

# Polymerization Mechanisms and Molecular Weight Distribution. II. AIBN-Initiated Polymerization of Styrene at 60°C

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## Synopsis

An experimental study was carried out on the AIBN-initiated polymerization of styrene at 60°C. The kinetic rate constants were determined by the method of moments and the MWD method, which was proposed in a previous paper. The results compared favorably with the data in the literature and the MWD method was noted to yield more consistent results than the method of moments, which indicates the importance of considering the whole molecular weight distribution. The theoretical MWD was found to approximate the experimental MWD well. The chain-transfer constant to AIBN was found to be between 0.09 and 0.14.

## INTRODUCTION

The molecular weight distribution (MWD) of a polymer is a function of its formation and as such should yield information which can be used to characterize the mechanism and the kinetics of polymerization. Westlake and Huang<sup>1,2</sup> have recently shown this to be the case for a complex reaction mechanism of styrene polymerized at low temperature by radiation where both ionic and free radical polymerization occurred simultaneously. The approach of Westlake and Huang is a qualitative method for simultaneous analysis of rate data and molecular weight distribution data. In the previous paper<sup>3</sup> we proposed a technique which utilized the molecular weight distribution on a quantitative basis to establish the mechanism and the associated kinetic rate constants. The experiments performed in this study were designed to demonstrate the validity of the proposed method.

## EXPERIMENTAL

### Monomer and Initiator Purification

Styrene (Eastman Organic Chemicals) was washed three times with 6% sodium hydroxide solution and three times with distilled water to remove inhibitor, then dried over anhydrous calcium chloride overnight in a refrigerator. The styrene was distilled at 32°C and 10 Torr absolute pressure. The middle fraction was redistilled again before use and only the middle fraction of the second distillation was retained.

Azobisisobutyronitrile (AIBN) (Eastman Organic Chemicals) was recrystal-

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lized three times from absolute ethanol and finally vacuum dried at room temperature.

### Polymerization Procedure

The reactions were carried out using 30 ml glass ampoules at 60°C. The ampoules were shaken vigorously during polymerization to ensure thorough mixing and uniform temperature in the ampoules. Also, smaller ampoules were used to check if different results would be obtained, however, no differences were observed. The monomer-initiator mixture was placed in these glass ampoules and were sealed under vacuum ( $10^{-3}$  Torr) after a series of three freeze-thaw cycles. Temperature control was obtained by using a Neslab TEV 40 thermostatic bath. The temperature in the cell was maintained to within  $\pm 0.05^\circ\text{C}$  of the desired value. Following the polymerization polystyrene was precipitated by washing the contents of ampoules with small amount of toluene into 2 l of cold methanol ( $-10^\circ\text{C}$ ). The precipitated polystyrene was filtered on sintered glass Gooch crucibles containing No. 2 Whatman filter paper and then dried to constant weight at 40°C in a vacuum oven. The percent conversions were determined gravimetrically.

### Molecular Weights and Molecular Weight Distributions

Molecular weights and molecular weight distributions were determined from gel permeation chromatography with a Waters Model 200 instrument. Tetrahydrofuran (THF) was used as the eluting solvent. The flow rate was maintained at 1.0 ml/min, and the oven temperature was kept at  $25 \pm 0.2^\circ\text{C}$ . Sample concentration was 0.10 wt %, and sample injection time was 60 sec, corresponding to a sample injection of 1.0 ml.

Calibration was performed by using eleven monodisperse polystyrene standard samples (Pressure Chemical Company) having peak molecular weights of 900, 2030, 4800, 10,000, 19,750, 50,000, 97,200, 171,000, 402,000, 830,000, and 1,987,000. Calibration followed the universal calibration concept proposed by Boni,<sup>4</sup> assuming the effective separation parameters to be the equivalent hydrodynamic volume. Resolution factors were determined by following the method proposed by Tung.<sup>5</sup>

The column specifications are as follows: (1)  $10^7$ ; (2)  $1.5 \times 10^5$ – $7 \times 10^5$ ; (3)  $1.5 \times 10^4$ – $5 \times 10^4$ ; and (4)  $7 \times 10^2$ – $2 \times 10^3$ .

Samples for analysis were made up as 0.10 wt % solutions and filtered to remove foreign material. Conditions of flow rate, temperature, and injection time were the same as those for calibration.

The number-average ( $\bar{M}_n$ ) and weight-average ( $\bar{M}_w$ ) molecular weights and the corrected molecular weight distributions were calculated according to the method of Chang and Huang.<sup>6</sup>

Since the molecular weight distributions are central to the arguments presented in this paper there should be no question as to their correctness. To prove that any GPC yields the true MWD is difficult. However, to show that a particular instrument yields the correct distribution in relative terms can be done by using a broad molecular weight distribution polymer which is well characterized, such as the NBS polystyrene standard 706.

This sample was injected into the GPC according to the above sampling pro-

cedure and upon correcting the MWD according to the method of Chang and Huang<sup>6</sup> the molecular weight averages are:  $\bar{M}_n = 132,500$  vs 136,500 as reported;  $\bar{M}_w = 268,000$  vs 257,800 as reported; and  $\bar{M}_z = 415,000$  vs 396,000 as reported. On the basis of the good agreement between the two sets of results and the fact that we were able to calculate the  $\bar{M}_n$  and  $\bar{M}_w$  values of the monodisperse polystyrene samples, we believe that the molecular weight distributions reported in this paper are of sufficient quality to make the claims we are making. The reproducibility of the experimental results were investigated by repeating each typical experiment several times for each sample, analyzing for molecular weights. The variation of these measurements from all experimental procedures including variations in monomer purity, ampoule preparation, reaction temperature, and precipitation conditions were investigated. A statistical analysis of the molecular weight distributions was carried out to show the reliability of the GPC data. A particular polystyrene sample was injected seven times into the GPC and the statistics were calculated. The average  $\bar{M}_n$ ,  $\bar{M}_w$ , and  $\bar{M}_n/\bar{M}_w$  were found to be 129,000, 221,000, and 1.71 and the standard deviations were calculated to be 2700 (or 2.1%) 2800 (1.3%) and 0.03, respectively.

The NBS-706 polystyrene standards were measured three times in the GPC and the standard deviations were calculated and found to be comparable to the above-mentioned polystyrene sample.

## THEORETICAL

The inverse of number-average degree of polymerization has been used extensively to determine the rate constants in vinyl polymerization. The number-average degree of polymerization ( $\bar{DP}_n$ ) is related to the free radical mechanism via the usual expression

$$\frac{1}{\bar{DP}_n} = \frac{(k_{tc} + 2k_{td})}{k_p^2} \frac{R_p}{[M]^2} + C_M + C_I \frac{[I]}{[M]} \quad (1)$$

where the various terms follow the usual terminology.

The conventional method, eq. (1), for determining the kinetic rate constants of vinyl polymerization reactions is based on the number-average molecular weight. The polymeric product, however, has a distribution of molecular sizes (or molecular chain lengths) and the distribution of these species is one of the kinetic consequences of the polymerization reaction because of "the propensity of chemical reactions to proceed in a random manner."<sup>1</sup> The logical augmentation of the conventional method was then to include two measures of the distribution rather than just the mean of the distribution, the number-average molecular weight. The method of moments<sup>7</sup> utilizes both the number and the weight-average molecular weights for the kinetic rate constant calculations. This method has the distinct advantage of incorporating the width of the distribution whereas the conventional method does not.

The rate constants obtained from the method of moments are based on the overall rate of polymerization, and number- and weight-average degrees of polymerization. The three quantities which can be evaluated from the following relationships are  $k_{tc}/k_p^2$ ,  $R_i$ , and  $(C_M + C_I[I]/[M])$ :

$$C_M + C_I[I]/[M] = (2A - 1)/(A - 1)\bar{DP}_n \quad (2)$$

$$k_{tc}/k_p^2 = [M]^2(1/\overline{DP}_n - C_M - C_I[I]/[M])/R_p \quad (3)$$

$$R_i = \frac{R_p^2}{(k_p^2/k_{tc})[M]^2} \quad (4)$$

where  $A = (1 - \overline{DP}_w/2\overline{DP}_n)^{1/2}$ .

The method proposed in a previous paper,<sup>3</sup> on the other hand, utilizes the whole distribution rather than just the moments of the distribution. The rate constants are calculated by fitting the theoretical MWD to the experimental MWD according to the following least-squares criteria:

Minimize

$$\theta \int_0^\infty [Y(r, \theta) - y_E(r)]^2 dr$$

where  $y(r, \theta)$  is the theoretical MWD,  $\theta$  is the vector of rate constants, and  $y_E(r)$  is the experimental MWD.

Chain transfer to polymer was not accounted for in this study since at these low conversions (5% maximum) the amount of branches formed is negligible, even though  $C$  polymer is comparable to  $C_M$ ; however, the concentration of polymer is much smaller than the concentration of monomer.

## RESULTS AND DISCUSSION

The investigation of chemically initiated polymerization of styrene was undertaken to show the applicability of the "MWD method" for determining the rate constants.

Several initiator concentrations were used to prepare low-conversion polystyrene (3–5%). As a check on the purity of the styrene monomer, an attempt to duplicate the rates obtained by May,<sup>8</sup> and Baysal and Tobolsky<sup>9</sup> was made. At an AIBN concentration of 0.00896  $M$  the experimental initial overall rate of polymerization of  $6.9 \times 10^{-5}$  mole  $l^{-1}$  sec $^{-1}$ , was obtained [calculated  $6.88 \times 10^{-5}$  (ref. 8) and  $6.86 \times 10^5$  mole  $l^{-1}$  sec $^{-1}$ ,<sup>6</sup> the agreement being good].

The inverse number-average degree of polymerization has been used extensively to determine the rate constants in vinyl polymerization [the application of eq. (1) to rate and molecular weight data]. Some typical results are shown in Table I. In the light of the numbers shown in Table I one must realize what type of errors are involved in the measurements of the molecular weights. If a colligative property measurement (membrane osmometry, for example) is used to determine the polymer molecular weight, then  $1/\overline{DP}_n$  is more likely to be normally distributed with constant variance than is  $\overline{DP}_n$ . If, however, viscosity

TABLE I  
Values of Rate Constants Reported in Literature for AIBN-Initiated Polymerization of Styrene at 60°C

Author	$k_{tc}/k_p^2$ sec mole $l^{-1}$	$C_M \times 10^5$	$C_I$
Tobolsky <sup>10</sup>	861	6	0
Saha <sup>11</sup>	826	6	0
Bonsall <sup>12</sup>	625	11.	0
May <sup>8</sup>	646	9.2	0.16
Pryor <sup>13</sup>	900 <sup>a</sup>	6	0.02

<sup>a</sup>Assumed  $k_{tc}/k_p^2$  to be 900.

TABLE II  
Summary of Data for the AIBN-Initiated Polymerization of Styrene at 60°C

$[I] \times 10^3 M$	$R_p \times 10^5$ moles/l sec	$\bar{M}_w \times 10^5$	$\bar{M}_n \times 10^5$	$1/\bar{DP}_n \times 10^4$
1.04	2.35	5.59	3.40	3.06
2.02	3.28	4.04	2.58	4.04
2.23	3.44	3.82	2.32	4.50
3.90	4.54	3.14	1.92	5.42
4.23	4.74	2.88	1.72	6.05
6.87	6.04	2.26	1.34	7.80
8.96	6.90	1.91	1.15	9.06
11.60	7.85	1.70	1.01	10.30

methods are used, the converse is true. It appears that some of the rate constants in Table I were derived without regard to proper error analysis. This conventional method was then applied to the experimental data of the present investigation. The experimental results of the AIBN-initiated polymerization of styrene in bulk at 60°C are shown in Table II.

Figure 1 shows the plot of  $1/\bar{DP}_n$  vs  $R_p/[M]^2$  for the data reported in the literature for AIBN-initiated polymerization of styrene at 60°C, the data of the present study is also included. The values of  $t_{tc}/k_p^2$ ,  $C_M$ , and  $C_I$  were determined by the application of eq. (1) to the data of the present study and yielded values of  $671 \text{ sec mole}^{-1} \text{ l}^{-1}$ ,  $5.8 \times 10^{-5}$ , and 0.176, respectively. On the application of eq. (1) to the data in the literature<sup>7,8,10</sup> and the data of present study, values of  $788 \text{ sec mole}^{-1} \text{ l}^{-1}$ ,  $3.0 \times 10^{-5}$ , and 0.091, respectively, were obtained for these rate constants.

The method of moments, as described above and the proposed "MWD method"<sup>3</sup> were then applied to determine the rate constants. The theoretical MWD,  $y(r, \theta)$ , used in the "MWD method" is the steady-state MWD derived by Bamford et al.,<sup>15</sup> and is

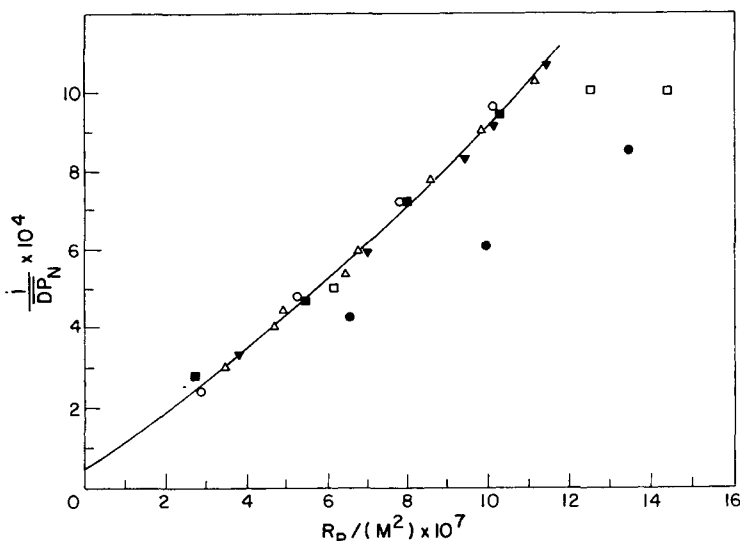


Fig. 1. Polymerization of styrene initiated by AIBN at 60°C;  $1/\bar{DP}_n$  vs  $R_p/[M]^2$ . ●, Data of Manabe<sup>14</sup>; ■, data of Baysal and Tobolsky<sup>9</sup>; ○, data of Saha<sup>11</sup>; □, data of Pryor<sup>13</sup>; ▼, data of May<sup>8</sup>; ▲, present study (corrected  $\bar{M}_n$ ).

$$W_r = r(1-p)p^{r-1} \left[ C_M + C_I \frac{[I]}{[M]} + \frac{R_p}{[M]^2} \frac{2k_{td}}{k_p^2} + \frac{r-1}{2} \frac{R_p}{[M]^2} \frac{2k_{tc}}{k_p^2} \left( C_I \frac{[I]}{[M]} + C_M + \frac{2(k_{tc} + k_{td})}{k_p^2} \cdot \frac{R_p}{[M]} \right) \right] \quad (2)$$

where  $W_r$  is the weight fraction of polymer with  $r$  monomer units, and  $p$  is the probability that a growing chain adds one more monomer unit rather than terminate and is defined as

$$p = \left( 1 + C_M + C_I \frac{[I]}{[M]} + \frac{R_p}{[M]^2} \cdot \frac{2(k_{tc} + k_{td})}{k_p^2} \right)^{-1}$$

The results of the calculations from both the method of moments and the "MWD method" are summarized in Table III.

It can be seen from Table III that the rate constants obtained by the method of moments are fairly scattered, the  $k_{tc}/k_p^2$  values range from 586 to 743 sec mole<sup>-1</sup> l<sup>-1</sup> with a standard deviation of 48. The results, perhaps indicate a scatter in the experimental data. The chain transfer constants were calculated from the plot of  $(C_M + C_I[I]/[M])$  vs.  $[I]/[M]$ ; whereby  $C_I$  is given as the slope of the line and  $C_M$  the intercept. A  $C_M$  value of  $5 \times 10^{-5}$  and  $C_I$  value of 0.22 were calculated from the data shown in Table III. On the other hand, the rate constants calculated via the proposed "MWD method" are fairly consistent. The average value of  $k_{tc}/k_p^2$  is 681 sec mole<sup>-1</sup> l<sup>-1</sup> and the standard deviation is 17. The  $(C_M + C_I[I]/[M])$  values shown in Table III were plotted against  $[I]/[M]$ , resulting in a  $C_M$  value of  $6.2 \times 10^{-5}$  and a  $C_I$  value of 0.14.

Figures 2 to 5 show typical plots of the experimental MWD and the theoretical MWD, which were obtained as a result of the optimization procedure on minimizing the error between the experimental and theoretical curves. It may be seen from these figures that the theoretical distribution closely approximates the experimental MWD. The error (or the area) between the two distributions is in the order of 0.05% relative to the total area under the curve. In general, the bulk of this error may be attributed to the lower molecular weight portion of the distribution. In most cases this problem is due to rough experimental data, that is, instability in the low molecular weight end of the corrected chromatogram resulted in fluctuations in the linearized MWD.

It may be seen from Table III that the kinetic rate constants via the method of moments and the proposed "MWD method" deviated sufficiently to warrant further consideration. The reason for this discrepancy is of fundamental im-

TABLE III  
Values of Rate Constants for AIBN-Initiated Polymerization of Styrene at 60°C

$[I] \times 10^3 M$	MWD method <sup>a</sup>		Method of Moments	
	$k_{tc}/k_p^2$	$(C_M + C_I[I]/[M]) \times 10^5$	$k_{tc}/k_p^2$	$(C_M + C_I[I]/[M]) \times 10^5$
1.04	686	8.1	669	8.1
2.02	689	9.6	743	5.4
2.23	706	10.4	671	11.9
3.90	674	8.4	627	13.3
4.23	683	12.8	608	19.2
6.87	691	17.7	586	27.3
8.96	705	20.0	640	27.2
11.60	712	25.6	641	30.8

<sup>a</sup> Proposed method.<sup>3</sup>

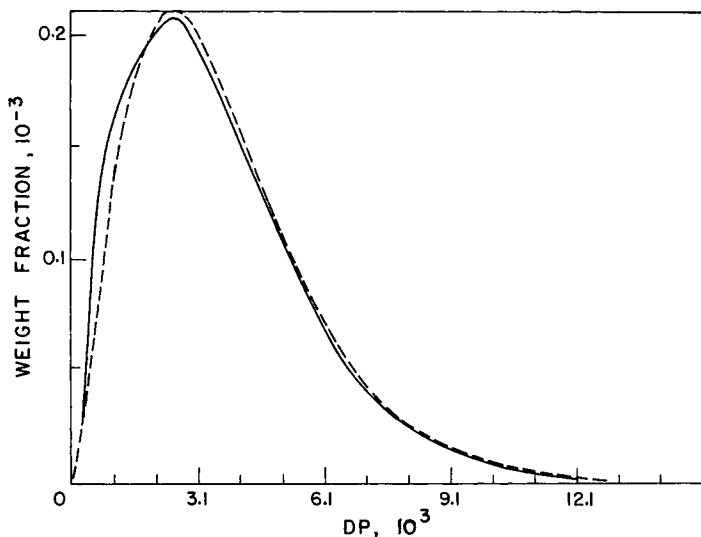


Fig. 2. Comparison of the experimental MWD and theoretical MWD obtained from optimization procedure: weight fraction vs degree of polymerization; ---, theoretical MWD; —, experimental MWD.  $[I]_0 = 0.00223$ ;  $k_{tc}/k_p^2 = 706$ ;  $C_M + C_I[I]/[M] = 10.4 \times 10^{-5}$ .

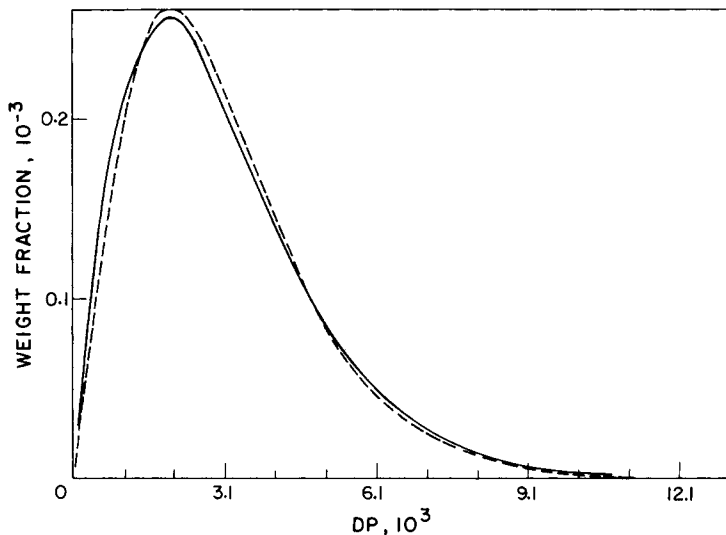


Fig. 3. Comparison of the experimental MWD and theoretical MWD obtained from optimization procedure: weight fraction vs degree of polymerization; ---, theoretical MWD; —, experimental MWD.  $[I]_0 = 0.0039$ ;  $k_{tc}/k_p^2 = 674$ ;  $C_M + C_I[I]/[M] = 8.4 \times 10^{-5}$ .

portance to the concept of molecular weight distribution and the moments of the distribution. It is evident that the  $\bar{M}_w$  and  $\bar{M}_n$  values are biased, in a statistical sense, when they are calculated from a GPC chromatogram that deviates from the theoretical distribution. Since all experimental distributions were noted to deviate from the expected distribution (i.e., the theoretical MWD) and since the sample size is very large in a statistical sense, the actual MWD should be exactly identical to the theoretical MWD. Thus the discrepancy must be due to experimental error. Therefore, the  $\bar{M}_w$  and the  $\bar{M}_n$  values are necessarily

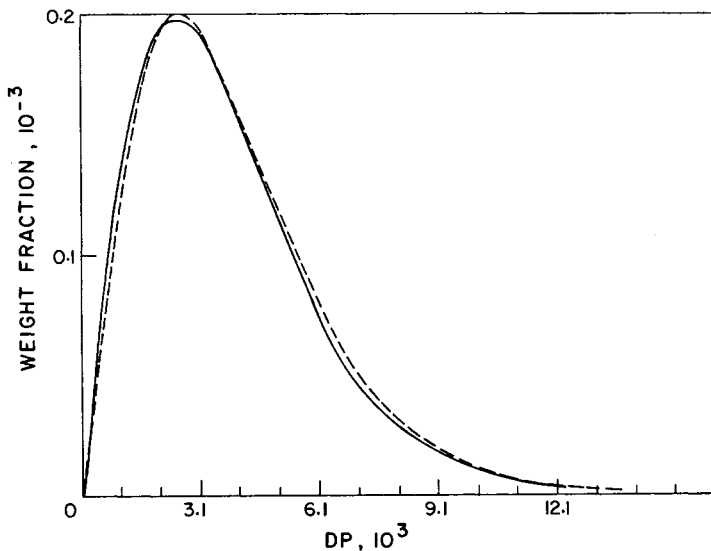


Fig. 4. Comparison of the experimental MWD and theoretical MWD obtained from optimization procedure: weight fraction vs degree of polymerization; --, theoretical MWD; —, experimental MWD.  $[I]_0 = 0.00202$ ;  $k_{tc}/k_p^2 = 689$ ;  $C_M + C_I[I]/[M] = 9.6 \times 10^{-5}$ .

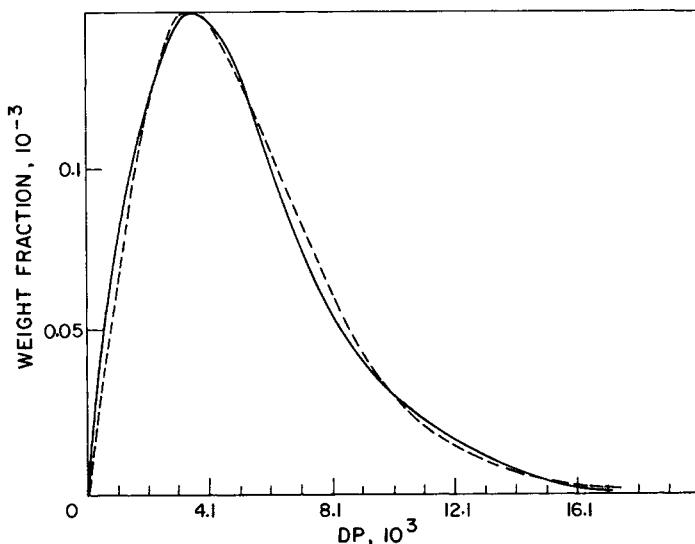


Fig. 5. Comparison of the experimental MWD and theoretical MWD obtained from optimization procedure: weight fraction vs degree of polymerization; --, theoretical MWD; —, experimental MWD.  $[I]_0 = 0.00104$ ;  $k_{tc}/k_p^2 = 686$ ;  $C_M + C_I[I]/[M] = 8.1 \times 10^{-5}$ .

in error because the  $\bar{M}_W$  is influenced more by the high molecular weight polymer, whereas the  $\bar{M}_n$  value is more influenced by the low molecular weight material. It follows then that the ratio,  $\bar{M}_W/\bar{M}_n$ , may not give a true indication of the polydispersity of the polymer. On the other hand, if the  $\bar{M}_W$  and  $\bar{M}_n$  values are determined by some other independent methods, the results will show utilizing similar arguments as above, that the  $\bar{M}_W/\bar{M}_n$  ratio will also be biased. However, the proposed method has an averaging effect on the whole distribution and hence is not as sensitive to some of the abnormalities which are experienced with GPC chromatograms.



Considerable confusion still remains concerning the value of chain-transfer constant to AIBN. May<sup>8</sup> and Pryor and Fiske<sup>13</sup> have suggested that AIBN has a finite transfer constant rather than zero as suggested by earlier investigators.<sup>10-12</sup> It is clear from the data presented here, and the data of May<sup>8</sup> and Pryor and Fiske,<sup>13</sup> that AIBN does have a finite transfer constant. The results of the present study certainly suggests that a finite value for  $C_1$  exists. However, to assign an exact value for it at this time is difficult. It is an accepted fact that curvature in the plot of  $1/\overline{DP}_n$  vs  $R_p$  is a direct consequence of chain transfer to the initiator molecule.<sup>15</sup> From the data shown in Figure 1 it may be seen that the line has some curvature thus indicating chain transfer to the initiator. Upon equal weighing of all the data<sup>8,9,11</sup> a  $C_I$  value of 0.091 was obtained. A word of caution is in order in that the data cannot in actual fact be weighted equally, statistically speaking, because of the several different methods of molecular weight determinations employed. Even in the light of this short coming, and the data obtained from the "MWD method," it appears that the value of  $C_I$  is in the range 0.09 to 0.14.

One may attempt to interpret the MWD's in terms of a small fraction of termination by disproportionation. Matheson et al.<sup>16</sup> have suggested that about 5% of the termination reaction may occur by disproportionation. However, since the "MWD method" yielded  $C_I$  values which are approximately equal to those calculated from Figure 1, it seems unlikely, then, that termination by disproportionation occurs to any detectable extent.

May<sup>8</sup> noted that abnormally long molecular weight tails were observed in the molecular weight distribution of AIBN-initiated bulk polymerization of styrene; no such high molecular weight tails were observed during the present investigation.

It is clear that a set of rules may be devised by which the mechanism and kinetics of polymerization reactions can be determined. The major criteria (or objective function) should be the molecular weight distribution. In the past, eq. (1) has been the major criteria by which the kinetic rate constants were obtained. However, since this equation must still be satisfied it would be appropriate to use it as a constraint.

In conclusion, a new method for studying the kinetics of polymerization reactions has been presented. The well known kinetics of bulk polymerization of styrene initiated by azobisisobutyronitrile were investigated to show the applicability of the proposed method.<sup>3</sup> This method may be considered very general in that any reaction, be it free radical, ionic or combination of both, may be studied if a theoretical molecular weight distribution model is available. The superiority of this new "MWD method" for determining the kinetic rate constants over the conventional average molecular weight method may not be obvious from the kinetic studies of styrene polymerizations performed here. However, it may be shown that when termination by disproportionation is extensive that the "MWD method" can be used to determine the fraction of each of the two bimolecular modes of termination, which is presented in a subsequent paper.<sup>17</sup>

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