$$\zeta = \frac{k_p M}{k_p M + k_{fs} S + k_{fm} M + \left[I(k_{tc} + k_{td}) \right]^{\frac{1}{2}}} \tag{20}$$

one may write:

$$R_n^o = \left[\frac{I}{k_{tc} + k_{td}} \right]^{\frac{1}{2}} (1 - \zeta)\, \zeta^{n-1} \tag{21}$$

and

$$R_{r-n}^o = \left[\frac{I}{k_{tc} + k_{td}} \right]^{\frac{1}{2}} (1 - \zeta)\, \zeta^{r-n-1} \tag{22}$$

The first term of equation (5) then becomes

$$(k_{fs} S + k_{fm} M) \left[\frac{I}{k_{tc} + k_{td}} \right]^{\frac{1}{2}} (1 - \zeta)\, \zeta^{r-1}$$

The second term of equation (5) becomes

$$k_{td} \left[\frac{I}{k_{tc} + k_{td}} \right]^{\frac{1}{2}} (1 - \zeta)\, \zeta^{r-1} R^o$$

which be replacing R^o gives

$$k_{td} \left[\frac{I}{k_{tc} + k_{td}} \right] (1 - \zeta)\, \zeta^{r-1}$$

The third term of equation (5) becomes

$$\tfrac{1}{2} k_{tc} \sum_{n=1}^{r-1} \left[\frac{I}{k_{tc} + k_{td}} \right]^{\frac{1}{2}} (1 - \zeta)\, \zeta^{n-1} \left[\frac{I}{k_{tc} + k_{td}} \right]^{\frac{1}{2}} (1 - \zeta)\, \zeta^{r-n-1} =$$

$$\tfrac{1}{2}\left[\frac{k_{tc} I}{k_{tc} + k_{td}}\right](1 - \varsigma)^2 \sum_{n=1}^{r-1} \varsigma^{\,n-1} \varsigma^{\,r-n-1} =$$

$$\tfrac{1}{2}\left[\frac{I\, k_{tc}}{k_{tc} + k_{td}}\right] (1 - \varsigma)^2 (r-1) \varsigma^{\,r-2}$$

Substituting these three terms back into equation (5) and remembering that

$$\varsigma^{-1} = \frac{k_p M + k_{fs} S + k_{fm} M + \left[I(k_{tc} + k_{td})\right]^{\frac{1}{2}}}{k_p M}$$

one gets:

$$\frac{dP_r}{dt} = \left[\frac{I}{k_{tc} + k_{td}}\right]^{\frac{1}{2}} (1 - \varsigma) \varsigma^{\,r-1} \Bigg[k_{fs} S + k_{fm} M +$$

$$\left[\frac{I}{k_{tc} + k_{td}}\right]^{\frac{1}{2}} \left\{ \frac{(r-1) k_{tc} \left(k_{fs} S + k_{fm} M + \left[I(k_{tc} + k_{td})\right]^{\frac{1}{2}}\right)}{2 k_p M} + k_{td} \right\} \Bigg] \qquad (23)$$

Further substitutions may be made for M and I in equations (20) and (23) and a substitution for ς in equations (23) may be made as well. However, equations (23) is already sufficiently unwieldy and equation (20) has therefore been maintained as a separate equation. Substituting for M and I in equation (20) gives

$$\varsigma = \frac{k_pM_o(1-X)}{k_pM_o(1-X) + k_{fs}S + k_{fm}M_o(1-X) + \left[2fk_dC_o \exp(-k_dt)(k_{tc} + k_{td})\right]^{\frac{1}{2}}} \tag{24}$$

and substituting for M and I in equation (21) gives

$$\frac{dP_r}{dt} = \left[\frac{2fk_dC_o \exp(-k_dt)}{k_{tc} + k_{td}}\right]^{\frac{1}{2}} (1-\varsigma)\,\varsigma^{r-1} \left[k_{fs}S + \left\{k_{fm}M_o(1-X) + \left[\frac{2fk_dC_o\exp(-k_dt)}{k_{tc} + k_{td}}\right]^{\frac{1}{2}} \left[\frac{(r-1)k_{tc}\left(k_{fs}S + k_{fm}M_o(1-X) + \left[2fk_dC_o\exp(-k_dt)(k_{tc} + k_{td})\right]^{\frac{1}{2}}\right)}{2k_pM_o(1-X)} + k_{td}\right]\right]\right\} \tag{25}$$

Simultaneous solution of equations (16), (24) and (25) gives P_r the polymer concentration of a species having chain length r. A plot of P_r versus r gives the so-called "frequency" distribution, whereas usually the weight fraction is the more desired quantity. But the weight fraction of polymer having a chain length r may easily be obtained. The amount of polymer of chain length r is $(r)(P_r)$, and the weight fraction is then:

$$W_r = \frac{r\ P_r}{M_o\ X} \tag{26}$$

The number-average chain length is defined as

$$\bar{r} = \frac{\sum_{r=1}^{\infty} rP_r}{\sum_{r=1}^{\infty} P_r} \tag{27}$$

The weight-average chain length is

$$\bar{r}_W = \frac{\sum_{r=1}^{\infty} r^2 P_r}{\sum_{r=1}^{\infty} r\ P_r} \tag{28}$$

which may also be written as

$$\frac{\sum_{r=1}^{\infty} r^2 P_r}{\sum_{r=1}^{\infty} M_o X\ W_r} = \frac{\sum_{r=1}^{\infty} r\ W_r}{\sum_{r=1}^{\infty} W_r} \tag{29}$$

Finally the Z-average chain length is defined as

$$\bar{r}_Z = \frac{\sum_{r=1}^{\infty} r^3 P_r}{\sum_{r=1}^{\infty} r^2 P_r} \tag{30}$$

4.5 Solution of Rate Equations

Equation (16) can be solved analytically but equation (25) does not lend itself to anything but numerical solution. To generate values of W_r, the weight fraction of polymer having a chain length of r monomer units, P_r must be calculated for each value of r for $(2 \leq r \leq \infty)$. The following scheme was therefore adopted.

Equation (16) was solved by a fourth-order Runge-Kutta process taking time interval steps of 3 minutes. (A step size of 1½ minutes gave essentially the same answer, deviating less than 1% from the 3 minute step process). All the values of X calculated every 3 minutes are stored and ξ is calculated at the same time intervals using equation (24). Equation (25) is then solved for all the stored values of X and t and ξ, using the trapezoidal rule at a fixed value of r, ranging from 1 to 6000. At W_r less than 10^{-6}, the contribution of higher chain length species is considered to be negligible, thus allowing a finite number of equations, which can be solved. Using equations (27), (28) and (30), the number, weight and Z-average chain lengths or degree of polymerization were then calculated.

5. EXPERIMENTAL DETAILS

5.1 Description of Batch Reactor

The basic apparatus consists of a one liter glass vessel fitted with a stainless-steel blind flange and a helical stainless-steel cooling coil following the wall contour. A variable speed axial stirrer is located centrally, approximately one third the vessel height above the bottom. In addition it has a thermistor temperature probe and an ordinary 0° - 100°C. laboratory thermometer. The thermistor probe is connected to an amplifier and Wheatstone bridge, which has as on-off solenoid switch connected to a solenoid valve located in the cooling water supply line. In series with the solenoid valve there is a manually controlled micro-needle valve to throttle the cooling water flow until adequate temperature control is achieved. The outside of the reactor was insulated with a Glas-Col electric heating mantel supplied through a variac. A normal variac setting was about 50 volts. Although the reaction is exothermic, most of the operating conditions were such that the temperature was not self-sustaining, requiring the external heating source. Temperature control thus is an on-off type but within $\pm 0.1^{\circ}$C. Figure 1 gives a schematic view of the apparatus.

5.2 Description of the Gel-Permeation Chromatograph

Chromatography is a well known technique in the

ISOTHERMAL STIRRED BATCH REACTOR

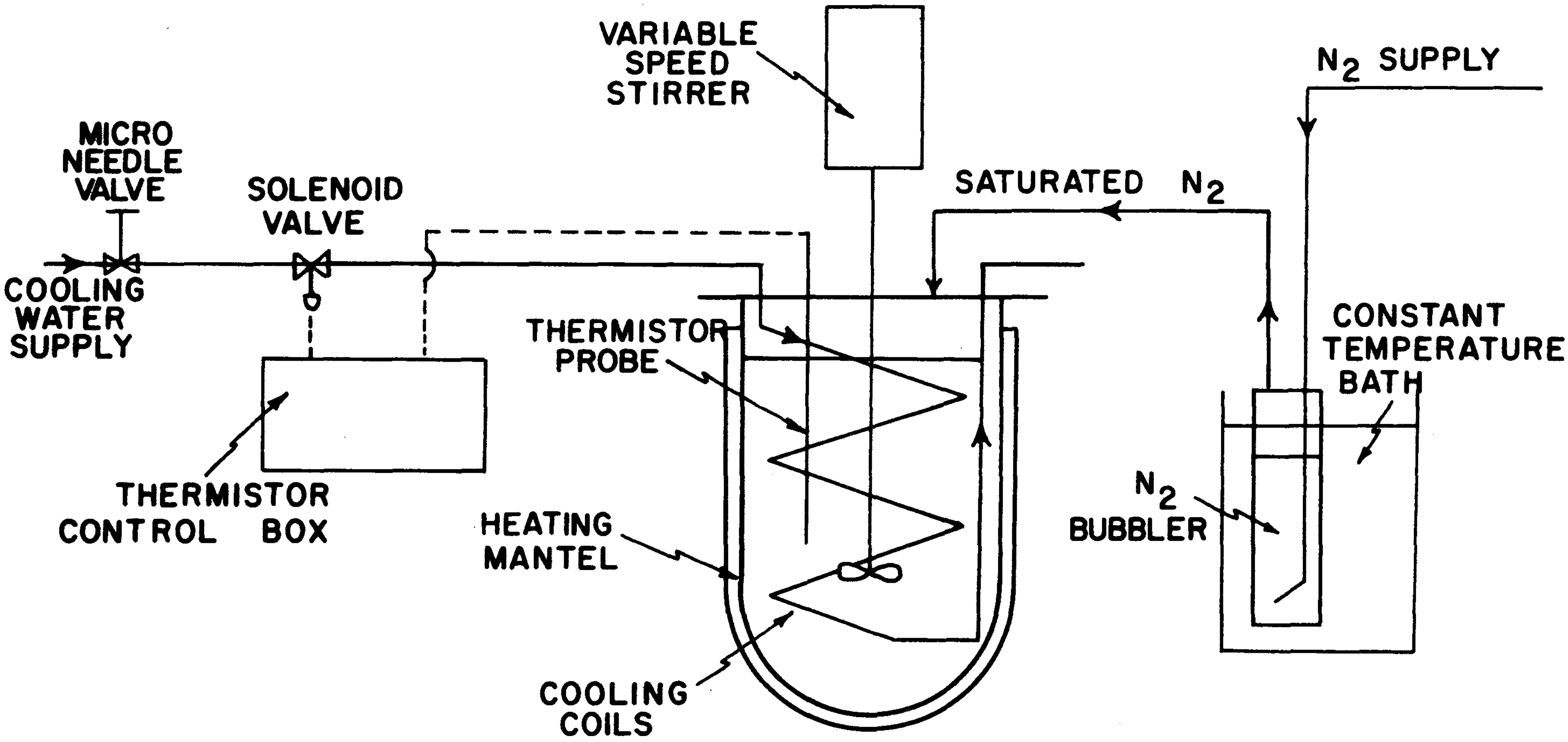


FIGURE 1

quantitative analyses of various chemical substances and needs no elaboration here. However, the use of the term chromatography in the characterization of polymer homologs is misleading for which reason its originators included the words gel-permeation. A brief description of the technique follows.

Polymer molecules when dissolved assume a more or less spherical configuration, the size and shape of the particles being related to the molecular chain length and the solvent being used (31, 40). This is further discussed in Appendix 4.1. The gel-permeation chromatograph gives a size distribution of the dissolved polymer molecules and since the size is related to the molecular chain length, this can be transformed into a molecular-weight distribution.

The gel-permeation chromatograph consists of a series of 3/8 inch diameter stainless steel columns which have been packed with porous polystyrene beads. The pore size of the beads varies from zero to some fixed upper limit and this limit decreases from column to column. The magnitude of the upper limit is selected on the basis of the size of the polymer molecules to be analyzed. Size separation is achieved as follows. A solution of polymer molecules permeates through the columns passing first through the column having the largest pore diameter followed by the one having the next largest pore diameter, and so on. As the solution contacts the beads the polymer molecules will tend to enter the pores, the only restriction being the pore size. Thus any molecules which

FIGURE 2 GEL PERMEATION CHROMATOGRAPH

are larger than the largest pore size pass straight through. Furthermore, the smaller molecules have a much greater chance of entering the pores than the larger ones since there are far more pores available to them. A short flow of polymer solution is followed by a continuous flow of pure solvent which will tend to displace the polymer molecules in the pores. For the same reason as above, the large molecules will be replaced more quickly than the small ones, the whole process causing an enrichment of the large molecules in the elution stream.

The effluent stream then passes through a differential refractometer which continuously monitors the difference in the refractive index between the polymer solution and the pure solvent. Thus any day to day variations in solvent refractive index are automatically corrected. The refractometer output signal is amplified and charted by a Honeywell recorder. This so-called trace can then be related to the polymer chain length or molecular weight distribution by means of a calibration curve. Figure 2 is a photograph of the equipment.

5.3 Techniques of Polymer Analysis

One of the best techniques for analyzing quantitatively the amount of polystyrene in a solution of styrene monomer or some other solvent is a gravimetric one and consists of precipitating the polymer by adding a five to ten-fold excess of methanol (25). Whether very low molecular weight material such as trimers and tetramers is precipitated is not known, however, it is assumed that it will. In any case, analysis of the theoretical chain length distribution shows that these materials are only present in negligible amounts and furthermore the method is used extensively by other workers (18, 26).

6. RESULTS AND DISCUSSION

6.1 Effect of Reaction Variables on Conversion and Molecular-Weight Distribution

6.1.1 Monomer concentration

Equations (3) and (4) or the more sophisticated form equation (16) predict that the rate of monomer consumption and thus conversion is first order in monomer concentration and the solution of such an equation is of the simple exponential-decay form. Equation (16), however, allows for a first-order decay in catalyst concentration as well which has to be incorporated. In any case, the general shape of the conversion versus time curve is not greatly altered because of this; Figure (3) is typical. It shows two curves of conversion versus time, one for an initial monomer concentration of 30.0% and the other for an initial monomer concentration of 60.0%. The reaction temperature was 65°C. and the initial catalyst concentration was 0.1%. The curves are based on the theoretically predicted values whereas the plotted points are experimentally observed values, averaged over three runs. Curves, representing higher monomer concentrations are given in the Appendices 3.1 and 3.2. It is seen that as the monomer concentration increases the rate of conversion increases as would be expected.

The effect of monomer concentration on the molecular-weight distribution is considerably more complex. None of the foregoing equations provides a simple overall picture, as to what influence the monomer concentration might be expected to

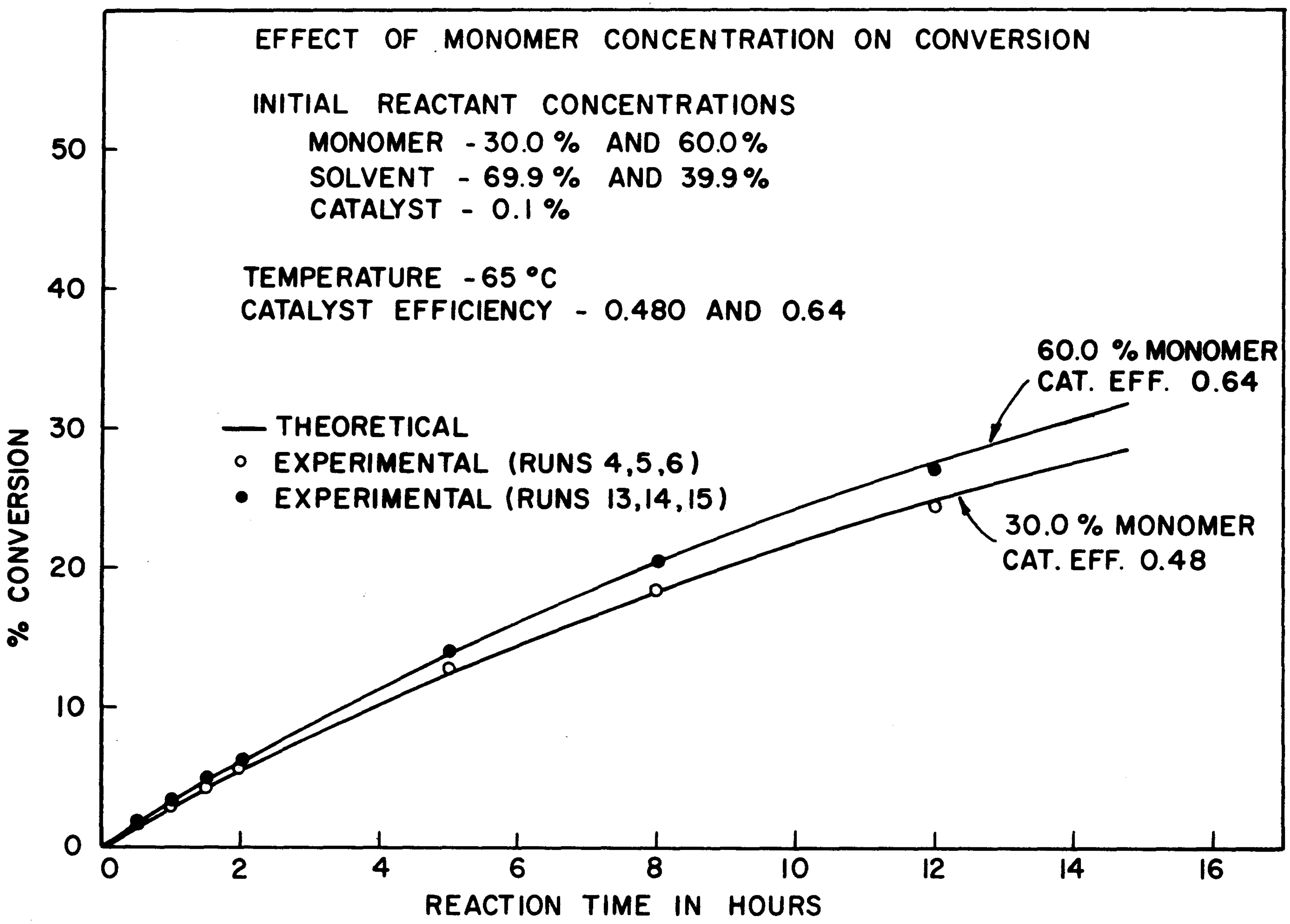

EFFECT OF MONOMER CONCENTRATION ON CONVERSION
INITIAL REACTANT CONCENTRATIONS
MONOMER - 30.0 % AND 60.0 %
SOLVENT - 69.9 % AND 39.9 %
CATALYST - 0.1 %
TEMPERATURE - 65 °C
CATALYST EFFICIENCY - 0.480 AND 0.64
— THEORETICAL
○ EXPERIMENTAL (RUNS 4,5,6)
● EXPERIMENTAL (RUNS 13,14,15)
60.0 % MONOMER
CAT. EFF. 0.64
30.0 % MONOMER
CAT. EFF. 0.48
% CONVERSION
0
10
20
30
40
50
0
2
4
6
8
10
12
14
16
REACTION TIME IN HOURS

FIGURE 3

have. However, some idea can be obtained by examining equation (35). This equation relates the number average degree of polymerization to all the reaction variables. The first two terms are often negligible and thus it is clear that if the monomer concentration is doubled, the number average degree of polymerization is about doubled. Figure 4 shows the cumulative distributions at 30% and 60% monomer concentrations and shows that the predicted shift indeed took place. The degree of polymerization shifted from 401 to 789 somewhat less than double. The fact that it is somewhat less is due to the first and second terms in equation (35) the chain transfer terms. As before, the solid lines are the theoretically predicted distribution whereas the plotted points are the distributions obtained by gel-permeation chromatograph measurement. Although the two do not completely coincide it is clear that the gel-permeation chromatograph measurements confirm the predicted shift. Thus in general, for solution polymerization, the lower the monomer concentration, the lower will be the molecular weight, the highest molecular weight being obtained for pure monomer (bulk) polymerization.

6.1.2 Catalyst concentration

The catalyst concentration is the variable most frequently manipulated in order to achieve a certain conversion or molecular weight. Examination of equation (16) shows that doubling the initial catalyst concentration increases the rate of conversion by a factor $\sqrt{2}$. Figure 5 shows two graphs of

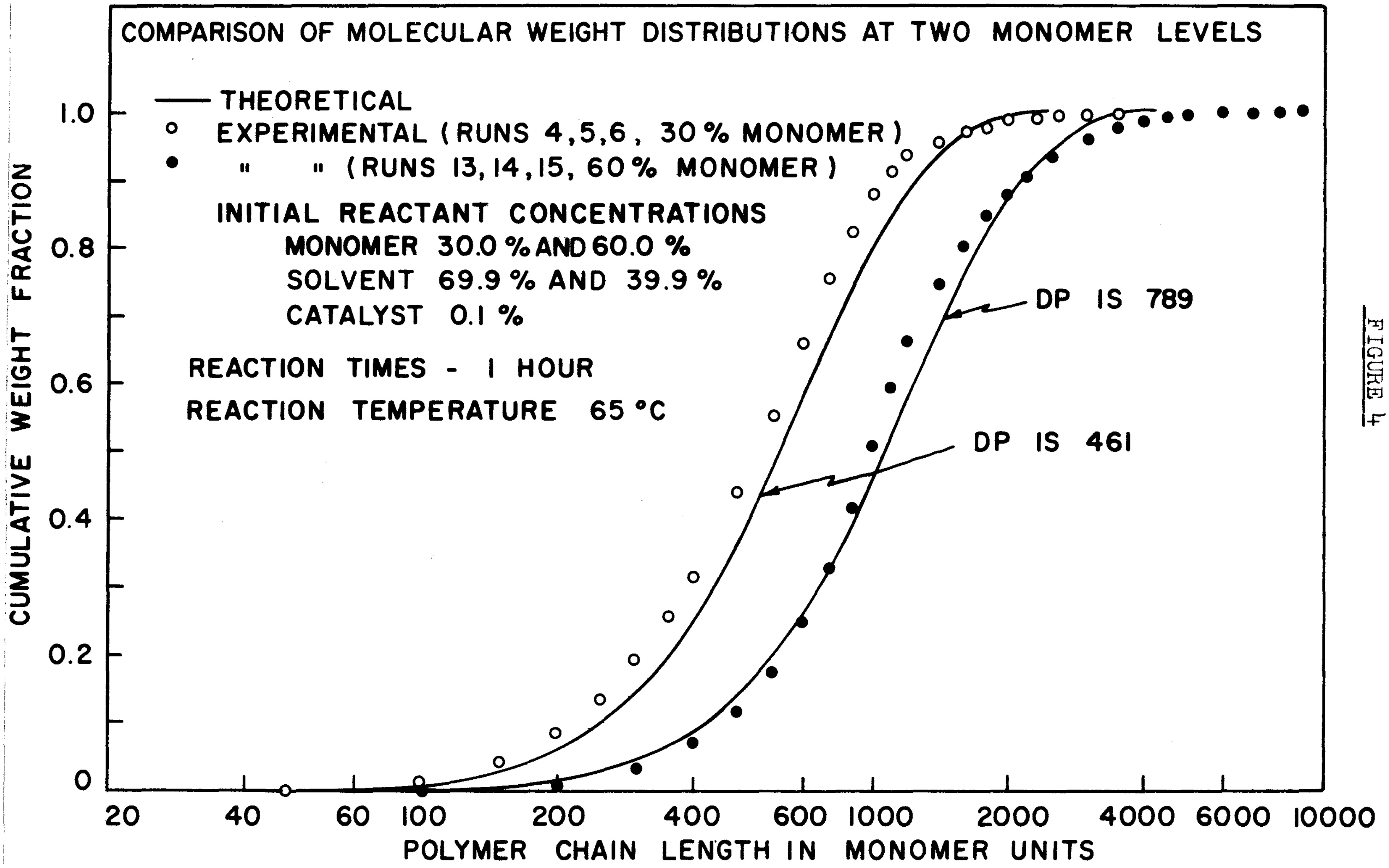

COMPARISON OF MOLECULAR WEIGHT DISTRIBUTIONS AT TWO MONOMER LEVELS
THEORETICAL
○ EXPERIMENTAL (RUNS 4,5,6, 30% MONOMER)
● " " (RUNS 13, 14, 15, 60% MONOMER)
INITIAL REACTANT CONCENTRATIONS
MONOMER 30.0% AND 60.0%
SOLVENT 69.9% AND 39.9%
CATALYST 0.1%
REACTION TIMES - 1 HOUR
REACTION TEMPERATURE 65 °C
DP IS 789
DP IS 461
CUMULATIVE WEIGHT FRACTION
1.0
0.8
0.6
0.4
0.2
0
POLYMER CHAIN LENGTH IN MONOMER UNITS
20
40
60
100
200
400
600
1000
2000
4000
6000
10000

FIGURE 4

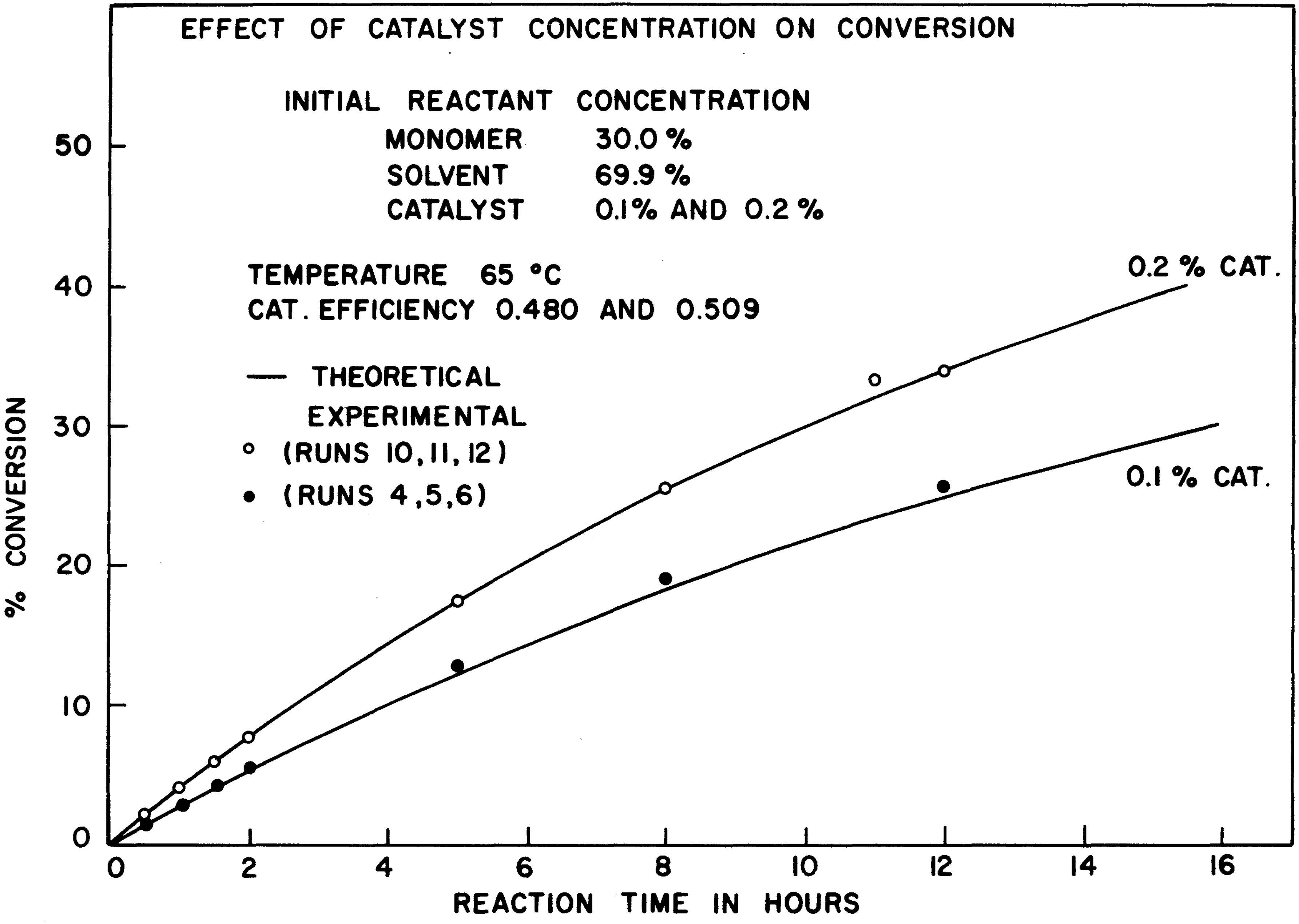

EFFECT OF CATALYST CONCENTRATION ON CONVERSION
INITIAL REACTANT CONCENTRATION
MONOMER 30.0 %
SOLVENT 69.9 %
CATALYST 0.1% AND 0.2 %
TEMPERATURE 65 °C
CAT. EFFICIENCY 0.480 AND 0.509
— THEORETICAL
EXPERIMENTAL
○ (RUNS 10, 11, 12)
● (RUNS 4, 5, 6)
0.2 % CAT.
0.1 % CAT.
% CONVERSION
0
10
20
30
40
50
REACTION TIME IN HOURS
0
2
4
6
8
10
12
14
16

FIGURE 5

conversion versus time, one at 0.1% catalyst and the other at 0.2%. In both cases the monomer concentration was 30.0% and the temperature 65°C. The plot is typical.

The effect of the catalyst concentration on the molecular-weight distribution may again be seen from equation (35) and is shown in Figure 6. Increasing the catalyst concentration increases the rate of initiation and the total free-radical concentration. As a result, the rate of termination also increases and the polymer chains cannot grow quite as long. Thus even though the total conversion increases, the molecular weight or chain length decreases. From equation (35) it is seen that doubling the catalyst concentration reduces the degree of polymerization by a factor of $\sqrt{2}$. The degree of polymerization decreases from 461 to 317, a factor of about $1/\sqrt{2}$. The agreement between the gel-permeation chromatograph results and the theoretical curve for the case of 0.1% catalyst (see also Figure 4) is not as good as it was hoped. There is no apparent reason for this, unless a clue is taken from the fact that the catalyst efficiency is abnormally low. Experiments performed under these particular conditions seemed to be exceptionally susceptable to random variations and as a result had to be repeated numerous times to obtain reproducible data. Likely some error has crept into the experimental runs, causing the below average conversion and molecular weight.

6.1.3 Reaction temperature

The third reaction variable that was investigated is

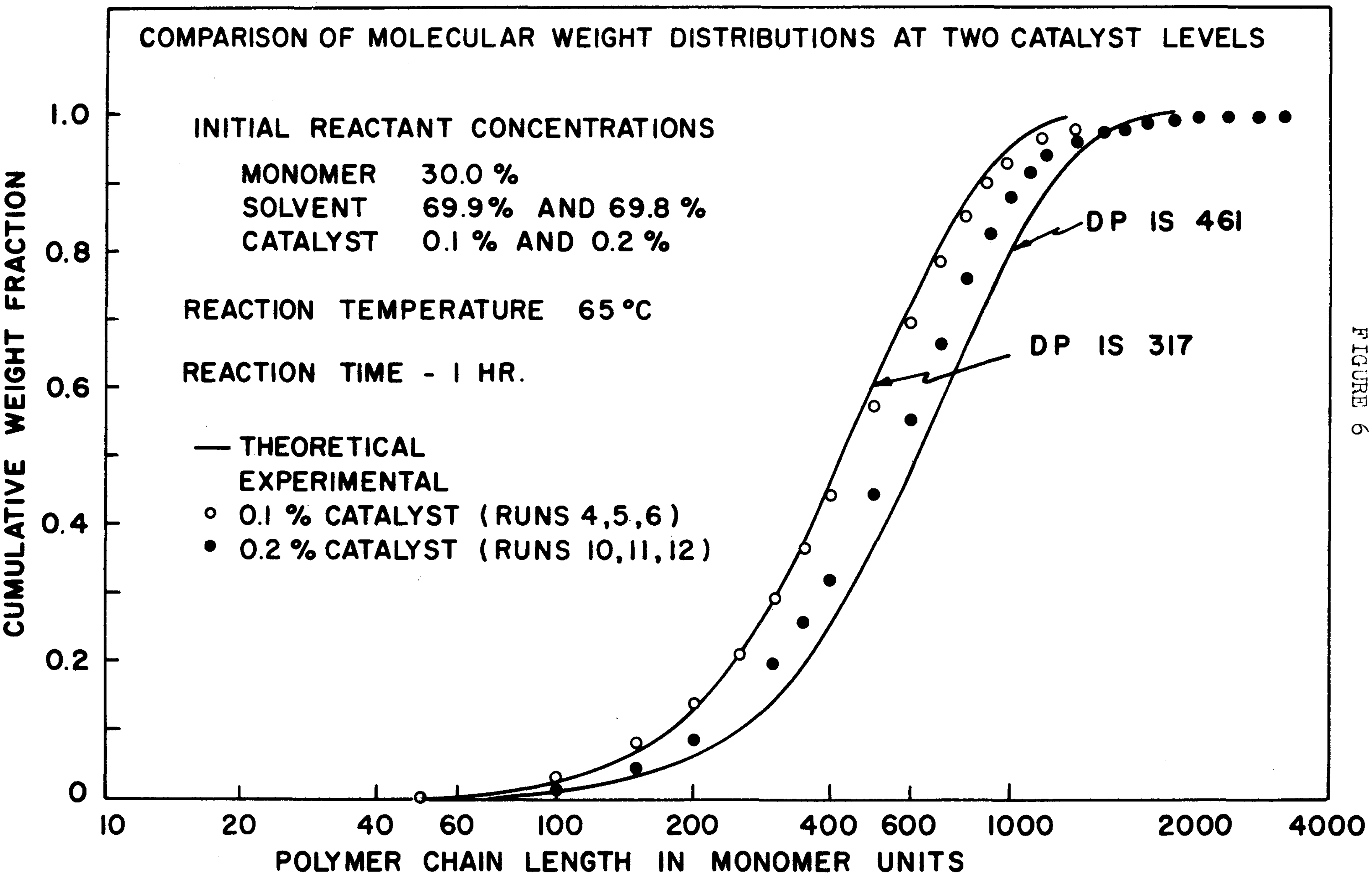

COMPARISON OF MOLECULAR WEIGHT DISTRIBUTIONS AT TWO CATALYST LEVELS
INITIAL REACTANT CONCENTRATIONS
MONOMER 30.0 %
SOLVENT 69.9 % AND 69.8 %
CATALYST 0.1 % AND 0.2 %
REACTION TEMPERATURE 65 °C
REACTION TIME - 1 HR.
— THEORETICAL
EXPERIMENTAL
○ 0.1 % CATALYST (RUNS 4, 5, 6)
● 0.2 % CATALYST (RUNS 10, 11, 12)
DP IS 461
DP IS 317
CUMULATIVE WEIGHT FRACTION
0
0.2
0.4
0.6
0.8
1.0
10
20
40
60
100
200
400
600
1000
2000
4000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE 6

the reaction temperature. Together with the catalyst concentration, this is by far the most important one. However, its effect it not easily foreseen. The reaction temperature affects the reaction rate through the rate constants and from equation (16) it is seen that no cursory glance will reveal these effects. If k_p increases less rapidly with increasing temperature than does the termination rate constant k_t, the molecular weight will be depressed and the conversion may or may not be lower. Usually k_d the catalyst decomposition constant also increases which results in an overall increase in conversion. Examination of the respective energies of activation in the Arrhenius equations, shows that this was the case. Figure (7) is typical and shows an increase in the rate of conversion. However, it should be noted that for the above case the increased rate is at the expense of an increase in catalyst consumption per unit conversion. This is illustrated in Figure (8). At 80°C. the initial rate is much greater but it falls quickly when all the catalyst is consumed. At 75°C. and lower, the initial rate is lower but the final conversion is higher. Thus, if a longer reaction time and increased molecular weight are no objection a lower reaction temperature will give a higher yield, which suggests an interesting optimization study.

The effect of temperature on the molecular-weight distribution is even more difficult to foresee, as equation (35) clearly shows. In this case two more rate constants enter the

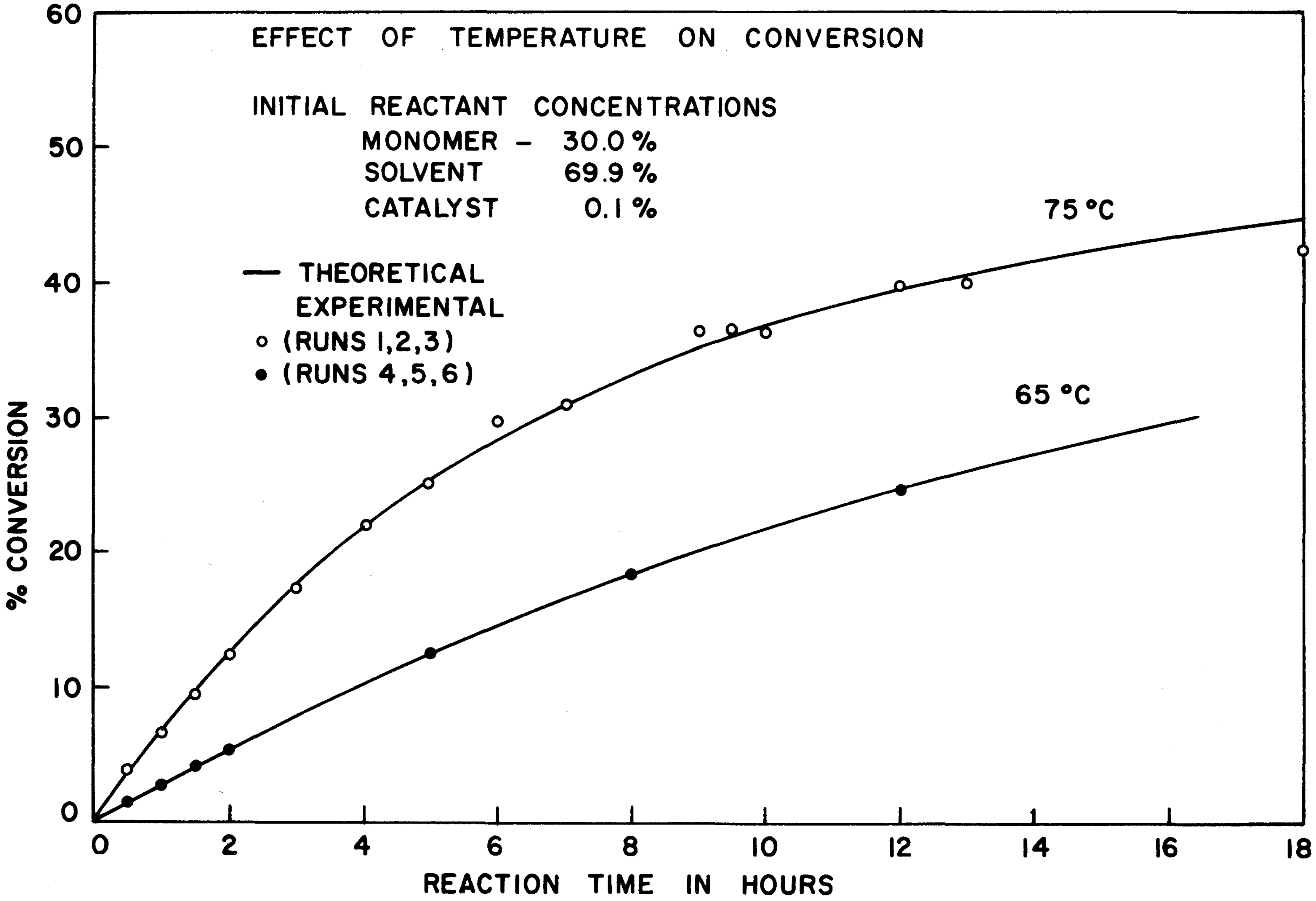

EFFECT OF TEMPERATURE ON CONVERSION
INITIAL REACTANT CONCENTRATIONS
MONOMER - 30.0 %
SOLVENT 69.9 %
CATALYST 0.1 %
— THEORETICAL
EXPERIMENTAL
○ (RUNS 1,2,3)
● (RUNS 4,5,6)
75 °C
65 °C
% CONVERSION
0
10
20
30
40
50
60
REACTION TIME IN HOURS
0
2
4
6
8
10
12
14
16
18

FIGURE 7

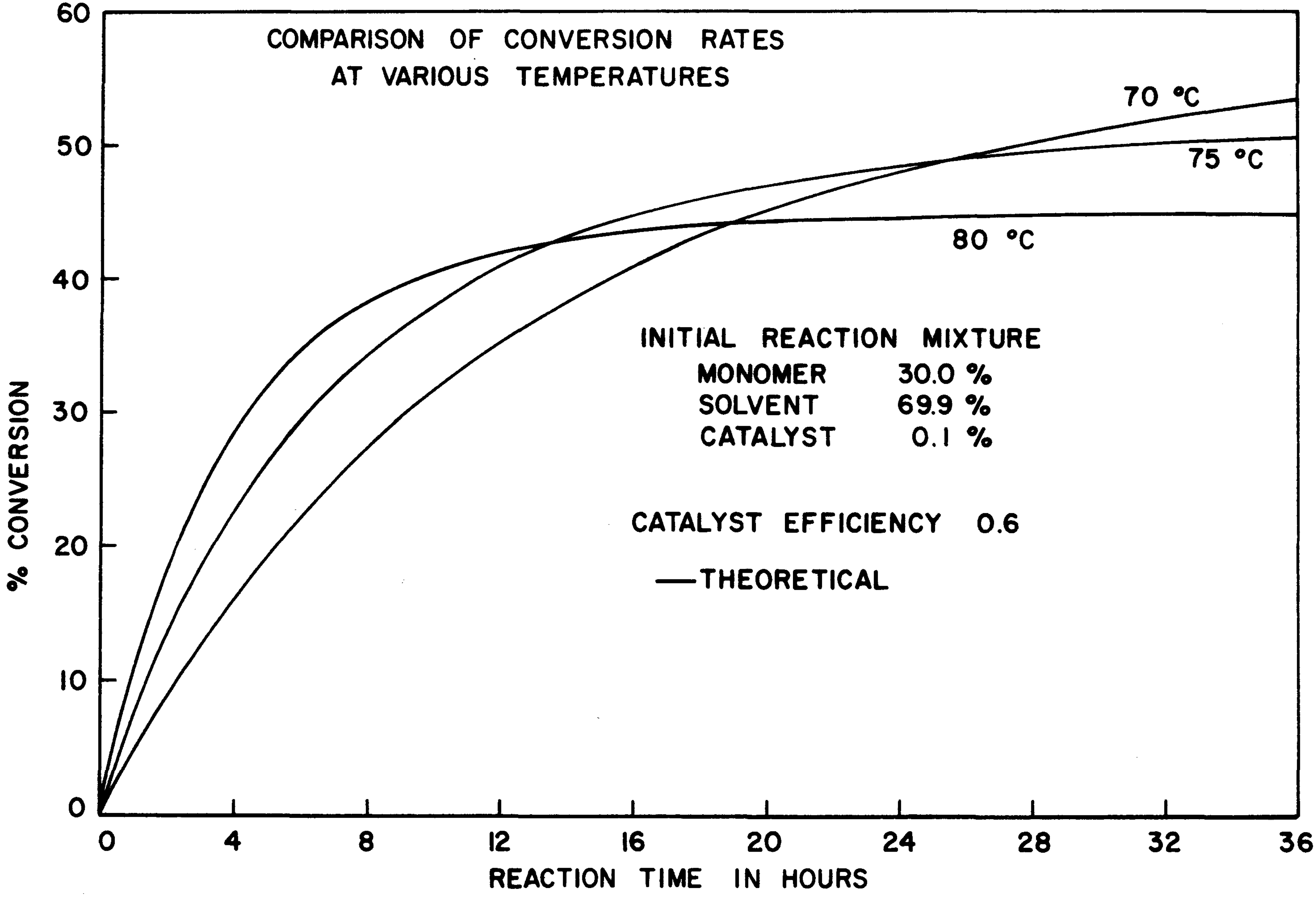

COMPARISON OF CONVERSION RATES
AT VARIOUS TEMPERATURES
70 °C
75 °C
80 °C
INITIAL REACTION MIXTURE
MONOMER 30.0 %
SOLVENT 69.9 %
CATALYST 0.1 %
CATALYST EFFICIENCY 0.6
—THEORETICAL
% CONVERSION
0
10
20
30
40
50
60
REACTION TIME IN HOURS
0
4
8
12
16
20
24
28
32
36

FIGURE 8

picture, providing added complexity. To best illustrate the effect of temperature actual cases have to be calculated for comparison, one such case being shown in Figure (9). In general, the higher the temperature, the higher will be the rate of initiation, resulting in a higher total free radical concentration. This in turn results in a higher rate of termination. Now, if the rate of termination increases faster than the rate of propagation, then as is the case here, the polymer chains cannot grow quite as long as at the lower temperature with the result that the molecular weight is lower. Under other conditions, it is of course quite possible, that the rate of propagation increases with temperature more rapidly than the rate of termination in which case the molecular-weight would increase with increasing temperature.

6.1.4 Reaction time

The last variable to be considered is the reaction time. A steady-state, free-radical concentration is achieved within one second, thus after a few seconds a complete chain-length distribution of dead polymer will exist. The amount will, of course, be infinitely small. Equation (35) gives a good idea as to how the degree of polymerization and therefore the distribution will change with time. As before, consider the first two terms in the right hand part of the equation to be negligible. Also, the term $C_o \exp(-k_d t)$ can be replaced by C, the catalyst concentration at any time t. Thus the only variables in the equation are C and M, in the ratio $\sqrt{C}/M$.

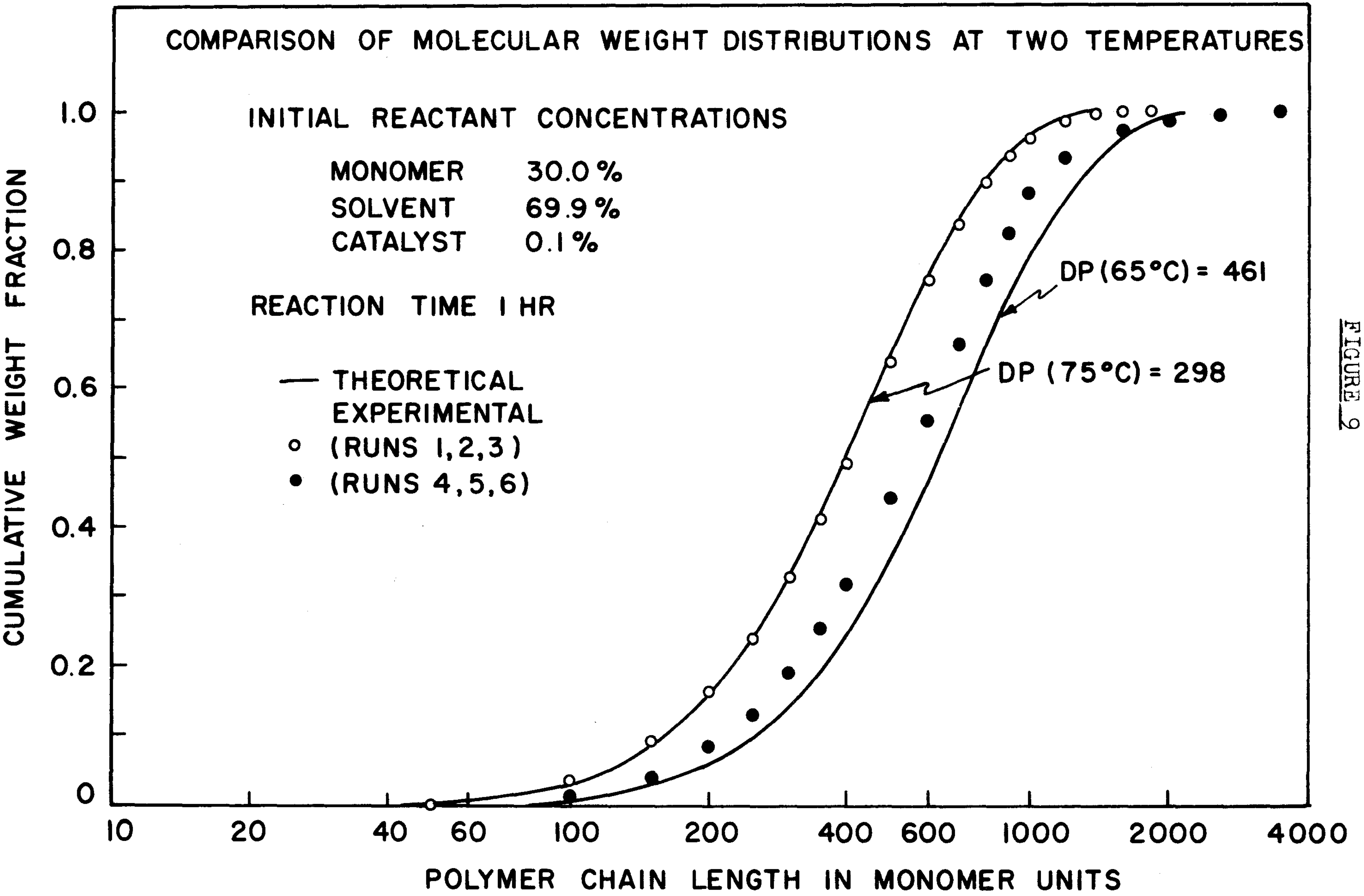

COMPARISON OF MOLECULAR WEIGHT DISTRIBUTIONS AT TWO TEMPERATURES
INITIAL REACTANT CONCENTRATIONS
MONOMER 30.0 %
SOLVENT 69.9 %
CATALYST 0.1 %
REACTION TIME 1 HR
— THEORETICAL
EXPERIMENTAL
○ (RUNS 1,2,3)
● (RUNS 4,5,6)
DP (65°C) = 461
DP (75°C) = 298
CUMULATIVE WEIGHT FRACTION
1.0
0.8
0.6
0.4
0.2
0
10
20
40
60
100
200
400
600
1000
2000
4000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE 9

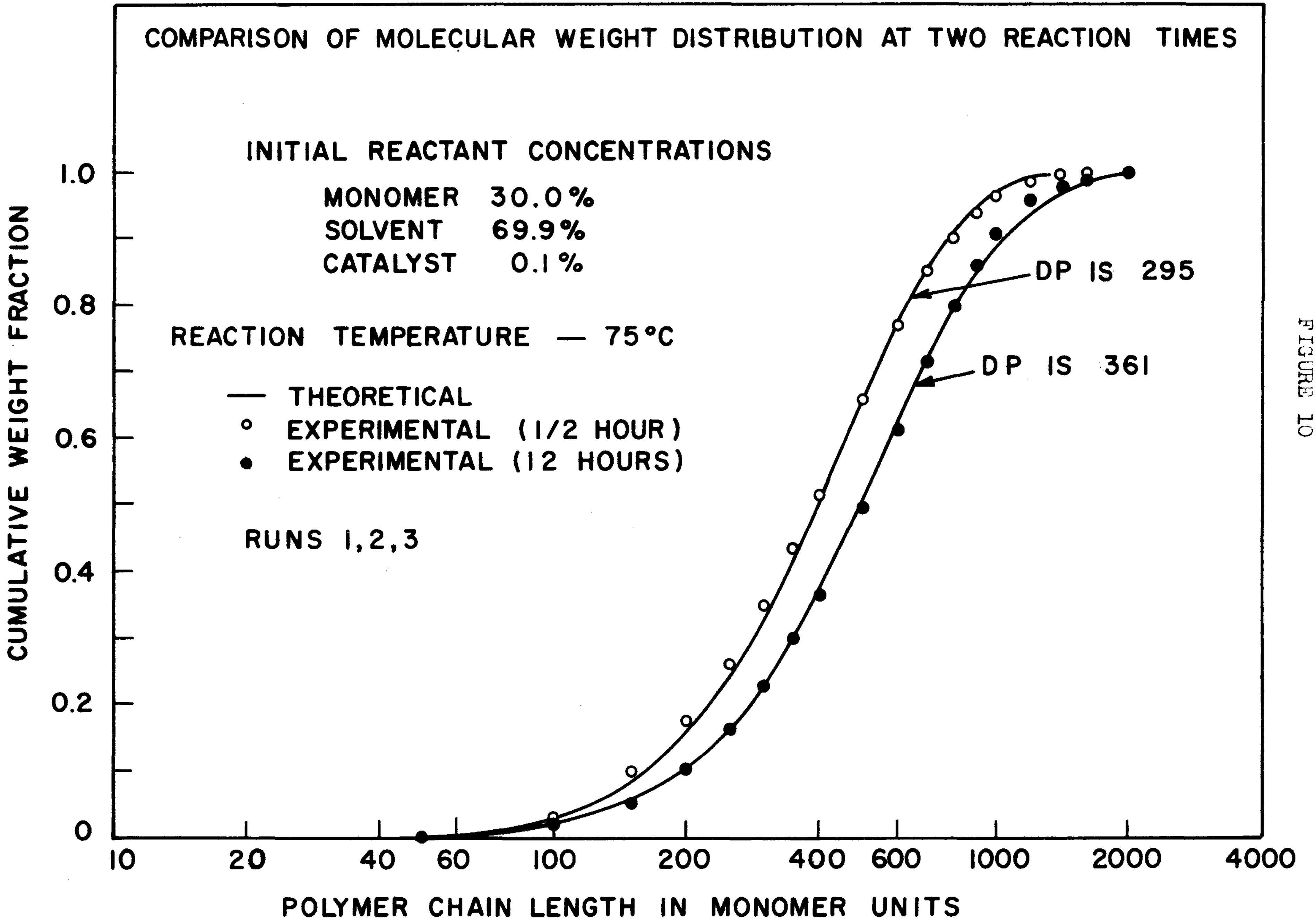

COMPARISON OF MOLECULAR WEIGHT DISTRIBUTION AT TWO REACTION TIMES
INITIAL REACTANT CONCENTRATIONS
MONOMER 30.0%
SOLVENT 69.9%
CATALYST 0.1%
REACTION TEMPERATURE — 75°C
— THEORETICAL
○ EXPERIMENTAL (1/2 HOUR)
● EXPERIMENTAL (12 HOURS)
RUNS 1,2,3
DP IS 295
DP IS 361
CUMULATIVE WEIGHT FRACTION
1.0
0.8
0.6
0.4
0.2
0
10
20
40
60
100
200
400
600
1000
2000
4000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE 10

If this ratio remains constant, then the degree of polymerization remains constant. Equation (16) shows that the monomer consumption rate is dependent on the catalyst decomposition rate, making the problem rather complex, but by combining Equations (16) and (35) conditions could be found at which the degree of polymerization remains constant, which incidentally is the condition at which the narrowest possible molecular-weight distribution is produced. A temperature of 65°C. seems to be approximately such a condition. Figure (10) shows the shift in distribution over a period of 12 hours at 75°C. and is typical of what can happen.

6.2 Steady-State Calculations

The derivation leading to the equation giving the total free radical concentration as a function of time has already been presented, resulting in Equation (12). Similarly, Equation (14) gives the rate of monomer consumption. Both equations were solved simultaneously using the fourth order Runge-Kutta Method. Equation (14) was solved by itself also. The results are presented in Tables (1) and (2). The catalyst efficiency was arbitrarily set at 0.6 but it is obvious that any other value between 0.5 and 1.0 would have given similar results. The rate constants were the same as those used in all other calculations. Table (1) and Figure (11) show the

TABLE 1

FREE RADICAL CONCENTRATION IN TRANSIENT STATE

Reaction Time (Sec.)	Conversion (X10^8)	Free Radical Concentration Gm. Moles/Liter (X10^8)
0.100	0.42098	0.94653692
0.200	0.84387	1.4363579
0.300	1.267	1.6073348
0.400	1.691	1.6584125
0.500	2.115	1.6729397
0.600	2.539	1.6770124
0.700	2.963	1.6781490
0.800	3.387	1.6784650
0.900	3.812	1.6785522
1.000	4.236	1.6785755
1.1	4.659	1.6785809
1.2	5.084	1.6785814
1.3	5.508	1.6785807
1.4	5.932	1.6785793
1.5	6.356	1.6785779
1.6	6.780	1.6785765
1.7	7.204	1.6785751
1.8	7.628	1.6785737
1.9	8.052	1.6785723
2.0	8.477	1.6785710

FIGURE 11

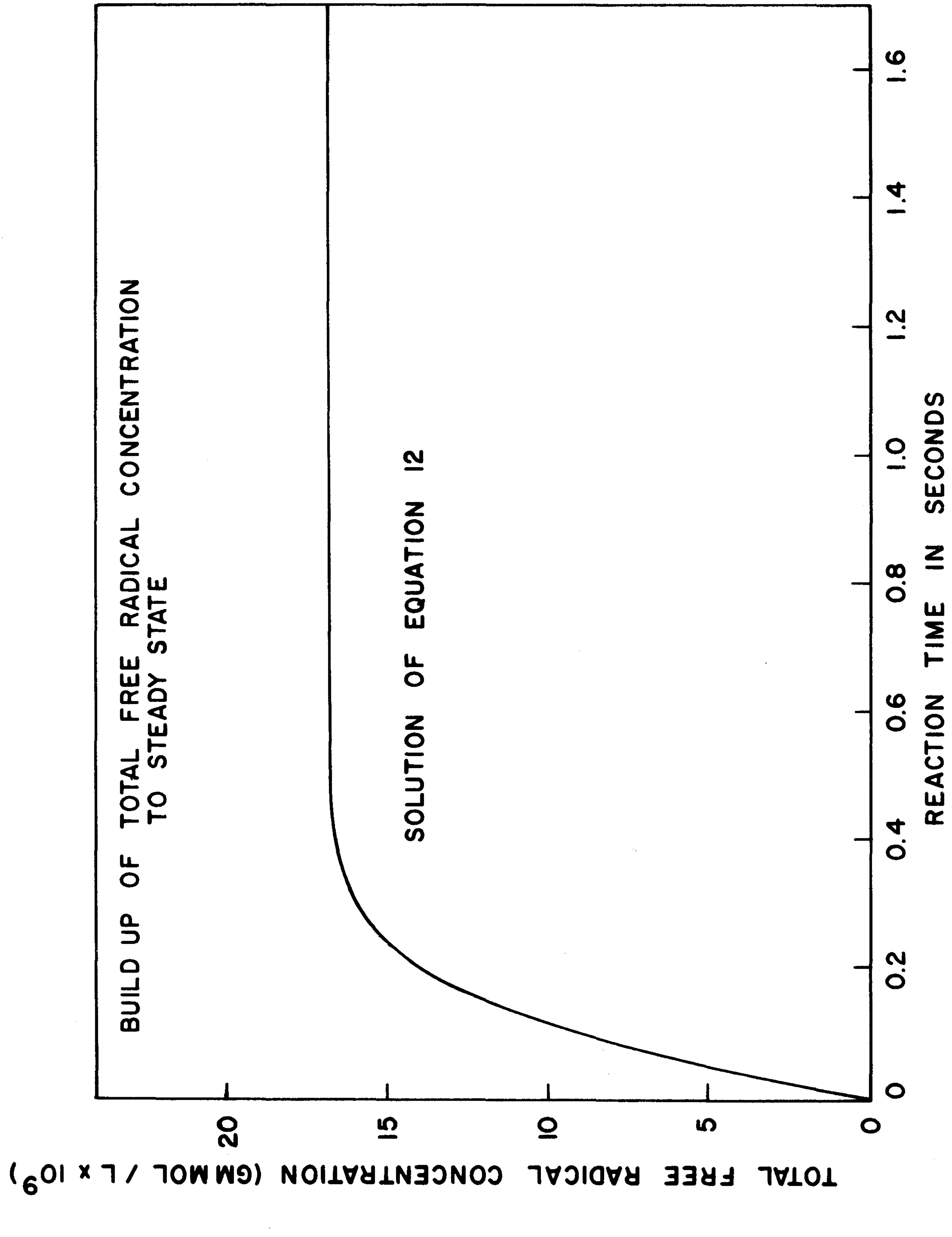

BUILD UP OF TOTAL FREE RADICAL CONCENTRATION
TO STEADY STATE
SOLUTION OF EQUATION 12
TOTAL FREE RADICAL CONCENTRATION (GM MOL / L x 10^9)
0
5
10
15
20
REACTION TIME IN SECONDS
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6

TABLE 2

FREE RADICAL CONCENTRATION IN THE TRANSIENT STATE

Reaction Time (Sec.)	Total Rad. Conc. Gm.Mol./L $X10^8$ (R^o)	Rate of Initiation Gm.Mol./L Sec. $X10^7$ I	Rate of Termination Gm.Mol/L. Sec. $X10^6$ $k_{tc}(R^o)^2$	Rate of Change in (R^o) $X10^{12}$ $\frac{d(R^o)}{dt}$
0.1	2.686	4.020	2.953	106633.94
0.2	3.097	4.020	3.926	9398.94
0.3	3.131	4.020	4.013	731.244
0.4	3.134	4.020	4.020	56.899
0.5	3.134	4.020	4.020	4.896
0.6	3.134	4.020	4.020	0.895
0.7	3.134	4.020	4.020	0.675
0.8	3.134	4.020	4.020	0.454
0.9	3.134	4.020	4.020	0.454
1.0	3.134	4.020	4.020	0.458
1.1	3.134	4.020	4.020	0.454
10	3.133	4.018	4.018	0.458
100	3.124	3.995	3.995	-0.881
1000	3.029	3.755	3.755	-0.867
1 hr.	2.803	3.215	3.215	-0.842
2 hr.	2.507	2.572	2.572	-0.760
3 hr.	2.242	2.058	2.058	-0.680
4 hr.	2.005	1.646	1.646	-0.607
5 hr.	1.794	1.318	1.318	-0.543
5½ hr.	1.697	1.179	1.179	-0.513

Reaction temperature was 75°C.

results for a temperature of 65°C. while Table (2) presents results for 75°C. From the graph it is seen that an overall steady state is reached in about half a second. Table (1) shows that a maximum free radical concentration is reached at 1.2 seconds and from then on it gradually declines. Table (2) shows the same result at 75°C. but includes the rates of initiation and termination and the rate of change in the total free radical concentration, $\frac{dR^o}{dt}$. It is clear that $\frac{dR^o}{dt}$ does approach zero, corresponding to a maximum free radical concentration but then it becomes negative showing the decline in R^o. The important conclusion, however, is that $\frac{dR^o}{dt}$ is very small compared with the rates of initiation and termination and therefore the steady-state assumption is justified.

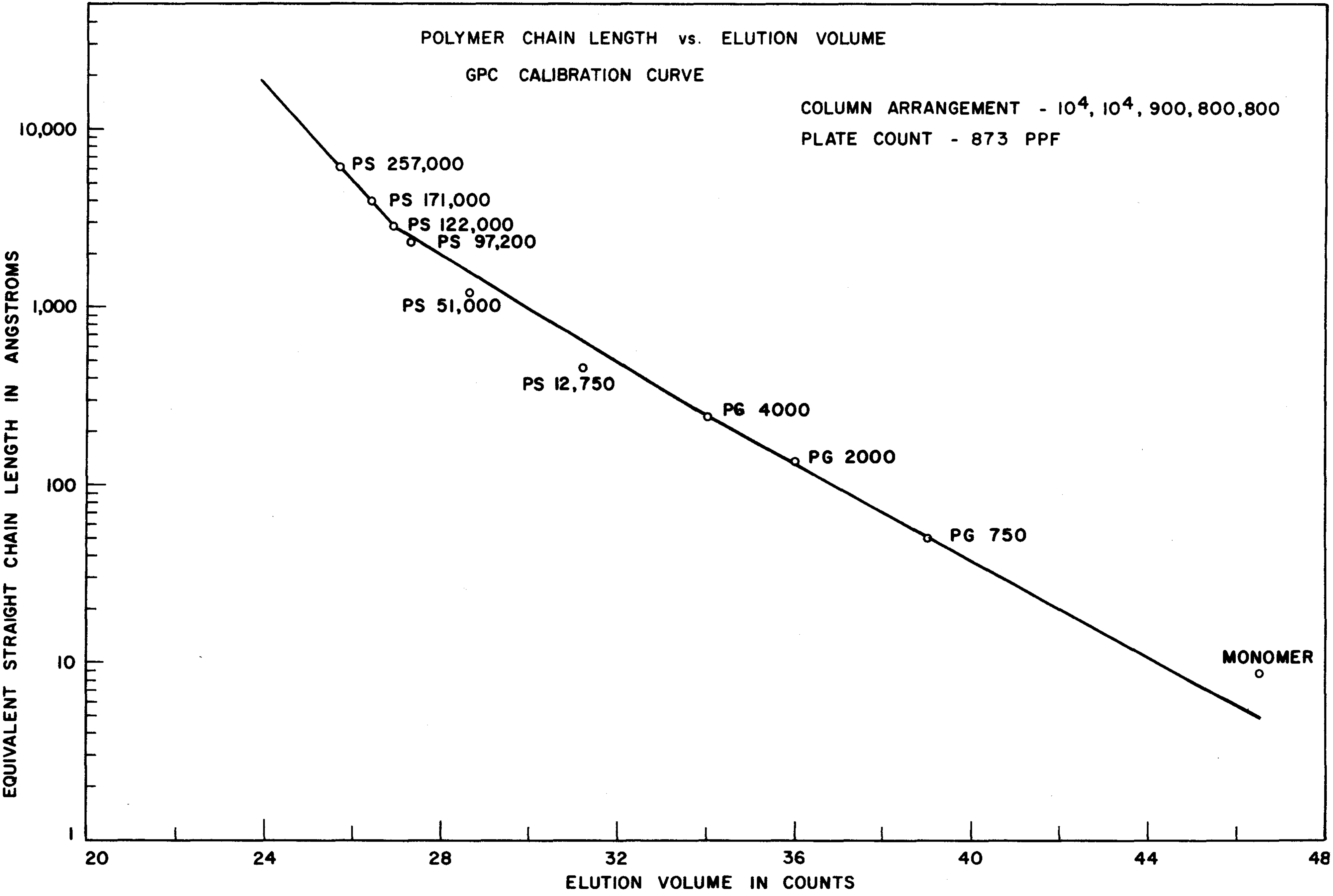
The results verify other workers' attempts at solving these equations analytically, to prove the steady-state condition. See for example Bamford[54]. The computer program for solving equations (12) and (14) simultaneously is given in Appendix (6).

6.3 Molecular Weight Measurement by Gel-Permeation Chromatography

6.3.1 Calibration curve

The gel-permeation chromatograph elution trace can be considered as a plot of the polymer concentration in the elution stream versus the elution volume as counts, one count being equivalent to 5 ml. of eluent. To transform the elution trace into a molecular-weight distribution plot, a relationship between elution volume and molecular-weight must be known. The reader is referred to Appendix 4.3 for details concerning the transformation technique. To obtain the above relationship a series of "standard" polymer samples whose molecular-weight is accurately known and which are mono-disperse or very nearly so are run. Preferably the standards should be of the same material as the samples to be analyzed and they should fall in roughly the same molecular-weight range. A semi-log plot of the equivalent-straight-chain length in angstroms versus the elution volume in counts is prepared from these standards. An increase in chain-length of one styrene unit is equivalent to 2.5 angstroms. Thus any point on the elution trace can now be related to the molecular-weight by finding the chain length for the same count on the calibration curve. The amount or fraction is obtained by normalizing the trace heights. In this work both polyglycol and polystyrene standards were used because the latter were not available in the lower molecular weight range. Standards are identified by two letters and a number, the letters signifying the type of material and the numbers the molecular-weight; PS means polystyrene and PG polyglycol. Figure (12) shows the calibration curve that was used to interpret the results of this work. It is clear that most regions can be closely approximated by straight lines. At the time of this investigation the standards PS-97,200 and PS-51,000 were not available and a straight line was therefore drawn from PG-4000 to PS-122,000, although it now appears that this region should really be represented by a curve.

FIGURE 12


POLYMER CHAIN LENGTH vs. ELUTION VOLUME
GPC CALIBRATION CURVE
COLUMN ARRANGEMENT - 10^4, 10^4, 900, 800, 800
PLATE COUNT - 873 PPF
PS 257,000
PS 171,000
PS 122,000
PS 97,200
PS 51,000
PS 12,750
PG 4000
PG 2000
PG 750
MONOMER
EQUIVALENT STRAIGHT CHAIN LENGTH IN ANGSTROMS
10,000
1,000
100
10
1
ELUTION VOLUME IN COUNTS
20
24
28
32
36
40
44
48

The existing computer program cannot be used for a curved calibration plot and it will require some changes. It is suggested that the calibration curve is read-in in the form of an array of elution count versus chain length and that a subroutine program be written to interpolate between read-in values.

It should be noted that the standard PS-19,750 does not fall on the curve as drawn and alternative curves were tried. For example, a curve in which the points PS-122,000 and PS-19,750 were connected and in which a line from PS-19,750 was drawn parallel to that through the polyglycol standards was tried. However, the results were rather discouraging in that poor agreement with the theoretically predicted distribution was obtained. Several other similar curves were tried with more or less the same result. The curve shown in Figure (12), however, gave good agreement between the experimental and theoretical distributions.

Some explanation concerning the monomer elution count seems to be in order also. When a monomer unit is added to a long polymer chain, it increases the chain length by two carbon-carbon bonds or 2.5 angstroms, the contribution of the phenyl group being neglected. In order to relate the polymer chain length in angstroms to its molecular weight it is multiplied by a "so-called" Q factor. This factor is simply the monomer molecular-weight divided by 2.5, its chain length contribution, and it is assumed to be constant regardless of the chain length. However, it is clear that for a single monomer unit or small multiples the contribution of the phenyl group to the equivalent-straight-chain length cannot be neglected. In fact, for pure monomer the end to end distance can be calculated to be 8.8 angstroms. But on the basis of a constant Q factor the monomer chain length should only be 2.5 angstroms. Thus either choice presents difficulties. If an angstrom value of 8.8 is adopted for pure monomer, a different Q factor must be used for each additional monomer unit in the polymer chain until a reasonable chain length (50 monomer units or more) has been built up. If on the other hand 2.5 angstroms is selected as the proper chain length, the calibration curve is no longer a plot of straight chain length versus elution count but rather the equivalent of a plot of molecular-weight versus elution count. The latter procedure likely is more accurate as long as only polystyrene analysis is involved. Fortunately the above difficulty introduces only small errors because all the distributions analyzed had very little material of chain length 50 or less.

In the absence of any polystyrene standards in the molecular-weight range below 20,000, polyglycol standards were used to establish the calibration cruve. Whether or not this is justified will not be known until polystyrene standards for that region are available. Under the circumstances it appeared to be the best procedure however. Further details are given in Appendices (2) and (5) for various column arrangement while Table(3) shows the calibration results for the present column arrangement.

TABLE 3

GEL-PERMEATION CHROMATOGRAPH CALIBRATION RESULTS

Standard	Angstrom Size	Elution Count
PG-750	51.4	39.0
PG-2000	139	36.0
PG-4000	247	34.0
PS-19,750	460	31.2
PS-51,000	1230	28.6
PS-97,200	2345	27.3
PS-122,000	2945	26.9
PS-171,000	4000	26.4
PS-257,000	6207	25.7

Column arrangement in direction of flow was 10^4, 10^4, 900, 800, 800.

Plate count based on orthodichlorobenzene was 873 plates per foot of column length.

6.3.2 Reproducibility of gel-permeation chromatograph trace interpretations

In the following paragraphs by reproducibility is meant agreement between two or more molecular-weight distributions obtained from separate gel-permeation chromatograph traces. The gel-permeation chromatograph traces may have been obtained from the same sample solutions or from two different solutions of the same concentration of polymer. Thus errors involved in making up the polymer are considered as part of the reproducibility.

Table (4) shows the results for one sample repeated three times. Columns (2) and (3) give the distribution for the same solution run a few days apart and column (1) gives it for a separate solution of the same polymer, run three months earlier. Several other polymer samples were subjected to similar repeat analyses, some showing worse and some better agreement. It is seen that there can be considerable variation. Several reasons that can cause variations are discussed in Appendix 4.5, but these were closely controlled. For example, all samples throughout this work were of the same concentration, 0.5 wt.% in tetrahydrofuran (T.H.F.) solvent and a standard injection time of 60 seconds was used. The cause of the variations had to be attributed, therefore, to other reasons. Careful examination of the gel-permeation chromatograph traces giving poor reproducibility showed that there was a considerable amount of baseline drift. The interpretation procedure as outlined in Appendix 4.3 makes allowance for baseline drift but

TABLE 4

GEL-PERMEATION CHROMATOGRAPH REPRODUCIBILITY

Run No. 1, Reaction Time - 7 Hours

Chain Length	Weight	Fraction	X10^5
	1	2	3
50	14.3	20.1	16.7
100	60.1	61.9	75.6
150	93.7	90.5	106.4
200	115.6	116.5	138.3
250	137.9	139.1	153.7
300	147.8	144.9	159.1
350	147.4	145.9	154.9
400	140.8	140.0	146.4
450	134.3	131.6	138.2
500	128.7	125.2	130.3
550	121.9	118.0	119.1
600	111.9	108.7	107.1
650	100.6	98.6	94.8
700	90.0	88.4	82.8
750	79.6	77.7	70.6
800	68.3	66.0	58.2
850	58.7	57.3	47.2
900	48.7	48.7	37.9
950	38.6	40.3	29.9
1000	31.6	33.0	24.5
1100	20.5	20.7	15.2
1200	11.3	11.1	8.0
1300	6.1	5.9	4.3
1400	4.8	4.7	3.6
1500	3.5	3.6	3.0
1600	3.0	2.9	2.5
1700	2.6	2.3	2.1
1800	2.1	1.8	1.8
1900	1.5	1.5	1.5
2000	1.0	1.3	1.2
No. Ave.	300	356	331
Wt. Ave.	451	565	504
Wt.Ave./No.Ave.	1.50	1.58	1.52

if the drift becomes excessive it is very difficult to establish where a trace starts or ends. As a result the point at which a trace starts or ends can vary as much as two counts. This was the case for the example shown in Table (3). Experienced judgment can to a large degree offset such variations, however, it is best to rerun samples which exhibit excessive baseline drift until satisfactory traces are obtained. Since baseline drift appears to be the most prominent source of error, future work should aim at closer control and improvement of this variable.

6.3.3 Effect of sample preparation

A far more serious error was found in the type of sample being used. One of the often suggested advantages of the gel-permeation chromatograph is that the polymer does not have to be isolated from the reaction mixture, to be suitable for injection into the gel-permeation chromatograph. It was found that this is not so. Figure (13) shows the distribution obtained from a precipitated sample and its original reaction mixture. Although the two distributions may not look too different there was a significant shift in the number average chain length, from 300 to 344. It is curious that the low molecular-weight material does not show up in the reaction mixture sample but does appear in the precipitated polymer. This suggests one of two things. Either the polymer is fractionated when precipitated, showing lower molecular-weight material than was originally produced, or, the monomer and

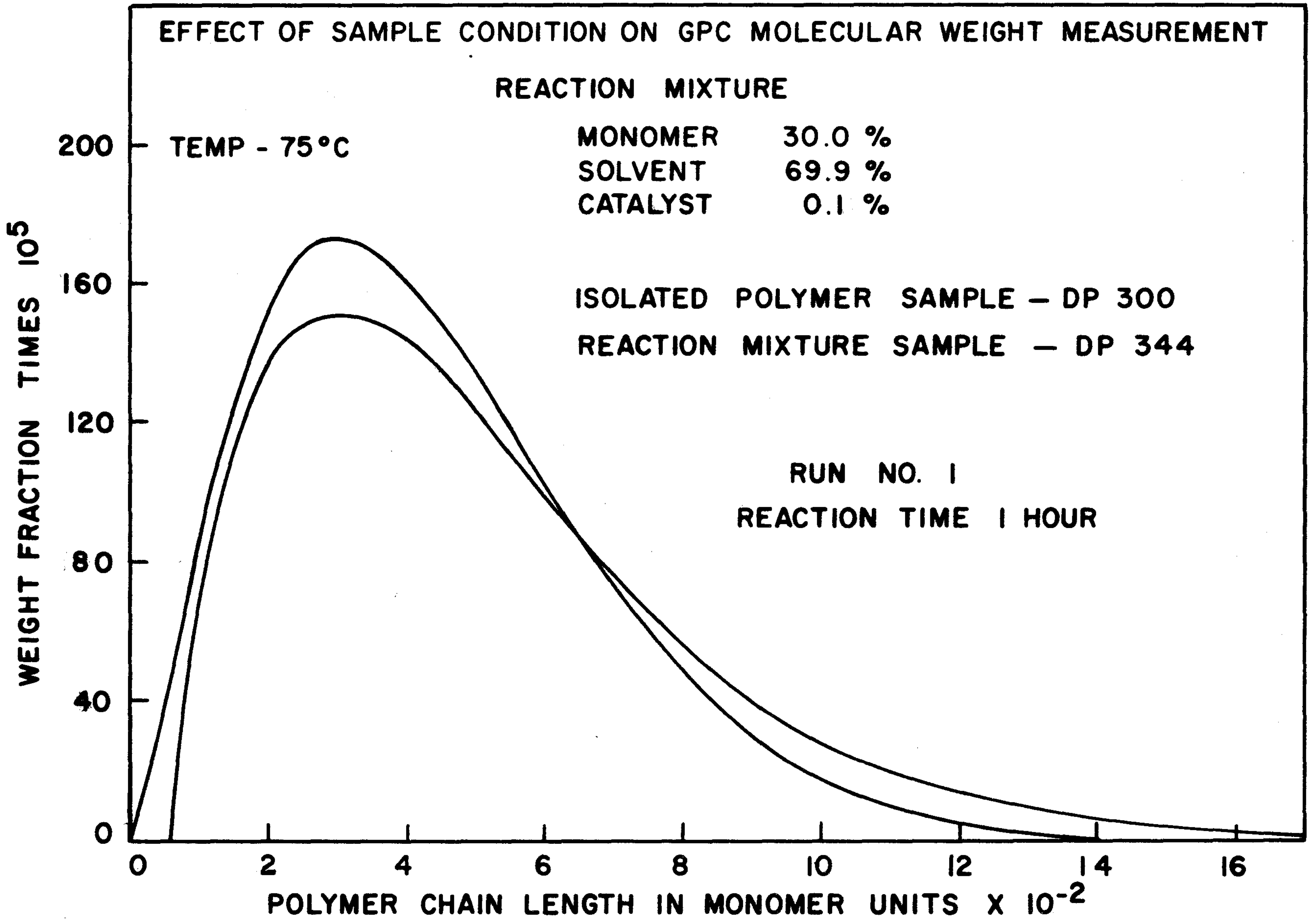

EFFECT OF SAMPLE CONDITION ON GPC MOLECULAR WEIGHT MEASUREMENT
REACTION MIXTURE
MONOMER 30.0 %
SOLVENT 69.9 %
CATALYST 0.1 %
TEMP - 75°C
ISOLATED POLYMER SAMPLE – DP 300
REACTION MIXTURE SAMPLE – DP 344
RUN NO. 1
REACTION TIME 1 HOUR
WEIGHT FRACTION TIMES 10^5
0
40
80
120
160
200
POLYMER CHAIN LENGTH IN MONOMER UNITS X 10^-2
0
2
4
6
8
10
12
14
16

FIGURE 13

benzene present in the reaction mixture sample for some reason interferes with its proper analysis in the gel-permeation chromatograph columns. The problem might be due to overloading but not likely so. Rather, it is suspected that the unreacted monomer and benzene or both remain trapped inside the long polymer chains even when the sample is considerably diluted in THF. The swelled particle then has a larger hydrodynamic diameter and thus exhibits a higher molecular weight than it would if no monomer were trapped inside. There is no doubt that the problem is real. Several other samples were similarly investigated showing very similar behaviour, as Table (5) shows. To further test this behaviour, two samples of polymer were dissolved in twice their weight of monomer, giving a 33% polymer in monomer sample, thus as it were a reconstituted reaction mixture of bulk polymerization. For this case there was no significant change, which shows that the phenomenon is not due to simple interference. Rather it seems to confirm the theory that monomer or benzene is trapped inside dissolved polymer molecules, which is removed in precipitation. In conclusion, therefore, it can be said that in order to obtain true molecular weight of a polymer in a reaction mixture, it should be precipitated first and then redissolved in THF, rather than the reaction mixture being diluted directly with THF.

TABLE 5

EFFECT OF MONOMER IN GEL-PERMEATION CHROMATOGRAPH SAMPLES

Run No.	Reaction Time (Hr.)	Number Average Chain Length Reaction Mixture	Precipitated Polymer
1	1	344	300
1	3	361	326
1	7	413	358
19	1	937	898
19	4	1045	1039
19	6	1220	1140
7,8,9*	6	354	364
7,8,9*	12	349	352

* The gel-permeation chromatograph sample was based on 1/3 by weight of isolated polymer from each run and the resulting polymer mixture was dissolved in twice its weight in monomer, before being diluted with THF.

7. CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

1. The conversion of the monomer and the molecular-weight distribution of polystyrene as predicted by the mathematical model are in good agreement with the experimental results except for bulk polymerization.

2. To obtain good agreement between predicted and experimental conversion at all monomer concentrations, the catalyst efficiency has to be increased or the ratio of the propagation to termination rate constant must be increased.

3. At higher monomer concentrations the experimentally determined molecular-weights are higher than the theoretically predicted values, even with an adjusted catalyst efficiency, which suggest that the rate constants rather than catalyst efficiency are monomer or solvent concentration dependent.

4. The steady-state assumption often used to simplify the kinetic equations is well justified; for styrene a steady-state is reached in less than one second.

5. The ratio of the weight to number average chain length is very close to 1.5 for styrene polymerization, which indicates that termination takes place largely by combination. For disproportionation the ratio is 2.0.

6. The probability of propagation is about 0.9975 or higher and no serious error would result if it were assumed to be constant.

7. In general the results from the gel-permeation chromatograph were in close agreement with the theoretically predicted values which confirms that under the proper conditions the gel-permeation chromatograph can be an accurate and efficient tool for determing molecular-weight distributions.

8. A general operating procedure for the gel-permeation chromatograph, including a computer program for interpreting the elution curve was established.

9. Gel-permeation chromatograph reproducibility is good provided the sample injection time is kept below 60 seconds and elution curves showing excessive baseline drift are rejected.

7.2 Recommendations

1. Future rate studies should be aimed at establishing a functional relationship between the monomer or solvent concentration or the viscosity of the mixture and the termination constant. A backmix reactor would lend itself best to such a project.

2. The existing apparatus should be easily adaptable to emulsion polymerization which is industrially of far greater importance, making it an attractive project.

3. Further studies on operating techniques of the gel-permeation chromatograph and trace interpretations are required. In particular, comparison studies with light scattering and viscosity techniques are suggested.

4. Bulk polymerization of acrylonitrile in water

using a peroxide or redox catalyst is suggested to test the so-called occlusion effect and to modify the present model to include this effect.

5. Ziegler catalysis has become of major industrial importance and with more and more papers being published on its kinetics, this field should be carefully considered for similar studies.

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REFERENCES

1. Thomas Graham, Trans. Roy. Soc., (London), 151, 183 (1861)
2. Wolfgang Ostwald, Kolloid Z., 1, 331 (1907)
3. J. H. van't Hoff, Z. Physik. Chem., 1, 481 (1887)
4. F. M. Raoult, Compt. Rend., 95, 1030 (1882)
5. F. Musculus and A. Meyer, Bull. Soc. Chem. France, 35, 370 (1881)
6. H. T. Brown and G. H. Morris, J. Chem. Soc., 53, 610 (1881)
7. H. Staudinger, Ber., 53, 1073 (1920)
8. W. H. Carothers, J. Am. Chem. Soc., 51, 2548 (1929)
9. W. Kuhn, Ber., 63, 1503 (1930)
10. H. Staudinger and W. Heuer, Ber., 63, 222 (1930)
11. W. A. Caspari, J. Soc. Chem. Ind., 32, 1041 (1913)
12. J. Craik and F. D. Miles, Trans. Far. Cos., 27, 756 (1931)
13. E. O. Kraemer, Ind. Eng. Chem., 30, 1200 (1938)
14. H. Mark and G. Saito, Monatsh., 68, 237 (1936)
15. D. H. Johnson and A. V. Tobolsky, J. Am. Chem. Soc., 74, 938 (1952)
16. Bamford, Barb, Jenkins and Onyon, "The Kinetics of Vinyl Polymerization", Butterworths (London), p-218 (1958)
17. Ibid, p-204
18. J. P. Van Hook and A. V. Tobolsky, J. Pol. Sci., 33, 429 (1958)
19. F. R. Mayo, R. A. Gregg and M. S. Matheson, J. Am. Chem. Soc., 73, 1691 (1951)
20. Bamford, Barb, Jenkins and Onyon, "The Kinetics of Vinyl Polymerization", Butterworths (London), pp 283, (1958)

21. Henn Kilkson, Ind. Eng. Chem., 3, 281 (1964)

22. R. J. Zeman and N. R. Amundson, Chem. Eng. Sci., 20, 331, (1965)

23. Shean-Lin Liu and Neal R. Amundson, Rubber Chem. and Technology, 34, 995 (1961)

24. Bamford, Barb, Jenkins and Onyon, "The Kinetics of Vinyl Polymerization", Butterworths (London), pp 205, (1958)

25. Boundy and Boyer, "Styrene-Its Polymers Copolymers and Derivatives", Reinhold (New York), pp 315, (1952)

26. J. C. Bevington, Trans. Far. Soc., 51, 1392 (1955)

27. Bamford, Barb, Jenkins and Onyon, "The Kinetics of Vinyl Polymerization", Butterworths (London), pp 205, (1958)

28. M. S. Matheson, J. Chem. Phys., 13, 584 (1945)

29. J. C. Bevington, J. Chem. Soc., 1127 (1956)

30. Bamford, Barb, Jenkins and Onyon, "The Kinetics of Vinyl Polymerization", Butterworths (London), pp 204, (1958)

31. P. J. Flory, Principles of Polymer Chemistry, Cornell Univ. Press, N. Y., pp 121, (1953).

32. F. R. Mayo, J. Amer. Chem. Soc., 65, 2324 (1943)

33. Boundy and Boyer, "Styrene, Its Polymers Copolymers and Derivatives", Reinhold (New York), pp 333, (1952)

34. Bamford, Barb, Jenkins & Onyon, "The Kinetics of Vinyl Polymerization", Butterworths (London), pp 39, (1958)

35. M. S. Matheson, E. E. Amer., Ellen B. Bevilaequa and E. J. Hart, Am. Chem. Soc., 71, 497 (1949)

36. Matheson et al., ibid, 73, 1700 (1951)

37. W. V. Smith, J. Am. Chem. Soc., 70, 3695 (1948)

38. W. V. Smith and R. H. Ewart, J. Chem. Phys., 16, 592 (1948)

39. S. Chandrasekhar, Revs. Modern Phys., 15, 1 (1943)

40. Tompa, "Polymer Solutions", Butterworths (London), pp 235, (1956)

41. Billmeyer, "Textbook of Polymer Science", Interscience (New York), pp 38, (1962)

42. Bamford, Barb, Jenkins and Onyon, "The Kinetics of Vinyl Polymerization", Butterworths (London), pp 219, (1958)

43. J. P. Van Hook and A. V. Tobolsky, J. Am. Chem. Soc., 80, 779 (1958)

44. A. V. Tobolsky and J. Offenbach, J. Pol. Sci., 26, 311 (1955)

45. A. V. Tobolsky and B. Baysol, J. Pol. Sci., 11, 471, (1953)

46. B. M. E. van der Hoff, Polymerization and Polycondensation Processes, Am. Chem. Soc., Adv. in Chem. Ser. No. 34, 6 (1962).

47. K. P. Paoletti and F. W. Billmeyer Jr., J. Pol. Sci., A-2, 2049 (1964)

48. Bamford, Barb, Jenkins and Onyon, "The Kinetics of Vinyl Polymerization", Butterworths (London), pp 238 (1958)

49. Von G. Henrici - Olive and S. Olive, Makromol. Chem., 55, 188 (1962)

50. M. Talat Erben and S. Bywater, J. Am. Chem. Soc., 77, 3712 (1955)

51. J. W. Breitenbach and A. Schindler, Mh. Chem., 83, 724 (1952)

52. D. H. Johnson and A. V. Tobolsky, J. Am. Chem. Soc., 74, 938 (1952)

53. L. M. Arnett and J. H. Peterson, J. Am. Chem. Soc., 74, 2032 (1952)

54. Bamford, Barb, Jenkins and Onyon, "The Kinetics of Vinyl Polymerization", Butterworths (London), pp 10, (1958)

55. Ibid - pp 76

56 Ibid - pp 251

57. Wilde, "Optimum Seeking Methods", Prentice-Hall, pp 33, (1964)

58. R. M. Wheaton and W. C. Bauman, Ann. N. Y. Acad. Sci., 57, 159 (1953)

59. G. H. Lathe and C. R. Ruthven, Biochem. J., 62, 665 (1956)

60. J. C. Moore, J. Pol. Sci., 2-A, 835 (1964)

61. J. C. Moore and J. G. Hendrickson, Pol. Div. Preprints, 1964 Fall National ACS Meeting, pp 706

62. A. V. Tobolsky, C. E. Rogers and R. Brickman, J. Am. Ch. Soc., 82, 1277 (1960)

APPENDIX

1. THEORY OF POLYMERIZATION KINETICS

1.1 Catalyst Efficiency

The principle reactions were outlined in Section 4.2 and will not be further elaborated upon here. However, in the initiation step a catalyst efficiency factor was introduced and assumed to be independent of the monomer concentration. Although this point is well discussed in the literature (18, 27, 28), some explanation seems to be in order. Matheson[18] introduced the concept of the so-called "cage effect" which is now generally accepted as representing the best mechanistic picture to date. Consider the following reaction scheme.

1. $\text{Cat.} \longrightarrow (2\ R_c^o) \qquad k_d$
2. $(2\ R_c) \longrightarrow Q \qquad k_R$
3. $(R_c^o) + M \longrightarrow R^o \qquad k_X$
4. $(R_c^o) \longrightarrow R_c^o \qquad k_D$
5. $R_c^o + R_c^o \longrightarrow X \qquad k_R'$
6. $R^o + M \longrightarrow R^o \qquad k_p$
7. $R^o + R^o \longrightarrow P \qquad k_t$

The parenthesis symbolize the cage in which the primary (catalyst) radicals are trapped and from which they can escape by diffusion. Q represents the reaction product of two caged radicals and may be a waste product or the same as the original catalyst. If the latter is the case the catalyst efficiency, which is defined as

$$f = \frac{\text{rate of initiation of polymerization chains}}{2\ (\text{rate of catalyst decomposition})}$$

is equal to 1.0.

Reaction 5 can easily be shown to be of little importance (27) and can therefore be neglected. Applying the steady-state procedure, as before, the rate of monomer consumption can be written as:

$$-\frac{dM}{dt} = k_pM\left[\frac{k_dCat}{k_t}\right]^{\frac{1}{2}}\left[\frac{k_D + k_XM}{k_R + k_D + k_XM}\right]^{\frac{1}{2}} \qquad (31)$$

If $k_D >> k_XM$ equation (31) may be simplified to

$$-\frac{dM}{dt} = k_pM\left[\frac{k_dCat}{k_t}\right]^{\frac{1}{2}}\left[\frac{k_D}{k_R + k_D}\right]^{\frac{1}{2}} \qquad (32)$$

The reaction is first order in monomer concentration and the order is constant. In this case f is independent of the monomer concentration. If on the other hand $k_D << k_XM$,

$$-\frac{dM}{dt} = k_pM\left[\frac{k_dCat}{k_t}\right]^{\frac{1}{2}}\left[\frac{k_XM}{k_R + k_XM}\right]^{\frac{1}{2}} \qquad (33)$$

In this case the reaction order varies from 1.0 to 1.5 as the monomer concentration decreases and f is now dependent upon the monomer concentration. Also, if Q is identical with the original catalyst in which case f = 1.0, the rate of catalyst decomposition is dependent upon the monomer concentration.

If f is less than 1.0, which appears to be the case (18), and f is independent of the monomer concentration a cage effect as illustrated by equation (32) must take place or part of the catalyst must decompose by a non-radical mechanism. There is some evidence that this is so for Azo, (29). From this work it appears that the catalyst efficiency is dependent upon the monomer and increases with initial monomer concentration but little or no variation is detected during the reaction. It may be of course that in this case we are not at all dealing with an increase in efficiency but rather a change in reaction constants. A possible explanation would be that the rate constants are dependent on the solvent concentration, which would explain why they do not change with monomer conversion. Matheson[28] was the first to derive equation (33) to explain the results of Schulz and Huseman [30] and their proposed mechanism. However, Flory's criticism (31) of the cage effect leads to equation (32) and thus f, although less than 1.0, would be independent of the monomer concentration. The findings of this work seem to indicate that this is not so. If f were dependent on the monomer concentration one would expect to see some deviation between the theoretically predicted and observed values of conversion as it progresses. Since this is not the case f could be independent of the monomer concentration.

1.2 Determination of Rate Constants

The most popular method for determining rate constants in polymerization work is to determine the degree of polymerization. It makes use of the fact that the intrinsic viscosity can be related to the number-average molecular weight or the degree of polymerization, DP.

The number average chain length is defined as the mean molecular chain length which is the average number of monomer molecules consumed per inactive (dead) polymer molecule formed.

$$DP = -\frac{dM}{dt} \Big/ \frac{dP}{dt}$$

$$DP = \frac{k_p M\, R^o \text{ (for long chains)}}{k_{fs} S\, R^o + k_{fm} M\, R^o + \frac{k_{tc}}{2} (R^o)^2} \qquad (34)$$

substituting for R^o from equation (15) and inverting gives:

$$\frac{1}{DP} = \left(\frac{k_{fs}}{k_p}\right)\left(\frac{S}{M}\right) + \left(\frac{k_{fm}}{k_p}\right) + \left(\frac{k_{tc}}{2k_p}\right)\left(\frac{1}{M}\right)\left(\frac{2fk_dC_o \text{ exp. } (-k_d t)}{k_{tc}}\right)^{\frac{1}{2}} \qquad (35)$$

For polymerization in pure monomer this reduces to

$$\frac{1}{DP} = \left(\frac{k_{fm}}{k_p}\right) + \left(\frac{k_{tc}}{2k_p}\right)^{\frac{1}{2}} \quad 2fk_dC_o \exp(-k_d t)^{\frac{1}{2}} \left(\frac{1}{M}\right) \qquad (36)$$

Thus if k_d and f are known, the ratio $\sqrt{k_{tc}/2k_p}$ may be obtained from the slope of a plot of 1/DP versus (1/M) and the ratio k_{fm}/k_p is given by the intercept. Once these two quantities are known polymerization in a solvent may be carried out and the ratio k_{fs}/k_p can then be obtained from equation (35). If k_d and f are not known polymerization rate studies can be made to yield these quantities. The rate of polymerization is given by:

$$R_p = k_p R^o M \tag{37}$$

and the rate of chain initiation by:

$$R_i = 2k_d f\ C_o \exp(-k_d t) \tag{38}$$

Finally the rate of termination is:

$$R_t = k_{tc}(R^o)^2 \tag{39}$$

As before, writing the steady-state equations, one obtains:

$$R_i = R_t$$

$$2k_d f\ C_o \exp(-k_d t) = k_{tc}(R^o)^2 \tag{40}$$

substituting for (R^o) from equation (37) yields

$$2k_d f\ C\ \exp(-k_d t) = k_{tc}\left[\frac{R_p}{k_p M}\right]^2 \tag{41}$$

and substituting equation (41) back into equation (36) gives:

$$\frac{1}{DP} = \frac{k_{fm}}{k_p} + \frac{k_{tc}}{2k_p^2}\left(\frac{R_p}{M^2}\right) \tag{42}$$

Normally, only initial rates are studies and an average monomer concentration may be used. Thus as before, a plot of 1/DP versus R_p/M^2 should yield a straight line with slope $k_{tc}/2k_p^2$.

This is the most widely used method of obtaining rate constants and these equations were first set forth by Mayo[32]. The number-average molecular weight or degree of polymerization usually is obtained from the intrinsic viscosity (33).

However, these methods all yield ratios of the rate constants and in order to obtain any one individual constant one of them or a ratio such as k_{tc}/k_p must be known. The ratio k_p/k_{tc} can be obtained by the so called "sector" method (34) and it was first used with styrene by Matheson et. al.[35,36]. For a detailed description the reader is referred to the original references, especially (35) and (34). There is a third method by which the individual rate constant for propagation, k_p, may be obtained, which is based on the emulsion-polymerization theory of Smith and Ewart[37, 38]. Having obtained k_p the other constants may then be obtained by the previously described viscosity method.

1.3 The Weight to Number Average Ratio and its Significance

The equations giving the number and weight average chain lengths have already been presented. However, the significance of these quantities has not been dealt with and will therefore be discussed in the following paragraphs.

The ratio of $\bar{r}_w$ to $\bar{r}$ is often taken as a measure of the degree of spreading of the distribution and it is therefore useful to see what one might expect this ratio to be in vinyl polymerization. From equations (27) and (28) it is seen that

$$\frac{\bar{r}_w}{\bar{r}} = \frac{\sum\limits_{r=1}^{\infty} r^2 P_r \sum\limits_{r=1}^{\infty} P_r}{\sum\limits_{r=1}^{\infty} r\, P_r^{\,2}} \qquad (43)$$

Thus the value of P_r needs to be known, which can only be obtained by integrating equation (5), and which may be written as:

$$\frac{dP_r}{dt} = \left[\frac{I}{k_{tc} + k_{td}}\right]^{\frac{1}{2}} (1 - \xi)\,\xi^{r-1} \left[k_{fs}S + k_{fm}M + k_{td}\left[\frac{I}{k_{fc} + k_{fd}}\right]^{\frac{1}{2}} + \tfrac{1}{2}k_{tc}\left[\frac{I}{k_{tc} + k_{td}}\right]^{\frac{1}{2}} (1 - \xi)\ \frac{(r-1)}{\xi}\right] \qquad (44)$$

If it is assumed that I, M and S are constant, then $\frac{dP_r}{dt}$ is constant and

$$P_r = \frac{dP_r}{dt}\, t$$

Also $\Delta M = - \frac{dM}{dt}\, t =$

or $\qquad t = \Delta M / k_p M \left[\frac{I}{k_{tc} + k_{td}}\right]^{\frac{1}{2}}$

Making these substitutions in equation (44) yields

$$P_r = \frac{\Delta M}{k_p M}\ (1 - \xi)\,\xi^{r-1} \Bigg\{ k_{fs}S + k_{fm}M + \left[\frac{I}{k_{tc} + k_{td}}\right]^{\frac{1}{2}} \Bigg[k_{td} +$$

$$\left.\left.\frac{(r-1)\ (1-\xi)\ k_{tc}}{2\xi}\right]\right\} \qquad (45)$$

Since

$$\frac{1-\xi}{\xi} = \frac{k_{fs}S + k_{fm}M + \left[I(k_{tc} + k_{td})\right]^{\frac{1}{2}}}{k_pM}$$

Equation (45) can be written as

$$P_r = \frac{\Delta M}{k_pM}\ (1-\xi)\,\xi^{r-1}\left[k_{fs}S + k_{fm}M + k_{td}\left[\frac{I}{k_{tc} + k_{td}}\right]^{\frac{1}{2}} + \right.$$

$$\left.\frac{k_{tc}}{2}\left[\frac{I}{k_{tc} + k_{td}}\right]^{\frac{1}{2}} (r-1) \left\{\frac{k_{fs}S + k_{fm}M + \left[I(k_{tc} + k_{td})\right]^{\frac{1}{2}}}{k_pM}\right\}\right] \qquad (46)$$

The first case to be considered is that in which termination is exclusively by disproportionation, i.e. $k_{tc} = 0$. This allows considerable simplification of equation (46).

$$P_r = \frac{\Delta M}{k_pM}\,(1-\xi)\,\xi^{r-1}\left[k_{fs}S + k_{fm}M + (Ik_{td})^{\frac{1}{2}}\right] \qquad (47)$$

equation (47) may be written as

$$P_r = \frac{\Delta M}{k_pM}\,(1-\xi)^2\,\xi^{r-1}\left[k_pM + k_{fs}S + k_{fm}M + (Ik_{td})^{\frac{1}{2}}\right]$$

and in the absence of chain transfer and for long chains

$$P_r = \Delta M(1 - \xi)^2 \xi^{r-1} \qquad (48)$$

The sums of the three infinite series that are required can now be evaluated:

$$\sum_{r=1}^{\infty} P_r = \Delta M(1 - \xi)^2 \sum_{r=1}^{\infty} \xi^{r-1}$$

$$\sum_{r=1}^{\infty} P_r = \frac{M(1 - \xi)^2}{(1 - \xi)} = \Delta M(1 - \xi) \qquad (49)$$

$$\sum_{r=1}^{\infty} rP_r = \Delta M \qquad (50)$$

Equation (50) is self-evident, since ΔM must equal the total amount of polymer produced.

$$\sum_{r=1}^{\infty} r^2 P_r = \Delta M(1 - \xi)^2 \sum_{r=1}^{\infty} r^2 \xi^{r-1}$$

$$\sum_{r=1}^{\infty} r^2 P_r = \Delta M(1 - \xi)^2 \cdot \frac{(1 + \xi)}{(1 - \xi)^3}$$

$$\sum_{r=1}^{\infty} r^2 P_r = \Delta M \frac{(1 + \xi)}{(1 - \xi)} \qquad (51)$$

The weight to number-average chain length ratio is then given by:

$$\frac{\bar{r}_w}{\bar{r}} = \frac{\Delta M(1 + \xi)}{(1 - \xi)} \cdot \frac{\Delta M(1 - \xi)}{(\Delta M)^2} = (1 + \xi) \qquad (52)$$

Since ξ is very close to 1.0, as a very good approximation

$$\frac{\bar{r}_w}{} = 2.0$$

The foregoing type of distribution ($k_{tc} = 0$) is often referred to as the most probable distribution and always arises in linear condensation polymerization. If the reactant concentrations change during the course of the polymerization process, the final distribution is made up of a series of most probable distributions, superimposed upon each other. It will therefore be wider than the most probable distribution. However, it was seen before that ξ is constant for all intents and purposes, thus the ratio should change little if any.

In the second case to be considered, termination is by combination only ($k_{td} = 0$), which is the actual case for styrene (15). From equation (46) it is seen that

$$P_r = \frac{\Delta M}{k_p M} (1 - \xi) \xi^{r-1} \left[k_{fs}S + k_{fm}M + \frac{(Ik_{tc})^2}{2} (r-1) \cdot \frac{k_{fs}S + k_{fm}M + (Ik_{tc})^{\frac{1}{2}}}{k_p M} \right] \tag{47a}$$

and in the absence of chain transfer

$$P_r = \frac{\Delta M}{k_p M} (1 - \xi) \xi^{r-1} \left[\frac{Ik_{tc}}{2k_p M} \right] \left[\frac{r-1}{2} \right] \tag{48a}$$

As before

$$\sum_{r=1}^{\infty} P_r = \frac{\Delta M}{k_p M} (1 - \xi) \frac{Ik_{tc}}{2k_p M} \left[\sum_{r=1}^{\infty} r \xi^{r-1} - \sum_{r=1}^{\infty} \xi^{r-1} \right]$$

$$= \frac{\Delta M}{k_pM}(1-\xi)\ \frac{Ik_{tc}}{2k_pM}\left[\frac{1}{(1-\xi)^2}-\frac{1}{(1-\xi)}\right]$$

$$= \frac{\Delta M}{k_pM}\ (Ik_{tc})^{\frac{1}{2}}\left[\frac{(1-\xi)^2}{2}\right]\left[\frac{\xi}{(1-\xi)^2}\right]$$

$$\sum_{r=1}^{\infty} P_r = \frac{\Delta M}{2k_pM}\ (I_{tc})^{\frac{1}{2}} \qquad (49a)$$

Likewise as before

$$\sum_{r=1}^{\infty} rP_r = \Delta M \qquad (50a)$$

and finally

$$\sum_{r=1}^{\infty} r^2P_r = \frac{\Delta M}{k_pM}\ \frac{(Ik_{tc})^{\frac{1}{2}}}{2}\ \frac{(1-\xi)^2}{\xi}\left[\sum_{r=1}^{\infty} r^3\xi^{r-1}-\sum_{r=1}^{\infty} r^2\xi^{r-1}\right]$$

$$\sum_{r=1}^{\infty} r^2P_r = \frac{\Delta M}{2k_pM}\ (Ik_{tc})^{\frac{1}{2}}\ \frac{(1-\xi)^2}{\xi}\left[\frac{\xi^2+4\xi+1}{(1-\xi)^4}-\frac{1+\xi}{(1-\xi)^3}\right]$$

$$\sum_{r=1}^{\infty} r^2P_r = \frac{\Delta M}{2k_pM}(Ik_{tc})^{\frac{1}{2}}\ \frac{(1-\xi)^2}{\xi}\ \ \frac{2\xi(\xi+2)}{(1-\xi)^4}$$

$$\sum_{r=1}^{\infty} r^2P_r = \frac{\Delta M}{k\ M}\ (Ik_{tc})^{\frac{1}{2}}\ \frac{\xi+2}{(1-\xi)^2} \qquad (51a)$$

Now

$$\frac{\bar{r}_w}{\bar{r}} = \frac{\frac{\Delta M}{k_pM}\ (Ik_{tc})^{\frac{1}{2}}\ \frac{\xi+2}{(1-\xi)^2}\ \ \frac{\Delta M}{2k_pM}\ (Ik_{tc})^{\frac{1}{2}}}{(\Delta M)^2}$$

$$\frac{\bar{r}_w}{\bar{r}} = \frac{Ik_{tc}}{2(k_pM)^2} \; \frac{\xi + 2}{(1-\xi)^2}$$

and remembering that

$$\frac{(Ik_{tc})^{\frac{1}{2}}}{k_pM} = \frac{1 - \xi}{\xi}$$

then

$$\frac{\bar{r}_w}{\bar{r}} = \frac{(1 - \xi)^2}{2\xi^2} \cdot \frac{(\xi + 2)}{(1 - \xi)^2} = \frac{\xi + 2}{2\xi^2} \qquad (52a)$$

with $\xi = 1.0$

$$\frac{\bar{r}_w}{\bar{r}} = 3/2 = 1.5$$

Thus it is seen that the ratio of $\bar{r}_w/\bar{r}$ may vary from 1.5 to 2.0, depending on the degree that each termination process takes place. It is also interesting to note that regardless of the actual reaction temperature and reagent concentrations, the same ratio is obtained, although the actual broadness or spread of the distribution itself will be very much influenced by the reaction conditions. The ratio of $\bar{r}_w/\bar{r}$ is therefore not a good indication of the spread of the distribution and should not be used for this purpose.

Sometimes one of the reactants, usually the monomer, is consumed at a much faster rate than the catalyst. In such a case the probability $\wp$ changes considerably, with the result that a considerable shift in distribution takes place, which may be undesirable. To avoid this problem, industrial reactors are often semi-batch, i.e. catalyst or monomer solution is being added continuously at a varying rate. The problem can be illustrated mathematically as follows. Using the expression for the degree of polymerization or number-average chain length of equation (34), which can be written as

$$DP = \frac{k_p M}{k_{fs} S + k_{fm} M + \left(k_{td} + \frac{k_{tc}}{2}\right) R^{o}} \qquad (53)$$

substituting for R^{o} from equation (7) and (10)

$$DP = \frac{k_p M}{k_{fs} S + k_{fm} M + \left(k_{td} + \frac{k_{tc}}{2}\right) \left[\frac{2f\ k_d C}{k_{td} + k_{tc}}\right]^{\frac{1}{2}}}$$

$$DP = \frac{k_p M}{k_{fs} S + k_{fm} M + \left(k_{td} + \frac{k_{tc}}{2}\right) (2f\ k_d C)^{\frac{1}{2}}} \qquad (54)$$

If chain transfer to the solvent can be neglected, it is clear that in order to keep the distribution from shifting, the ratio $M/\sqrt{C}$ must be kept constant. Since both can easily be calculated, it is a simple matter to determine beforehand their actual flow rates into a semi-batch system.

2. LITERATURE REVIEW

2.1 Source and Selection of Rate Constants

2.1.1 Selection of propagation and termination constants

The detailed methods by which rate constant may be obtained have already been discussed and such terms as viscosity methods, rotating sector, etc. are assumed to be familiar.

An extensive lists of propagation constants as well as catalyst decomposition and chain-transfer constants are given by Bamford[42] and a glance at some immediately reveals the large discrepancies between various workers, it seemed therefore expedient to review briefly the literature dealing with their determination.

Matheson et al[35,36] were the first to apply the rotating-sector method to styrene polymerization to obtain an Arrhenius expression for k_p/k_{tc}, as shown by the data in Table IV of their paper, and graphically in Figure 3.

Their value of k_{tc} is one half that of k_{tc} used here, due to a difference in definition.

Expressed in the form of an Arrhenius equation they found

$$\frac{k_p}{k_{tc}} = 4.26 \times 10^{-3} \exp\left(-\frac{5380}{RT}\right) \qquad (55)$$

Matheson then continues by measuring the rate of initiation from the catalyst decomposition rate which can be related to the rate of polymerization by combining equations (38) and (41) giving

$$R_i = \frac{k_{tc}}{k_p^2}\left[\frac{R_p}{M}\right]^2 \qquad (56)$$

which yields k_{tc}/k_p^2, and by combining equations (55) and (56) a value for k_p can be obtained. In calculating R_i Matheson assumed f, the catalyst efficiency to be unity which in light of later work is a doubtful assumption. The second method which was used to determine R_i consisted of adding 2,2-diphenyl-1-picrylhydrazyl as an inhibitor and measuring the induction period for a fixed amount of inhibitor. As before, the basic assumption is that each inhibitor radical stops one kinetic chain or the catalyst efficiency being 100%. Finally, Matheson et al. measured the degree of polymerization using the intrinsic viscosity method (19). It is clear that equation (42) will yield the ratio (k_p^2/k_{tc}). The first two methods gave good agreement but the latter deviated considerably. For example, the viscosity method gave a value of 55.2×10^{-5} l/m/sec. for (k_p^2/k_{tc}) at 60°C., whereas the first two methods gave an average value of 36.6×10^{-5}. If the rate of initiation used in the first method is recalculated using a k_d value based on Van Hook's equation (43), a value of 45.7×10^{-5} is obtained for (k_p^2/k_{tc}), which is in better agreement with the last method. This value can be brought in line even further if an efficiency factor of less than 1.0 is used. A further comparison of (k_p^2/k_{tc}) values may be made with those reported by Tobolsky and Offenbach[44]. Using the same equation (44) relating intrinsic viscosity and degree of polymerization as Matheson, they combined their findings with those in the literature and found

$$\frac{k_{tc}}{k_p^2} = 1.136 \times 10^{-5} \exp(12{,}460/RT) \qquad (57)$$

which compares well with a previous equation by Tobolsky and Baysal[45]. From equation (57) a value of (k_p^2/k_{tc}) was calculated at 60°C., which was 54.8×10^{-6} and which compares well with the 60°C. value of 55.2×10^{-6} reported by Matheson. The viscosity method is strongly preferred because it is simple and does not require any knowledge about the catalyst efficiency which as will be shown later is a rather capricious quantity. One more and final reason for rejecting the k_p and k_{tc} values reported by Matheson is that in the case of bulk polymerization the predicted conversion using these constants is much lower than the conversion obtained experimentally, requiring a catalyst efficiency greater than 100% for agreement between the two whereas in solution polymerization the catalyst efficiency is less than 100%.

In order to obtain individual rate constants, equation

(55) from Matheson's data and equation (51) from Tobolsky's were combined to yield the following Arrhenius expression for k_p

$$k_p = 2.06 \times 10^7 \ \exp(-\frac{7080}{RT}) \tag{58}$$

By substituting equation (58) back into equation (57) or (55) a value for k_{tc} can then be obtained giving:

$$k_{tc} = 4.83 \times 10^9 \ \exp(-\frac{1700}{RT}) \tag{59}$$

From equation (16) conversion can be predicted, provided the catalyst efficiency f is known. Since f was found to vary, a "Golden Section Search" program was written to find a value for f which best fits the experimental data. By examining equation (16) it is seen that if the ratio $(k_p/\sqrt{k_{tc}})$ is too small, f conceivably could be greater than 1.0 in order to get agreement between the experimental and predicted conversion. As already mentioned, if Matheson's constants are used, then $f > 1.0$ in the case of bulk polymerization, as shown in Table A-1. This is of course impossible, throwing grave doubt on the accuracy of Matheson's data. If, on the other hand, equations (58) and (59) are used no such problem arises, as shown also in Table A-1.

There is a third source from which rate constants can be obtained, namely emulsion-polymerization studies. This method, however, only gives k_p the propagation rate constant. According to the Smith-Ewart theory (38) the rate of emulsion polymerization can be expressed as

$$R_p = k_p \frac{N}{2} \ (M) \tag{60}$$

where N is the number of particles per $cm.^3$ of water. Similarly

$$\overline{DP} = k \ N \left(\frac{M}{\rho}\right) \tag{61}$$

where ρ is the rate of free radical generation and involves a knowledge of f the catalyst efficiency. If the rate of polymerization is known then by counting N, the rate constant k_p can be obtained. Smith and Ewart present an equation for obtaining N and the reader is referred to the original papers for further details. It should be pointed out, however, that there are many obstacles in obtaining an accurate value of N. If the degree of polymerization is also known, equations (60) and (61) can be combined and N need not be known, but the catalyst efficiency and the catalyst rate of decomposition must be known, which makes it a much less attractive procedure than the viscosity method used in solution polymerization. In any case, only k_p is obtained and in order to solve equation (16) k_t must be known as well, requiring further solution polymerization experiments. Van der Hoff (46) has made an extensive survey of all k_p values in the literature and gives the following equation

$$k_p = 1.66 \times 10^9 \ \exp\left(\frac{-10,500}{RT}\right) \tag{62}$$

Equation (62) represents a good average of most other workers values. A more recent value for k_p in emulsion polymerization has been reported by Paoletti and Billmeyer[47] giving

$$k_p = 2.24 \times 10^{14} \exp(-\frac{17,570}{RT}) \tag{63}$$

which is far from being in even close agreement with any previous values.

If equation (62) is combined with equation (60) a value for k_{tc} is obtained giving

$$k_{tc} = 3.132 \times 10^{13} \exp(-\frac{8540}{RT}) \tag{64}$$

which does not compare well with equation (59). If equations (62) and (64) are used with equation (16) to obtain the catalyst efficiency, the same value is obtained as with equations (58) and (59). That is of course to be expected, since it is the ratio $(k_p/\sqrt{k_{tc}})$ which governs f and which has not changed. Similarly it is seen from Table A-2 that as before the molecular-weight distribution has not changed. This is not surprising, since it is the ratio of the constants k_t/k_p which is important and from which k_{fm} and k_{fs} have been calculated. Then if equation (57) is taken to be correct, any individual value for k_p or k_{tc} is immaterial as long as the ratio $(k_p/\sqrt{k_{tc}})$ remains the same.

There is one further possible combination for obtaining k_{tc} and that is a combination of equations (55) and (62), which ignores the data of Tobolsky et al (45). Multiplying the two equations and inverting gives

$$\frac{k_{tc}}{k_p^2} = 3.035 \times 10^{-8} \exp(\frac{15,880}{RT}) \qquad (65)$$

which compares poorly with equation (57).

The following is a comparison of different values for $(k_p/\sqrt{k_{tc}})$ at 65°C., obtained from equations (57) and (65), and from the rate constants from Matheson et al.

TABLE A-1

	Matheson et al	Equation 57	Equation 65
$k_p/\sqrt{k_t}$	2.293	2.695	1.874
f	1.136	0.824	1.194

Since the value from equation (65) is not significantly larger than that obtained from the equations by Matheson et al, the catalyst efficiency would have to be over 1.0 again. This suggests that either the k_p value by Van der Hoff, equation (62), or Matheson's sector experiments, equation (55) are in error. This means that equation (57) is probably the most reliable one and it has therefore been adopted for all calculations in this work. As pointed out before, it has been combined with Matheson's sector experiment, equation (55) to give individual rate constants. The equation by Van der Hoff is rejected because it is based on emulsion polymerization work, which may not be equivalent to solution polymerization. In any case if equation (62) is combined with equation (57), as it would have to be, the results are unchanged as shown before.

2.1.2 Determination of chain transfer constants

Tobolsky and Offenbach (44) also give an equation for transfer to monomer based on the same data as equation (57).

$$\frac{k_{fm}}{k_p} = 0.22 \exp(- \frac{5600}{RT}) \qquad (66)$$

which when combined with equation (58) yields

$$k_{fm} = 4.53 \times 10^6 \exp(- \frac{12,680}{RT}) \qquad (67)$$

and which has been adopted for all calculations.

Chain transfer to solvent data were obtained from Bamford, Barb, Jenkins and Onyon[48], noting that E_p the activation energy for polymerization is (- 7080)cal./mole giving a value for the activation energy of transfer of (+ 7720)cal./mole and a rate constant.

$$k_{fs} = 6.66 \times 10^{-9} \exp(+ \frac{7720}{RT}) \qquad (68)$$

2.1.3 Determination of catalyst decomposition constant

The determination of the rate of catalyst decomposition is closely associated with its efficiency causing great difficulty in getting an accurate understanding of it. For Azo, Bamford[42] gives an exhaustive list of values and references for k_d as well as an Arrhenius equation for the case of thermal decomposition in a solvent or monomer. For aromatic hydrocarbons

$$k_d = 1.0 \times 10^{15} \exp(-\frac{30,450}{RT}) \tag{69}$$

However, equation (69) may not hold true in pure monomer or mixtures of monomer and benzene, as suggested by the rather large variations in k_d at certain temperatures in the data reported by Bamford.

Van Hook[43] made a further exhaustive study of the subject and states that the rate of decomposition has been shown to be independent of the nature of the solvent. He measured the rate of decomposition in benzene and toluene spectrophotometrically and combined his findings with those of the literature giving an Arrhenius equation of

$$k_d = 1.58 \times 10^{15} \exp(-\frac{30,800}{RT}) \tag{70}$$

which in the 60°-70°C. range varies less than 5% from equation (69). Equation (70) has been adopted in this work.

Henrici and Olive[49] on the other hand claim that k_d is dependent on the nature of the solvent and that for a mixture of two materials

$$k_d = k_{d1}\gamma_1 + k_{d2}\gamma_2 \tag{71}$$

where γ_1 and γ_2 are the mole fractions of each substance. To back their claim they quote various values for k_d in benzene, toluene and styrene by themselves and other workers (50, 51), whereas Van Hook, using the same values considers them as random variations. They further claim that the catalyst efficiency is constant for all solvents and the differences in f that have been observed are due to variations in k_d. In particular, they point to k_d for pure styrene as determined by Breitenback and Schindler[51]. If differs considerably from those after Van Hook. Breitenbach and Schindler propose

$$k_d = 1.29 \times 10^{15} \exp(-\frac{30,500}{RT}) \tag{72}$$

Combining values from equation (69) with that from the above equation, composite k_d values were calculated and the catalyst efficiency determined. The following table shows the results:

TABLE A-2

Mon.Conc.%	Solv.Conc.%	Cat.Conc.%	Temp°C.	k_d x10^4	Cat.Eff.f
30.0	69.9	0.1	75	0.646	0.5447
30.0	69.9	0.1	65	0.190	0.4379
30.0	69.85	0.15	65	0.190	0.4775
30.0	69.8	0.2	65	0.190	0.4635
60.0	39.9	0.1	65	0.204	0.5491
99.7	0.0	0.3	65	0.210	0.6760

It is clear that there is still considerable variation in f and it appears that it may be temperature dependent also. At a concentration of 60% monomer f increases significantly from the 30% monomer concentration value, except the 75°C. value. A further rise to 0.676 occurs for pure monomer. This compares with 0.72 from Breitenbach and Schindler. Henrici only studied solvent mixtures, not solvent and monomer and then only at one temperature. Furthermore, they completely ignore the much higher value of f, 0.72, in pure styrene, by Breitenbach and Schindler, whereas they cite their k_d value as proof for their claims. A close inspection of Breitenbach and Schindler's paper showed that they measured k_d only twice at 50° and 70°C., upon which they based their Arrhenius equation, equation (72) which can therefore be assumed to have considerable error associated with it. Although Table A-2 does not show sufficient evidence to refute Henrici-Olive and Henrici's claims, neither does it confirm it. It seems that at this stage the evidence is insufficient and k_d and f values based on Van Hook's equation have been adhered to. In any case, there does not appear to be any chemical reason why f should remain the same from solvent to solvent while k_d changes. Also, the effect of dissolved polymer would have to be known, making the question extremely complicated.

2.2 Selection of Catalyst Efficiency from the Literature

The theory and possible mechanism causing the rate of initiation to vary with monomer concentration as well as the reason for a catalyst efficiency factor of less than 1.0 has already been discussed. The following will show that there is clear evidence that the efficiency is less than 1.0 for Azo and possibly monomer dependent.

Johnson and Tobolsky[52] determined the rates of initiation from rates of polymerization studies and intrinsic viscosity measurements, by relating equations (60), (38) and (41). For bulk polymerization of styrene they calculated f to be 0.69 or 0.83 depending on what value of k_d was used and assuming no disproportionation took place. Arnett and Peterson[53] believed that Azo yields only one free radical instead of two and thus should exhibit an efficiency of 0.50. They performed radioactive tracer studies using Azo synthesized from sodium cyanide containing the C^{14} isotope. For styrene they found an efficiency of about 0.8, in bulk polymerization, which was in agreement with other workers but perhaps based on a wrong value for k_d. Bevington[26] also used the radioactive tracer technique, but he analyzed both the isolated polymer and possible waste reaction products. His polymerizations were carried out in various solvent (benzene) concentrations instead of bulk polymerization. Bevington believed that the rate of decomposition used by previous workers was about 20% too low. He arrives at this conclusion by plotting the efficiency calculated from the rate of initiation and the efficiency calculated from the amount of waste product formed versus k_d. The point of intersection of the two curves is then the correct k_d (see Figure (2) in his paper). The rate of initiation is calculated from the rate of polymerization and the kinetic chain length. The latter is determined from radioactive measurements of the isolated polymer. Bevington's methods certainly are unique in that none of the classical measurements for intrinsic viscosity and catalyst decomposition rate need to be made. Monomer concentrations varying from 6.17 down to 0.015 gm.mole/l. were investigated and no significant effect on the efficiency was shown to exist above monomer concentrations of 1 gm.mole/l. Using his own values for k_d, Bevington found the efficiency to be about 0.62.

Van Hook[18,43] analyzed the efficiency of Azo, using the same method as Johnson and Tobolsky[52]. However, as already pointed out, this method requires an accurate knowledge of the decomposition rate constant and an exhaustive study of the rate of decomposition of Azo was made first (18), which led to the formulation of equation (69). Furthermore, accurate values of $k_p/\sqrt{k_{tc}}$ had to be available, which were obtained from Tobolsky and Offenbach's work (44).

Equation (41) may be written as

$$\frac{R_p^2}{M_{ave.}} = \frac{2k_p^2}{k_{tc}} k_d f \qquad (73)$$

The efficiency f or the product $k_d f$ is then obtained by plotting

$(R_p / M_{ave.})^2$ versus $C_{ave.}$. To obtain f, Van Hook plots various values of $k_d f$ versus 1/T which yields the Arrhenius equation:

$$k_d f = 9.80 \times 10^{14} \exp(-\frac{30,800}{RT}) \tag{74}$$

By dividing equation (74) by the Arrhenius expression for k_d (equation (70)) f is then extracted and found to be 0.62, which is in good agreement with Bevington's[26] work. To determine the effect of the catalyst concentration on f, Van Hook plotted f calculated from equation (73) versus $C_{ave.}$. This plot showed the peculiar behaviour of f being steady at 0.66 at $C_{ave.} > 0.05$. At a lower catalyst concentration, f increased sharply. In the case of methylmethacrylate, which was investigated along with styrene, no such behaviour was observed. Since the plot of f versus $C_{ave.}$ involves the $C_{ave.}$ terms in in both the dependent and independent variables the phenomena probably is an artifact, to use Van Hook's description, i.e. due to a magnification of errors.

3. DETERMINATION OF CONVERSION

3.1 Experimental Results and Discussion

The technique for determining quantitatively the amount of polymer in a reaction mixture has already been described. The following is a detailed description of the various experiments that were run and the analytical results. The first set of experimental runs were made at 75°C. and Table A-3 shows the results. The data were subjected to analysis for determining the f value that would best fit equation (16), which was found to be 54.8%. Based on that value equation (16) was integrated and the comparable calculated values are shown in the last column. Table A-4 through A-9 are similar, but each representing different reaction conditions. In all cases the experimental results are in good agreement with the calculated values. This is to be expected of course since f was determined on the basis of the experimental results. However, the curvature of the calculated graph is the same as that of the experimental one which suggests that equation (16) gives an adequate description of the rate of polymer formation if f is properly adjusted. For bulk polymerization some deviation appears although the curve is still quite good. The rather large increase in the catalyst efficiency is significant and has already been discussed. For clarification the results of Table A-8 have been plotted as shown in Figure A-1. Note that as the reaction time passes the four or five hour period, the experimentally observed conversions rise above

TABLE A-3

Run No.	1	2	3	Ave.	Calculated
Reaction Time Hours	% Conversion				
½	3.05				3.72
1	6.11	7.0		6.56	7.00
1½	9.19				10.19
2	11.95	12.7	12.56	12.40	12.85
3	16.95	17.62		17.29	17.77
4			22.12		21.93
5	24.90	25.10		25.00	25.48
6			29.76		28.51
7	31.20	30.75		30.98	31.12
9			36.72		35.32
9½	36.55				36.18
10		36.32			37.02
12	39.75		40.04	39.90	39.79
13		40.0			40.93
15			42.37		42.80
18			42.42		44.85
22½			42.49		

Reactant concentrations

Monomer 30.0%
Solvent 69.9%
Catalyst 0.1%

Temp. - 75°C.

Cat. Eff. - 0.548

TABLE A-4

Run No.	4	5	6	Ave.	Calc.
Reaction Time Hours	% Conversion				
½	1.30	1.48	1.42	1.40	1.40
1	2.65	3.03	2.83	2.84	2.76
1½	4.21	4.21	4.40	4.27	4.08
2	5.47	5.49	5.69	5.55	5.36
5	12.89	12.22	13.46	12.86	12.36
8	19.22	17.13	18.83	18.39	18.30
12	26.47	24.39	22.65	24.50	24.91
18		29.18			
24		30.81			

Reactant Concentrations

Temp. - 65°C.

Monomer - 30.0%

Solvent - 69.9%

Catalyst - 0.1%

Cat. Eff. - 0.480

TABLE A-5

Run No.	7	8	9	Ave.	Calc.
Reaction Time Hours	% Conversion				
½	1.69				1.79
1	3.24	3.59	3.54	3.46	3.52
1½	4.83				5.19
2		6.66	6.65	6.66	6.81
2½	8.00				8.38
4	12.49	12.52	12.72	12.58	12.80
6	17.89	17.89	18.30	18.03	18.10
8	24.79	24.88	25.61	25.09	24.94
12	30.70	30.14	31.52	30.79	30.69

Reactant Concentrations

Monomer - 30.0%

Solvent - 69.85%

Catalyst - 0.15%

Reaction Temp. - 65°C.

Catalyst Efficiency - 0.524

TABLE A-6

Run No.	10	11	12	Ave.	Calc.
Reaction Time Hours	% Conversion				
½	2.22	2.04	2.12	2.13	2.03
1	4.10	3.98	3.97	4.02	3.99
1½	5.98	5.78	6.01	5.92	5.89
2	7.73	7.32	7.81	7.62	7.72
5	18.02	16.40	17.88	17.43	17.48
8	26.10	24.38	26.13	25.50	25.50
11	33.39				32.16
12		33.44	34.09	33.77	34.12

Reactant Concentrations

Monomer - 30.0%

Solvent - 69.8%

Catalyst - 0.2%

Reaction Temp. - 65°C.

Catalyst Eff. - 0.509

TABLE A-7

Run No.	13	14	15	Ave.	Calc.
Reaction Time Hours	% Conversion				
½	1.72	1.70	1.64	1.69	1.58
1	3.36	3.26	3.30	3.31	3.12
1½	4.99	4.81	4.97	4.92	4.61
2	6.51	6.32	6.56	6.46	6.06
5	14.26	13.78	14.38	14.14	13.88
8	20.29	19.98	21.16	20.48	20.45
11	25.79				26.05
12		26.97	27.32	27.15	27.72

Reaction Mixture

Monomer - 60.0%

Solvent - 39.9%

Catalyst - 0.1%

Reaction Temp. - 65°C.

Catalyst Eff. - 0.64

TABLE A-8

Run No.	16	17	18	Ave.	Calc.
Reaction Time Hours		% Conversion			
½	3.03				3.15
1	6.09	6.04	5.97	6.03	6.15
1½	8.81				9.02
2	11.46	11.21	11.33	11.33	11.76
3	17.94	16.39	15.96	16.76	16.88
4	21.44	20.71	20.53	20.89	21.57
5	25.51	25.30	25.07	25.29	25.87
6	31.46	29.47	29.67	30.20	29.81
7	35.21	33.97	33.45	34.21	33.44

Reactant Concentrations

Monomer - 99.7%

Catalyst - 0.3%

Reaction Temp. - 65°C.

Catalyst Eff. - 0.824

TABLE A-9

Run No.	19	Calc. F=0.8	Calc. F=0.6
Reaction Time Hours	% Conversion		
½	4.57	4.41	-
1	8.23	8.40	7.32
1½	11.99	12.02	-
2	15.23	15.32	13.41
3	20.41	21.06	18.52
4	25.62	25.87	22.83
5	30.14	29.92	26.49
6	33.83	33.34	29.62

Reactant Concentrations

Monomer - 99.9%

Catalyst - 0.1%

Reaction Temp. 75°C.

Catalyst Efficiency - 0.800

The results were corrected for thermal polymerization

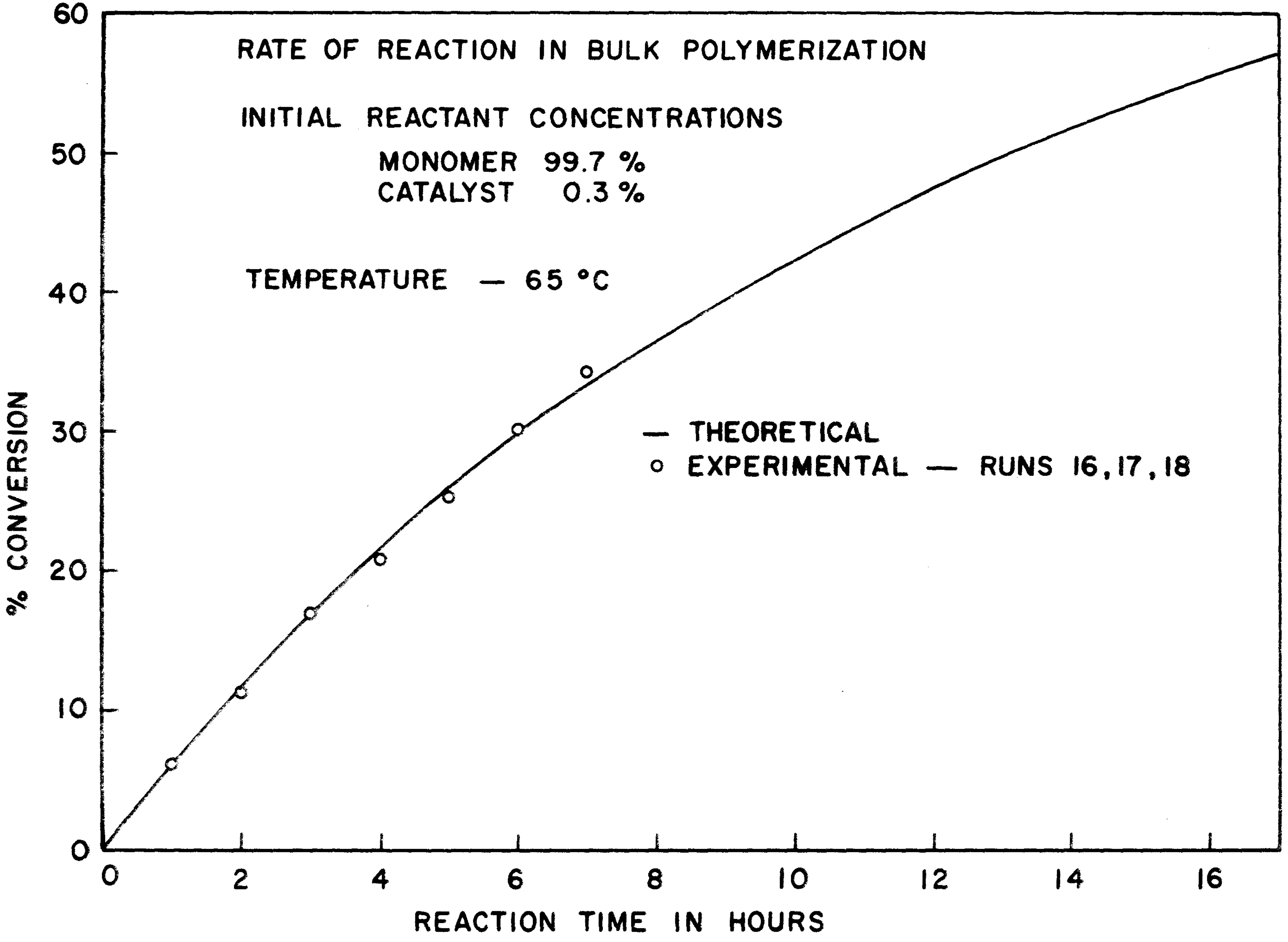
RATE OF REACTION IN BULK POLYMERIZATION
INITIAL REACTANT CONCENTRATIONS
MONOMER 99.7 %
CATALYST 0.3 %
TEMPERATURE — 65 °C
— THEORETICAL
○ EXPERIMENTAL — RUNS 16, 17, 18
% CONVERSION
0
10
20
30
40
50
60
REACTION TIME IN HOURS
0
2
4
6
8
10
12
14
16

FIGURE A-1

the curve. There appears to be a definite discontinuity in the experimental curve at this point which is likely due to the termination reaction being diffusion controlled, the so-called Tromsdorff-Norrish "gel" effect (55), (62).

Although only 19 experimental runs are reported, a total of 32 runs were actually done. Polymerization studies reported in the literature usually consist of initial rate studies made by polymerizing the monomer in sealed ampules, to exclude any possibility of oxygen contamination. The purpose of this work was to simulate a possible industrial set-up. It is clear therefore that oxygen is a very strong contaminant in that it acts as a free radical scavenger, causing the conversion to be low. This was suspected to be the case with most of the other 13 experimental runs. In every one the conversion was lower. Whether this was due solely to oxygen is of course not known. Any trace of inhibitor or scavenger contaminating the mixture would have the same effect, lower conversion. Also, a number of rejected experiments were made with a different experimental arrangement. Instead of the present temperature control by cooling coils, the solvent-monomer mixture temperature was controlled by refluxing. This caused considerable fuming and a gradual increase in the temperature as the reaction proceeded. Furthermore, choice of reaction temperature was severely limited because it was fixed by the initial solvent-monomer concentrations. Four runs were made with this particular apparatus, but none of these was successful. Other runs were rejected because of definite errors having been made which were discovered during or after completion of the run. Sometimes no apparent cause of failure was known, but as already pointed out since the reaction is extremely sensitive to contamination by scavengers, improper cleaning of the apparatus between runs could easily result in failure.

There is an interesting aspect to the case of bulk polymerization which should be noted. Van Hook[18], using the same rate constants as adopted in this work, obtained a catalyst efficiency of 0.62 by studying the polymerization of pure styrene in sealed ampules. In this work, using a batch reactor, the catalyst efficiency is 0.82, that is the rate of conversion was 32% higher. This is very surprising and no ready explanation is available. There is no doubt, however, that Van Hook's rate of polymerization was much less. If it is assumed that the rate constants used were correct only one explanation is available, namely a lack of stirring causing temperature gradients. Certainly, his procedures were sufficiently elaborate to eliminate any possible trace of oxygen. However, it is possible that monomer polymerization in a small ampule becomes diffusion controlled. There is some evidence that oxygen although initially retarding the reaction later on causes the rate to increase due to the oxygen-monomer copolymer being fractionated into two free radical fragments which are subject to further polymerization (56), the implication being that this is what might have happened in our batch reaction. However, it is doubtful whether a temperature of 65°C. is sufficiently high to cause polymer fractionation and no sudden acceleration in polymerization was observed.

3.2 Theoretical Calculation of Conversion and Catalyst Efficiency

Equation (16) gives the basic relationship between conversion and reaction time and its limitations have already been discussed. If f, the catalyst efficiency (or k_{tc}, the termination constant) are independent of conversion the equation may be solved analytically, otherwise, a numerical method is more suitable. The latter method was adopted using the fourth order Runge Kutta process with a stepsize in the time variable of 180 seconds. With this time interval computation time on the IBM 7040 computer was about 1.5 minutes for a total reaction time of 25 hours. A time increment of 90 seconds gave essentially the same answer as shown in Table A-10. The 180 seconds time increment was therefore adopted for all calculations. The program was written as an integral part of a much larger program for calculating the molecular-weight distribution. It can easily be used by itself, however, without any modifications. If a functional relationship between f and the conversion, X, or between the termination constant, k_{tc}, and the conversion becomes necessary the program is still valid and only a few statements need to be revised. If it is desired to use the program on a permanent basis it should be closely reviewed for further simplification. Since this was written further logic

TABLE A-10

EFFECT OF TIME INCREMENT ON CONVERSION CALCULATION

Reaction Time Hours	% Conversion Delt - 180	% Conversion Delt - 90
1	7.01	7.00 *
2	12.86	12.85
3	17.79	17.77
4	21.95	21.94
5	25.50	25.48
6	28.53	28.51
7	31.14	31.12
8	33.40	33.37
9	35.35	35.32
10	37.05	37.02
11	38.53	38.50
12	39.82	39.79 †
13	40.96	40.93
14	41.95	41.92
15	42.83	42.80
16	43.60	43.57
17	44.29	44.25
18	44.89	44.86

* Change - 0.143%

† Change - 0.075%

improvements have been discovered as well, making a review quite desirable. For a program listing the reader is referred to Appendix 6.

In order to calculate the conversion X by means of equation (16) the rate constants, initial reactant concentrations and the catalyst efficiency f must be known. For reasons already discussed, Tobolsky and Offenbach's k_p^2/k_{tc} constants were adopted as well as the k_d constant determined by Van Hook and Tobolsky. It is clear that if equation (16) does adequately describe the polymerization process, and the experimental results are correct, then it ought to be possible to find a value of f by trial and error, which gives good agreement between the calculated and experimental conversions. A search program for f, using the so-called "Golden Section" technique (57) was written. In it f was assumed to lie between 0.3 and 1.2. A value for f is assumed and substituted into equation (16) which is then integrated. The calculated values are compared with experimental values for the same reaction time, and the difference is calculated and squared. The squared deviations are then summed. Using the golden section technique a new value of f is selected and the calculation process repeated. The two sums of squared deviations are then compared and a new value of f corresponding to the lowest sum of squared deviations is chosen. When the last two values of f differed by less than 0.005 the desired accuracy was considered to have been achieved.

About 9 to 10 trials were necessary to home-in on the proper f value. Table A-11 shows the final results.

TABLE A-11

CATALYST EFFICIENCIES

Mon.Conc. %	Solv.Conc. %	Cat.Conc. %	Temp.	f	k_d
30.0	69.9	0.1	75	0.548	0.6204
30.0	69.9	0.1	65	0.480	0.1654
30.0	69.85	0.15	65	0.524	0.1654
30.0	69.8	0.2	65	0.509	0.1654
60.0	39.9	0.1	65	0.640	0.1654
99.7	0.0	0.3	65	0.824	0.1654
99.9	0.0	0.1	75	0.800	0.6204

It is clear that at a monomer concentration of 30% the catalyst efficiency is about 0.52, regardless of the temperature and catalyst concentration. At a monomer concentration of 60% the efficiency rises to 0.64 and for bulk polymerization it is 0.85. Thus there appears to be a definite increase in efficiency as the monomer concentration increases. At this point it is instructive to compare the efficiencies calculated on the basis of a k_d for a mixture of solvents as shown in Table A-2 with those of Table A-11. The f values of Table A-2 vary from 0.44 to 0.55, excluding the case for pure monomer whereas the comparable values of Table A-11 vary from 0.48 to 0.64. The latter spread is greater, but if only the first four values are considered, all calculated at a 30% monomer concentration, the values of Table A-2 show a spread of 0.44 to 0.54 compared with 0.48 to 0.55 of these in Table A-11. Thus no concrete conclusions can be drawn as to whether or not f does vary. One thing is sure, for bulk polymerization it is definitely higher than for solution polymerization, i.e. if the rate constantsdo not change.

The theory that either f or k_d or both vary with the amount and type of solvent, i.e. the monomer concentration in solution polymerization, has an interesting implication. If f is monomer-concentration dependent then as polymerization proceeds in a batch reactor, f might be expected to decrease and as a result the rate of polymerization would decrease. This should show in comparing the calculated conversion with the experimental values. During the early part of the polymerization the experimental rate should be higher than the theoretically calculated since f is based on an average over the entire reaction period. However, during the second half of polymerization, the experimental values should lie below the curve. Examination of the results shown in Tables A-3 to A-9 shows no such behaviour, except perhaps the results of Table A-3 after 15 hours of reaction time. The fact that this was not observed suggests that either f is not the parameter that varies or considerable changes in f only slightly affect the calculated conversion. The last column of Table A-9 shows the conversion calculated with f = 0.6 instead of 0.8. It is clear that although there is a difference, the change is not great and in view of the fairly large variation in experimental results it may not easily be detected. To clarify this point many more very carefully controlled experiments will have to be made.

4. THEORY OF MOLECULAR-WEIGHT DISTRIBUTIONS BY GEL-PERMEATION CHROMATOGRAPHY

4.1 Relationship Between Polymer Chain Length and Hydrodynamic Diameter

The mechanism of achieving size separation of polymer molecules by gel permeation has already been discussed; however, the parameters governing the size a certain polymer molecule acquires in solution were not considered.

The so-called random chain configuration which a polymer molecule assumes in solution is usually expressed as either the root-mean-square distance between its ends, $(\overline{Y^2})^{\frac{1}{2}}$ or as the radius of gyration, the root-mean-square distance of the elements of a chain from its center of gravity, $(\overline{S^2})^{\frac{1}{2}}$. For linear polymers the two are related by: $\overline{Y^2} = 6\overline{S^2}$.

A simple model of a polymer chain may be thought of as a series of r links of length l, joined in a linear sequence with no restrictions on the angles between successive bonds and no interaction between any links. The question now is - what is the end to end distance of such a chain and is it always the same? This problem is equivalent to that of a random walk in one or two directions or that of a random flight in three directions and was first solved by Chandrasckhar[39]. For a detailed discussion the reader is referred to Tompa[40]. The important conclusion of these calculations is that the end-to-end distance of a random coil is proportional to the square root of the number of links:

$$(\overline{Y_o^2})^{\frac{1}{2}} = 1\ r^{\frac{1}{2}}$$

I
(~~55~~)

where Y_o is the unperturbed or random flight end-to-end distance. The distribution of the end-to-end distances is given by the Gaussian distribution function. Real systems have, of course, restrictions on their bond angles and rotation about bonds, which must be corrected for. Different links may also approach each other closer than the average thickness of the real chain, because of molecular interaction. In general, real polymer chains are expanded by a factor α such that

$$(\overline{Y^2})^{\frac{1}{2}} = \alpha (\overline{Y_o^2})^{\frac{1}{2}}$$

II
(~~56~~)

where α may be calculated from:

$$\alpha^5 - \alpha^3 = 2\ C_m\ \psi_1\ (1 - \frac{\theta}{T}) M^{\frac{1}{2}}$$

III
(~~57~~)

See Billmeyer[41] for more details.

The important conclusion to be drawn from all this is that in solution even a mono-disperse polymer exhibits the same properties as a polymer distribution. A solution of a real polymer can therefore be thought of as the sum of many Gaussian distributions of single molecular species. This is potentially a serious source of error in molecular-weight measurements, with the ultra-centrifuge and the gel-permeation chromatograph. Nevertheless, a separation on the basis of particle size (in solution) can be related to molecular chain length. From equation I (~~55~~) and II (~~56~~) it is seen that a plot of the r.m.s. particle size versus (r^2) the chain length in monomer units squared should give a straight line. This is the basis of separation in the gel-permeation chromatograph and the elution volume is a function of the particle size eluted.

4.2 Relationship Between Gel-Permeation Chromatograph Elution Volume and Polymer Chain Length

In the previous section it was shown how the dissolved polymer particle size might be related to its chain length and thus its molecular-weight. The gel-permeation chromatograph gives an eluted volume versus concentration curve, where the elution volume has to be related to the molecular chain length. Consider first of all a truly mono-disperse polymer standard. In solution it will behave like a size distribution of particles all having the same chain length r, having a r.m.s. diameter

$$(\overline{Y^2})^{\frac{1}{2}} = \alpha 1\, r^2$$

But the elution volume E.V. is a function of Y

$$E.V. = f(Y)$$

More specifically, the peak of the distribution curve of E.V. versus concentration is related to $(\overline{Y^2})^{\frac{1}{2}}$ and the curve itself should be Gaussian.

$$(E.V.)_p = f(\overline{Y^2})^{\frac{1}{2}} = f(\alpha 1\, r^2)$$

where $(E.V.)_p$ is the elution volume at the peak.

From the calibration curve, which is a plot of $E.V.)_p$ versus log r it is seen that the semi-log relationship may be considered linear.

$$(E.V.)_p = a - b \operatorname{Log}(r) \qquad (75)$$

For an unknown distribution, consisting of the same polymer as the calibration standards, the elution volume can then be related to the chain length r through equation (75). However, this equation gives the elution volume at the peak of the curve and no correction is applied for spreading. For example if an unknown species r is analyzed, it will elute at count X; which let us say is where the peak occurs. But some of the same species elutes earlier and some later. Thus if a gel-permeation chromatograph output trace were cut into several small increments and each increment related to the chain length (r) by means of equation (75), an erroneous distribution of several species would be the assumed answer whereas in fact only one molecular species was present. Ideally then the output trace should be a pulse of infinite height and pulses from two neighbouring species should not overlap. But the distribution curves of neighbouring species do overlap, compounding the problem. Finally, it is not known whether each species, regardless of its size or its concentrations, within limits of course, exhibits the same spread in the output trace.

In addition to the above mentioned difficulties there is the problem of longtitudinal diffusion, causing spreading of the output trace. The magnitude of this error like the first is not known and furthermore it definitely can be expected to change with species size since rates of diffusion are usually dependent on the molecular size of the diffusing species.

Finally there is the problem of imperfect resolution in the gel-permeation chromatograph columns, i.e. two or more species are eluted so closely together that no distinction can be made between them. From the calibration curve it can be seen that the elution volume of a single species, which corresponds to a difference in chain length of about 2.5 A^o for polystyrene, increases logarithmically as the chain length decreases, in other words, the smaller the molecular-weight, the better is the resolution. The reason for this is not known but it may be related to the pore-size distribution of the gel.

Fortunately, some degree of correction can be made for all these errors, provided certain assumptions are accepted. The first and most important one is that the amount of spreading of each species is the same and that the shape of the curve due to spreading is the same. The second assumption is that no backmixing takes place in the differential refractometer or is at least negligible. Other assumptions are involved, which will become apparent as the method of interpretating output traces is described.

4.3 Interpretation of the Gel-Permeation Chromatograph Trace*

The gel-permeation chromatograph output trace is obtained from a continuous electrial signal from a differential

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* All the work related to the calibration of the gel-permeation chromatograph and the interpretation of the output trace was done jointly by the author and his colleague, Mr. J. H. Duerksen whose contribution is gratefully acknowledged.

refractometer which compares the refractive index of the T.H.F. solvent with that of the eluted polymer solution. Thus any effect of impurities in the solvent is minimized. The signal is amplified and monitored continuously by a Honeywell recorder. Since the differential refractive index is proportional to the polymer concentration in the elution stream, the output trace is in essence a plot of the polymer concentration in the elution stream versus the eluted volume. Figure A-2 represents a typical output trace. However, the desired form of the output consists of a plot giving the weight fraction of polymer versus its chain length or molecular weight. To transform the gel-permeation chromatograph trace to such a form the following procedure was used, which incidentally differs from that suggested by Waters Associates.

If the analytical relationship between the elution count and the polymer chain length cannot be expressed as a straight-line function the following procedure cannot be used without modification. However, from the calibration curve, figure 10, it is seen that straight lines can be drawn through the three polyglycols. Straight line approximations appear therefore to be justified. For this work, the calibration curve was divided into three straight line sections, one through the polyglycols up to the PG-4000 standard, one from the PG-4000 standard to the PS-122,000 standard, and one through the upper three polystyrene standards. Thus each region is approximated by a different form of equation (75).

The procedure for relating the gel-permeation chromatograph output trace to the molecular-weight distribution is best illustrated with a hypothetical example. Suppose e.g. that it is desired to know the weight fraction of a species of chain length 1780, if the elution curve or gel-permeation chromatograph trace output is known to start at a species size of 2500 and ends at a species size of 25. The highest molecular-weight species is eluted first. One procedure would be to substitute these numbers into the appropriate form of equation (75). This would have to be done for each species from 25 to 2500 and the corresponding elution volume or count noted. Then the trace height corresponding to each species elution count is measured and all the heights summed. To get the weight fraction of species 1780, its trace height is divided by the sum of the species trace heights. In effect then trace height readings for each species could be normalized as for species 1780 and then the weight fraction of each species calculated. It is clear that such a procedure takes due account of the changing resolution, but it does assume that the output trace height of a certain count is due to one species only which is known not to be so. The procedure requires the counting of several thousand trace heights, a nearly impossible task.

The following relatively simple procedure was adopted: The gel-permeation chromatograph trace base line is divided into four increments for each count and the corresponding trace heights are measured, normally about 45 readings. These readings are then corrected for any drift in base line by subtracting the base line heights. Next, the most prevalent species count which should be at the peak of the curve, is located and from equation (75) the corresponding angstrom size is obtained. The equivalent angstrom size of one monomer unit, 2.5 in the case of styrene, is added, giving a new angstrom size which is substituted back into equation (75) to give a new count value. The difference between the two counts is then the differential elution volume of one species, occurring at the peak. The same differential count increment to the left of the peak will contain more than one species and to the right less. The first count value at which elution begins is now considered. Two count limits are calculated, the upper one by adding one half the differential volume and the lower one by subtracting one half the volume. The corresponding difference in angstrom size is then obtained, from which the corresponding number of species is obtained. The corrected trace height for the first count is calculated as the read trace height, corrected for baseline drift, divided by the number of species. The process is repeated for each count at which a trace height measurement was made. Trace heights corresponding to each species are now calculated by calculating the corresponding count for each species and the trace height is obtained by linear interpolation between the trace heights corresponding to the read in counts on either side of the species being considered. The height for each species is then calculated, the values summed and through normalization of the height the corresponding weight fractions are calculated. The entire procedure is easily computerized, a typical calculation taking about 2.5 minutes on the IBM 7040.

The foregoing procedure is really only a linearization procedure in that it changes the gel-permeation chromatograph trace which is a refractive index versus elution volume curve into a refractive index versus molecular species curve, but more than just a change in variable is involved, because the areas under the respective curves must be the same. The program takes account of the changing resolution by basing the correction on the middle species. Similarly the correction could be based on the first or last species being eluted. The middle species was chosen as being most representative and since this procedure still involves an averaging process the errors involved should be balanced. To get some idea as to the magnitude of the figures involved several programs were run with the same data but the correction based on the first species. The number of species per unit volume for the last species being eluted was found to be 80, a considerable increase. To see the effect of a change in volume, the calculated volume was increased ten fold. For this case the number of species per unit volume changed from 17 to 799. The number average degree of polymerization shows no change but there was a slight change in the actual distribution.

At the volume equal to one half, no change was detected.

These calculations were based on a polybutadiene sample whose number of species ranged from 2 to 5000. The calculations show that this type of averaging process is not too sensitive to the actual incremental volume selected, although for samples whose maximum number of species is only 2000, a ten-fold increase might have a significant effect. In any case, the assumption that if an incremental volume increase has more than one species, then each one of them is present in the same concentration appears to be reasonable. To keep this averaging process to a minimum, that is to keep the number of species per unit incremental volume as close to one as possible, the center species was chosen for calculating the incremental volume.

4.4 Effect of Column Arrangement on Gel-Permeation Chromatograph Calibration Curve

The original colums shipped with the instrument consisted of a 10^6, a 10^4, a 900 and a 400 angstrom size column. The original calibration is shown in Figure A-2 by curve No. 1. As soon as it was known what molecular weight region the experimental results would lie in, more columns were ordered to improve the instrument resolution. It is clear that the less steep the curve is, the better is its resolution.

Curve number 2 shows the first attempt at a new arrangement. The 10^6 angstrom column was removed since no material was anticipated in this region, an upper molecular-weight range of 4.2×10^4. An extra column was inserted in the 10^3 A region

TABLE A-12

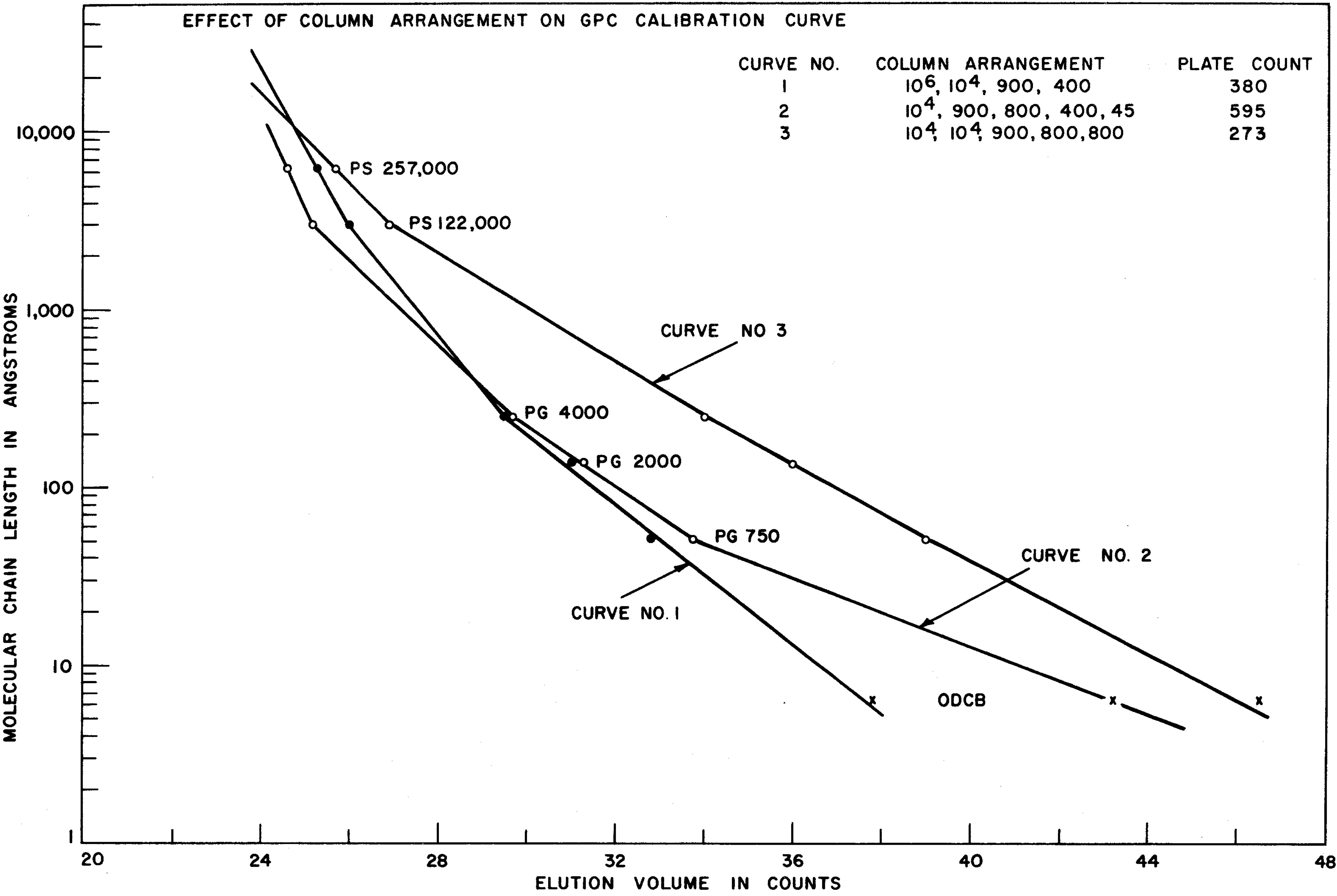
EFFECT OF COLUMN ARRANGEMENTS ON THE CALIBRATION CURVE

Standard	Angstrom Size	Elution Counts		
		Curve No. 1	Curve No. 2	Curve No. 3
PG 750	51.4	32.6	33.7	39.0
PG 2000	139	31.0	31.3	36.0
PG 4000	247	29.5	29.6	34.0
PS 19750	460	-	-	31.2
PS 122000	2945	26.0	25.2	26.9
PS 171000	4000	-	-	26.4
PS 257000	6207	25.3	24.6	25.7

Curve No.	Column Arrangement	Plate Count
1	10^6, 10^4, 900, 400	380
2	10^4, 900, 800, 400, 45	595
3	10^4, 10^4, 900, 800, 800	873

Plate counts were based ODCB, orthodichlorobenzene

FIGURE A-2


EFFECT OF COLUMN ARRANGEMENT ON GPC CALIBRATION CURVE
CURVE NO. COLUMN ARRANGEMENT PLATE COUNT
1 10⁶, 10⁴, 900, 400 380
2 10⁴, 900, 800, 400, 45 595
3 10⁴, 10⁴, 900, 800, 800 273
PS 257,000
PS 122,000
PG 4000
PG 2000
PG 750
CURVE NO 3
CURVE NO. 2
CURVE NO. 1
ODCB
MOLECULAR CHAIN LENGTH IN ANGSTROMS
10,000
1,000
100
10
1
ELUTION VOLUME IN COUNTS
20
24
28
32
36
40
44
48

corresponding to a molecular weight of 4.2×10^4. The results were discouraging. The slope of the curve improved very little in 10^3Å region but a significant improvement was obtained in the 10 to 100 Å region due to the addition of a 45 Å column. As to why there was so little improvement is not known for sure. It is true of course that the angstrom size of a column is its upper maximum size and no data are given as the actual distribution of the pore size. Thus the major portion of the gel in the column might have angstrom sizes well below the reported upper size, which would at least in part explain such behaviour. This is what was suspected to be the case and led to the third choice of arrangement.

Curve number 3 shows the results for the third arrangement, which has been adopted for all this work. The 45 Å and 400 Å columns were removed and a second 10^4 Å and 800 Å installed. This time the improvement was quite encouraging especially in the region below 10^3 Å. There was some improvement in the region above 10^3 Å as well, but not as good as was hoped for. Note, that as was the case for curve numbers 1 and 2 all the polyglycol standards lie pretty well in a straight line. Furthermore the extrapolation for curves 1 and 3 shows that the ODCB lies on the same straight line, which was not the case for curve number 2, probably because of the 45 Å column in this arrangement.

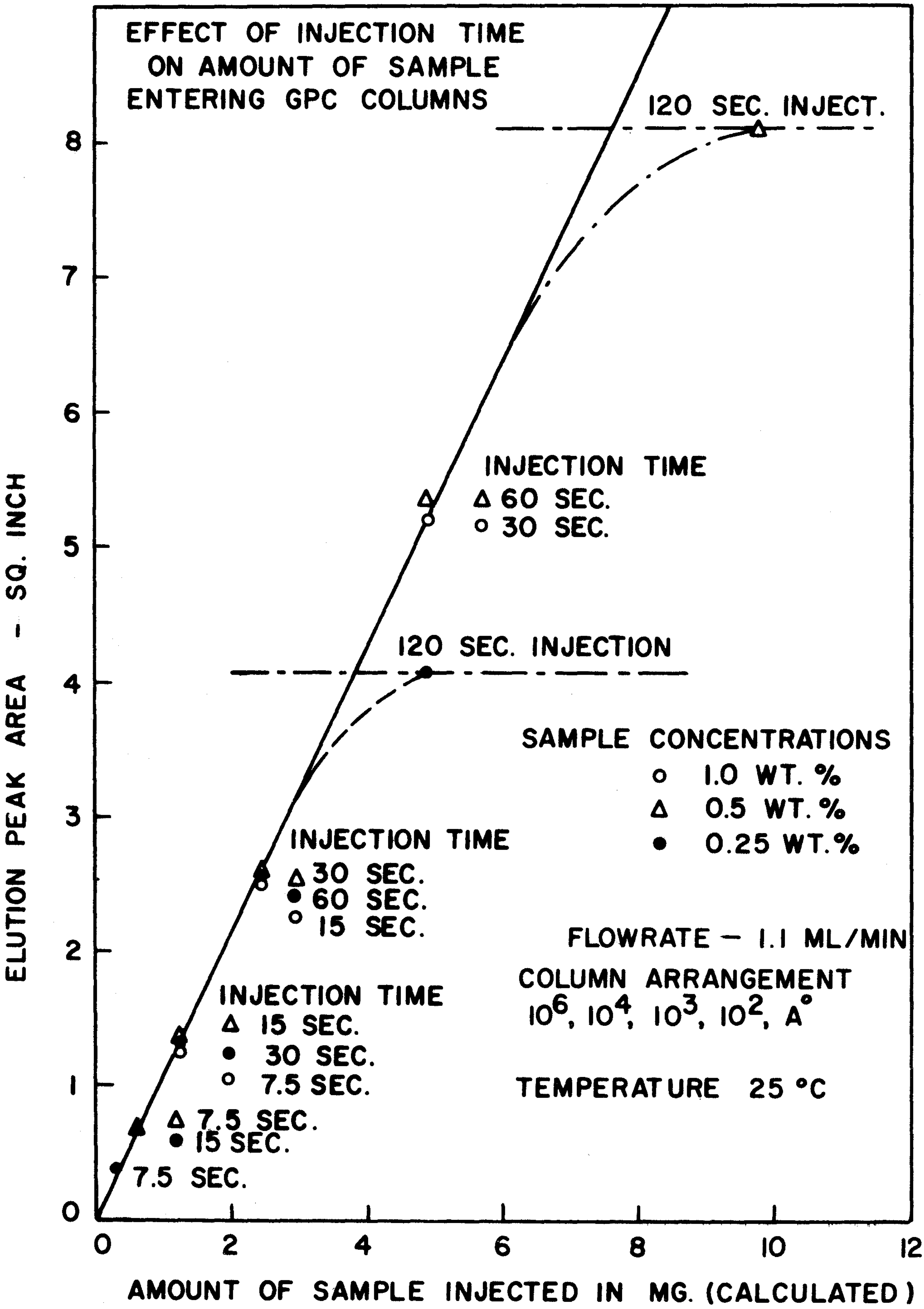
The foregoing results suggest a number of important points. First, the upper angstrom limit, which is the present basis of column selection, can only be used as a very rough guide and is no substitute for actual experimentation with different arrangements. It would appear that a fruitful field of study would be to completely characterize the bead pore structure and relate this to column resolution. Second, for polymers of very wide distributions, e.g. ranging from 5000 to 5×10^6 molecular weight, one single set of five columns may not be sufficient to effectively characterize such a sample. It would therefore be useful to outfit the instrument such that at least ten columns in series could be installed. Third, the resolution decreases quickly with increasing molecular weight, especially in the region above 10^5 angstroms. Since the resolution decreases at higher molecular weight the errors also increase at higher molecular weights. Thus it is imperative that the choice of columns be such that maximum resolution is obtained in the region where the sample is expected to peak. In conclusion it can be said that gel-permeation chromatograph is still very much an art and the best method for obtaining the desired results is by selecting columns on a trial basis.

4.5 Effect of Injection Time and Sample Concentration

Some of the reasons why a monodisperse polymer standard shows an elution curve like a polymer distribution have already been mentioned. It is easy to understand why a very long injection time would cause excessive spreading of the elution curve and similarly a very high concentration could cause overloading again resulting in excessive spreading. In order to get a better understanding of these effects the following tests were made in the hope that operating conditions would be found where these effects are negligible. It was felt that the best way to study these effects was to use a polymer standard and the polystyrene standard S-103, having a molecular weight of 122,000 was used. The column arrangement consisted of four columns having pore sizes of 10^6, 10^4, 10^3 and 10^2 angstroms, in that order. Calibration curve number 1 and Water's method of trace interpretations were used. The elution solvent (T.H.F.) flow rate was 1 ml./min.

The effect of injection time on the amount of sample swept from the sample loop (2 ml. volume) into the columns should be linearly proportional if plug flow exists. The amount of sample actually swept into the columns is proportional to the area under the elution curve and thus a plot of injection time versus peak area gives an indication of how closely the flow pattern in the sample loop is to plug flow. Figure A-3 shows a plot of peak area versus the calculated amount of sample injected, the latter being calculated from the flow rate, sample concentration and injection time. Two graphs are shown, one for 0.5 wt.% and one for 0.25 wt.% concentrations. At injection times of 120 seconds the plot deviates from linearity suggesting a parabolic profile. At 60 seconds this is not so. This is because the apex of the profile still has not reached the sample loop exit after 60 seconds. Thus, in order to ensure

FIGURE A-3


EFFECT OF INJECTION TIME
ON AMOUNT OF SAMPLE
ENTERING GPC COLUMNS
120 SEC. INJECT.
INJECTION TIME
Δ 60 SEC.
○ 30 SEC.
120 SEC. INJECTION
SAMPLE CONCENTRATIONS
○ 1.0 WT. %
Δ 0.5 WT. %
● 0.25 WT. %
INJECTION TIME
Δ 30 SEC.
● 60 SEC.
○ 15 SEC.
FLOWRATE – 1.1 ML/MIN
COLUMN ARRANGEMENT
10^6, 10^4, 10^3, 10^2, A°
INJECTION TIME
Δ 15 SEC.
● 30 SEC.
○ 7.5 SEC.
TEMPERATURE 25 °C
Δ 7.5 SEC.
● 15 SEC.
7.5 SEC.
ELUTION PEAK AREA - SQ. INCH
0
1
2
3
4
5
6
7
8
0
2
4
6
8
10
12
AMOUNT OF SAMPLE INJECTED IN MG. (CALCULATED)

that the same amount of sample is always injected, the injection time should be kept below 60 seconds.

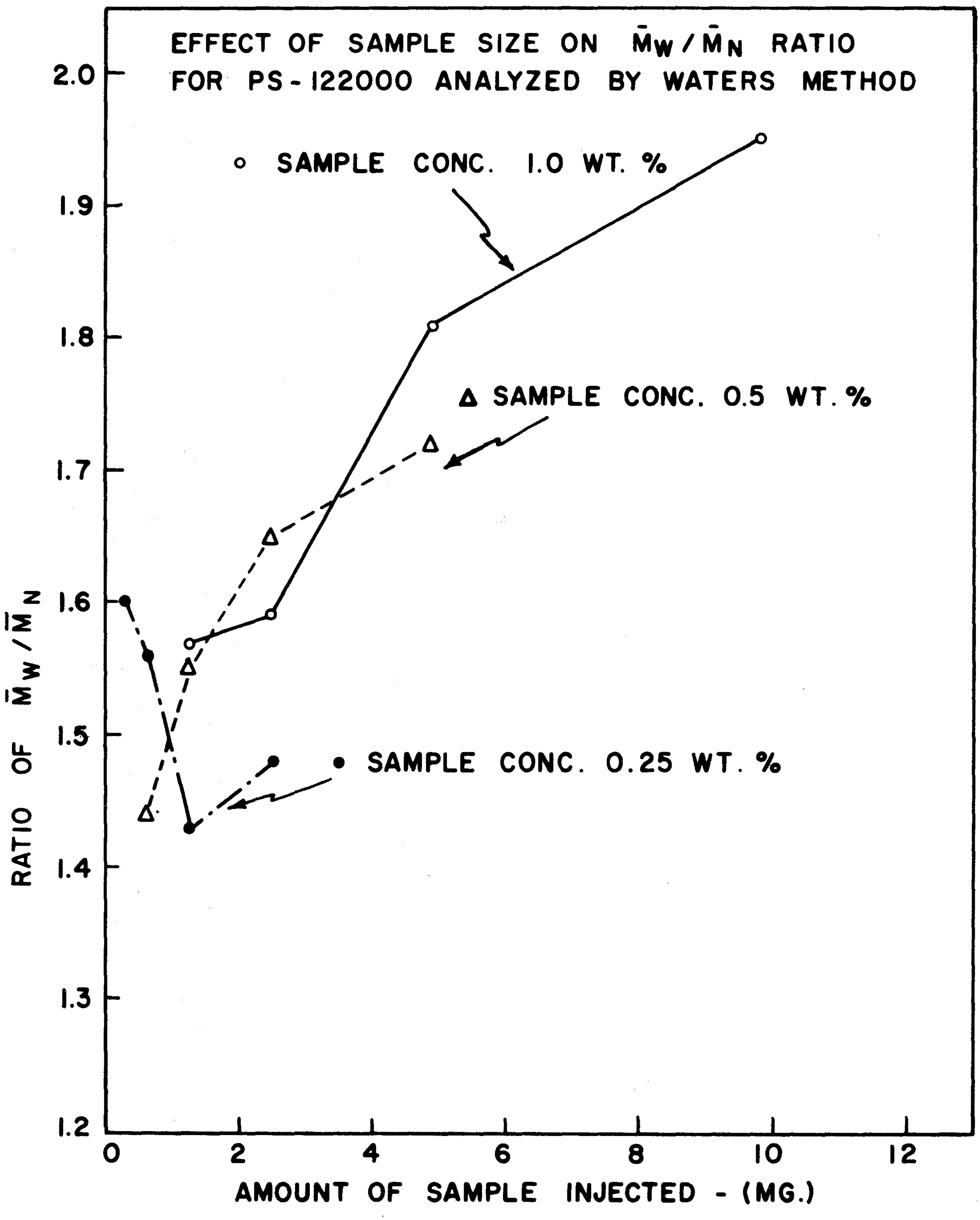
The effect of the sample concentration which indirectly also involves the injection time was investigated next. There is no effective criteria for measuring peak spreading except by actual comparison of traces. Nevertheless, a trace from the S-103 standard was subjected to the normal (Waters' method) method analysis for obtaining a molecular weight distribution. Table A-13 shows the results. For each injection time and concentration the number and weight-average molecular weights and their ratio are given. Figure A-4 shows the results in graphical form. Note that at a fixed concentration $\bar{M}_n$ and $\bar{M}_w$ increase with decreasing injection time but the ratio $\bar{M}_w/\bar{M}_n$ decreases, suggesting the peak spreading becomes less upon dilution. At a fixed injection time and decreasing sample concentration the same behaviour is observed which suggests the effect is due to sample concentration and not injection time although the latter may have an effect as well. To test this, samples of decreasing injection times were compensated by increasing their concentration. There is a steady decrease in the $\bar{M}_w/\bar{M}_n$ ratio with injection time for the 1.0 wt.% and the 0.5 wt.% case but at 0.25 wt.% no such pattern emerges. From all these results it is seen that no limiting concentration at which $\bar{M}_w/\bar{M}_n$ remains constant was reached except perhaps for the case of 0.25 wt.% but it is clear that the spread of the

TABLE A-13

EFFECT OF SAMPLE SIZE ON PEAK SPREADING

Inj. Time (Sec)	Sample Conc. (Wt.%)	THF Flow rate (Ml/Mn)	Temp (°C)	Sensitivity Selection	$\bar{M}_n\text{x}10^{-5}$	$\bar{M}_w\text{x}10^{-5}$	$\frac{\bar{M}_w}{\bar{M}_n}$
60	1.0	1.1	23.5	1X	0.65	1.26	1.95
30	1.0	1.1	23.2	1X	0.81	1.47	1.81
15	1.0	1.1	23.4	1X	1.03	1.64	1.59
7.5	1.0	1.1	23.2	2X	1.34	2.10	1.22
120	0.5	1.1	23.6	1X	0.64	1.30	2.02
60	0.5	1.1	23.7	1X	0.83	1.42	1.72
30	0.5	1.1	23.7	2X	1.04	1.71	1.65
15	0.5	1.1	23.6	4X	1.19	1.85	1.55
7.5	0.5	1.1	23.6	4X	1.46	2.10	1.44
120	0.25	1.1	26.0	1X	0.99	1.67	1.69
60	0.25	1.1	24.0	2X	1.20	1.77	1.48
30	0.25	1.1	23.9	4X	1.39	1.99	1.43
15	0.25	1.1	23.6	4X	1.66	2.58	1.56
7.5	0.25	1.1	23.5	8X	1.86	2.97	1.60
60	0.5	1.0	23.6	1X	1.03	1.63	1.59
60	0.25	1.0	23.6	2X	1.25	1.79	1.43
40	0.5	1.0	23.5	2X	1.14	1.67	1.46
60	0.5	1.0	23.5	1X	1.08	1.58	1.46
60	0.25	1.0	23.8	2X	1.19	1.71	1.44
60	0.5	1.0	23.6	1X	0.99	1.55	1.56
60	0.25	1.0	23.3	2X	1.07	1.74	1.62

FIGURE A-4


EFFECT OF SAMPLE SIZE ON $\bar{M}_W/\bar{M}_N$ RATIO FOR PS-122000 ANALYZED BY WATERS METHOD
○ SAMPLE CONC. 1.0 WT. %
△ SAMPLE CONC. 0.5 WT. %
● SAMPLE CONC. 0.25 WT. %
RATIO OF $\bar{M}_W/\bar{M}_N$
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
0
2
4
6
8
10
12
AMOUNT OF SAMPLE INJECTED - (MG.)

elution peak is affected by these variables. In order to correct actual sample output traces the amount of spreading must of course be accurately known and the first question that comes to mind is this, is the peak spreading the same for two different standards? This effect was not tested and probably should be, as well as the foregoing work further extended.

5. DETERMINATION OF MOLECULAR-WEIGHT DISTRIBUTIONS

5.1 Theoretical Calculation of Molecular-Weight Distribution

The equation required for calculating the concentration of a certain species of polymer, P_r, have already been presented in the form of equations (16), (24) and (25) and the actual distribution can then be obtained from equations (26), (27) and (28). Whenever analytical solutions of these equations are attempted, the probability function ξ usually is assumed to be constant as in the rate of initiation. It was therefore considered worthwhile to calculate ξ for each value of P_r for various reaction times to test this assumption. Table A-14 shows a typical result, verifying the assumption of constant ξ. It is also interesting to note how close ξ is to 1.0. To solve equations (16), (24) and (25) the following procedure was adopted.

As before, the conversion X was calculated by numerically integrating equation (16) using the fourth-order Runge-Kutta method. All the values of X calculated at each step were stored and used to calculate values for ξ for the same step increments, which were stored also. Equation (25) was then integrated using the trapezoidal rule, the required value for X and ξ for each step being called from storage. An alternative method of solution would be to combine equations (24) and (25) and to solve the resulting equation simultaneously with equation (16) using the Runge-Kutta method. However, it was desired to get values for ξ making the calculation of equation (24) necessary

TABLE A-14

CHANGE IN PROPAGATION PROBABILITY

Reaction Time (hrs)	Conversion (%)	Probability
1	7.00	0.9935
2	12.85	0.9938
3	17.77	0.9941
4	21.94	0.9944
5	25.48	0.9948
6	28.51	0.9951
7	31.12	0.9955
8	33.37	0.9958
9	35.32	0.9961
10	37.02	0.9964
11	38.50	0.9967
12	39.79	0.9970
13	40.93	0.9973
14	41.92	0.9975
15	42.80	0.9977
16	43.57	0.9979
17	44.25	0.9981
18	44.85	0.9983
19	45.03	0.9983

Run No. 1

Reaction Temperature - 75°C.

Initial Reactant Concentrations - Monomer - 30.0 Wt.%
Solvent - 69.9 Wt.%
Catalyst - 0.1 Wt.%

anyway, and the adopted scheme is simpler from a bookkeeping standpoint. The time required to do a complete calculation varies greatly depending on the reaction time. For example, to get the conversion and molecular-weight distribution after one hour takes 4 minutes and 46 seconds but a distribution after twelve hours takes 36 minutes, 27 seconds. For a complete listing of the program, refer to Appendix 6. The program is subject to further simplification with perhaps considerable time saving and should be closely scrutinized before being used on a continuous basis. To get an idea of the error buildup, the quantity ($\sum_{r=1}^{\infty} r\ P_r$) is calculated. It is clear that this quantity should be identical to (M_oX) the total no. of gm. moles of monomer converted. For the case of 30% monomer, 0.1% catalyst and 75^oC. this was

$$\sum_{r=1}^{\infty} r\ P_r = 1.022$$

$$M_oX = 1.018$$

Thus the calculation of P_r is reasonably accurate showing a round-off error of less than one half of one percent.

As in the case for solving equation (16) alone, the choise of delt affects the calculation error. A comparison of the molecular-weight distribution at delt = 90 with that at delt = 180 showed no difference and delt = 180 seconds was therefore adopted as standard.

5.2 Comparison of Theoretical with Experimental Results

The effect of the various reaction variables on the molecular-weight distribution has already been discussed to some extent. The following Figures (A-5 to A-19) show the results of the molecular-weight distribution calculation as actual distribution curves. The cumulative distribution curves are shown as well and here the gel-permeation chromatograph results have been superimposed for comparison.

Figures (A-5 to A-7) are the results for the use of 30% monomer, 0.1% catalyst at 75°C., Runs 1, 2 and 3. Both the normal and cumulative distributions have been plotted, the latter showing the gel-permeation chromatograph results as well. Note that the agreement between the gel-permeation chromatograph results and the theoretically predicted curve is excellent in all cases. For this particular case at least, the theoretical model in the form of equations (16), (24) and (25) is confirmed experimentally even though the gel-permeation chromatograph calibration curve was selected on the basis of getting agreement for the case shown in Figure A-5b. Note the shift in distribution with time, especially after twelve hours, when the high-molecular-weight tail becomes more and more important. Table A-15 gives a comparison of the averages. As was to be expected, as the distribution became broader with increasing reaction time, the weight to number average ratio increased accordingly.

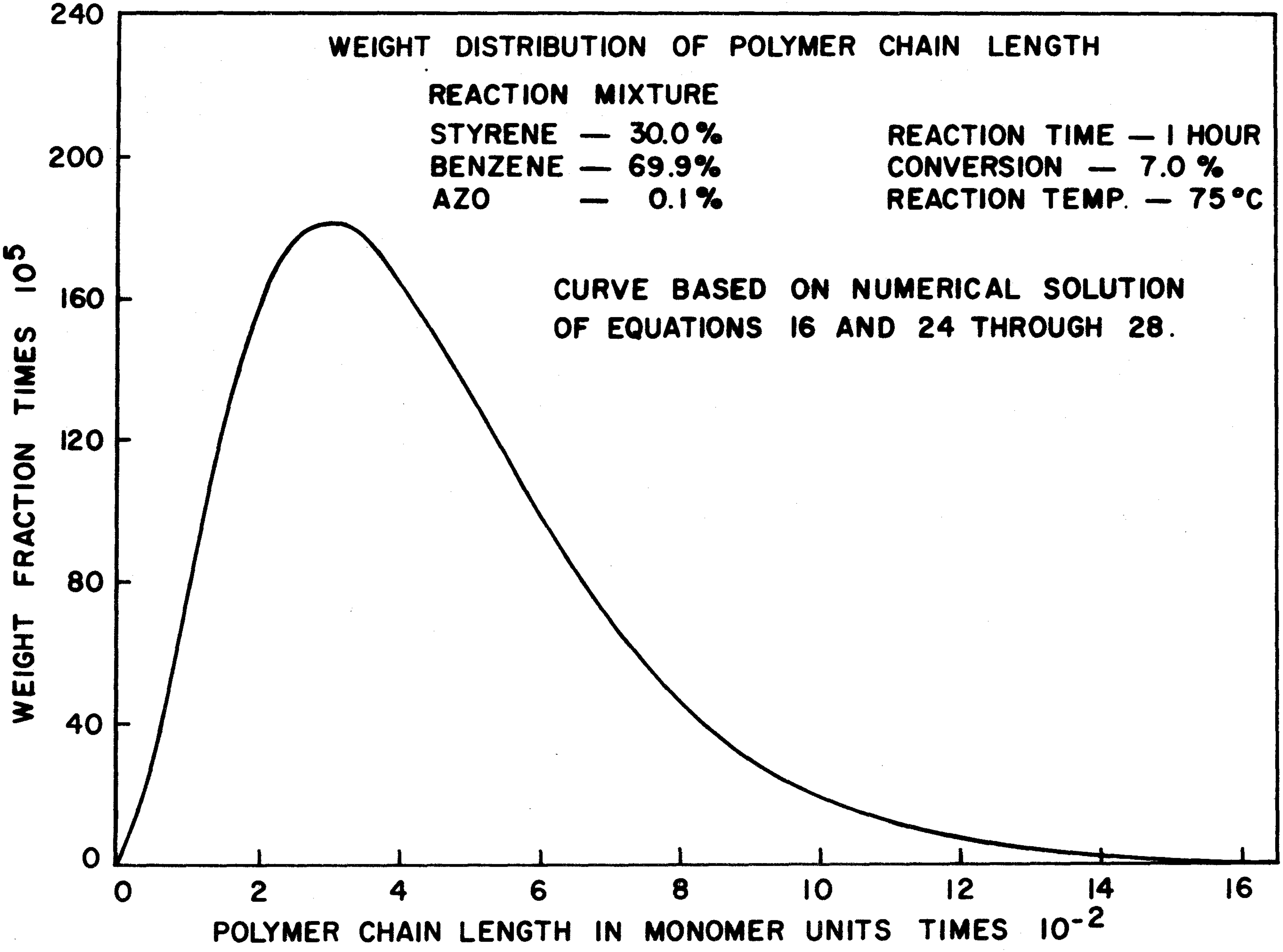

WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
REACTION MIXTURE
STYRENE — 30.0 %
BENZENE — 69.9%
AZO — 0.1 %
REACTION TIME — 1 HOUR
CONVERSION — 7.0 %
REACTION TEMP. — 75 °C
CURVE BASED ON NUMERICAL SOLUTION
OF EQUATIONS 16 AND 24 THROUGH 28.
WEIGHT FRACTION TIMES 10^5
240
200
160
120
80
40
0
0
2
4
6
8
10
12
14
16
POLYMER CHAIN LENGTH IN MONOMER UNITS TIMES 10^-2

FIGURE A-5a

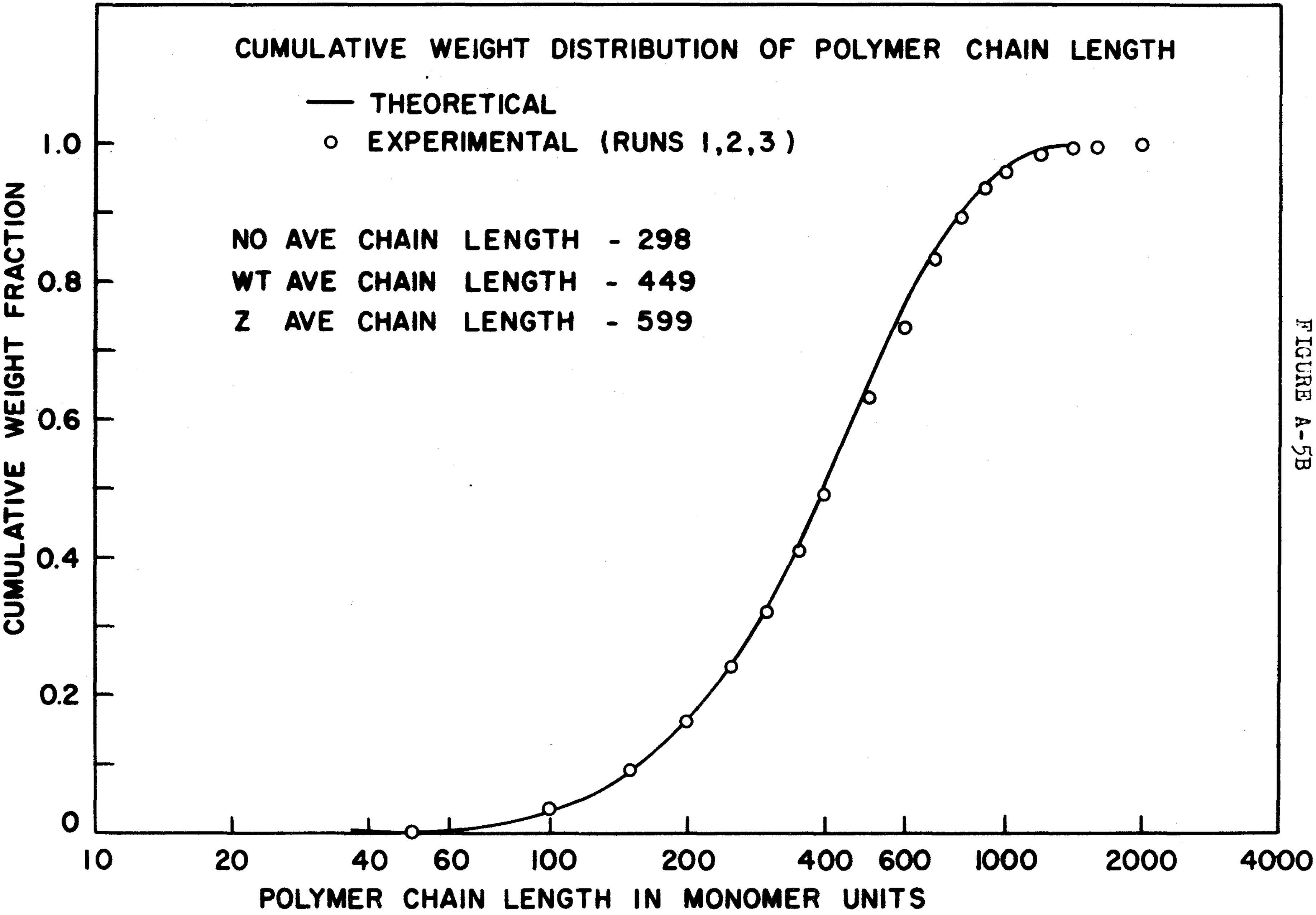

CUMULATIVE WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
THEORETICAL
EXPERIMENTAL (RUNS 1,2,3)
NO AVE CHAIN LENGTH - 298
WT AVE CHAIN LENGTH - 449
Z AVE CHAIN LENGTH - 599
CUMULATIVE WEIGHT FRACTION
1.0
0.8
0.6
0.4
0.2
0
10
20
40
60
100
200
400
600
1000
2000
4000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE A-5B

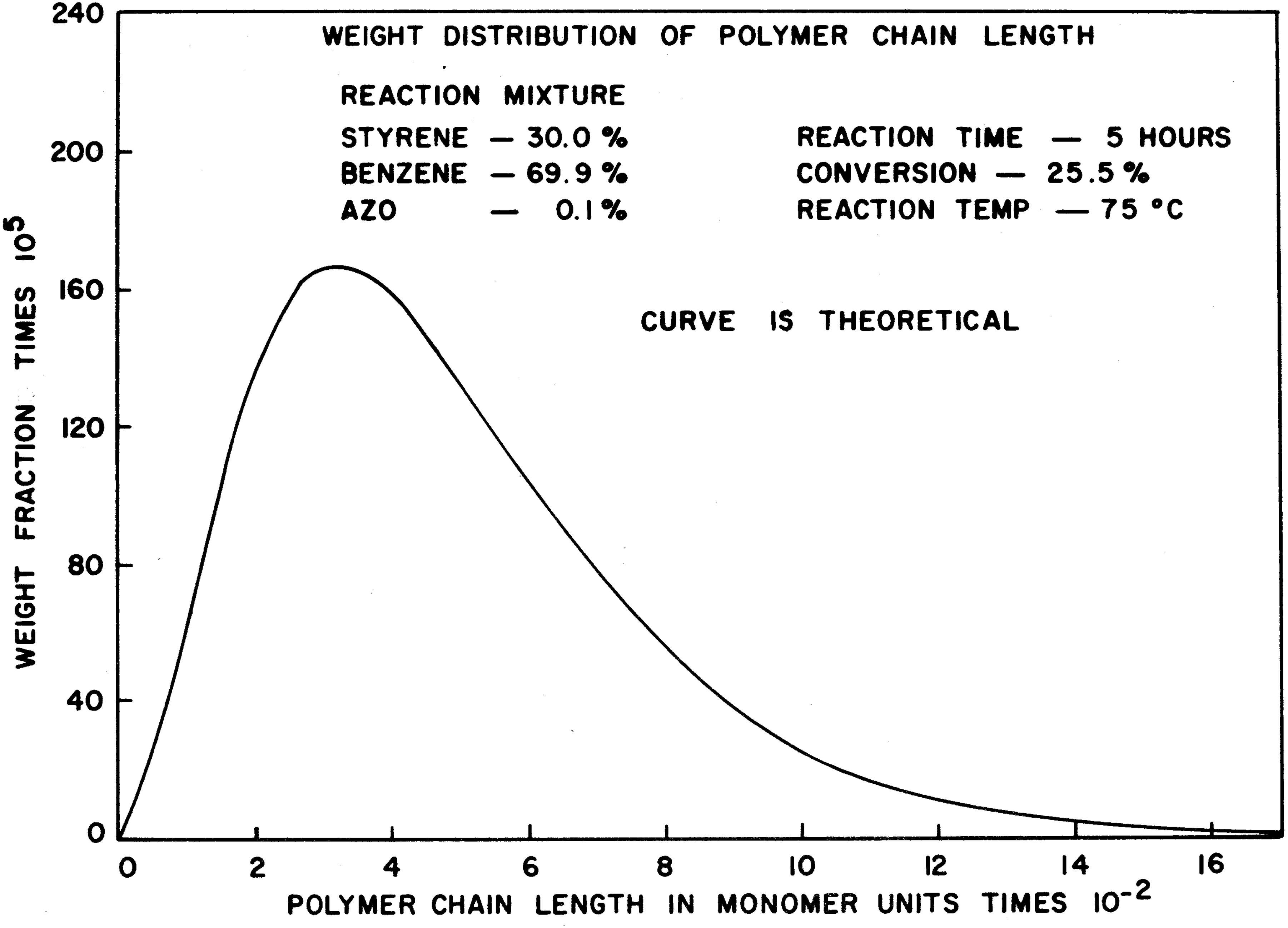

WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
REACTION MIXTURE
STYRENE — 30.0 %
BENZENE — 69.9 %
AZO — 0.1 %
REACTION TIME — 5 HOURS
CONVERSION — 25.5 %
REACTION TEMP — 75 °C
CURVE IS THEORETICAL
WEIGHT FRACTION TIMES 10^5
240
200
160
120
80
40
0
0
2
4
6
8
10
12
14
16
POLYMER CHAIN LENGTH IN MONOMER UNITS TIMES 10^-2

FIGURE A-6a

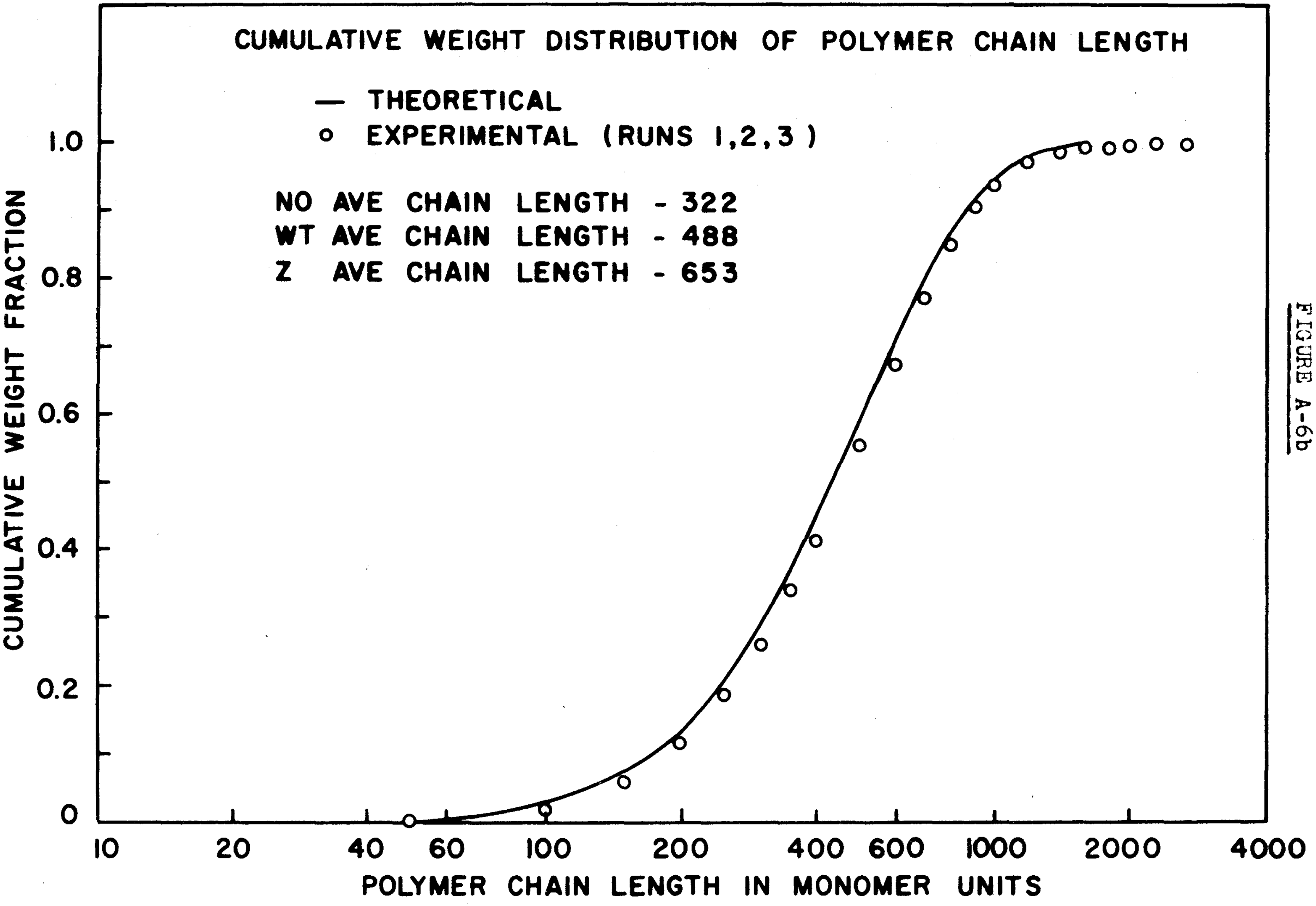

CUMULATIVE WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
— THEORETICAL
○ EXPERIMENTAL (RUNS 1,2,3)
NO AVE CHAIN LENGTH - 322
WT AVE CHAIN LENGTH - 488
Z AVE CHAIN LENGTH - 653
CUMULATIVE WEIGHT FRACTION
1.0
0.8
0.6
0.4
0.2
0
10
20
40
60
100
200
400
600
1000
2000
4000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE A-6b

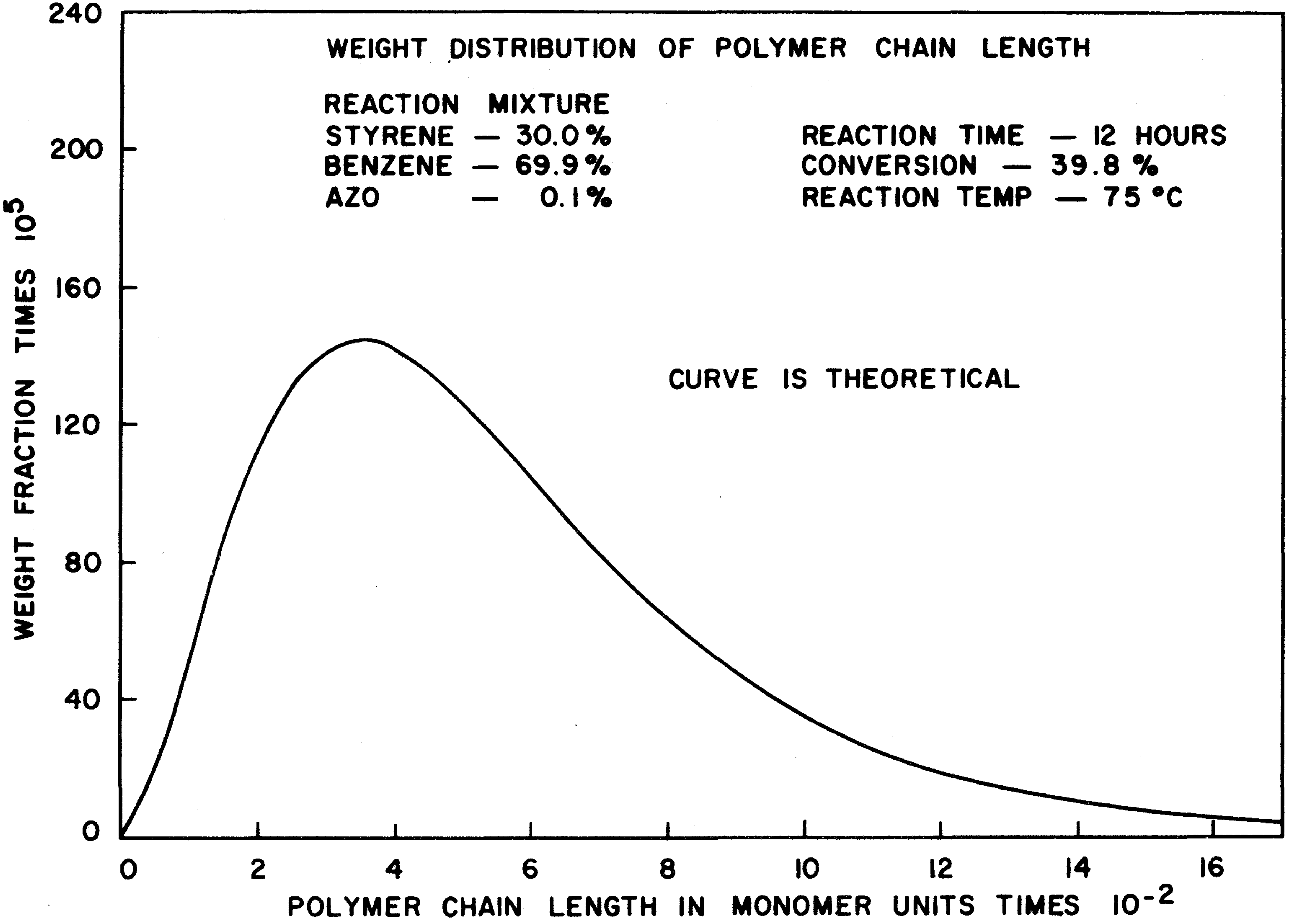

WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
REACTION MIXTURE
STYRENE — 30.0 %
BENZENE — 69.9 %
AZO — 0.1 %
REACTION TIME — 12 HOURS
CONVERSION — 39.8 %
REACTION TEMP — 75 °C
CURVE IS THEORETICAL
WEIGHT FRACTION TIMES 10^5
240
200
160
120
80
40
0
0
2
4
6
8
10
12
14
16
POLYMER CHAIN LENGTH IN MONOMER UNITS TIMES 10^-2

FIGURE A-7a

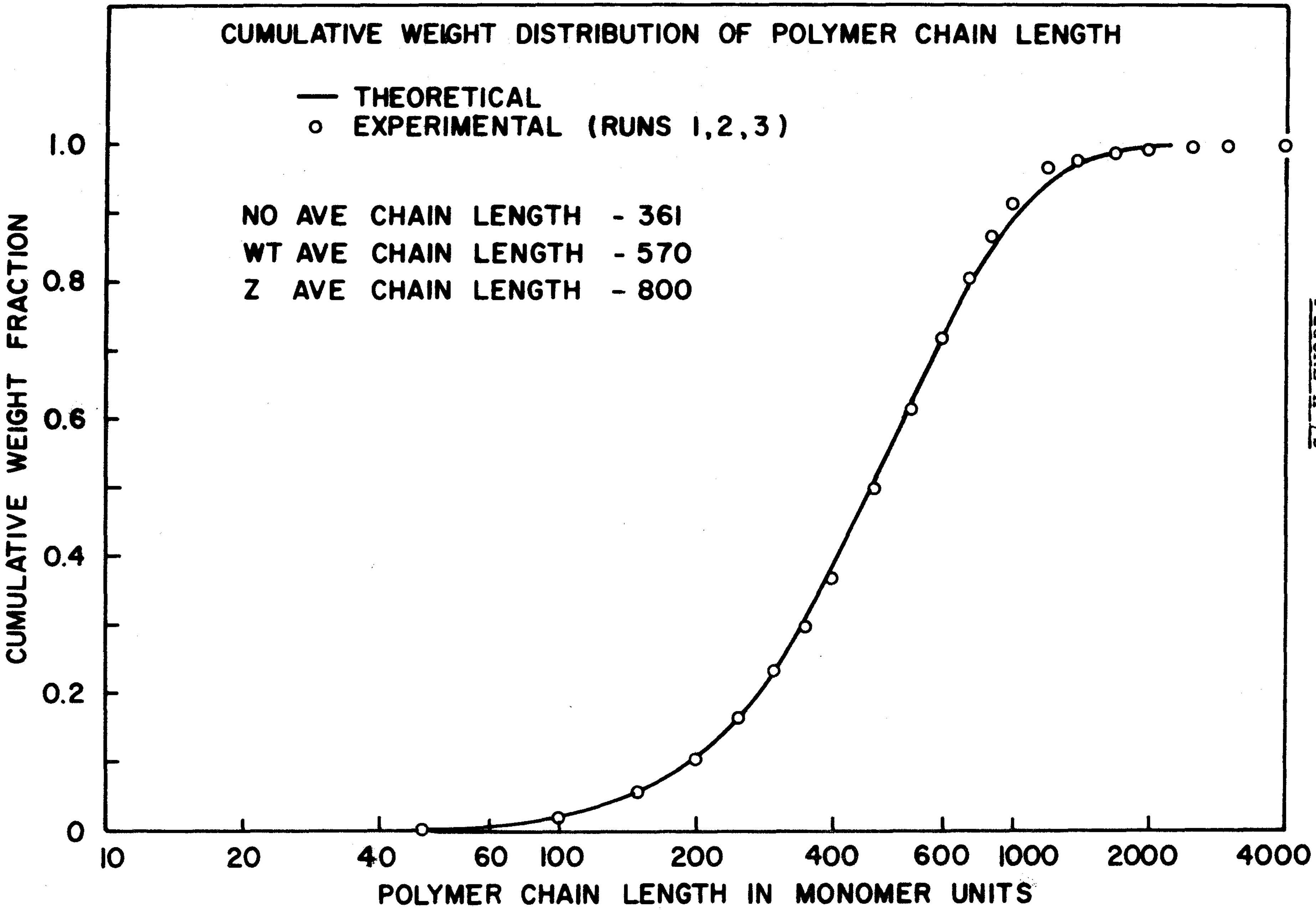

CUMULATIVE WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
— THEORETICAL
○ EXPERIMENTAL (RUNS 1,2,3)
NO AVE CHAIN LENGTH - 361
WT AVE CHAIN LENGTH - 570
Z AVE CHAIN LENGTH - 800
CUMULATIVE WEIGHT FRACTION
1.0
0.8
0.6
0.4
0.2
0
10
20
40
60
100
200
400
600
1000
2000
4000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE A-7b

TABLE A-15

AVERAGE MOLECULAR-WEIGHTS FOR RUNS 1, 2 AND 3

Reaction Time Hours	No. Ave. CH .L.	Wt. Ave. CH.L.	Z Ave. CH.L.	Wt. Ave. To No. Ave.Ratio
1	298	449	599	1.51
5	322	488	653	1.52
12	361	570	800	1.58

The results for the same reaction mixture but a reaction temperature of 65°C., Runs 4, 5 and 6 are shown in Figure A-8 and A-9. As before, the second curve is the same as the first one but plotted on a cumulative basis. Only the one and twelve hour reaction time cases are shown since no significant shift in molecular-weight took place. The number average degree of polymerization increased significantly over the 75°C. runs. This is not surprising since, although the activation energy of the termination constant is less than that of the propagation constant, it is much higher for the catalyst decomposition constant. Agreement with the gel-permeation chromatograph results is poor and the cause is not known. The catalyst efficiency was rather low too, perhaps suggesting premature termination due to oxygen or some other inhibitor which would depress the molecular-weight. Further duplication of these runs might shed more light, since it was the most troublesome condition to establish good reproducibility.

Figures A-10 and A-11 show the results for Runs 7, 8

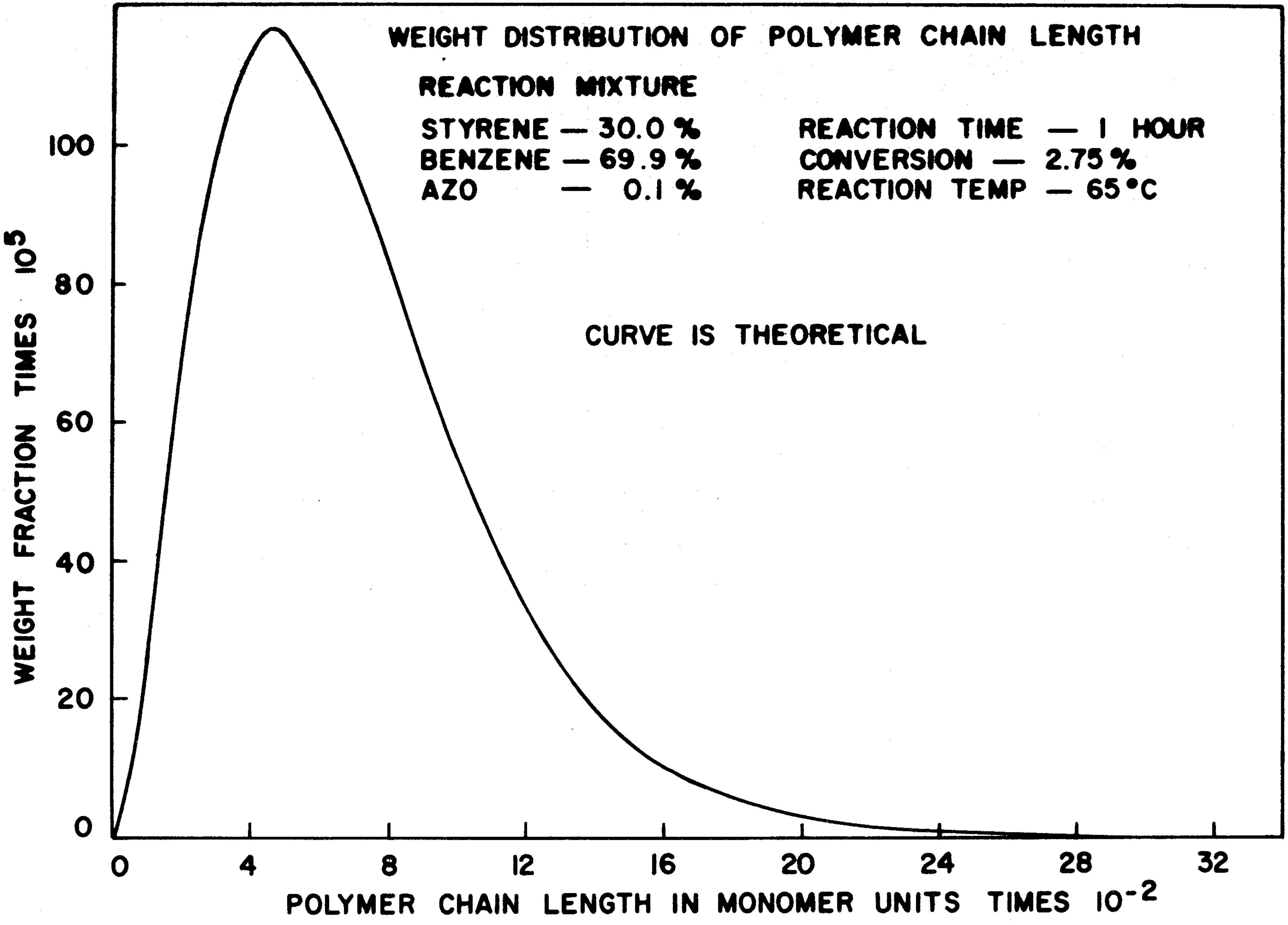

WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
REACTION MIXTURE
STYRENE — 30.0 %
BENZENE — 69.9 %
AZO — 0.1 %
REACTION TIME — 1 HOUR
CONVERSION — 2.75 %
REACTION TEMP — 65 °C
CURVE IS THEORETICAL
WEIGHT FRACTION TIMES 10^5
0
20
40
60
80
100
0
4
8
12
16
20
24
28
32
POLYMER CHAIN LENGTH IN MONOMER UNITS TIMES 10^-2

FIGURE A-8a

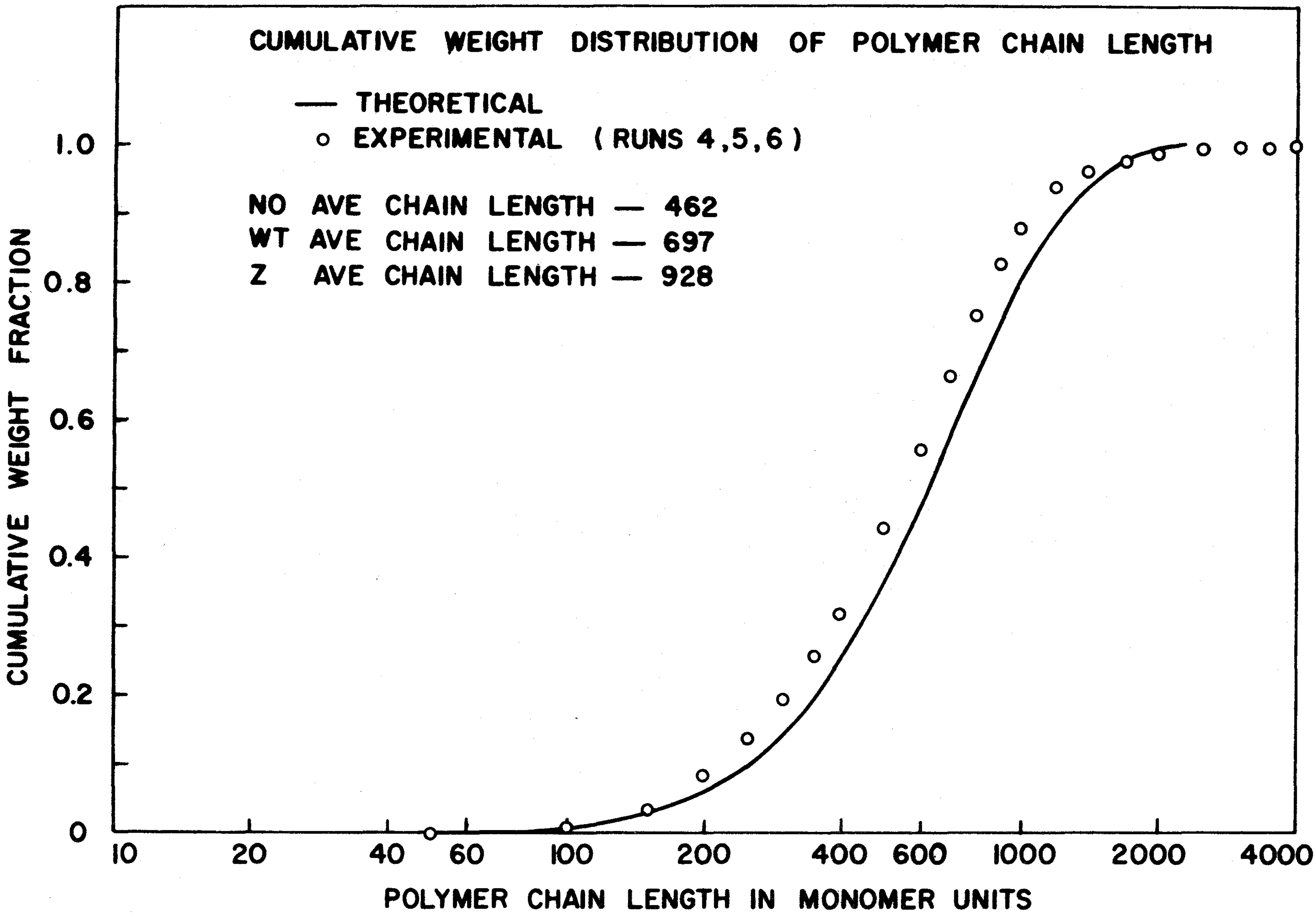

CUMULATIVE WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
— THEORETICAL
○ EXPERIMENTAL (RUNS 4,5,6)
NO AVE CHAIN LENGTH — 462
WT AVE CHAIN LENGTH — 697
Z AVE CHAIN LENGTH — 928
CUMULATIVE WEIGHT FRACTION
1.0
0.8
0.6
0.4
0.2
0
10
20
40
60
100
200
400
600
1000
2000
4000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE A-8b

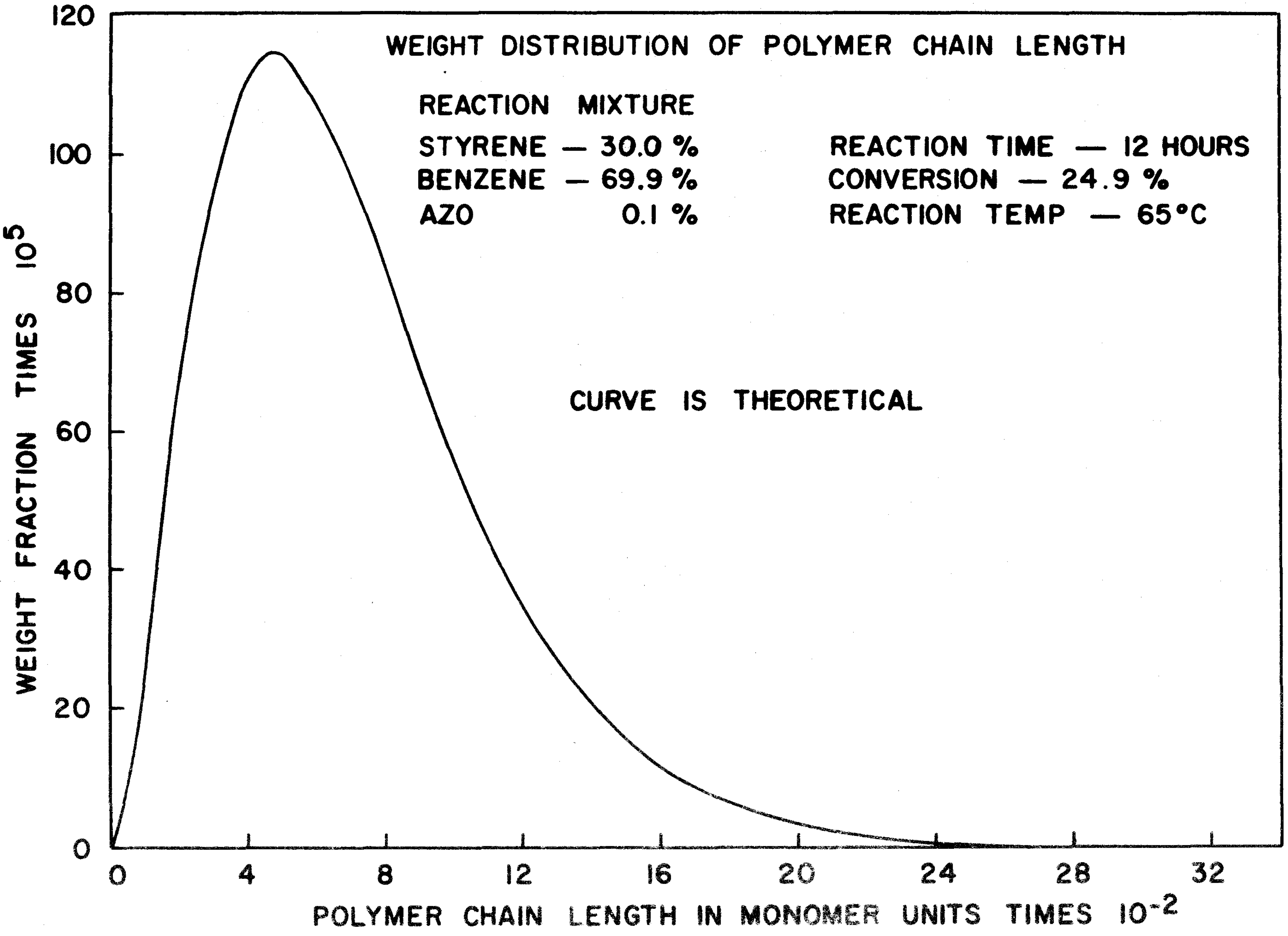

WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
REACTION MIXTURE
STYRENE — 30.0 %
BENZENE — 69.9 %
AZO 0.1 %
REACTION TIME — 12 HOURS
CONVERSION — 24.9 %
REACTION TEMP — 65°C
CURVE IS THEORETICAL
WEIGHT FRACTION TIMES 10^5
0
20
40
60
80
100
120
POLYMER CHAIN LENGTH IN MONOMER UNITS TIMES 10^-2
0
4
8
12
16
20
24
28
32

FIGURE A-9a

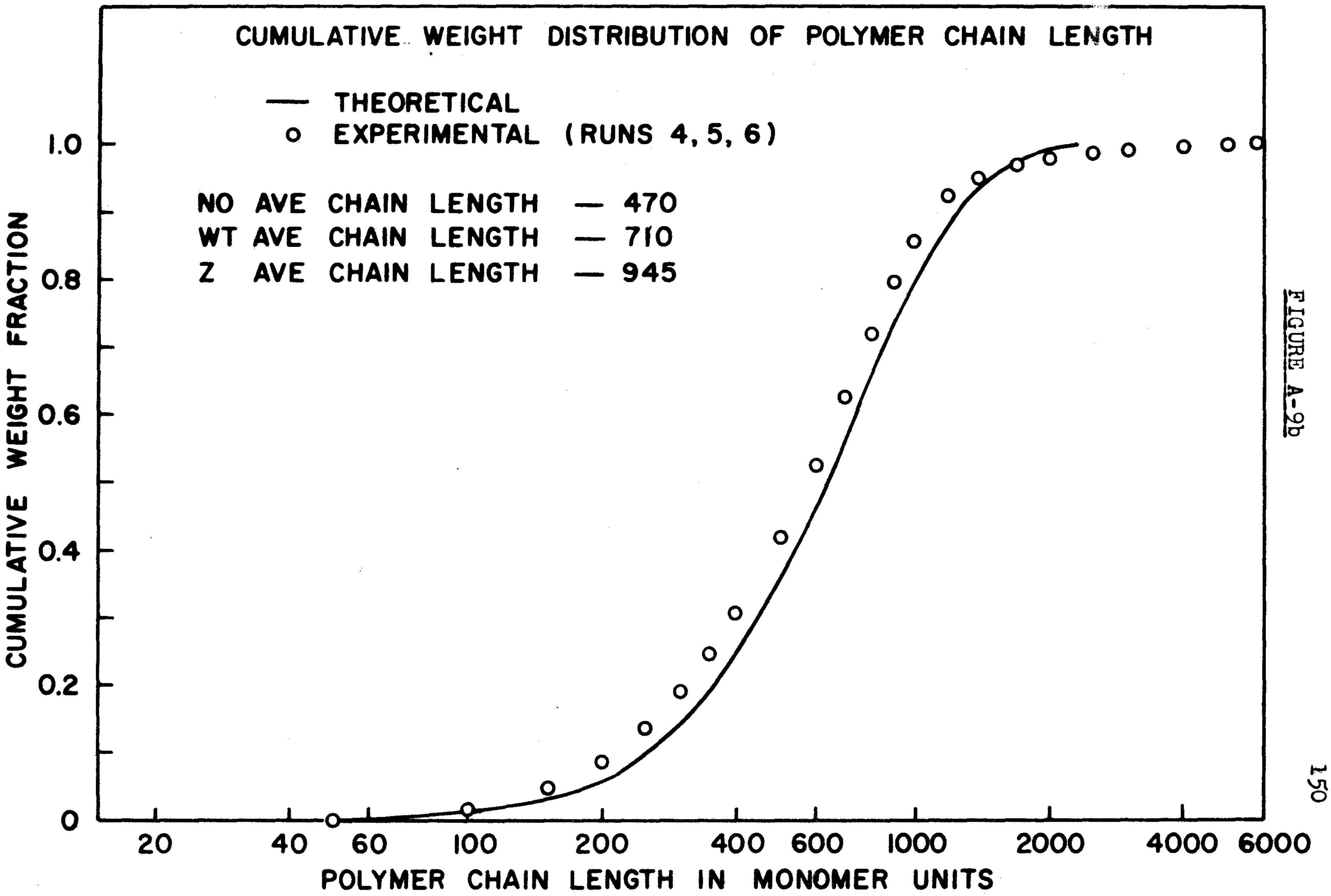

CUMULATIVE WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
— THEORETICAL
○ EXPERIMENTAL (RUNS 4, 5, 6)
NO AVE CHAIN LENGTH — 470
WT AVE CHAIN LENGTH — 710
Z AVE CHAIN LENGTH — 945
CUMULATIVE WEIGHT FRACTION
0
0.2
0.4
0.6
0.8
1.0
20
40
60
100
200
400
600
1000
2000
4000
6000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE A-9b

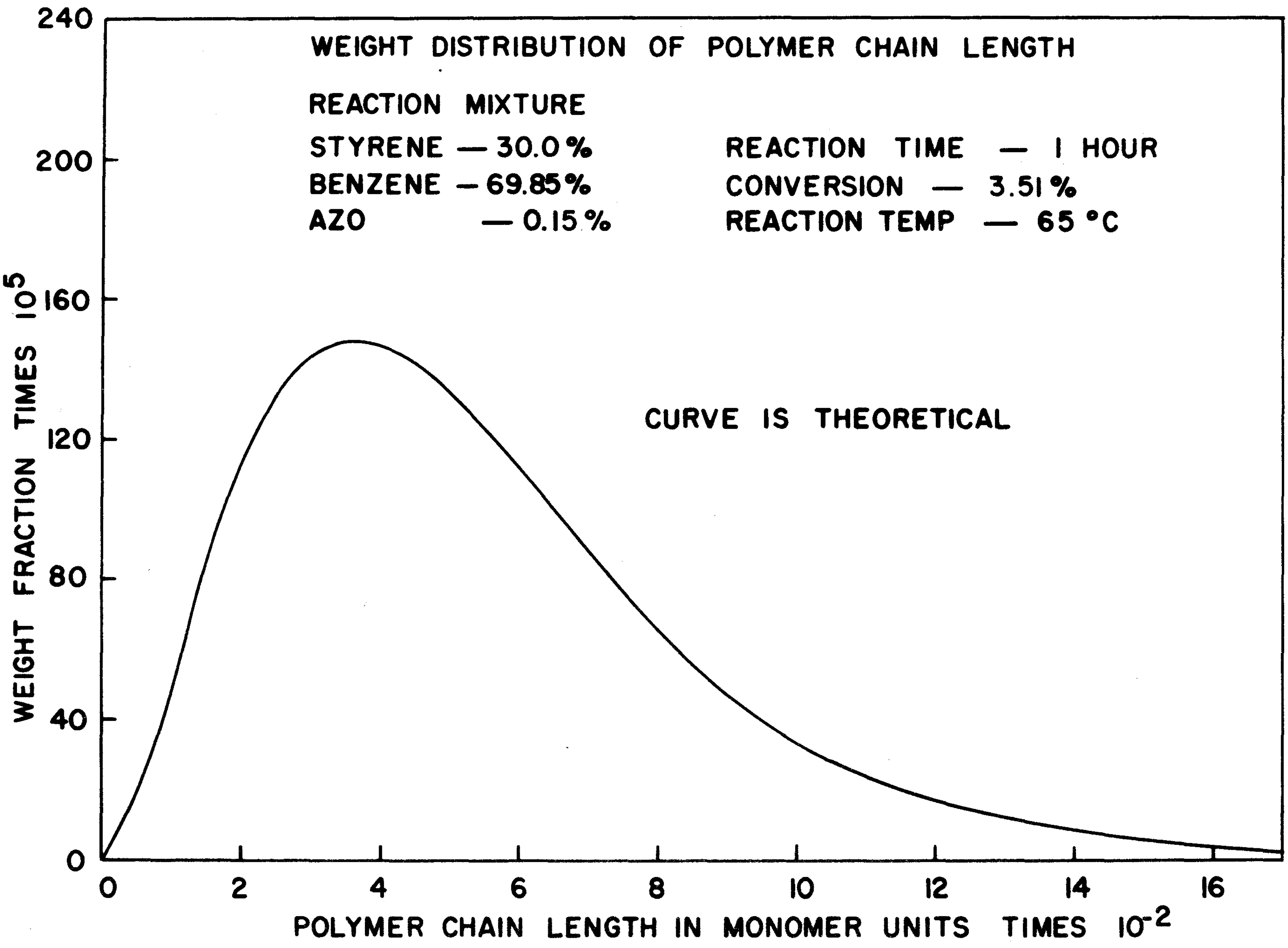

WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
REACTION MIXTURE
STYRENE — 30.0 %
BENZENE — 69.85 %
AZO — 0.15 %
REACTION TIME — 1 HOUR
CONVERSION — 3.51 %
REACTION TEMP — 65 °C
CURVE IS THEORETICAL
WEIGHT FRACTION TIMES 10^5
0
40
80
120
160
200
240
POLYMER CHAIN LENGTH IN MONOMER UNITS TIMES 10^-2
0
2
4
6
8
10
12
14
16

FIGURE A-10a

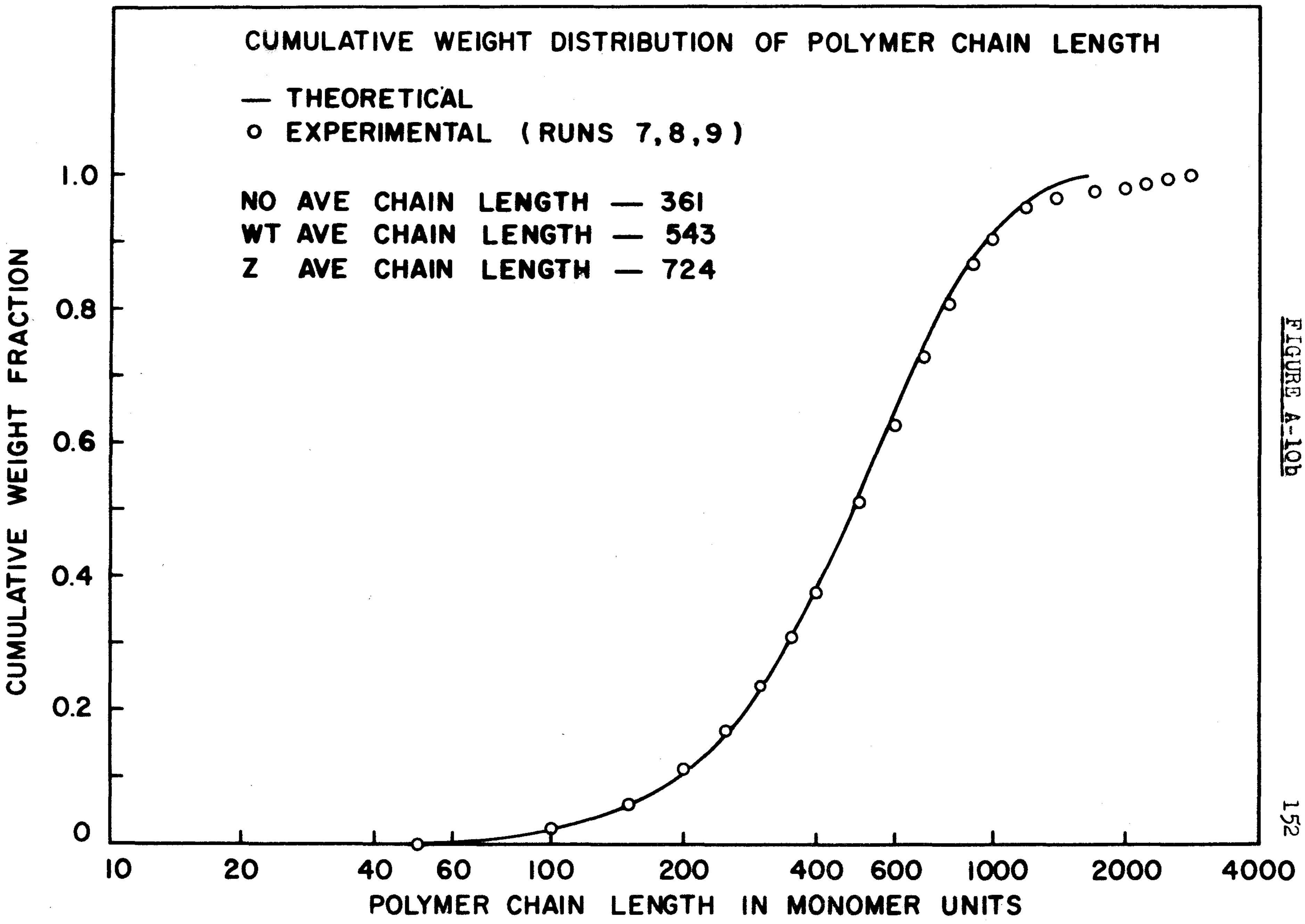

CUMULATIVE WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
— THEORETICAL
o EXPERIMENTAL (RUNS 7,8,9)
NO AVE CHAIN LENGTH — 361
WT AVE CHAIN LENGTH — 543
Z AVE CHAIN LENGTH — 724
CUMULATIVE WEIGHT FRACTION
1.0
0.8
0.6
0.4
0.2
0
10
20
40
60
100
200
400
600
1000
2000
4000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE A-10b

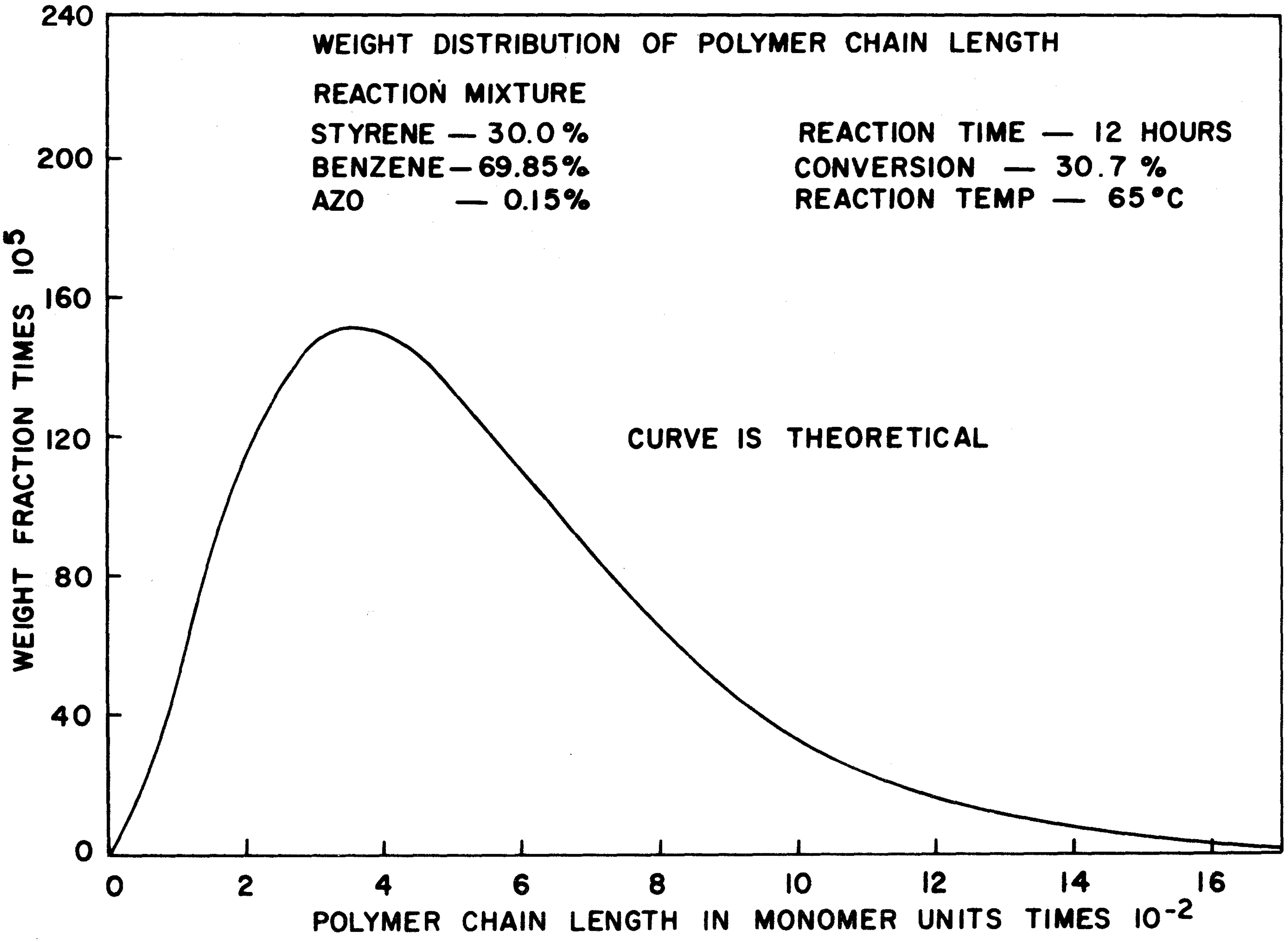

WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
REACTION MIXTURE
STYRENE — 30.0 %
BENZENE — 69.85 %
AZO — 0.15 %
REACTION TIME — 12 HOURS
CONVERSION — 30.7 %
REACTION TEMP — 65 °C
CURVE IS THEORETICAL
WEIGHT FRACTION TIMES 10^5
0
40
80
120
160
200
240
POLYMER CHAIN LENGTH IN MONOMER UNITS TIMES 10^-2
0
2
4
6
8
10
12
14
16

FIGURE A-11a

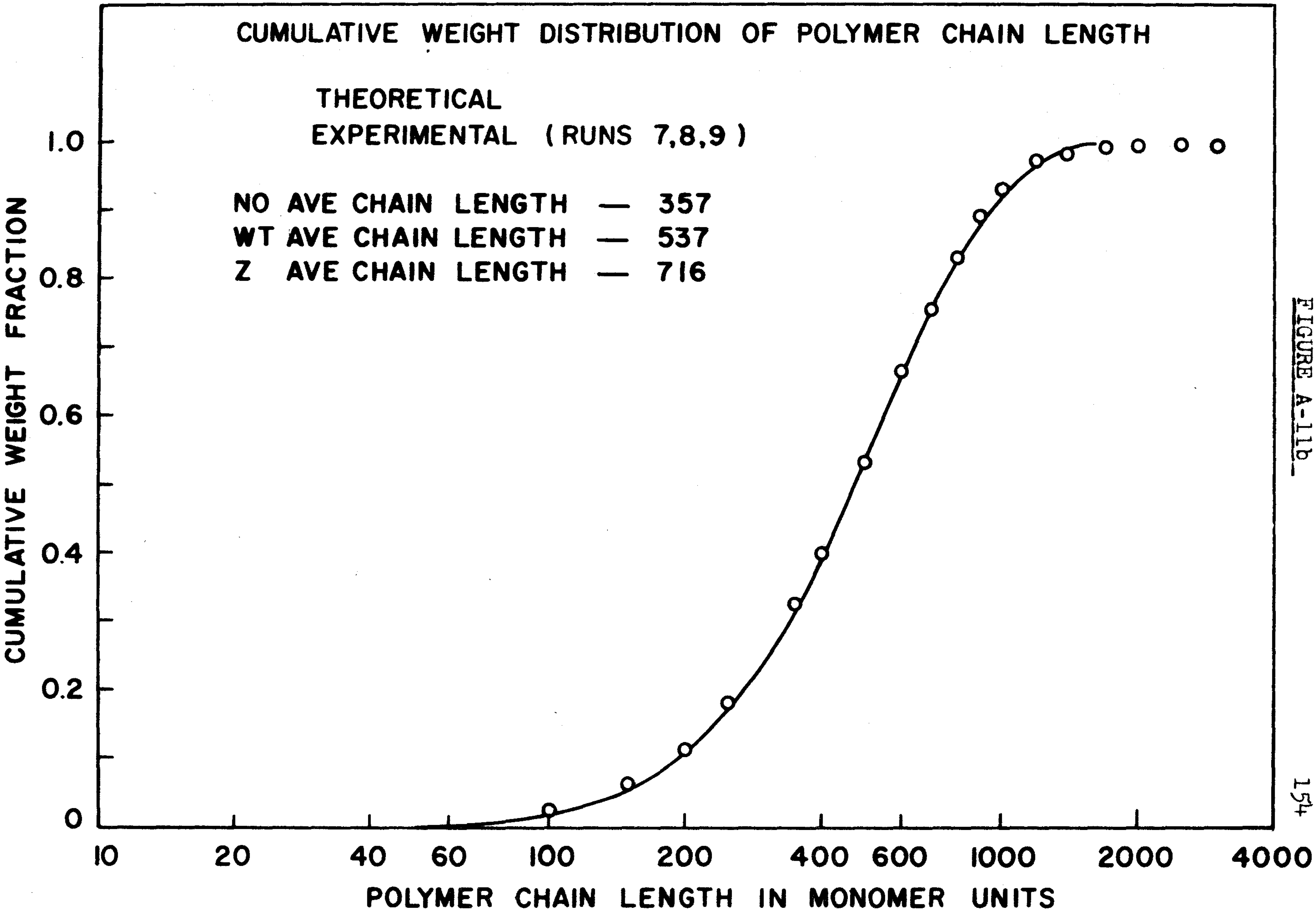

CUMULATIVE WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
THEORETICAL
EXPERIMENTAL (RUNS 7,8,9)
NO AVE CHAIN LENGTH — 357
WT AVE CHAIN LENGTH — 537
Z AVE CHAIN LENGTH — 716
CUMULATIVE WEIGHT FRACTION
1.0
0.8
0.6
0.4
0.2
0
10
20
40
60
100
200
400
600
1000
2000
4000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE A-11b

and 9, which were the same as Runs 6, 7 and 8 except for an increase in catalyst concentration from 0.1 to 0.15%. Again, only the one and twelve hour results are shown, since there was no significant shift in molecular weight with time. Because of the increased catalyst concentration the degree of polymerization dropped from 462 to 361 almost exactly as is to be expected on the basis of equation (35). Agreement with the gel-permeation chromatograph results is good. It should be pointed out that except for Runs 1, 2 and 3, the gel-permeation chromatograph samples were based on an equal weight mixture of polymer from each run.

Figures A-12 and A-13 show the results for Runs 9, 10 and 11, in which the catalyst concetration was further increased to 0.2%. As expected no shift in molecular weight with reaction time took place, but there was a further drop compared with the previous run, from 361 to 317. Again, agreement with the gel-permeation chromatograph results is good.

Figures A-14 and A-15 are for Runs 13, 14 and 15. The catalyst concentration was 0.1%, the temperature 65°C., and the monomer concentration 60.0%. On the basis of equation (35) this should result in the molecular weight being doubled over that of Runs 4, 5 and 6. Comparison of Figures A-5 with A-14 shows this is so. The number-average degree of polymerization increased from 361 to 789, nearly twice the amount. Also, Figure A-14 shows a distribution about twice as wide as Figure A-5 with the peak being reduced to one half the height. Agree-

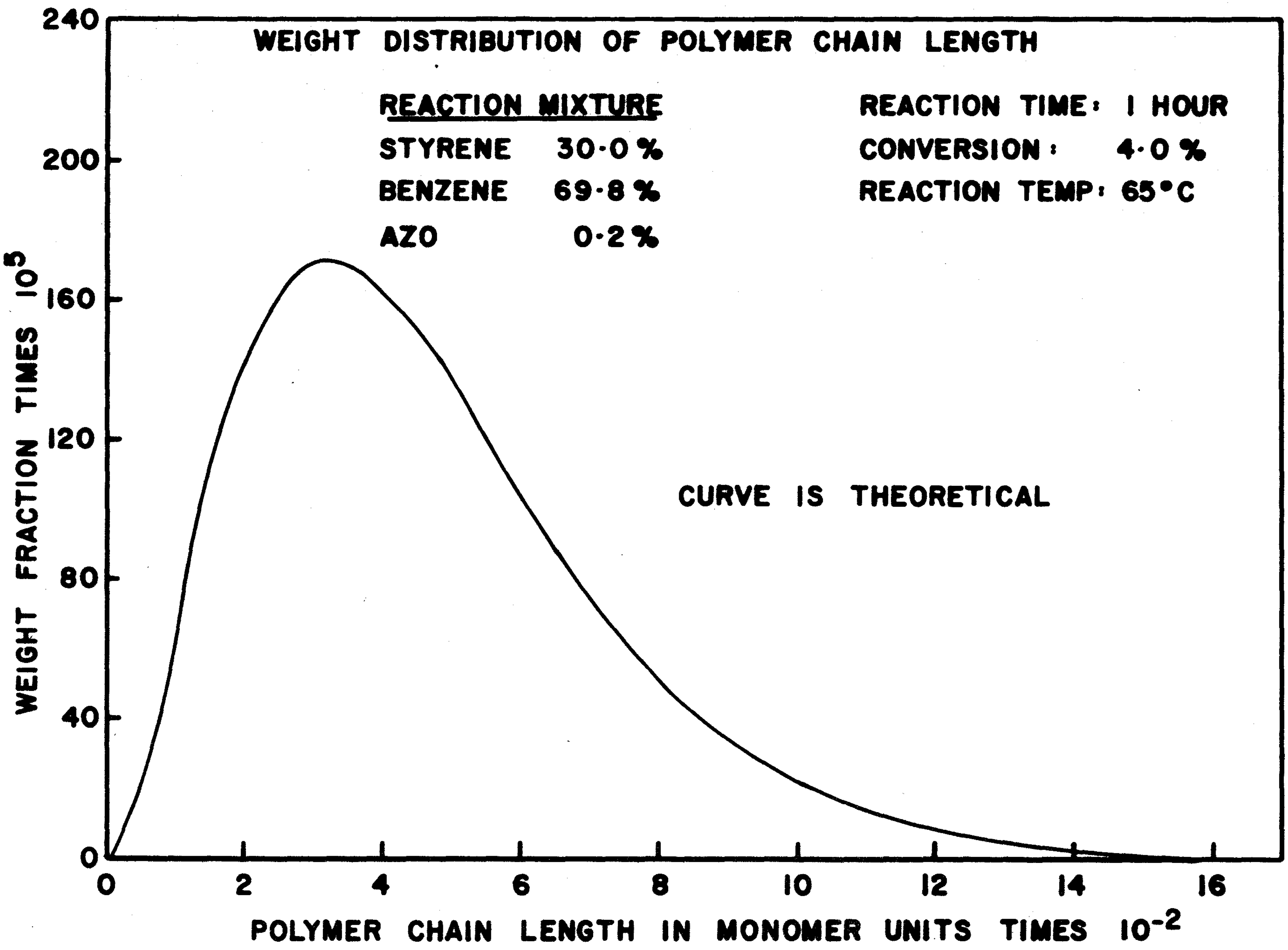
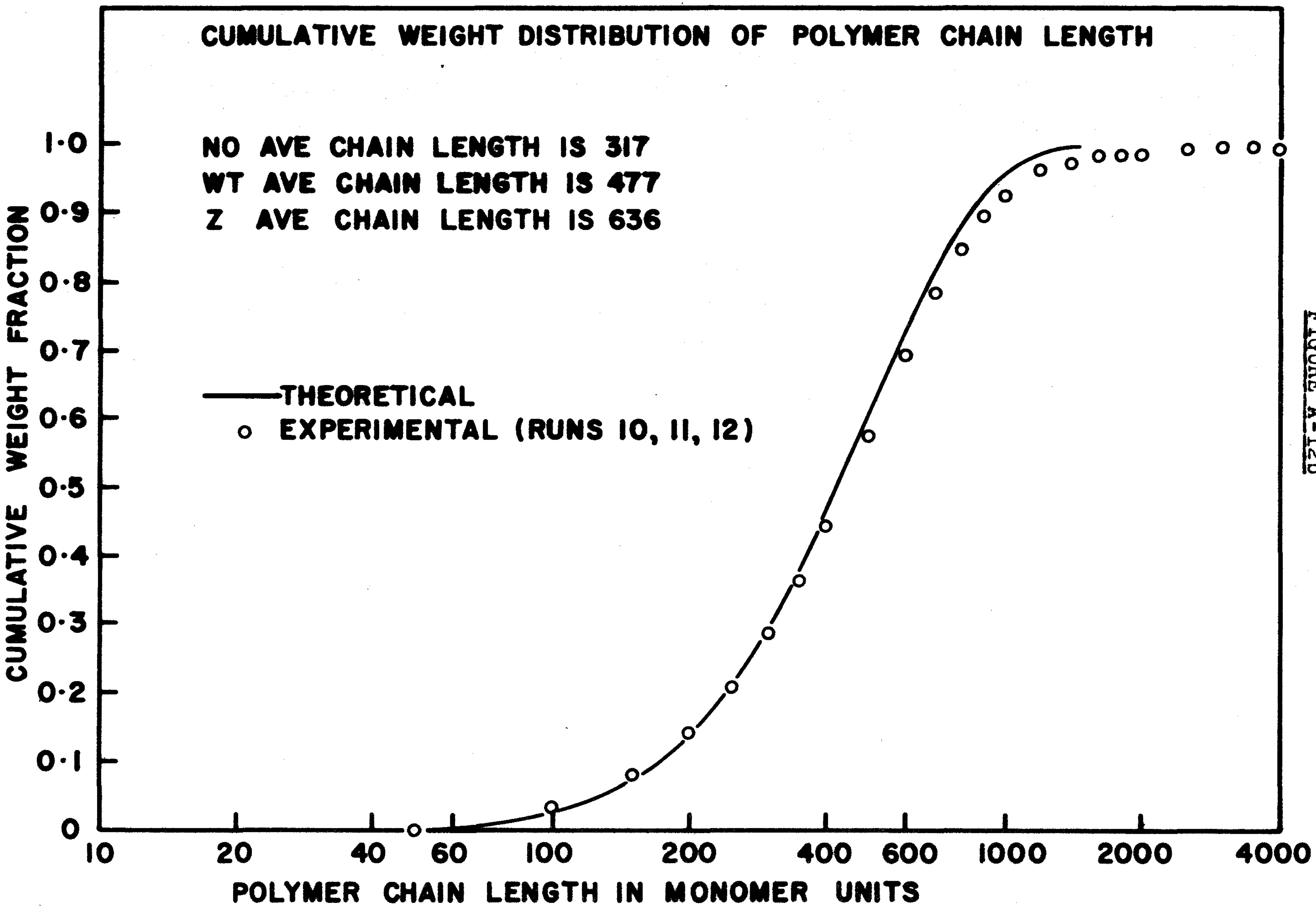

WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
REACTION MIXTURE
STYRENE 30·0 %
BENZENE 69·8 %
AZO 0·2 %
REACTION TIME: 1 HOUR
CONVERSION: 4·0 %
REACTION TEMP: 65°C
CURVE IS THEORETICAL
WEIGHT FRACTION TIMES 10^5
0
40
80
120
160
200
240
POLYMER CHAIN LENGTH IN MONOMER UNITS TIMES 10^-2
0
2
4
6
8
10
12
14
16

FIGURE A-12a


CUMULATIVE WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH

NO AVE CHAIN LENGTH IS 317
WT AVE CHAIN LENGTH IS 477
Z AVE CHAIN LENGTH IS 636

FIGURE A-12b

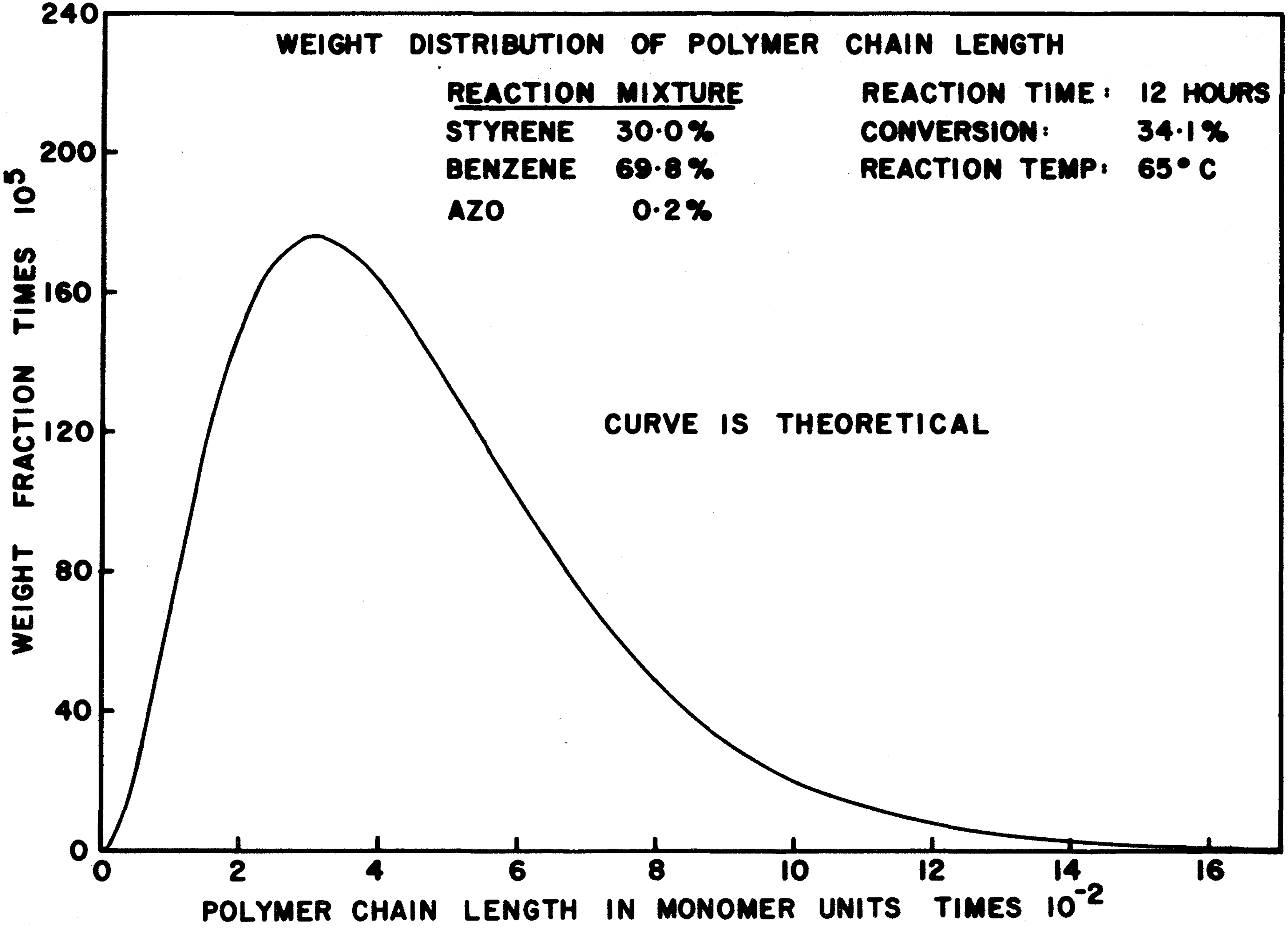

WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
REACTION MIXTURE
STYRENE 30·0%
BENZENE 69·8%
AZO 0·2%
REACTION TIME: 12 HOURS
CONVERSION: 34·1%
REACTION TEMP: 65° C
CURVE IS THEORETICAL
WEIGHT FRACTION TIMES 10⁵
POLYMER CHAIN LENGTH IN MONOMER UNITS TIMES 10⁻²
0
40
80
120
160
200
240
0
2
4
6
8
10
12
14
16

FIGURE A-13a

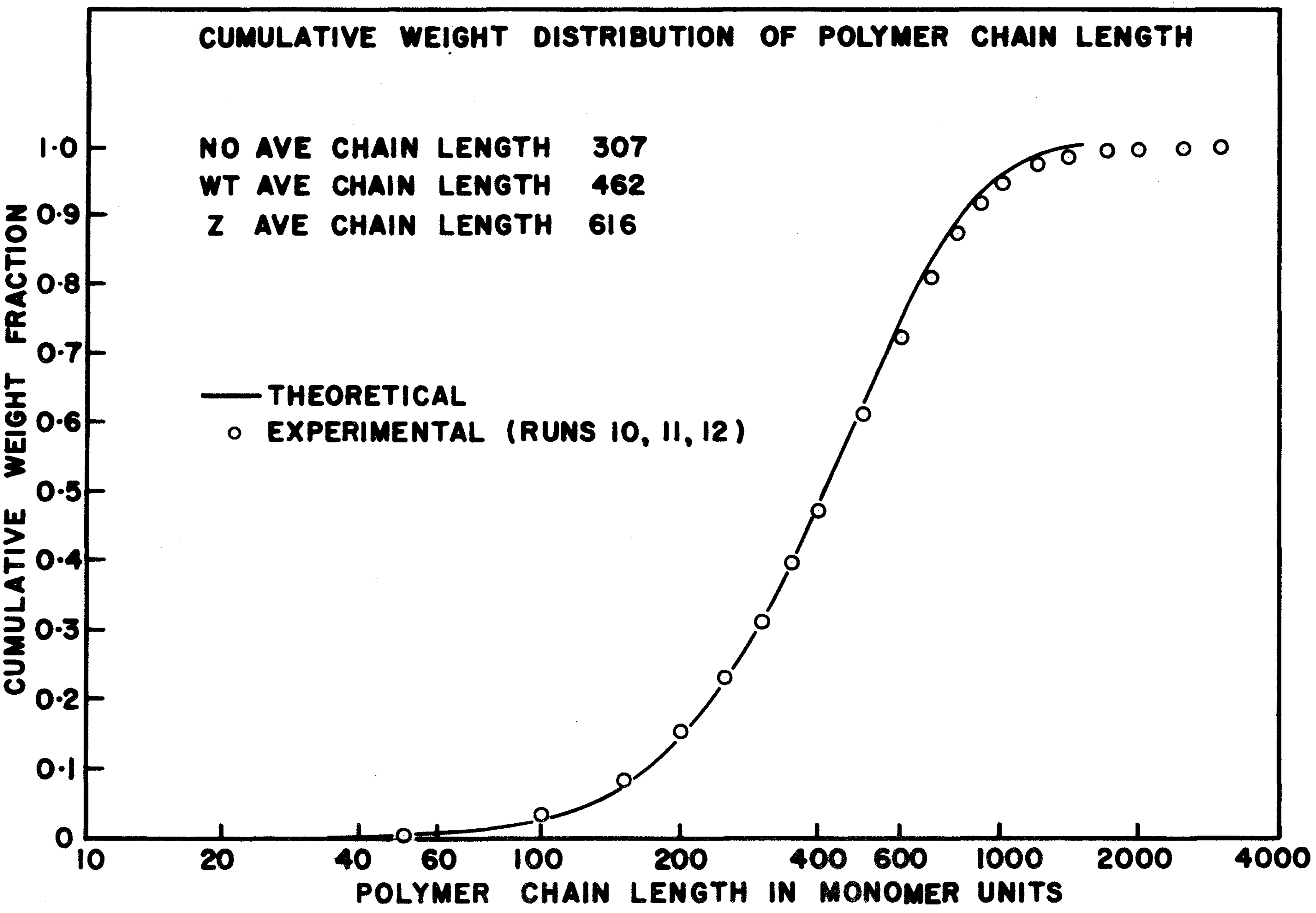

CUMULATIVE WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
NO AVE CHAIN LENGTH 307
WT AVE CHAIN LENGTH 462
Z AVE CHAIN LENGTH 616
THEORETICAL
EXPERIMENTAL (RUNS 10, 11, 12)
CUMULATIVE WEIGHT FRACTION
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
10
20
40
60
100
200
400
600
1000
2000
4000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE A-13b

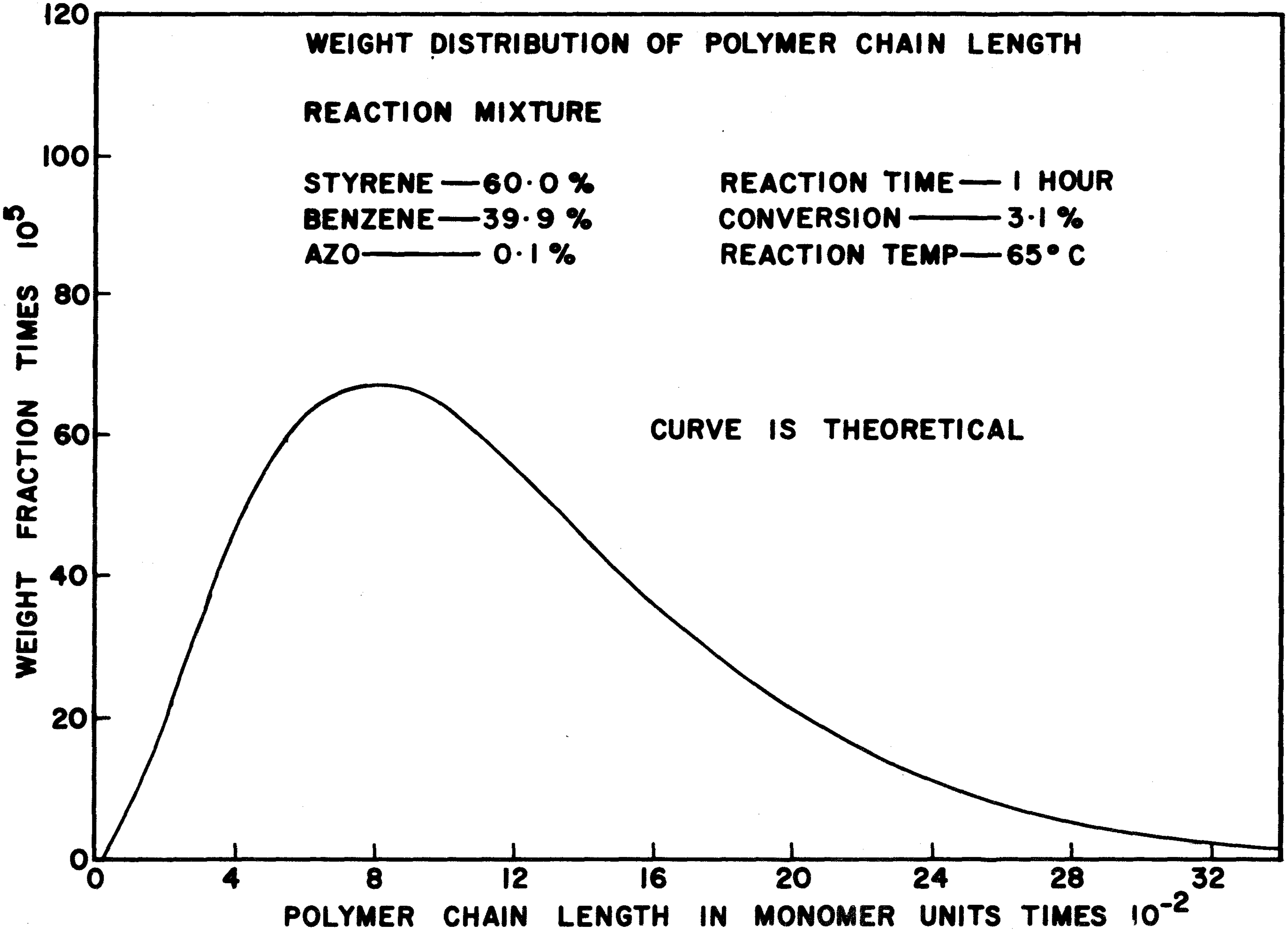

WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
REACTION MIXTURE
STYRENE —60·0 %
BENZENE—39·9 %
AZO——— 0·1 %
REACTION TIME— 1 HOUR
CONVERSION ——— 3·1 %
REACTION TEMP—65° C
CURVE IS THEORETICAL
WEIGHT FRACTION TIMES 10^5
0
20
40
60
80
100
120
0
4
8
12
16
20
24
28
32
POLYMER CHAIN LENGTH IN MONOMER UNITS TIMES 10^{-2}

FIGURE A-14a

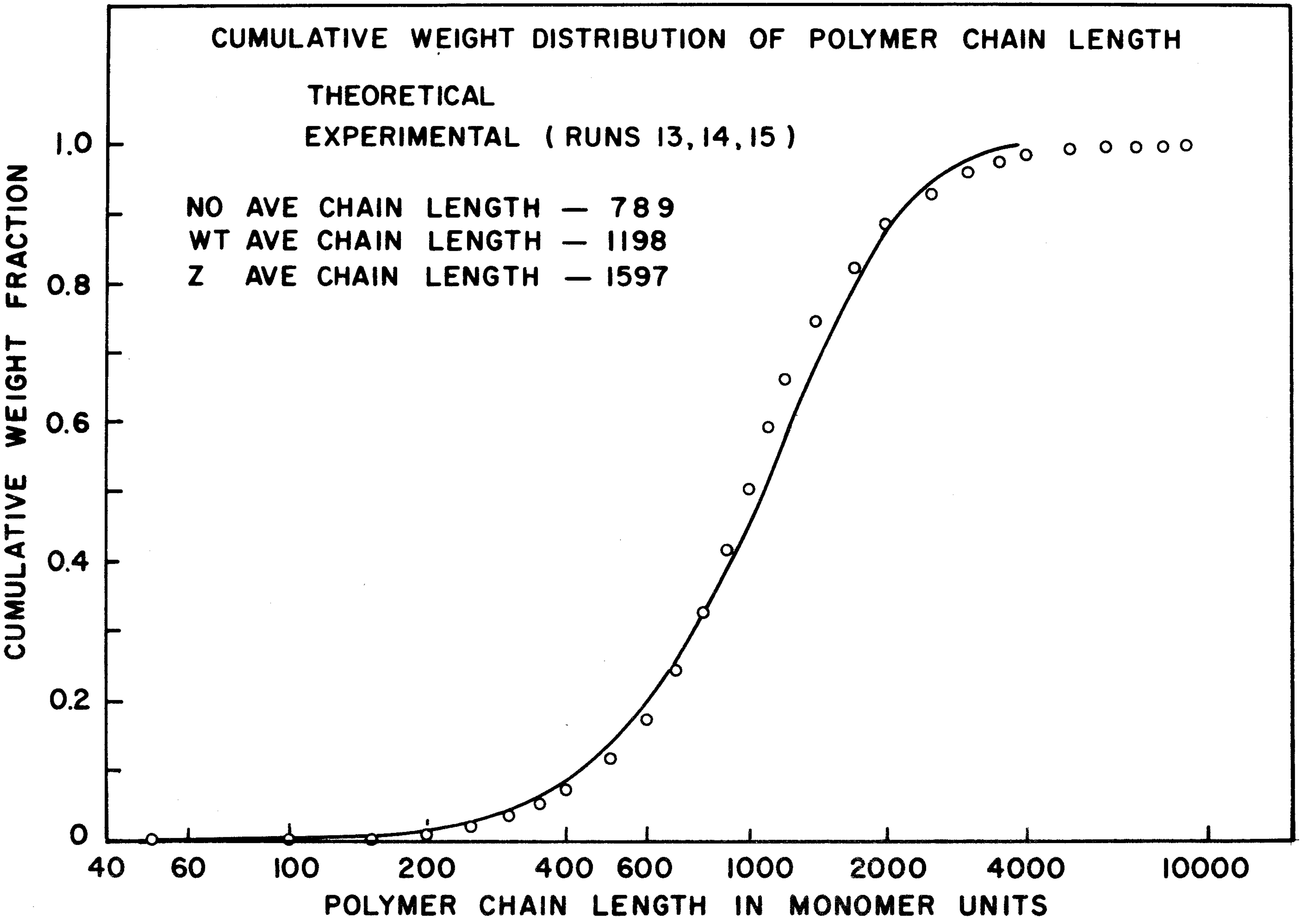

CUMULATIVE WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
THEORETICAL
EXPERIMENTAL (RUNS 13, 14, 15)
NO AVE CHAIN LENGTH — 789
WT AVE CHAIN LENGTH — 1198
Z AVE CHAIN LENGTH — 1597
CUMULATIVE WEIGHT FRACTION
0
0.2
0.4
0.6
0.8
1.0
40
60
100
200
400
600
1000
2000
4000
10000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE A-14b

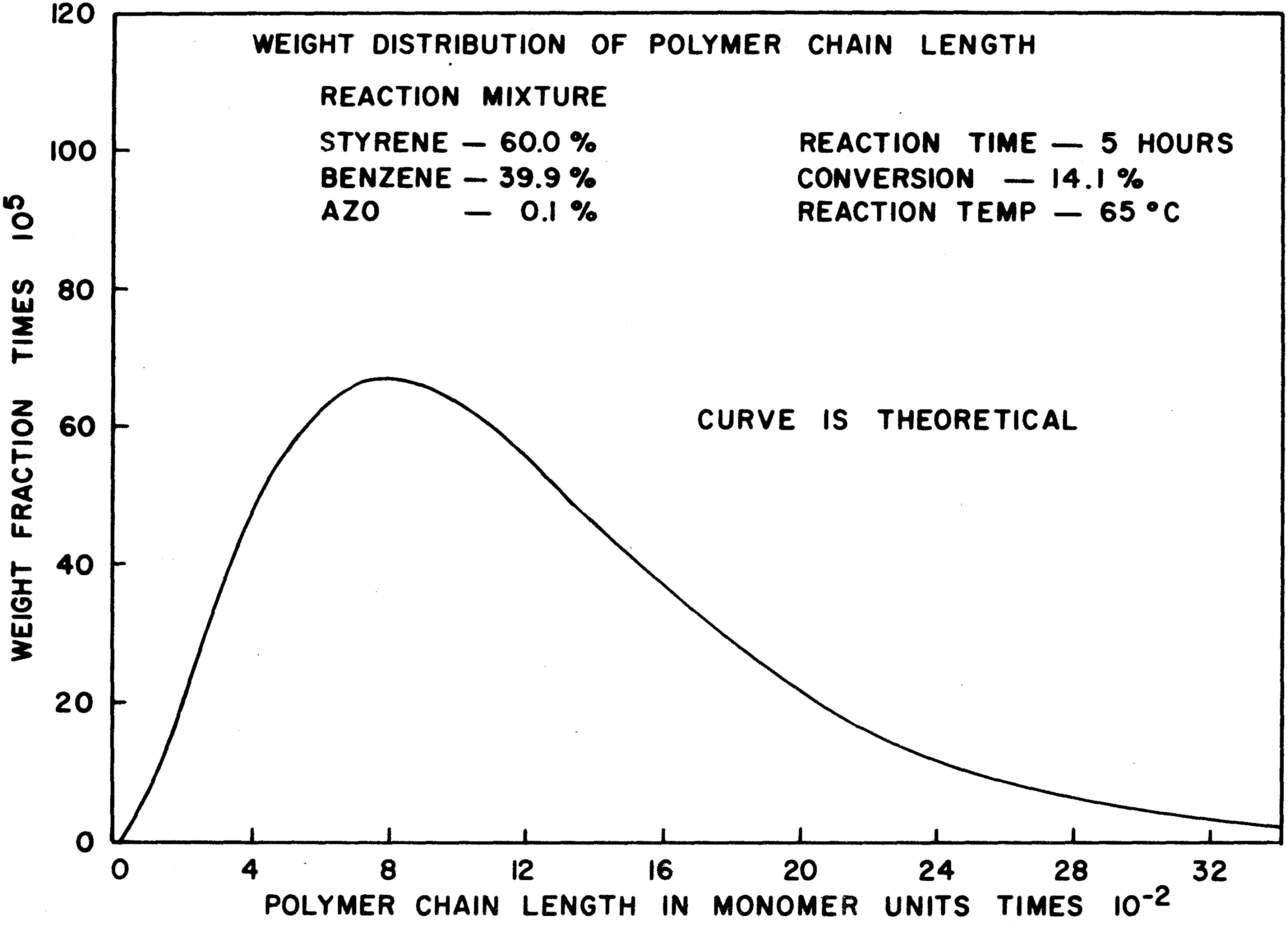

WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
REACTION MIXTURE
STYRENE — 60.0 %
BENZENE — 39.9 %
AZO — 0.1 %
REACTION TIME — 5 HOURS
CONVERSION — 14.1 %
REACTION TEMP — 65 °C
CURVE IS THEORETICAL
WEIGHT FRACTION TIMES 10^5
0
20
40
60
80
100
120
POLYMER CHAIN LENGTH IN MONOMER UNITS TIMES 10^-2
0
4
8
12
16
20
24
28
32

FIGURE A-15a

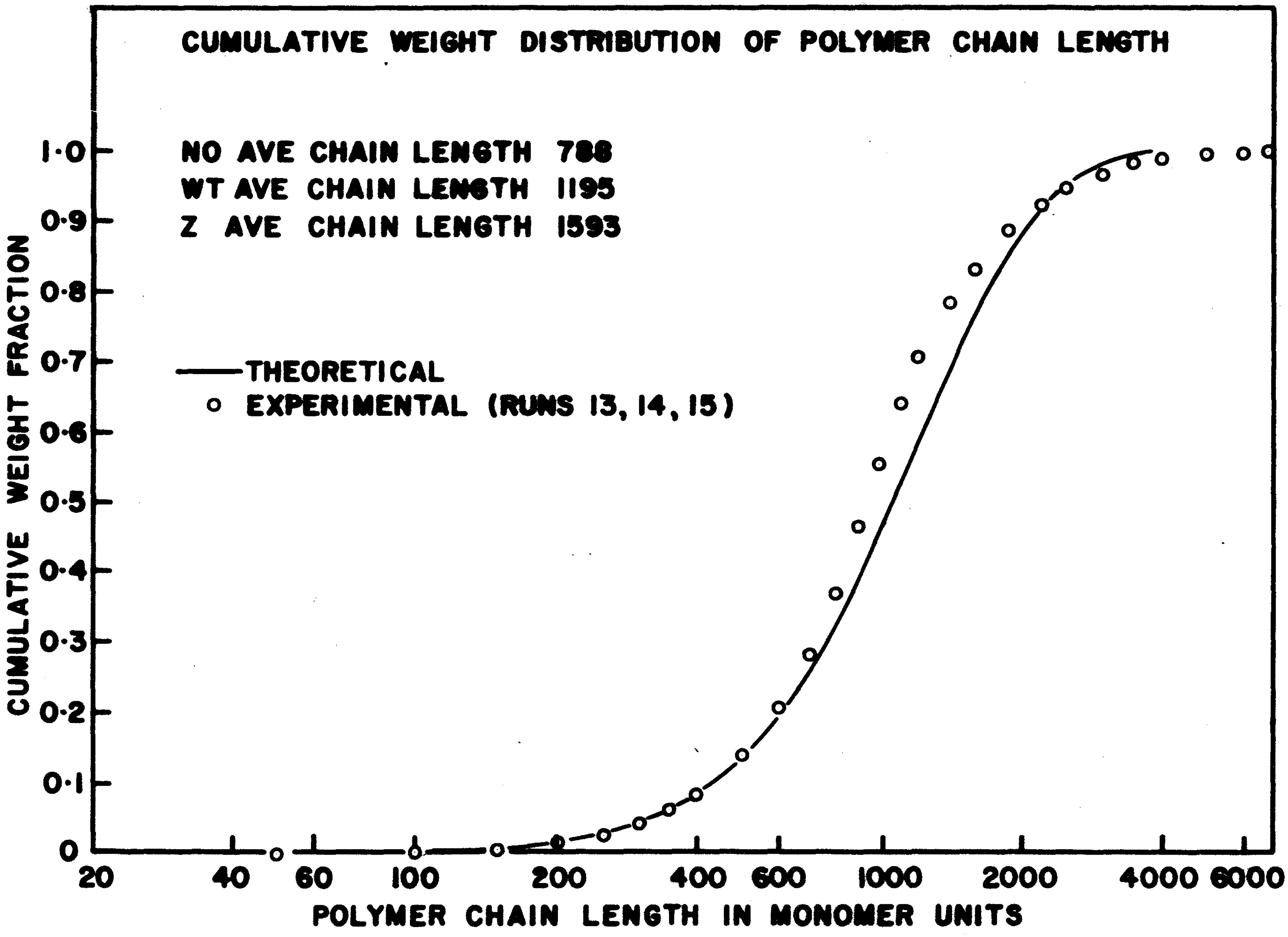

CUMULATIVE WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
NO AVE CHAIN LENGTH 788
WT AVE CHAIN LENGTH 1195
Z AVE CHAIN LENGTH 1593
THEORETICAL
EXPERIMENTAL (RUNS 13, 14, 15)
CUMULATIVE WEIGHT FRACTION
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
20
40
60
100
200
400
600
1000
2000
4000
6000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE A-15b

ment with the gel-permeation chromatograph is not too bad but deviations are beginning to show.

Runs 16, 17 and 18 consisted of bulk polymerization at 65°C. with a catalyst concentration of 0.3% and the results are shown in Figures A-16 and A-17. Because of the increased catalyst concentration the molecular weight did not increase, in fact it dropped slightly. Still no significant change in molecular weight with time was evident and therefore only two cases are shown again, one hour reaction time and 4 hours reaction time. Agreement with gel-permeation chromatograph determinations is definitely poor, the gel-permeation chromatograph results being much higher. This is believed to be significant. For bulk polymerization the catalyst efficiency was found to be significantly higher than in solution polymerization. From equation (16), which was used to calculate the catalyst efficiency, it is seen that if k_{tc} or k_p had been adjusted instead, good agreement in the conversion versus time relationship could have been obtained as well. If, therefore, f was not the variable quantity but say e.g. k_{tc} then on the basis of equation (35) the DP would be seriously in error with an adjusted f factor, in fact if f is erroneously increased by say 20% instead of k_{tc} being reduced 20%, the resulting error would be 40%. The gel-permeation chromatograph number-average molecular weight was 827, see figures in brackets of Figure A-16 which does suggest that not f but k_{tc} is the monomer or solvent

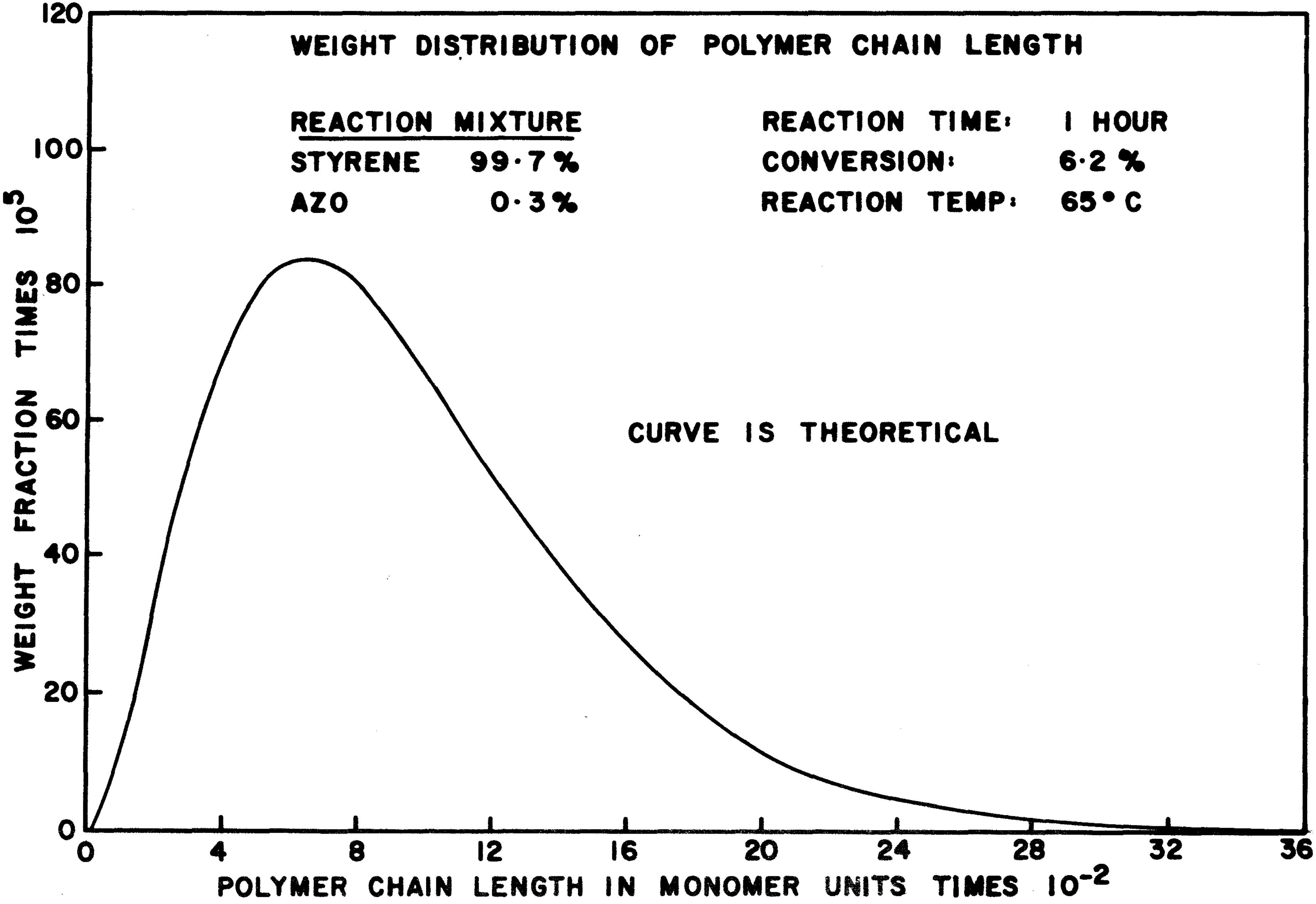

WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
REACTION MIXTURE
STYRENE 99·7 %
AZO 0·3 %
REACTION TIME: 1 HOUR
CONVERSION: 6·2 %
REACTION TEMP: 65° C
CURVE IS THEORETICAL
WEIGHT FRACTION TIMES 10^3
0
20
40
60
80
100
120
POLYMER CHAIN LENGTH IN MONOMER UNITS TIMES 10^{-2}
0
4
8
12
16
20
24
28
32
36

FIGURE A-16a

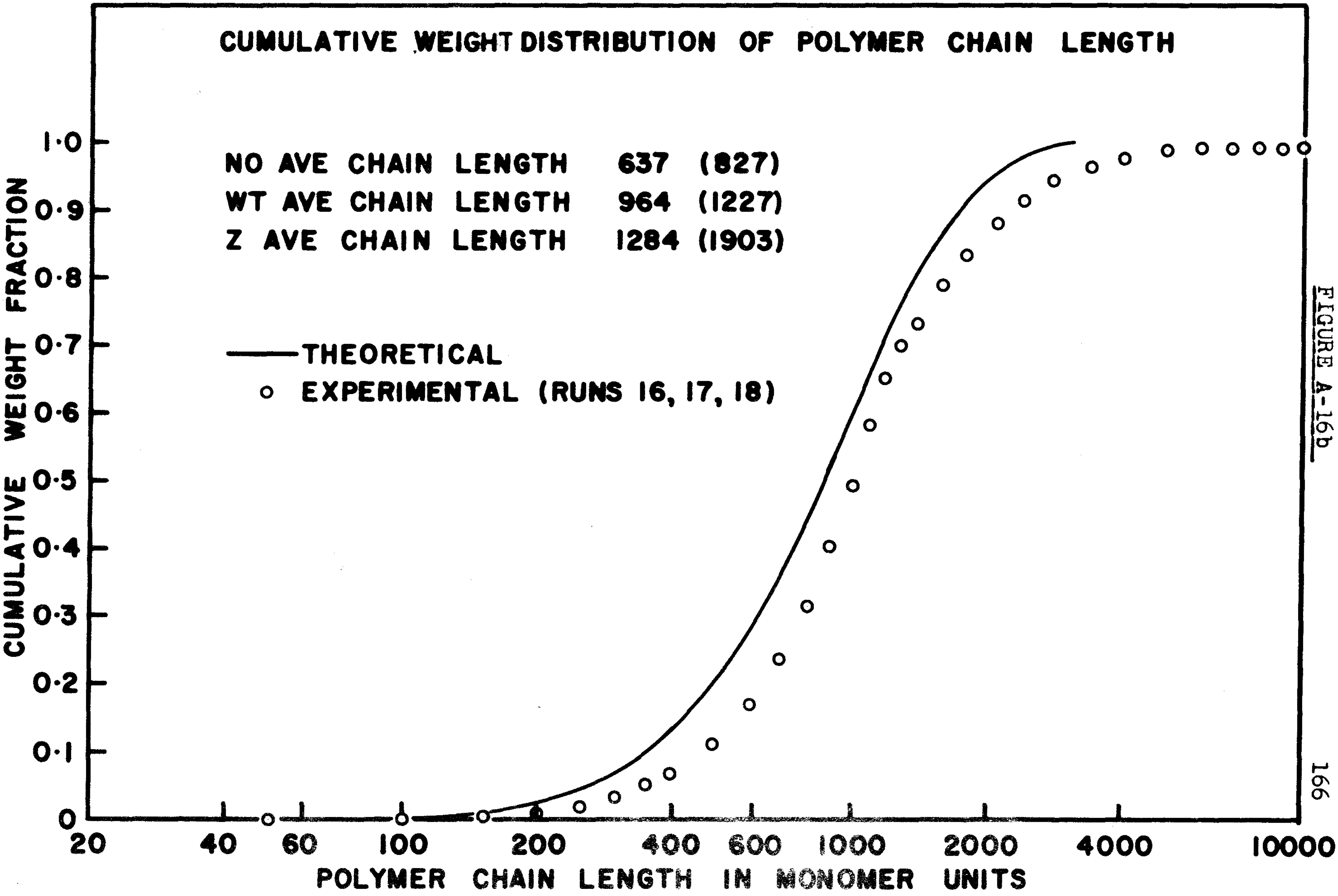

CUMULATIVE WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
NO AVE CHAIN LENGTH 637 (827)
WT AVE CHAIN LENGTH 964 (1227)
Z AVE CHAIN LENGTH 1284 (1903)
THEORETICAL
EXPERIMENTAL (RUNS 16, 17, 18)
CUMULATIVE WEIGHT FRACTION
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
20
40
60
100
200
400
600
1000
2000
4000
10000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE A-16b

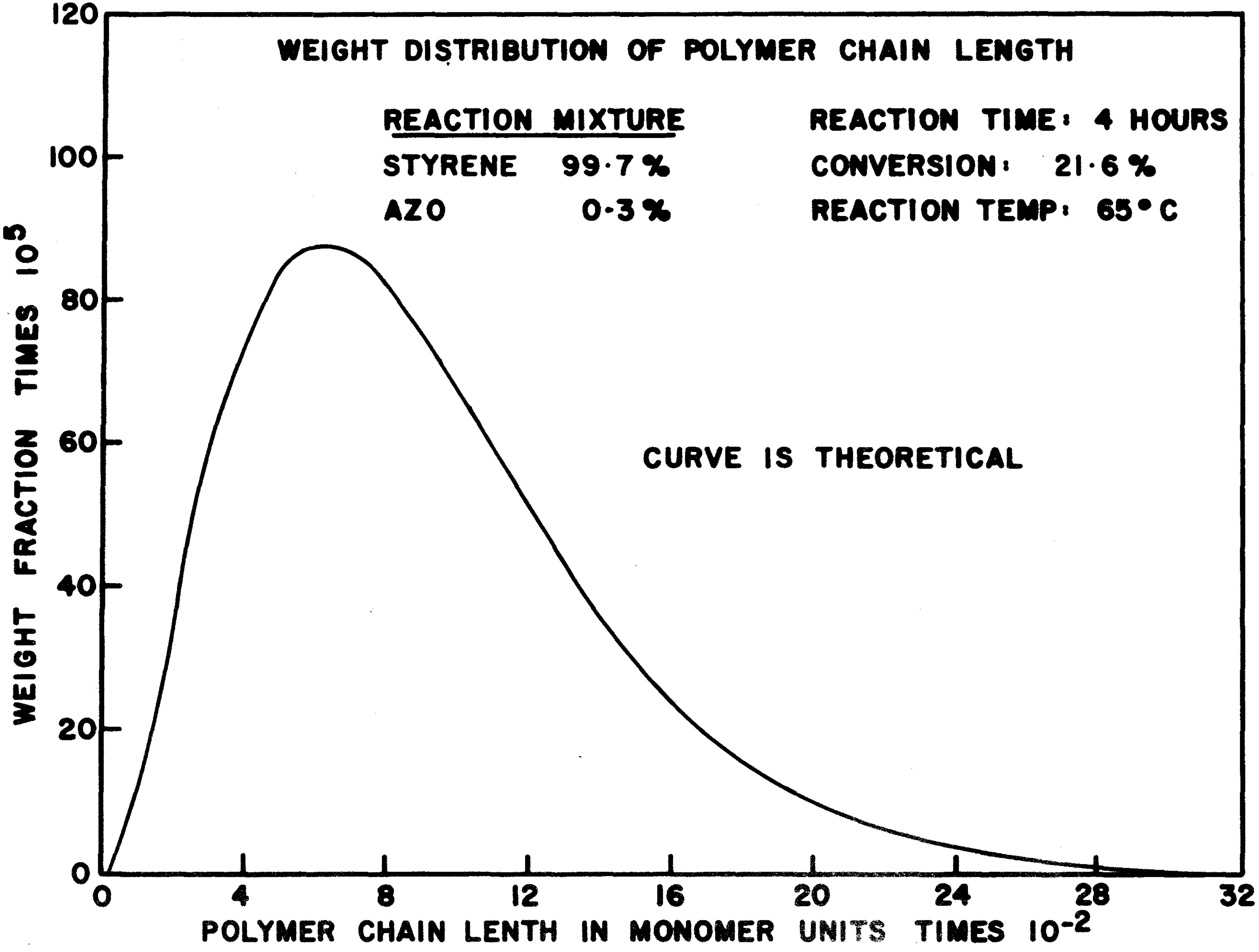

WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
REACTION MIXTURE
STYRENE 99·7 %
AZO 0·3 %
REACTION TIME: 4 HOURS
CONVERSION: 21·6 %
REACTION TEMP: 65° C
CURVE IS THEORETICAL
WEIGHT FRACTION TIMES 10^5
120
100
80
60
40
20
0
0
4
8
12
16
20
24
28
32
POLYMER CHAIN LENTH IN MONOMER UNITS TIMES 10^-2

FIGURE A-17a

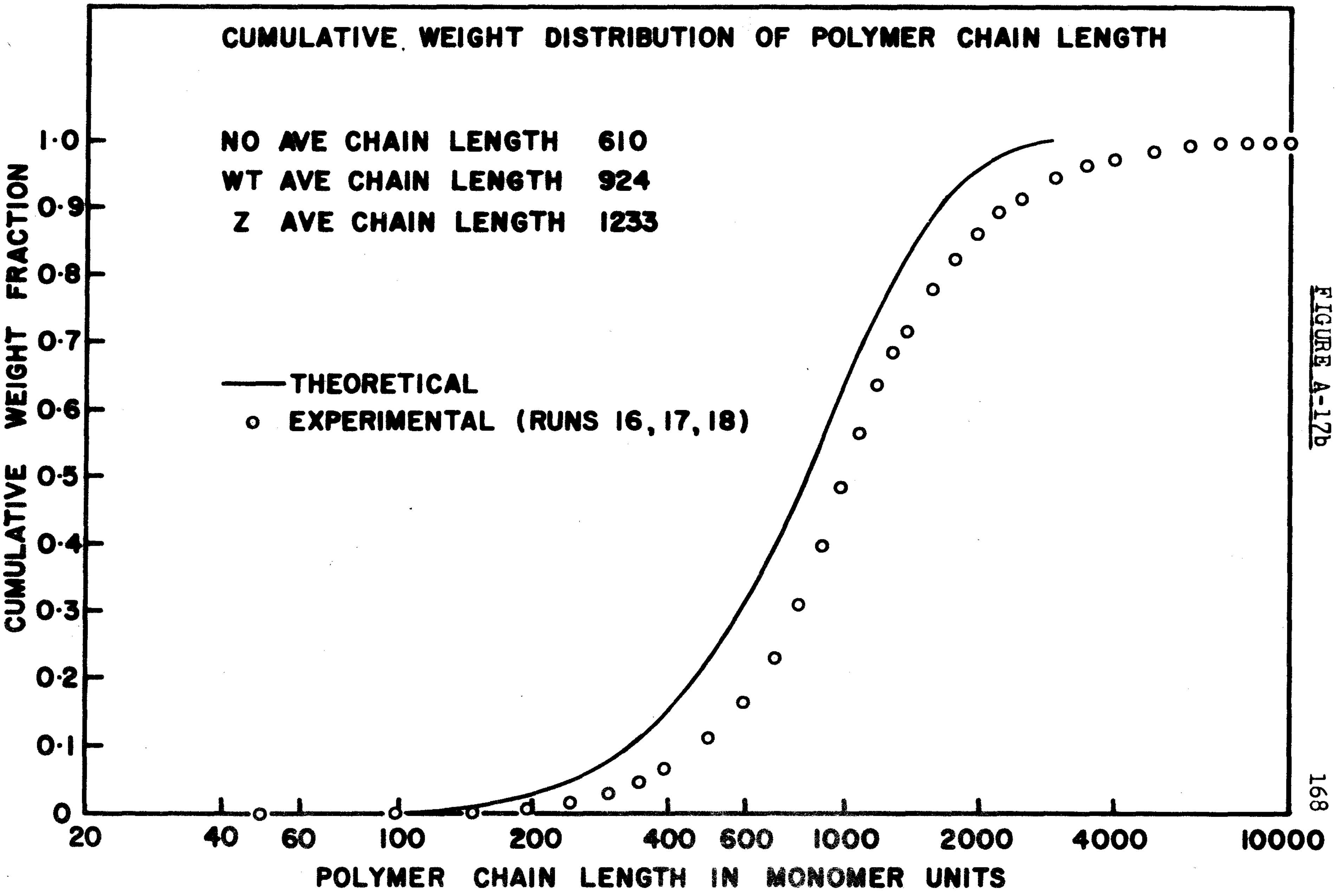

CUMULATIVE WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
NO AVE CHAIN LENGTH 610
WT AVE CHAIN LENGTH 924
Z AVE CHAIN LENGTH 1233
THEORETICAL
o EXPERIMENTAL (RUNS 16, 17, 18)
CUMULATIVE WEIGHT FRACTION
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
20
40
60
100
200
400
600
1000
2000
4000
10000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE A-17b

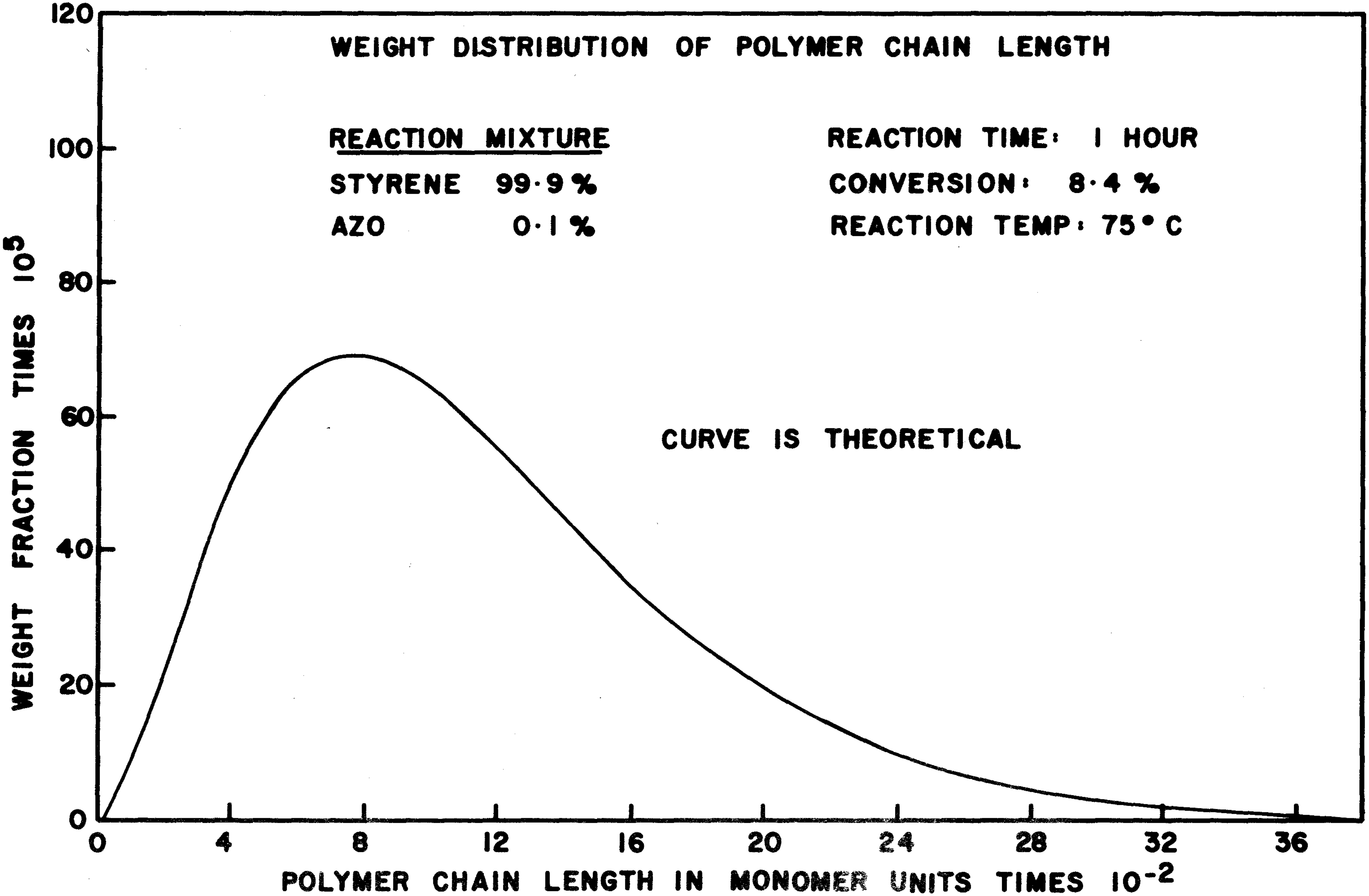

WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
REACTION MIXTURE
STYRENE 99·9 %
AZO 0·1 %
REACTION TIME: 1 HOUR
CONVERSION: 8·4 %
REACTION TEMP: 75° C
CURVE IS THEORETICAL
WEIGHT FRACTION TIMES 10^5
0
20
40
60
80
100
120
0
4
8
12
16
20
24
28
32
36
POLYMER CHAIN LENGTH IN MONOMER UNITS TIMES 10^-2

FIGURE A-18a

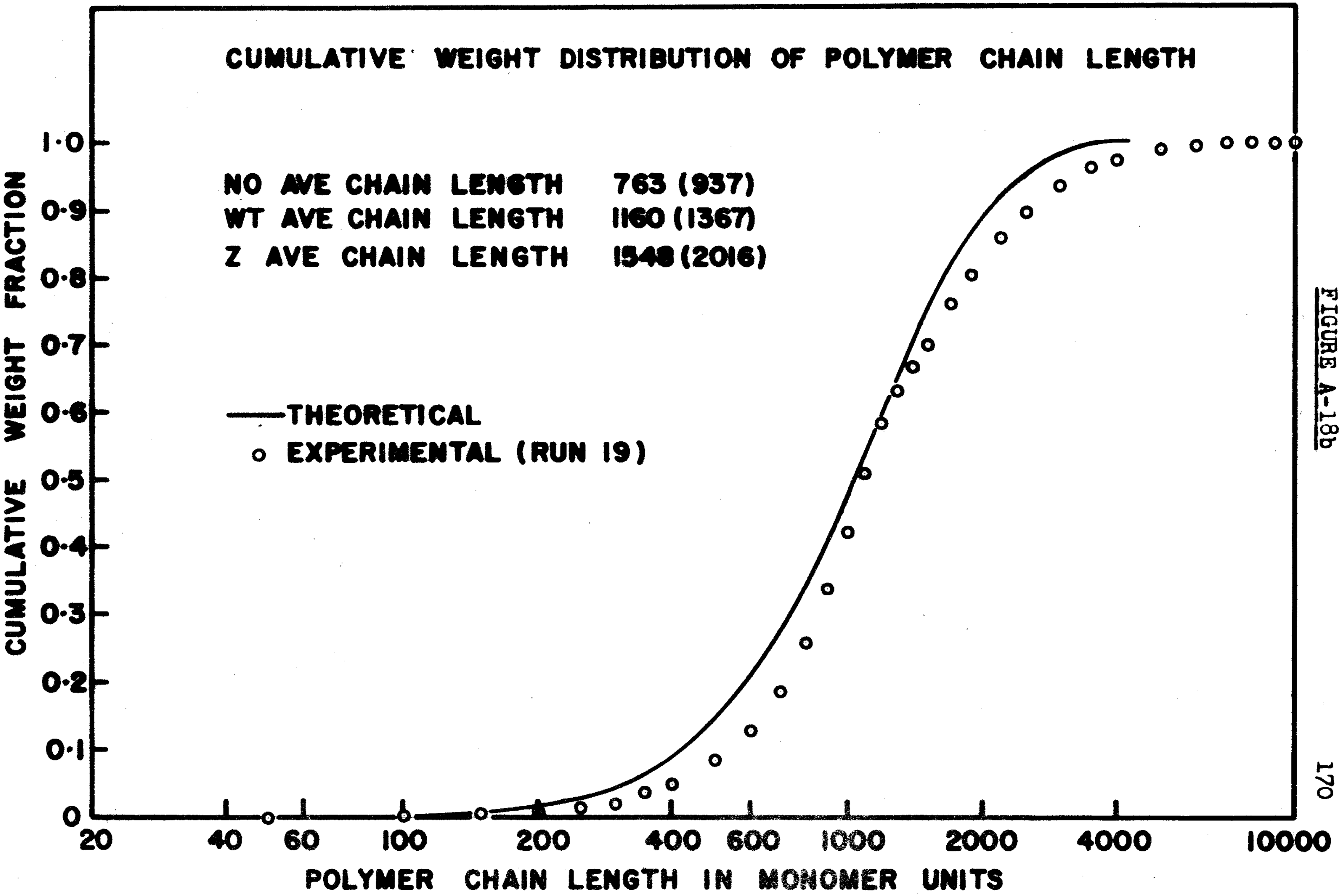

CUMULATIVE WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
NO AVE CHAIN LENGTH 763 (937)
WT AVE CHAIN LENGTH 1160 (1367)
Z AVE CHAIN LENGTH 1548 (2016)
THEORETICAL
EXPERIMENTAL (RUN 19)
CUMULATIVE WEIGHT FRACTION
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
20
40
60
100
200
400
600
1000
2000
4000
10000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE A-18b

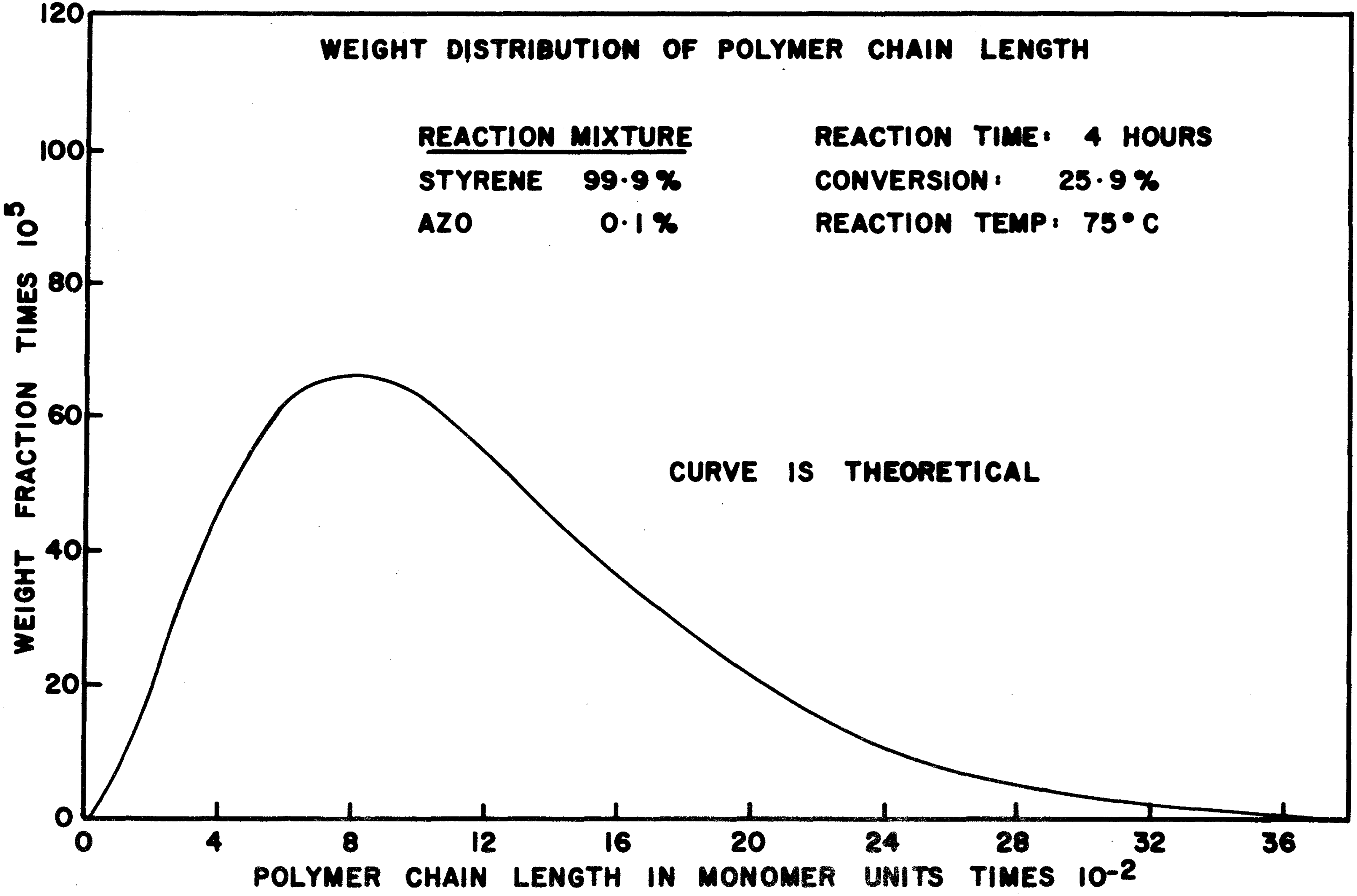

WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
REACTION MIXTURE
STYRENE 99·9 %
AZO 0·1 %
REACTION TIME: 4 HOURS
CONVERSION: 25·9 %
REACTION TEMP: 75° C
CURVE IS THEORETICAL
WEIGHT FRACTION TIMES 10^5
120
100
80
60
40
20
0
0
4
8
12
16
20
24
28
32
36
POLYMER CHAIN LENGTH IN MONOMER UNITS TIMES 10^-2

FIGURE A-19a

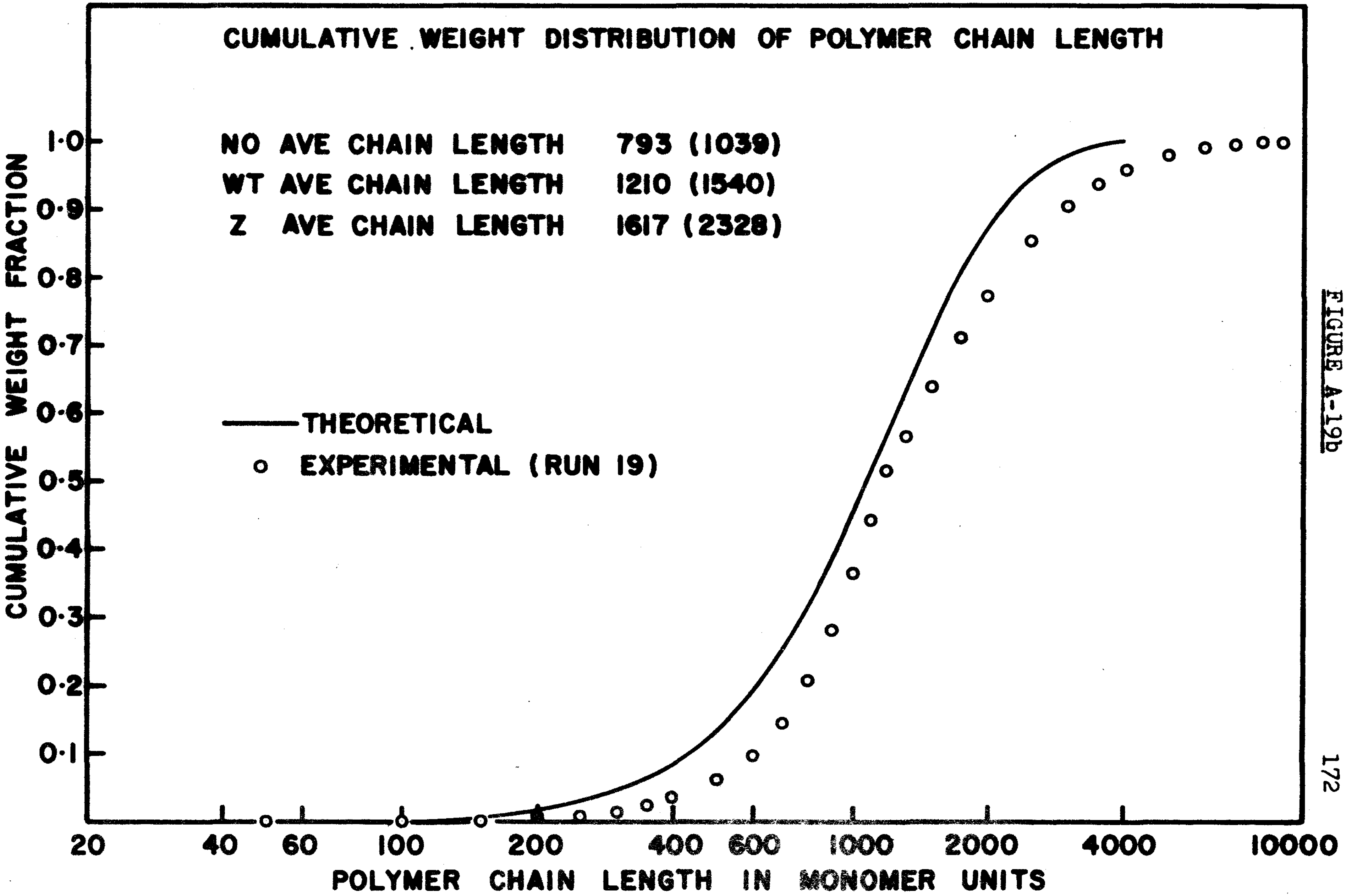

CUMULATIVE WEIGHT DISTRIBUTION OF POLYMER CHAIN LENGTH
NO AVE CHAIN LENGTH 793 (1039)
WT AVE CHAIN LENGTH 1210 (1540)
Z AVE CHAIN LENGTH 1617 (2328)
THEORETICAL
○ EXPERIMENTAL (RUN 19)
CUMULATIVE WEIGHT FRACTION
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
20
40
60
100
200
400
600
1000
2000
4000
10000
POLYMER CHAIN LENGTH IN MONOMER UNITS

FIGURE A-19b

concentration dependent variable. The question then is, whether this is a true gel effect. There is no doubt that the effect is real. The gel-permeation chromatograph results were recalculated based on a number of different calibration curves, drawn only through the polystyrene standards, showing very similar results. To do any extensive work in bulk polymerization therefore, a proper relationship between the monomer concentration or reaction mixture viscosity and the termination or propagation constant must be determined.

Finally, Figures A-18 and A-19 show the results for Run 19. For this condition only one was done because of the extremely viscous reaction mixture after about one hour of polymerization. Thus the catalyst concentration was reduced to 0.5% but the temperature increased to 75°C. The experimentally determined conversions were corrected for thermal polymerization, whereupon f was determined. Agreement with the gel-permeation chromatograph results is somewhat better, which is surprising since the effect of thermal polymerization would be to increase the molecular weight, although if this effect is very small it might become insignificant. The general tendency is the same though as for the 65°C. case, experimental molecular weights being higher than the theoretical. As was the case in solution polymerization at 75°C., the degree of polymerization increases with reaction time.

In conclusion, the following points are clear. The theoretical model, in the form of equations (16) and (24) through (30), appears to provide a good description of conversion and molecular-weight distribution for solution polymerization of styrene in benzene. For bulk polymerization the model probably is alright but a relationship between k_{tc} and the monomer concentration or solvent concentration should be obtained and tested. Further mathematical improvement of the treatment of the equations no doubt is possible. Chain transfer does not play a significant role and future work should center on a system where chain transfer is important. Other catalyst systems also should be tested, including perhaps an oxidation-reduction catalyst. Further refinements in the reactor should be looked for and the sampling technique improved. For the case of bulk polymerization stirring speed may be an important variable which was not considered. The greatest source of uncertainty is of course the gel-permeation chromatograph. Until and only until its results are on an absolute basis, comparable with other methods, can it be used as a truly quantitative tool. Thus it remains the most fruitful area of immediate further research.

6. COMPUTER PROGRAMS

6.1 Program to Calculate Time Required to Reach Steady State

```
C     CONVERSION AND FREE RADICAL CONCENTRATION IN BATCH REACTOR
C                    NON STEADY STATE
      DIMENSION X(5001),T(5001),R(5001)
      READ 1,TE,SMO,CO,S,N
    1  FORMAT(4F10.5,1I10)
      PRINT 2
    2 FORMAT(//6X,4HTEMP,4X,8HMON CONC,2X,8HCAT CONC,2X,8HSOL CONC,2X,
     111HNO OF STEPS/)
      PRINT 3,TE,SMO,CO,S,N
    3 FORMAT(1H 4F10.4,1I10///)
C     CALCULATION OF REACTION CONSTANTS
      AKD=1.58E15*EXP(-15550./TE)
      AKP=2.06E07*EXP(-3575./TE)
      AKTC=4.83E09*EXP(-859./TE)
      AKFS=6.66E-09*EXP(3895./TE)
      AKFM=4.53E06*EXP(-6410./TE)
      AKTD = 0.0
      PRINT 4
    4 FORMAT(9X,3HAKD,11X,4HAKTD,11X,4HAKTC,11X,4HAKFM,11X,4HAKFS,12X,
     13HAKP/)
      PRINT 5 ,AKD,AKTD,AKTC,AKFM,AKFS,AKP
    5 FORMAT(1H 6E15.5///)
C     CALCULATION OF CONVERSION AND RAD CONC BY RUNGE KUTTA
      F=0.6
      XB=1.0E-06
      A1=2.0*F*AKD*CO
      A2=A1/SMO
      RADC(TI,R)=A1*EXP(-AKD*TI)-AKTC*R*R
      CONV(TI,R,X)=A2*EXP(-AKD*TI)+AKD*(1.0-X)*R+AKFM*(1.0-X)*R
      X(1)=0.0
      R(1)=0.0
      T(1)=0.0
      PRINT 6
    6 FORMAT(6X,9HTIME(SEC),5X,10HCONVERSION,8X,8HRAD CONC/)
      DELT=0.001
      J=101
      DO 10 I=1,5000
      T1=T(I)+DELT/2.0
      T4=T(I)+DELT
      BK1=DELT*RADC(T(I),R(I))
      R1=R(I)+BK1/2.0
      BK2=DELT*RADC(T1,R1)
      R2=R(I)+BK2/2.0
      BK3=DELT*RADC(T1,R2)
      R3=R(I)+BK3
      BK4=DELT*RADC(T4,R3)
      R(I+1)=R(I)+(BK1+2.0*BK2+2.0*BK3+BK4)/6.0
      CK1=DELT*CONV(T(I),R(I),X(I))
      CK2=DELT*CONV(T1,R1,X(I)+CK1/2.0)
      CK3=DELT*CONV(T1,R2,X(I)+CK2/2.0)
      CK4=DELT*CONV(T4,R3,X(I)+CK3)
      X(I+1)=X(I)+(CK1+2.0*CK2+2.0*CK3+CK4)/6.0
      T(I+1)=T(I)+DELT
       IF (I+1.NE.J) GO TO 10
       PRINT 7, T(I+1),X(I+1),R(I+1)
    7 FORMAT(1H 1F12.4,1E18.9,1E19.9)
      J=J+100
       IF(X(I+1).GE.XB) GO TO 15
   10 CONTINUE
```

```
15 PRINT 7, T(I+1),X(I+1),R(I+1)
   STOP
   END
```

```
                   CD TOT    0062
```

6.2 Program to Calculate Catalyst Efficiencies

```
C     CALCULATION OF CATALYST EFFICIENCY IN BATCH REACTOR BY CURVE
C     FITTING OF LEAST SQUARE SUM OF DEVIATIONS
      DIMENSION X(3000),T(3000),XX(50,5),SUMSQ(50),FF(5)
      READ 60, ((XX(K,L), L=1,3),K=1,12)
   60 FORMAT (9F8.4)
      PRINT 61, ((XX(K,L), L=1,3),K=1,12)
   61 FORMAT (9F8.4/)
      READ 46,TE,SMO,CO,S
   46 FORMAT (4F10.5)
      PRINT 47
   47 FORMAT(//6X,4HTEMP,4X,8HMON CONC,2X,8HCAT CONC,2X,8HSOL CONC/)
      PRINT 48, TE,SMO,CO,S
   48 FORMAT (1H 4F10.5///)
C     CALCULATION OF REACTION CONSTANTS
      AKTD = 0.0
      AKD=1.58E15*EXP(-15550./TE)
      AKP=2.06E07*EXP(-3575./TE)
      AKTC=4.83E09*EXP(-859./TE)
      AKFM=4.53E06*EXP(-6410./TE)
      AKFS=6.66E-09*EXP(3895./TE)
      PRINT 49
   49 FORMAT(9X,3HAKD,11X,4HAKTD,11X,4HAKTC,11X,4HAKFM,11X,4HAKFS,12X,
     13HAKP/)
      PRINT 50,AKD,AKTD,AKTC,AKFM,AKFS,AKP
   50 FORMAT(1H 6E15.5///)
C     CALCULATION OF CONVERSION BY RUNGE KUTTA AND ITS DEVIATIONS
      FF(1)=0.3
      FF(4)=1.2
      FF(2)=FF(4)-(FF(4)-FF(1))/1.618
      FF(3)=FF(1)+(FF(4)-FF(1))/1.618
      SUMSQ(1)=0.0
      SUMSQ(2)=0.0
      SUMSQ(3)=0.0
      SUMSQ(4)=0.0
      N=4
      DO 30 J=1,N
      F=FF(J)
      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)
      CONV(TA,XA)=AKP*(1.0-XA)*D2*SQRT(EXP(-AKD*TA))
      X(1) = 0.0
      T(1) = 0.0
      DELT = 180.0
      JJ=11
      K=1
      DO 10 I=1,2000
      BK1=DELT*CONV(T(I),X(I))
      BK2 = DELT*CONV(T(I)+DELT/2.,X(I)+BK1/2.)
      BK3=DELT*CONV(T(I)+DELT/2.,X(I)+BK2/2.)
      BK4 = DELT*CONV(T(I)+DELT,X(I)+BK3)
      X(I+1)=X(I)+(BK1+2.*BK2+2.*BK3+BK4)/6.
      T(I+1) = T(I)+DELT
      IF ((I+1).EQ.JJ) GO TO 15
      GO TO 10
```

```
15 DO 16 L=1,3
   IF (XX(K,L).EQ.0.0) GO TO 16
   SQ=(ABS(X(I+1)-XX(K,L)))**2.0
   SUMSQ(J)=SUMSQ(J)+SQ
16 CONTINUE
   JJ=JJ+10
   K=K+1
   IF (K.EQ.13) GO TO 30
10 CONTINUE
30 CONTINUE
   IF (SUMSQ(2).LT.SUMSQ(3)) GO TO 40
25 FF(1)=FF(2)
   FF(2)=FF(3)
   FF(3)=FF(4)-FF(2)+FF(1)
   SUMSQ(1)=SUMSQ(2)
   SUMSQ(2)=SUMSQ(3)
   N=3
   SUMSQ(N)=0.0
   GO TO 38
40 FF(4)=FF(3)
   FF(3)=FF(2)
   FF(2)=FF(1)+FF(4)-FF(3)
   SUMSQ(4)=SUMSQ(3)
   SUMSQ(3)=SUMSQ(2)
   N=2
   SUMSQ(N)=0.0
38 F=FF(N)
   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)
   X(1) = 0.0
   T(1) = 0.0
   DELT = 180.0
   JJ=11
   K=1
   DO 37 I=1,2000
   BK1=DELT*CONV(T(I),X(I))
   BK2 = DELT*CONV(T(I)+DELT/2.,X(I)+BK1/2.)
   BK3=DELT*CONV(T(I)+DELT/2.,X(I)+BK2/2.)
   BK4 = DELT*CONV(T(I)+DELT,X(I)+BK3)
   X(I+1)=X(I)+(BK1+2.*BK2+2.*BK3+BK4)/6.
   T(I+1) = T(I)+DELT
   IF ((I+1).EQ.JJ) GO TO 35
   GO TO 37
35 DO 36 L=1,3
   IF (XX(K,L).EQ.0.0) GO TO 36
   SQ=(ABS(X(I+1)-XX(K,L)))**2.0
   SUMSQ(N)=SUMSQ(N)+SQ
36 CONTINUE
   JJ=JJ+10
   K=K+1
   IF((K-1).EQ.12) GO TO 20
37 CONTINUE
20 IF ((FF(3)-FF(2)).LT.0.005) GO TO 26
```

```
   IF (SUMSQ(2).LT.SUMSQ(3)) GO TO 40
   GO TO 25
26 PRINT 51
51 FORMAT (20H CATALYST EFFICIENCY,5X,8HSUMSQ(2),5X,8HSUMSQ(3)/)
   PRINT 52,F,SUMSQ(2),SUMSQ(3)
52 FORMAT (1H 1F10.7,12X,1F10.7,3X,1F10.7///)
   PRINT 56
56 FORMAT (6X,10HCONVERSION,6X,9HTIME(SEC)/)
   DO 53 I=1,JJ,10
54 PRINT 55, X(I),T(I)
55 FORMAT (1H 1F15.9,1F15.2)
53 CONTINUE
   STOP
   END

                  CD TOT   0131
```

6.3 Program to Calculate Molecular Weight Distribution

```
C     PROGRAM FOR MOL WT DISTRIBUTION IN BATCH REACTOR
C        STEADY STATE FREE RADICAL CONCENTRATION
      DIMENSION X(3000),T(3000),Y(3000),Z(3000),Z1(3000),Z2(3000)
      READ 46,TE,SMO,CO,S,N
   46 FORMAT (4F10.5,1I10)
      PRINT 47
   47 FORMAT(//6X,4HTEMP,4X,8HMON CONC,2X,8HCAT CONC,2X,8HSOL CONC,2X,
     111HNO OF STEPS/)
      PRINT 48, TE,SMO,CO,S,N
   48 FORMAT (1H 4F10.4,1I10///)
C     CALCULATION OF REACTION CONSTANTS
      AKD=1.58E15*EXP(-15550./TE)
      AKTD = 0.0
      AKP=2.06E07*EXP(-3575./TE)
      AKTC=4.83E09*EXP(-859./TE)
      AKFM=4.53E06*EXP(-6410./TE)
      AKFS=6.66E-09*EXP(3895./TE)
      PRINT 49
   49 FORMAT(9X,3HAKD,11X,4HAKTD,11X,4HAKTC,11X,4HAKFM,11X,4HAKFS,12X,
     13HAKP/)
      PRINT 50,AKD,AKTD,AKTC,AKFM,AKFS,AKP
   50 FORMAT(1H 6E15.5///)
C     CALCULATION OF CONVERSION BY RUNGE KUTTA
      F=0.64
      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)
      CONV(TA,XA)=AKP*(1.0-XA)*D2*SQRT(EXP(-AKD*TA))
      X(1) = 0.0
      T(1) = 0.0
      XB=0.55
      DELT = 180.0
      PRINT 51
   51 FORMAT(6X,10HCONVERSION,4X,11HPROBABILITY,6X,9HTIME(SEC)/)
      JJ = 21
      DO 10 I=1,N
      BK1=DELT*CONV(T(I),X(I))
      BK2 = DELT*CONV(T(I)+DELT/2.,X(I)+BK1/2.)
      BK3 = DELT*CONV(T(I)+DELT/2.,X(I)+BK2/2.)
      BK4 = DELT*CONV(T(I)+DELT,X(I)+BK3)
      X(I+1)=X(I)+(BK1+2.*BK2+2.*BK3+BK4)/6.
      T(I+1) = T(I)+DELT
C     CALCULATION OF PROPAGATION PROBABILITTIES
      Z1(I)=(1.0-X(I))
      Z2(I)=SQRT(EXP(-AKD*T(I)))
      Z(I)=C3*Z1(I)/(C3*Z1(I)+C5+C4*Z1(I)+D1*Z2(I))
      IF (I-JJ)13,14,13
   14 PRINT 52,X(I),Z(I),T(I)
   52 FORMAT(1H 2F15.9,1F15.2    )
      JJ = JJ+20
   13 NN=I
      IF (XB-X(I)) 11,11,10
   10 CONTINUE
   11 PRINT 52,X(NN),Z(NN),T(NN)
C     CALCULATION OF MOL WTS BY TRAP RULE
```

```
      NM=241
      SPR = 0.0
      SRPR = 0.0
      SRRPR = 0.0
      SRRRPR=0.0
      Q=50.0
      PRINT 53
   53 FORMAT(///1X,19HCUM WEIGHT FRACTION,8X,15HWEIGHT FRACTION,6X,
     112HCHAIN LENGTH/)
      DO 15 L=1,6000
      R=L
      DO 20 K=1,NM
      Y(K)=D2*Z2(K)*(1.0-Z(K))*Z(K)**(R-1.0)*(C5+C4*Z1(K)+D2*Z2(K)*
     1((R-1.0)*AKTC*(C5+C4*Z1(K)+    D1*Z2(K))/(2.0*C3*Z1(K))+AKTD))
   20 CONTINUE
      SA = 0.0
      DO 25 II=2,NM
      A = DELT*(Y(II-1)+Y(II))/2.
      SA = A+SA
   25 CONTINUE
      PR=SA
      SPR=SPR+PR
      SRPR=PR*R+SRPR
      SRRPR=PR*R*R+SRRPR
      SRRRPR=PR*R*R*R+SRRRPR
      WR=R*PR/(SMO*X(NM))
      IF(Q.GE.2050.0.AND.WR.LE.1.0E-06) GO TO 17
      SWR=WR+SWR
      IF(R-Q)15,16,16
   16 PRINT 54, SWR, WR, Q
   54 FORMAT (1H 1F16.9,1F23.9,1F18.2)
      Q=Q+50.0
   15 CONTINUE
   17 PRINT 54, SWR,WR,R
      RAV = SRPR/SPR
      RAVMW=RAV*104.150
      WAV = SRRPR/SRPR
      WAVMW=WAV*104.150
      ZAV=SRRRPR/SRRPR
      ZAVMW=ZAV*104.150
      RAT=WAV/RAV
      PRINT 55
   55 FORMAT(///13X,3HSPR,15X,4HSRPR,13X,5HSRRPR,14X,3HRAV,14X,3HWAV,
     114X,3HZAV/)
      PRINT 56,SPR,SRPR,SRRPR,RAV,WAV,ZAV
   56 FORMAT(1H 6F18.6///)
      PRINT 57, RAV
   57 FORMAT (35H THE NUMBER AVERAGE CHAIN LENGTH IS, F8.2,2X,
     1 13HMONOMER UNITS//)
      PRINT 58,RAVMW
   58 FORMAT (39H THE NUMBER AVERAGE MOLECULAR WEIGHT IS,F10.2//)
      PRINT 59, WAV
   59 FORMAT (35H THE WEIGHT AVERAGE CHAIN LENGTH IS, F8.2,2X,
     1 13HMONOMER UNITS//)
      PRINT 60, WAVMW
   60 FORMAT (39H THE WEIGHT AVERAGE MOLECULAR WEIGHT IS,F10.2//)
      PRINT 61, ZAV
   61 FORMAT (32H THE ZEE AVERAGE CHAIN LENGTH IS, F8.2,2X,
```

```
  1 13HMONOMER UNITS//)
   PRINT 62, ZAVMW
62 FORMAT(36H THE ZEE AVERAGE MOLECULAR WEIGHT IS,F10.2//)
   PRINT 63, RAT
63 FORMAT (46H THE WEIGHT AVERAGE TO NUMBER AVERAGE RATIO IS,F6.3///)
   STOP
   END

                                CD TOT   0124
```

6.4 Program to Interpret Gel-Permeation Chromatograph Traces

```
C PROGRAM FOR WT FRACTION OF SINGLE MOLECULAR SPECIES FROM GPC TRACE
      DIMENSION HBASE(100),COUNT(100),HITE(100),CHITE(100),SPITE(2000),
     1 WF(2000),CUM(2000),CUMWP(2000),CHITE1(100),CLIM(10),RANG(10)
      READ 5,NN
    5 FORMAT (I5)
      DO 12 II=1,NN
C DATA FROM GPC TRACE  AND CALIBRATION CURVE
      READ 10,N,NRUN,NO,NDATE,NTIME,NNN,NI,WM,Q,AS108,CS108,AP750,CP750,
     1 CROSS1,CROSS2,HBASE(1),HBASE(N),COUNT(1),COUNT(N),CINC,
     2 CINTR1,CINTR2,(HITE(I),I=1,N)
   10 FORMAT (7I10/6F10.4/7F10.3/2F10.3/(16F5.0))
      PRINT 15,N,NRUN,NO,NDATE,NTIME,NNN,NI,WM,Q,AS108,CS108,AP750,
     1 CP750,CROSS1,CROSS2,HBASE(1),HBASE(N),COUNT(1),COUNT(N),CINC,
     2 CINTR1,CINTR2,(HITE(I),I=1,N)
   15 FORMAT (1H1,7I10/1X,6F10.3/1X,9F14.5/(1X,25F5.0))
      B1=-ALOG(CROSS1/AS108)/(CINTR1-CS108)
      A1=ALOG(CROSS1)+B1*CINTR1
      B2=-ALOG(CROSS2/CROSS1)/(CINTR2-CINTR1)
      A2=ALOG(CROSS2)+B2*CINTR2
      B3=-ALOG(AP750/CROSS2)/(CP750-CINTR2)
      A3=ALOG(AP750)+B3*CP750
      SUMN=0.0
      SUMH=0.0
      SUMMH=0.0
      SUMM2H=0.0
      NP=NNN*NI/50
      DO 120 JJ=1,NP
      CUM(JJ)=0.0
  120 SPITE(JJ)=0.0
      JJ=1
C GPC CALIBRATION CURVE AS ARITHMETIC STATEMENT FUNCTIONS
      CAL1(Z)=(A1-ALOG(Z))/B1
      CAL2(Z)=(A2-ALOG(Z))/B2
      CAL3(Z)=(A3-ALOG(Z))/B3
C CORRECTION OF TRACE HEIGHTS TO ACCOUNT FOR NON-HORIZONTAL BASELINE
C HEIGHT CORRECTION PER COUNT INCREMENT(HINC)
      HINC=CINC*(HBASE(1)-HBASE(N))/(COUNT(1)-COUNT(N))
C CALCULATION OF FRACTIONAL COUNTS AND CORRESPONDING BASELINE HEIGHTS
C (HBASE) AND CORRECTED TRACE HEIGHTS(CHITE)
      DO 13 I=1,N
      COUNT(I+1)=COUNT(I)+CINC
      HBASE(I+1)=HBASE(I)+HINC
      CHITE1(I)=HITE(I)-HBASE(I)
      IF (CHITE(I).LT.CHITE(I-1).AND.CHITE(I-1).LT.CHITE(I-2)) GO TO 13
      IF (CHITE(I).LT.CHITE(I-1)) COUNT1=COUNT(I-1)
   13 CONTINUE
C TRACE HEIGHT CORRECTION DUE TO CHANGING RESOLUTION IN GPC
      IF (COUNT1.LE.CINTR1) ANG1=EXP(A1-B1*COUNT1)
      IF (COUNT1.GE.CINTR2) ANG1=EXP(A3-B3*COUNT1)
      IF (COUNT1.LT.CINTR2.AND.COUNT1.GT.CINTR1) ANG1=EXP(A2-B2*COUNT1)
      DANG1=WM/Q
      ANG2=ANG1+DANG1
      IF(ANG2.GE.CROSS1) COUNT2=CAL1(ANG2)
      IF(ANG2.LE.CROSS2) COUNT2=CAL3(ANG2)
      IF(ANG2.LT.CROSS1.AND.ANG2.GT.CROSS2) COUNT2=CAL2(ANG2)
      VOL1=COUNT1-COUNT2
      DO 105 I=2,N
      CLIM(1)=COUNT(I)+0.5*VOL1
      CLIM(2)=COUNT(I)-0.5*VOL1
```

```
      DO 110 IJ=1,2
      IF(CLIM(IJ).LE.CINTR1) RANG(IJ)=EXP(A1-B1*CLIM(IJ))
      IF(CLIM(IJ).GE.CINTR2) RANG(IJ)=EXP(A3-B3*CLIM(IJ))
      IF(CLIM(IJ).LT.CINTR2.AND.CLIM(IJ).GT.CINTR1) RANG(IJ)=EXP(A2-B2*
     1 CLIM(IJ))
  110 CONTINUE
      DANG=RANG(2)-RANG(1)
      SPNO=DANG*Q/WM
      CHITE(I)=CHITE1(I)/SPNO
  105 CONTINUE
C CALCULATION OF COUNTS AND HEIGHT CORRESPONDING TO EACH SPECIES
      INSUM=1
      DO 17 J=1,NNN
      DO 14 IN=1,NI
      INSUM=INSUM+1
      SMW=WM*(FLOAT(INSUM))
      ANG=SMW/Q
      IF (ANG.GE.CROSS1) SCOUNT=CAL1(ANG)
      IF (ANG.LE.CROSS2) SCOUNT=CAL3(ANG)
      IF (ANG.LT.CROSS1.AND.ANG.GT.CROSS2) SCOUNT=CAL2(ANG)
      IF (SCOUNT.GE.COUNT(1)) GO TO 100
      IF(SCOUNT.LE.COUNT(N)) GO TO 26
      DO 18 I=2,N
      IF ((SCOUNT-COUNT(I)).LT.0.000) GO TO 18
   27  SITE =   (SCOUNT-COUNT(I-1))*(CHITE(I)-CHITE(I-1))/(COUNT(I)-
     1 COUNT(I-1))+CHITE(I-1)
      GO TO 23
   18 CONTINUE
   23 SUMH=SUMH+SITE
      SUMN=SUMN+SITE/SMW
      SUMMH=SUMMH+SMW*SITE
      SUMM2H=SUMM2H+SITE*SMW*SMW
      IF ((INSUM-50*JJ).NE.0) GO TO 14
      CUM(JJ)=SUMH
      SPITE(JJ)=SITE
  100 IF ((INSUM-50*JJ).EQ.0) JJ=JJ+1
   14 CONTINUE
   17 CONTINUE
   26 PRINT 85,NRUN,NO,NDATE,NTIME
   85 FORMAT (///24H THE SAMPLE NUMBER IS B ,I7,2H -,I7,2H -,I7,2H -,
     1 I5//)
      PRINT 80
   80 FORMAT (1X,100(1H-)//)
      PRINT 54
   54 FORMAT (4X,13H CHAIN LENGTH,1X,16H WEIGHT FRACTION,
     1 17H MOLECULAR WEIGHT,3X,26H CUMULATIVE WEIGHT PERCENT//)
      PRINT 80
C CALCULATION OF SPECIES WEIGHT FRACTION AND MOLECULAR WEIGHT
      DO 24 JJ=1,NP
      J=50*JJ
      CUMWP(JJ)=CUM(JJ)*100./SUMH
      WF(JJ)=SPITE(JJ)/SUMH
      SMW=WM*(FLOAT(J))
      PRINT 30,J,WF(JJ),SMW,CUMWP(JJ)
   30 FORMAT (1H ,I10,F20.8,F20.1,F20.2)
      IF(WF(JJ).LT.1.0E-09.AND.JJ.GT.20) GO TO 56
   24 CONTINUE
   56 PRINT 80
```

```
C CALCULATION OF NO AVG AND WT AVG CHAIN LENGTH AND MW
      AVNMW=SUMH/SUMN
      AVNCH=AVNMW/WM
      AVWMW=SUMMH/SUMH
      AVWCH=AVWMW/WM
      AVZMW=SUMM2H/SUMMH
      RATIO=AVWMW/AVNMW
      PRINT 55,AVNCH
   55 FORMAT (35H THE NUMBER AVERAGE CHAIN LENGTH IS, F10.0,
     1 14H MONOMER UNITS//)
      PRINT 60,AVNMW
   60 FORMAT (39H THE NUMBER AVERAGE MOLECULAR WEIGHT IS,F10.0//)
      PRINT 65,AVWCH
   65 FORMAT (35H THE WEIGHT AVERAGE CHAIN LENGTH IS, F10.0,
     1 14H MONOMER UNITS//)
      PRINT 70,AVWMW
   70 FORMAT (39H THE WEIGHT AVERAGE MOLECULAR WEIGHT IS,F10.0//)
      PRINT 71,AVZMW
   71 FORMAT (34H THE Z AVERAGE MOLECULAR WEIGHT IS,F10.0//)
      PRINT 75,RATIO
   75 FORMAT (46H THE WEIGHT AVERAGE TO NUMBER AVERAGE RATIO IS,F5.2///)
      PRINT 90
   90 FORMAT (1X,131(1H*)//)
   12 CONTINUE
      STOP
      END

                                   CD TOT   0143
```