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corresponds to an unannealed sample and the "after quench" sample was previously heated to 187 °C and cooled at 320 °C/min. The values of T_m and ΔH_m of the unannealed samples are almost independent of the chain length. However, the values for the quenched samples decrease clearly with increasing chain length. The marked drop in the T_m of high molecular weight HPB samples ($\bar{M}_n > 50\,000$) may be associated with a decrease in the crystallinity caused by a quenching treatment.

Table III lists the glass transition temperature (T_g), T_m, and ΔH_m of the atactic and syndiotactic HPB samples 5–10, together with the data of isotactic poly(1-butene) samples 1 and 2. The syndiotactic HPB samples 6–10 with nearly 100% 1,2 addition can be referred to syndiotactic poly(1-butene) samples. The T_g values of syndiotactic HPB samples increase with increasing chain length. On comparison of the T_g values at almost the same $\bar{M}_n$, a clear dependence upon the stereoregularity of poly(1-butene) is noted. The T_g value decreases in the series T_g(syndiotactic) > T_g(atactic) > T_g(isotactic). Similar dependence of T_g on the stereoregularity has been found for polypropylene[19] and poly(methyl methacrylate).[20] The difference in T_g between syndiotactic and isotactic poly(1-butene) is 9 ± 1 °C, which is much smaller than ~14 °C for polypropylene and ~81 °C for poly(methyl methacrylate). The result may correlate with the observation[15] that ^{13}C NMR spin–lattice relaxation times, T_1's, are longer for isotactic than for syndiotactic poly(1-butene) sequences. Taking these findings together, we can conclude that the isotactic sequences of 1-butene units possess a less restricted segmental mobility than do the syndiotactic sequences.

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A Calculation of Thermal Degradation Initiated by Random Scission. 1. Steady-State Radical Concentration

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ABSTRACT: Changes in molecular weight distribution and in sample volume were calculated for thermal degradation of a polymer. The thermal degradation scheme consists of random scission initiation, depropagation, and disproportionation termination reactions. A steady-state radical concentration was used in this study. The initial molecular weight distribution of the sample was expressed by a logarithmic normal distribution. Results were obtained in two ways: one was by approximate analytical solutions describing changes in molecular weight and in the sample volume, including effects of initial polydispersity of the sample; the other was by numerical calculation. Comparison among the analytical solutions obtained in this study, previously published solutions, and the numerically calculated results indicates that the solutions obtained in this study can apply to more general initial molecular weight distributions and agree better with the numerical results than previously published results. Effects of initial molecular weight, average zip length, initial polydispersity, and order of the termination reaction on changes in molecular weight, polydispersity, and the volume of the sample are discussed. A method to determine values of kinetic constants of random scission initiation and average zip length is described using experimental data in conjunction with the calculated results.

1. Introduction

The thermal degradation of polymers involves a large number of different lengths of polymer chains, both stable molecules and free radicals. Their interaction makes the degradation of polymers very complex. For this reason, many degradation studies have been oriented toward a global approach with the main emphasis on experimental studies. However, detailed understanding of the complex thermal degradation mechanism requires a close collaboration between theoretical and experimental approaches. The experimental approach has advanced significantly with improvements in modern instrumentation. On the other hand, it appears that advancement in the theoretical study of thermal degradation has not kept up even though more powerful computers have become available. The objectives of this study are to contribute to the understanding of thermal degradation by formulating and calculating a degradation model and to demonstrate the usefulness of theoretical results for understanding of the degradation mechanism.

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The thermal degradation of polymers can be described by a radical chain reaction mechanism involving initiation, depropagation, transfer, and termination reactions. Based on this degradation scheme, theoretical models have been formulated and solved numerically.[1-3] These calculations were based on the steady-state approximation for radical concentration and on a monodisperse distribution for initial molecular weight. Although the results were intended to apply to the thermal degradation of various polymers, there was some difficulty in the calculation because of many unknown values of kinetic constants of the various reactions as described above. Another approach has been to obtain analytical solutions for molecular weight and the sample weight with a specified molecular weight distribution during the degradation period or at limited extreme cases. Typical of the former cases are Boyd[4] using the most probable distribution and Gordon[5] using an exponential distribution. Typical of the latter cases are Jellinek[6] and MacCallum.[7] However, these solutions cannot describe the effects of initial polydispersity of the sample on degradation. Also all these studies, including the numerical study, used the steady-state approximation without rigorous justification of its use. Therefore, the theoretical study of polymer thermal degradation has not been fully explored and the results are not yet advanced enough to correlate closely with experimental studies.

In this study, a simpler degradation scheme based on random initiation, depropagation, and termination reactions is considered as a first step to avoid many unknown parameters. Even this simple degradation scheme can describe degradation of poly(methyl methacrylate),[8] poly(α–methylstyrene),[9] poly(tetrafluoroethylene),[10] and other polymers. Two approaches were used in this study: one was to obtain approximate analytical solutions and the other was to obtain exact numerical solutions. A steady-state approximation of the radical concentration was used in part 1 of this study. Results were obtained numerically without using this approximation in part 2 of this study. The effects of the initial molecular weight, average zip length, initial polydispersity, and the order of the termination reaction on changes in molecular weight distribution, polydispersity, and the volume of the sample are examined and discussed in this paper.

2. Theoretical Model

2.1. Basic Equations. The following chain reactions are considered for degradation of a polymer:

(i) random initiation

$$\mathrm{M}_n \xrightarrow{k_{\mathrm{ir}}} \mathrm{P}_x + \mathrm{R}_{n-x}$$

(ii) depropagation of free radicals

$$\mathrm{R}_n \xrightarrow{k_{\mathrm{d}}} \mathrm{R}_{n-1} + \mathrm{M}_1$$

(iii) termination of free radicals

$$\mathrm{R}_n + \mathrm{X} \xrightarrow{k_{\mathrm{t}_1}} \mathrm{M}_n + \mathrm{X}^{\bullet} \qquad \text{(first order)}$$

$$\mathrm{R}_n + \mathrm{R}_m \xrightarrow{k_{\mathrm{t}_2}} \mathrm{M}_n + \mathrm{M}_m \qquad \text{(second order)}$$

where M is a molecule and R is a radical. The subscript is the degree of polymerization. Also, k_{ir}, k_{d}, and k_{t} are the rate constants of initiation, depropagation, and termination, respectively. The second subscript of k_{t} denotes the reaction order of termination. It is assumed that these rate constants are independent of the degree of polymerization of the molecules and radicals.

From the above reaction scheme, the following ordinary differential equations can be formulated.[4]

$$\frac{\mathrm{d}[\mathrm{M}_n]V}{\mathrm{d}\tau} = -(n-1)[\mathrm{M}_n]V + \frac{1}{Z'}[\mathrm{R}_n]V \qquad n \geq 2 \quad (1)$$

$$\frac{\mathrm{d}[\mathrm{R}_n]V}{\mathrm{d}\tau} = \frac{Z}{Z'}([\mathrm{R}_{n+1}] - [\mathrm{R}_n])V + 2\sum_{i=n+1}^{\infty}[\mathrm{M}_i]V - \frac{1}{Z'}[\mathrm{R}_n]V \qquad n \geq 2 \quad (2)$$

$$\frac{\mathrm{d}[\mathrm{R}_1]V}{\mathrm{d}\tau} = \frac{Z}{Z'}[\mathrm{R}_2]V + 2\mathbf{M}_0\mathrm{V} - \frac{1}{Z'}[\mathrm{R}_1]V \quad (3)$$

$Z = k_{\mathrm{d}}/k_{\mathrm{t}_1}$ for first-order termination (4a)

$Z = k_{\mathrm{d}}/(k_{\mathrm{t}_2}\mathbf{R}_0)$ for second-order termination (4b)

$Z' = k_{\mathrm{ir}}/k_{\mathrm{t}_1}$ for first-order termination (5a)

$Z' = k_{\mathrm{ir}}/(k_{\mathrm{t}_2}/\mathbf{R}_0)$ for second-order termination (5b)

$[\mathrm{M_n}]$ denotes the concentration of molecules with the degree of polymerization n. V is the volume of the residual polymer sample during degradation. Correspondingly, $[\mathrm{R}_n]$ is the concentration of radicals with an n degree of polymerization. The term Z has been called the average zip length (the average number of monomer units successively released by depropagation along the length of a polymer chain). The term Z' represents the ratio of the rate constant of the initiation reaction to the rate constant of the termination reaction. When Z' is large, it is expected that radical concentration is high. The term τ represents dimensionless time, $k_{\mathrm{ir}}t$.

$\mathbf{M}_0$ and $\mathbf{R}_0$ are the total concentration of molecules and radicals, respectively. Then

$$\mathbf{M}_0 = \sum_{n=2}^{\infty}[\mathrm{M}_n] \quad (6)$$

$$\mathbf{R}_0 = \sum_{n=1}^{\infty}[\mathrm{R}_n] \quad (7)$$

Equations 1–3, 6, and 7 are derived on the assumption that monomer radicals stay in the polymer sample but monomer molecules vaporize immediately after they are produced. This assumption has been commonly used in previous studies. Further experimental studies are needed to clarify whether a significant number of monomer radicals can vaporize without further reaction in the polymer sample. The importance of this approximation for monomer radicals on calculated results will be discussed in part 2 of this study.

The total concentration of monomer units in the polymer residue sample is equal to the summation of monomer unit concentrations in molecules and radicals that remain in the sample. Therefore

$$\rho/m_0 = \mathbf{M}_1 + \mathbf{R}_1 \quad (8)$$

where $\mathbf{M}_1$ and $\mathbf{R}_1$ are defined as follows:

$$\mathbf{M}_1 = \sum_{n=2}^{\infty}n[\mathrm{M}_n] \quad (9)$$

$$\mathbf{R}_1 = \sum_{n=1}^{\infty}n[\mathrm{R}_n] \quad (10)$$

The term ρ is the density of the polymer residue, which is assumed to be a constant during degradation, and m_0 is the molecular weight of a monomer unit.

Equation 8 can be modified to

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\left(\frac{\rho \mathrm{V}}{m_0}\right) = \frac{\mathrm{d}}{\mathrm{d}\tau}(\mathbf{M}_1V) + \frac{\mathrm{d}}{\mathrm{d}\tau}(\mathbf{R}_1V) \quad (11)$$

Substituting eq 1–3 into the right-hand side of eq 11 gives

$$-\frac{\mathrm{d}}{\mathrm{d}\tau}\left(\frac{\rho V}{m_0}\right) = \frac{1}{Z'}[\mathrm{R}_1]V + \frac{Z}{Z'}\sum_{i=2}^{\infty}[\mathrm{R}_i]V = \frac{1}{Z'}\{1 - Z\}[\mathrm{R}_1]V + \frac{Z}{Z'}[\mathbf{R}_0]V \quad (12)$$

Equations 1–3 and 12 are the basic differential equations for calculating concentrations of molecules and radicals in the polymer residue and the change in the residue sample volume.

The initial molecular weight distribution of the sample must be specified in order to solve the above differential equations. In this study, a logarithmic normal distribution is used because this distribution allows that polydispersity can be varied. However, the previously used monodisperse distribution[2] and the most probable distribution[11,12] do not allow that polydispersity can be varied. Mathematically, this distribution is expressed as[13]

$$V_n = \frac{x_0}{\rho\sigma(2\pi)^{1/2}}\exp\left\{-\left[\ln\left(\frac{n}{x_0}\right) + \frac{\sigma^2}{2}\right]/2\sigma^2\right\} \quad (13)$$

where

$$\sigma^2 = \ln P_0$$

The term P_0 is the initial polydispersity of the sample.

The number-average degree of polymerization, x, and polydispersity, P, of the polymer residue during degradation can be calculated as follows:

$$x = (\rho/m_0)/(\mathbf{R}_0 + \mathbf{M}_0) \quad (14)$$

$$P = (\mathbf{M}_2 + \mathbf{R}_2)(\mathbf{M}_0 + \mathbf{R}_0)/(\rho/m_0)^2 \quad (15)$$

where $\mathbf{M}_2$ and $\mathbf{R}_2$ are second moments, defined as

$$\mathbf{M}_2 = \sum_{n=2}^{\infty} n^2[\mathrm{M}_n] \quad (16)$$

$$\mathbf{R}_2 = \sum_{n=1}^{\infty} n^2[\mathrm{R}_n] \quad (17)$$

In eq 14 and 15, the contribution from radicals is included because its contribution may be significant under certain conditions, especially in the calculation using an unsteady radical concentration. Further discussion regarding the contribution from radicals will be given in part 2 of this study.

2.2. Steady-State Radical Concentration. Without rigorous examination, previous degradation calculations assumed that the radical concentration did not change significantly during the degradation. Also, the contribution from radicals to the sample volume and molecular weight was assumed to be negligible compared with that from molecules. This assumption allows one to remove the time-dependent terms in eq 2 and 3, and the calculation becomes simpler. Furthermore, analytical solutions can be obtained under certain limited conditions.

With the assumption of a steady-state radical concentration, the value of the radical concentration can be derived from eq 1 and the steady-state form of eq 2 as[12]

$$[\mathrm{R}_n] = \left(\frac{2Z'}{1 + Z}\right)\sum_{j=n+1}^{\infty}\{K_1^{\,j-(n+1)}\sum_{i=j}^{\infty}[\mathrm{M}_i]\} \qquad n \geq 2 \quad (18)$$

where $K_1 = Z/(1 + Z)$.

It is important to note that eq 3 is not needed to derive eq 18. Therefore, there are no assumptions about the behavior of R_1, whether such radicals react or vaporize or stay in the sample as an inert species. As long as monomer molecules vaporize, monomer radicals do not appear in the basic equations with the steady-state radical concentration. The substitution of eq 18 into eq 1 gives the differential equations for $[\mathrm{M}_n]V$ as

$$\frac{\mathrm{d}[\mathrm{M}_n]V}{\mathrm{d}\tau} = -(n - 1)[\mathrm{M}_n]V + \frac{2}{1 + Z}\sum_{j=n+1}^{\infty}(K_1^{\,j-(n+1)}\sum_{i=j}^{\infty}[\mathrm{M}_i]V) \quad (19)$$

Also, eq 11 becomes

$$\frac{\mathrm{d}V}{\mathrm{d}\tau}\frac{\rho}{m_0} = \frac{\mathrm{d}\mathbf{M}_1 V}{\mathrm{d}\tau} \quad (20)$$

The integration of eq 19 and 20 will yield changes in molecular concentration and the sample residue volume. It is important to note that these changes are only a function of Z and are independent of Z'.

The term Z can be calculated from eq 4. It is straightforward for first-order termination. However, additional information is needed for second-order termination to determine $\mathbf{R}_0$. This additional information is the specification of the monomer radicals because the summation of eq 2 in order to obtain $\mathbf{R}_0$ produces an unknown, $[\mathrm{R}_2]$. If it is assumed, as discussed in the previous section, that monomer radicals do not vaporize, eq 3 will provide the necessary relation between $[\mathrm{R}_2]$ and $[\mathrm{R}_1]$ as

$$[\mathrm{R}_1] = Z[\mathrm{R}_2] + 2Z'\sum_{n=2}^{\infty}[\mathrm{M}_i] \quad (21)$$

Then

$$\mathbf{R}_0 = 2Z'\sum_{n=2}^{\infty}(n - 1)[\mathrm{M}_n] \quad (22)$$

$$Z = k_{\mathrm{d}}/k_{\mathrm{t}_1} \quad (23)$$

or

$$= k_{\mathrm{d}}/[k_{\mathrm{t}_2}(2k_{\mathrm{ir}}/k_{\mathrm{t}_2})(\sum_{n=2}^{\infty}(n - 1)[\mathrm{M}_n])^{1/2}]$$

Therefore, if the termination reaction is first order, the steady-state assumption does not need to describe the behavior of monomer radicals. If the termination reaction is second order, then some description is needed to specify Z although the basic equations, (19) and (20), still do not include any $[\mathrm{R}_1]$.

When the termination reaction is first order, eq 23 indicates that Z is constant. It appears that Z would change with time when the termination reaction is second order. However, if the degree of polymerization, n, of the sample residue is much larger than 1 (generally true for polymers), then

$$n - 1 \approx n$$

With the steady-state assumption

$$\mathbf{M}_1 \gg \mathbf{R}_1 \quad (24)$$

and

$$\sum_{n=2}^{\infty}(n - 1)[\mathrm{M}_n] \approx \mathbf{M}_1 \approx \rho/m_0 \quad (25)$$

with eq 8, 9, and 24. Therefore, for second-order termination

$$Z = k_{\mathrm{d}}/[k_{\mathrm{t}_2}(k_{\mathrm{ir}}/k_{\mathrm{t}_2})(\rho/m_0)^{1/2}] \quad (26)$$

Then it is expected that Z would be constant during degradation even though termination is second order. The term Z is the only parameter in the calculation dependent upon the assumption of a steady-state radical concentration.

The normalized number-average degree of polymerization and polydispersity with the steady-state assumption can be derived from eq 14, 15, and 24 as follows:

$$x/x_0 = (\rho/m_0)/(\mathbf{M}_0 x_0) \tag{27}$$

$$P = \mathbf{M}_2\mathbf{M}_0/(\rho/m_0)^2 \tag{28}$$

where x_0 is the initial number-average degree of polymerization. The results of the integration of eq 19 and 20 with the appropriate values of Z are referred to as "numerical solutions" (results derived from numerical analysis of the steady-state approximation model) in section 3.

2.3. Numerical Integration Scheme. For the integration of the ordinary differential equations such as eq 1–3 for the unsteady radical concentration and eq 19 and 20 with a steady-state radical concentration, the integral method of Shampine[14] was used. The maximum lengths of molecules and radicals were assumed to be seven times that of the initial number-average degree of polymerization instead of infinity. The contribution beyond seven times of x_0 is less than 0.001% of the total and does not create detectable difference in the calculated results. Therefore, the largest calculation with the steady-state approximation based on a set of 7000 ordinary differential equations for the case of x_0 = 1000 took about 1 min using the CYBER 205 computer at NBS.

2.4. Simplified Solutions with the Steady-State Radical Concentration. The calculation of the number-average degree of polymerization and of the sample residue volume described in section 2.2 can be simplified greatly with additional approximations.

(a) Approximate Solution by Jellinek.[6] In his derivation, it was assumed that

$$\mathbf{M}_1 \gg [\mathrm{R}_1]/Z'$$

Strictly speaking, this assumption is valid only when Z is very small. The derived analytical solutions are

$$\ln (V/V_0) = -2Z\tau \tag{29}$$

$$x/x_0 = (V/V_0)/\{(1 - V/V_0)/(2Z/x_0 + 1)\} \tag{30}$$

It is interesting to note that the effects of polydispersity do not appear in the solutions. The behavior of monomer radicals is described by eq 3 in this method.

(b) With the Most Probable Distribution. Another simplified solution was found by Boyd[4] by assuming that the molecular weight distribution of the polymer sample can be expressed by the most probable distribution over the entire degradation process. Then the expression for $[\mathrm{R}_1]$ by this method becomes

$$[\mathrm{R}_1] = 2ZZ'\mathbf{M}_0/(1 + Z/x) \tag{31}$$

Boyd's solutions are

$$\frac{1}{x} - \frac{1}{x_0} = \tau \tag{32}$$

$$\frac{V}{V_0} = \left\{1 + \frac{x_0\tau}{1 + x_0/Z}\right\}^{-2} \tag{33}$$

These solutions are valid for any values of Z. Since the polydispersity is kept at 2 due to the specified molecular weight distribution, the effects of polydispersity do not appear in the above solutions. The behavior of monomer radicals is described by eq 3 in this method.

(c) Approximate Solution Including Initial Polydispersity. Although the above-described simplified solutions are useful, these solutions are valid only under certain limited conditions. In particular, they do not show any effects of polydispersity on x/x_0 and V/V_0 during degradation. For this reason, approximate solutions including the effects of polydispersity are derived in this study.

The summation of eq 19 from n = 2 to ∞ can be written as

$$\frac{\mathrm{d}\mathbf{M}_0 V}{\mathrm{d}\tau} = -(\mathbf{M}_1 - \mathbf{M}_0)V + \frac{2}{1 + Z}\sum_{n=2}^{\infty}[\sum_{j=n+1}^{\infty} K_1^{j-(n+1)}(\sum_{i=j}^{\infty}[\mathrm{M}_i]V)] \tag{34}$$

The summation term in eq 34 is a function of K_1. Since $K_1 = Z/(1 + Z)$, values of K_1 can change from 0 to 1, corresponding to $Z = \infty$ and $Z = 0$, respectively. The actual value of K_1 is between 0 and 1, depending on the value of Z. At the two extremes, the values of the summation term in eq 34 become

$$\sum_{n=2}^{\infty}[\sum_{j=n+1}^{\infty} K_1^{j-(n+1)}(\sum_{i=j}^{\infty}[\mathrm{M}_i]V)] = \sum_{n=2}^{\infty}\frac{(n-1)(n-1)}{2}[\mathrm{M}_n]V \approx \frac{1}{2}\mathbf{M}_2 V \qquad \text{for } K_1 = 1 \tag{35a}$$

$$\sum_{n=2}^{\infty}(n-2)[\mathrm{M}_n]V \approx \mathbf{M}_1 V \qquad \text{for } K_1 = 0 \tag{35b}$$

If the value of this summation is approximately linearly interpolated for values of K_1 between 0 and 1 using the summation values at the two extremes, then

$$\sum_{n=2}^{\infty}[\sum_{j=n+1}^{\infty} K_1^{j-(n+1)}(\sum_{k=j}^{\infty}[\mathrm{M}_i]V)] \approx \frac{\mathbf{M}_1(\mathbf{M}_2/2)V}{(1 - K_1)(\mathbf{M}_2/2) + K_1\mathbf{M}_1} \tag{36}$$

Then eq 34 becomes

$$\frac{\mathrm{d}\mathbf{M}_0 V}{\mathrm{d}\tau} = -(\mathbf{M}_1 - \mathbf{M}_0)V + \frac{2\mathbf{M}_1 V}{1 + 2Z(\mathbf{M}_1/\mathbf{M}_2)} \tag{37}$$

Dividing both sides of eq 37 by $\mathbf{M}_1$ and using eq 25, 27, and 28, one may rewrite eq 37 as

$$\frac{\mathrm{d}(1/x)V}{\mathrm{d}\tau} = \left[-\left(1 - \frac{1}{x}\right) + \frac{2}{1 + 2Z/px}\right]V \approx \left(-1 + \frac{2}{1 + 2Z/px}\right)V \tag{38}$$

Another relationship between x and V can be derived by taking a summation of eq 1 and 2 and then adding it to the summation of (n × eq 1) and (n × eq 2). Then

$$(1 - Z)\frac{\mathrm{d}\mathbf{M}_0 V}{\mathrm{d}\tau} - \frac{\mathrm{d}\mathbf{M}_1 V}{\mathrm{d}\tau} = (1 + Z)(\mathbf{M}_1 - \mathbf{M}_0)V \tag{39}$$

Using eq 25 and 27, one can write eq 39 as

$$-\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}\tau} = \frac{Z}{Z + x}\left(x - \frac{1}{x}\frac{\mathrm{d}x}{\mathrm{d}\tau}\right) \tag{40}$$

From eq 38 and 40, the next set of simplified differential equations can be derived.

$$\frac{\mathrm{d}(x/x_0)}{\mathrm{d}(x_0\tau)} = \frac{(x/x_0)^2\{2(Z/x_0) - 2P(Z/x_0) - P(x/x_0)\}}{(x/x_0)P + 2(Z/x_0)} \tag{41}$$

$$\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}(x_0\tau)} = -\frac{2P(x/x_0)(Z/x_0)}{(x/x_0)P + 2(Z/x_0)} \tag{42}$$

If it is assumed that P remains constant during degrada-

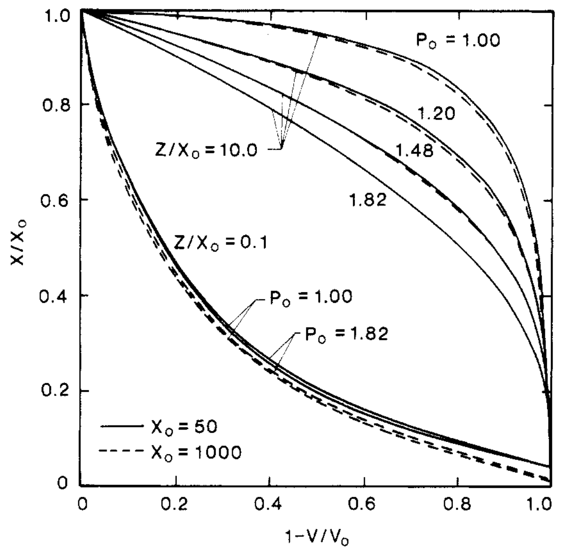

Figure 1. Relationships between normalized number-average molecular weight and conversion for various values of initial polydispersity.

tion, then analytical solutions of eq 41 and 42 can be obtained as

$$\frac{a}{b}\left(\frac{1}{x/x_0}-1\right)+\frac{b-a}{b^2}\ln\frac{(x/x_0)+b}{(x/x_0)(1+b)}=x_0\tau \qquad (P \neq 1) \quad (43a)$$

$$\left(\frac{1}{x/x_0}-1\right)+\frac{Z}{x_0}\left(\frac{1}{(x/x_0)^2}-1\right)=x_0\tau \qquad (P = 1) \quad (43b)$$

and

$$\left(\frac{x}{x_0}\right)=\frac{b(V/V_0)^{b/(2Z/x_0)}}{(b+1)-(V/V_0)^{b/(2Z/x_0)}} \qquad (P \neq 1) \quad (44a)$$

$$\left(\frac{x}{x_0}\right)=1-\ln\,(V/V_0)^{1/(2Z/x_0)} \qquad (P = 1) \quad (44b)$$

where

$$a = 2Z/(x_0P)$$

$$b = 2\left(\frac{Z}{x_0}\right)\left(1-\frac{1}{P}\right)$$

If $P = 2$, the above solutions become exactly the same as those derived by Boyd, eq 32 and 33. Therefore, these solutions are more general than the previously published simplified solutions because they are based on a more realistic molecular weight distribution, described by eq 13, including variable initial polydispersity.

The above three sets of analytical solutions, eq 29, 30, 32, 33, 41, and 42, are expressed as a function of only Z/x_0. This is also true for the numerical solutions of the steady-state model as discussed above. Therefore, Z/x_0 is the most important parameter for describing x/x_0 and V/V_0 during degradation with the assumption of a steady-state radical concentration.

3. Results and Discussion

3.1. Effects of Initial Molecular Weight and Polydispersity. The relationships between the normalized number-average degree of polymerization and the sample residue volume are shown in Figure 1. These curves were obtained by numerically integrating eq 19 and 20 with the initial molecular distribution described by eq 13. The results show clearly that the initial number-average degree of polymerization, x_0, has little effect on the relationship between x/x_0 and $1 - V/V_0$. If the average zip length is much shorter than the initial degree of polymerization, the effects of initial polydispersity on the relationship are negligible. Since the majority of polymer chains terminate during the depropagation process, the memory of the initial molecular weight distribution is quickly lost. Therefore, effects of the initial polydispersity on the relationship shown in Figure 1 are negligible. However, when the average zip length becomes much longer than the initial degree of polymerization, the majority of polymer chains unzip fully and the memory of the initial molecular weight distribution is kept throughout the degradation. Therefore, in this case the effects of initial polydispersity on the relationship become significant as shown in Figure 1. An increase in polydispersity increases the fraction of longer polymer chains in the molecular weight distribution relative to a low-polydispersity sample; this increases the probability of termination and reduces the molecular weight. Therefore, with $Z/x_0 = 10.0$ an increase in polydispersity decreases x/x_0 at any constant value of $(1 - V/V_0)$.

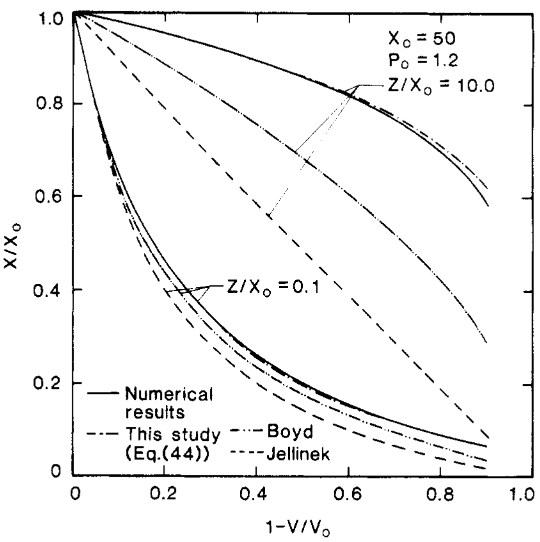

Figure 2. Comparison of x/x_0 with $1 - V/V_0$ calculated from various simplified solutions with numerically calculated results.

It is important to point out that x/x_0 decreases even though $Z/x_0 = 10.0$ and $P_0 = 1.0$. This indicates that a small number of terminations occur during the depropagation process and complete unzipping for all polymer chains does not happen.

The results shown in Figure 1 were calculated numerically. As discussed in section 2.4, there are simplified approximate solutions available. A comparison of these solutions, Jellinek's solutions (eq 29 and 30), Boyd's solutions (eq 32 and 33), and the solution from this study (eq 43a and 44a) with the numerically calculated results is shown in Figure 2. The results show clearly that the solutions from this study agree best with the numerically calculated results for $Z/x_0 = 0.1$ and 10.0. This also will be demonstrated for various values of the initial polydispersity later in this work. As discussed in section 2.4, the solutions of this study become the same as Boyd's solutions when $P_0 = 2.0$.

A cross plot of the relationships in Figure 1 is shown in Figure 3 at a specific value of $V/V_0 = 0.5$. The results are calculated for $x_0 = 50$, because Figure 1 shows clearly that the effects of x_0 on the relationship are negligible. When Z/x_0 becomes larger, the numerically calculated results

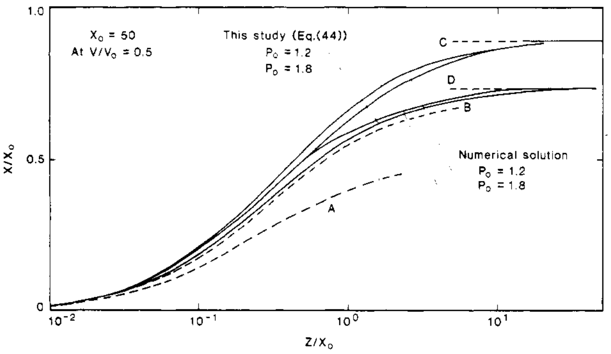

Figure 3. Comparison of the relationship between x/x_0 and Z/x_0 at $V/V_0 = 0.5$ calculated from various simplified solutions by (a) Jellinek,[6] (b) Boyd,[4] (c) MacCallum,[7] ($P_0 = 1.2$), and (d) MacCallum[7] ($P_0 = 1.8$).

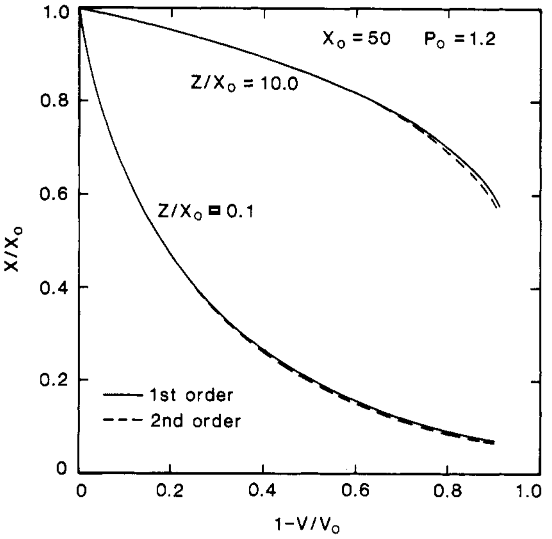

Figure 4. Effect of the order of disproportionation termination on the relationship between x/x_0 and $1 - V/V_0$.

show that the difference in initial polydispersity has a significant effect on x/x_0. This trend is also predicted by the solutions from this study (eq 43a and 44a), but neither Jellinek's nor Boyd's solutions predict this trend. As indicated in section 2.4, Jellinek's solutions are reasonably accurate only at very small values of Z/x_0. The solutions of this study agree reasonably well with the numerically calculated results even though the solutions assume that polydispersity is kept at the initial value during degradation.

The relationship shown in Figure 3 is useful to determine the value of Z from an experimentally measured value of x/x_0 for the sample residue at the corresponding V/V_0. The relationship between x/x_0 and Z/x_0 for a specific V/V_0 can be calculated easily from eq 43a and 44a. Then using known x/x_0, V/V_0, and P_0, one can determine the value of Z/x_0 by using a similar curve to that shown in Figure 3. Therefore, the combination of the simplified solutions of this study with a limited number of experimental measurements allows the determination of this important degradation parameter relatively easily.

3.2. Effects of Termination Reaction Order. Probably the least understood reaction step in the degradation process is the termination reaction. However, it is relatively easy to examine the effects of reaction order of disproportionation termination on degradation. A comparison of the results obtained with first-order termination and with second-order disproportionation termination is shown in Figure 4. It shows that the effect of reaction order of disproportionation termination on the relationship between x/x_0 and $1 - V/V_0$ is negligible.

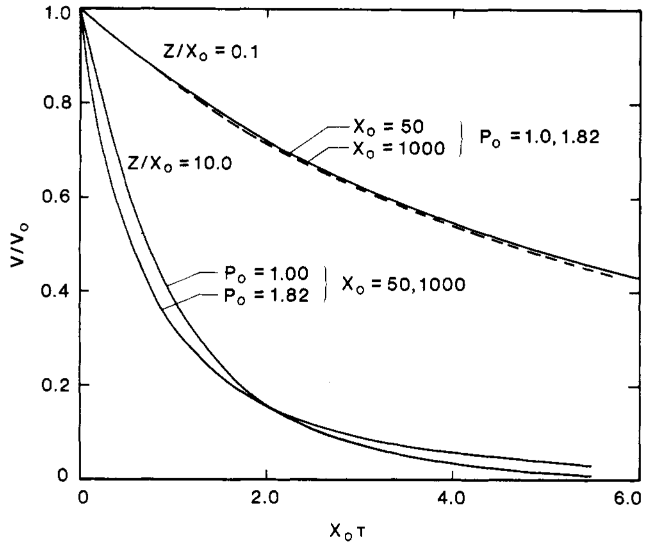

Figure 5. Change in V/V_0 with nondimensionalized time at two different values of Z/x_0, 0.1 and 10.0, and normalized average zip length of 1.0 and 1.82.

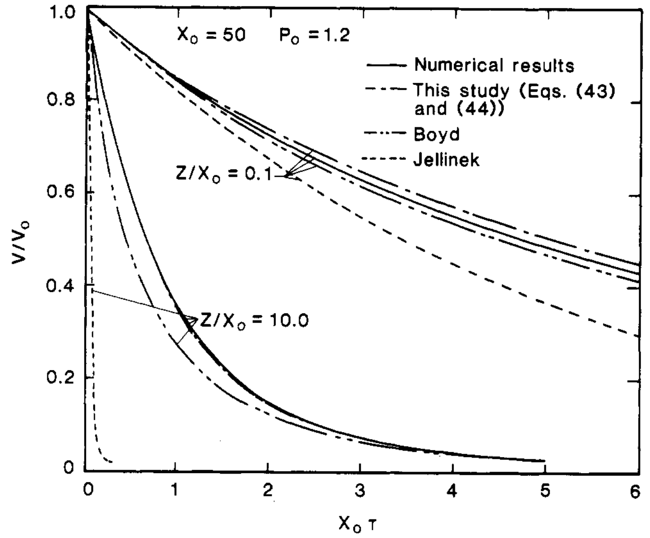

Figure 6. Comparison of the relationship between V/V_0 and $x_0\tau$ calculated from various simplified solutions with numerically calculated results.

3.3. Degradation with Time. The relationships between the residue volume and nondimensionalized degradation time, $x_0\tau = x_0 k_{ir} t$, were calculated numerically; they are shown in Figure 5 for various values of x_0, P_0, and Z/x_0. These results show that both values of x_0 and P_0 have little effect on the relationship with $Z/x_0 = 0.1$. With $Z/x_0 = 10.0$, effects of x_0 and P_0 on the relationship become more noticeable but they are still not really significant. The results also show that the residue volume decreases more rapidly with $Z/x_0 = 10.0$ than with $Z/x_0 = 0.1$. Large values of Z/x_0 indicate more efficient depropagation of polymer radicals resulting from random scissions so that more monomer units are lost from the sample even with the same number of random scissions than are lost from those with small values of Z/x_0.

The relationships between $x_0\tau$ and $1 - V/V_0$ calculated from the various simplified solutions have been compared against the numerically calculated results to assess their accuracy. Since the effects of x_0 on the relationship are negligible, as shown in Figure 5, the case of $x_0 = 50$ was used for the comparison. The results are shown in Figure 6. They indicate that Boyd's solutions and the solutions

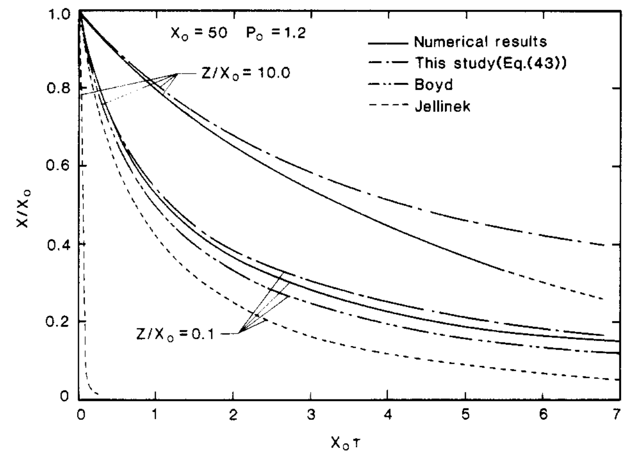

Figure 7. Comparison of the relationship between x/x_0 and $x_0\tau$ calculated from various simplified solutions with numerically calculated results.

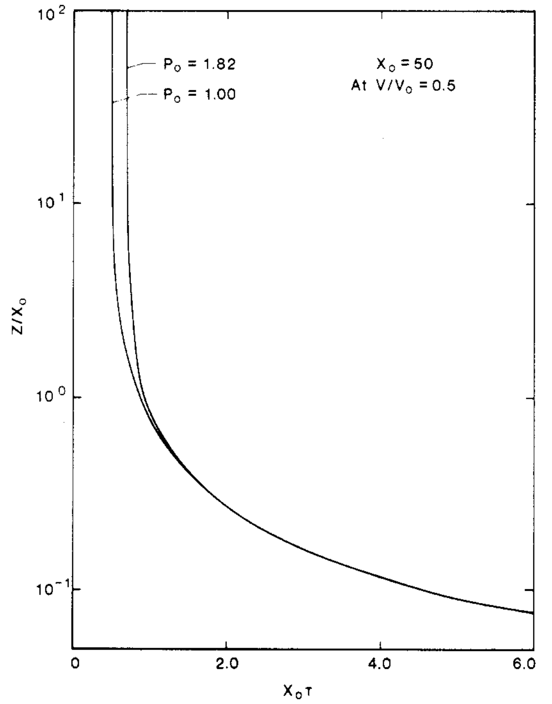

Figure 8. Relationship between Z/x_0 and $x_0\tau$ at $V/V_0 = 0.5$.

of this study agree reasonably well with those calculated numerically, but Jellinek's solutions significantly overestimate the change in the residue volume.

A similar comparison was made for the relationships between $x_0\tau$ and x/x_0; the results are shown in Figure 7. The results show that Boyd's solutions significantly overestimate the change in x/x_0 unless P_0 is close to 2.0, and Jellinek's solutions also overestimate it significantly, even when P_0 is close to 2.0. The solutions from this study underestimate it when $P_0 = 1.2$ but they agree reasonably well with the numerically calculated results. From the comparisons shown in Figure 2, 3, 6, and 7, it is clear that the results obtained from the simplified solutions derived in this study agree best with the numerically calculated results compared to Jellinek's and Boyd's solutions.

The relationship between the normalized average zip length and the nondimensionalized time at $V/V_0 = 0.5$ is shown in Figure 8. The curves in this figure were calculated with $x_0 = 50$ to demonstrate the trend because the initial length of the sample does not have a significant effect on the curves. This figure is useful for determining the value of k_{ir} from experimental results. After the value of Z/x_0 is determined experimentally by using Figure 3, the value of k_{ir} can be determined from similar curves to those shown in Figure 8 for the experimentally measured value of V/V_0. By repeating the isothermal experiments at different temperatures, one can determine kinetic constants for k_{ir} and Z from experimentally measured values of x/x_0 and V/V_0 using figures similar to Figures 3 and 8 corresponding to specific values of V/V_0. .

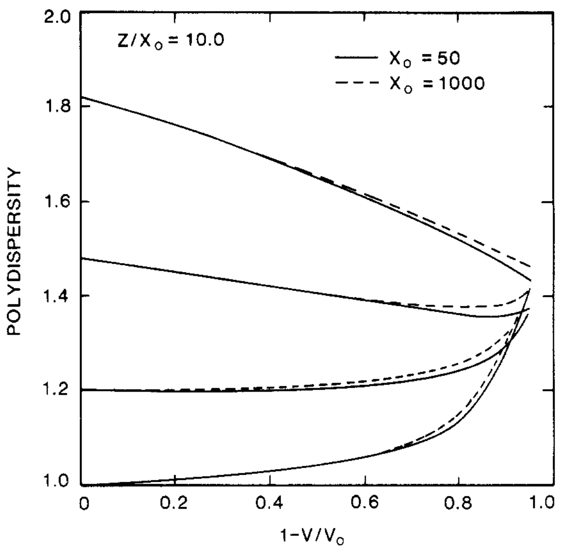

Figure 9. Change in polydispersity with $1 - V/V_0$ under two different values of initial molecular weight at $Z/x_0 = 10.0$.

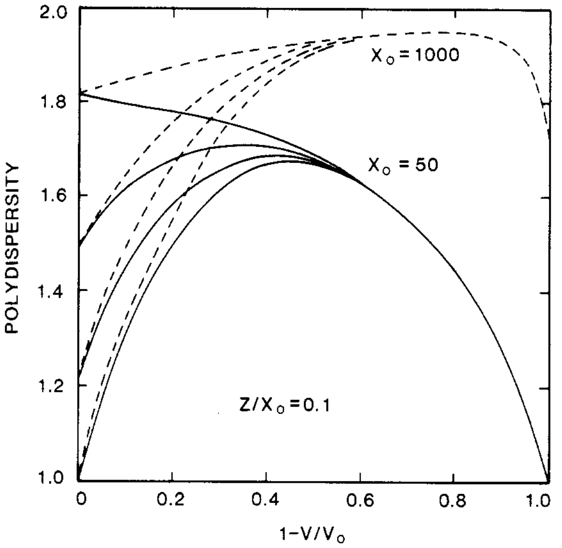

Figure 10. Change in polydispersity with $1 - V/V_0$ under two different values of initial molecular weight at $Z/x_0 = 0.1$.

3.4. Change in Polydispersity. The change in polydispersity with conversion is shown in Figure 9 for the case of long average zip length and in Figure 10 for short average zip length. When average zip length is long, the majority of polymer chains unzip so that the effects of the length of the polymer sample on change in polydispersity are negligible. Also, the change in polydispersity is gradual with conversion due to the small number of termination reactions (the number of termination reactions is not negligible even at $Z/x_0 = 10.0$ as shown in Figure 1). The results in Figure 9 indicate that, in the case of small initial polydispersity, polydispersity increases with increase in conversion due to the addition of short polymer chains by termination reactions. However, in the case of large initial polydispersity, long polymer chains terminate more often than short polymer chains, which produces many short

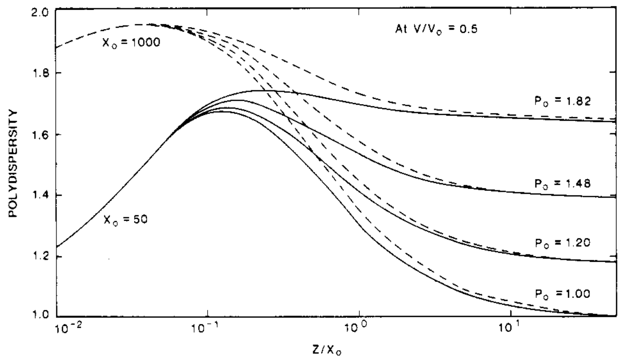

Figure 11. Change in polydispersity with Z/x_0 with various values of initial polydispersity at $V/V_0 = 0.5$.

polymer chains with few longer polymer chains and polydispersity decreases.

When the average zip length is short, the majority of polymer chains are terminated during the depropagation process. This produces many different lengths of polymer chains, and polydispersity of the sample with small initial polydispersity increases significantly with an increase in conversion up to about 0.5. With a large value of x_0, there is the possibility of a wider span of polymer chain length than there is with a small value of x_0 so that the polydispersity with larger x_0 is bigger than that with small x_0, thus showing the strong effect of x_0 on the change in polydispersity. The sample rapidly loses its initial characteristics with conversion due to termination reactions, and the polydispersity of samples with different initial polydispersities and the same value of x_0 becomes the same after a conversion of about 0.6.

The above discussion on the changes in polydispersity is summarized in Figure 11. When Z/x_0 is large, the effects of x_0 on the change in polydispersity are negligible but the effects of initial polydispersity are significant. On the other hand, when Z/x_0 is small, the effects of x_0 on changes in polydispersity are significant, but the effects of P_0 are negligible. The crossover point in Z/x_0 depends on the value of conversion as shown in Figures 9 and 10.

3.5. Degradation with Temperature. Current degradation studies use thermogravimetric analysis (TGA) more often than the isothermal approach. In TGA, a sample is heated to high temperatures at a specified heating rate. The model described in section 2 can be used to obtain TGA-type results, providing values of degradation kinetic constants such as the preexponential factor (A) and activation energy (E) are available. Unfortunately, in this case, the number of parameters is no longer one, Z/x_0, as it is for the isothermal case but four for the TGA case. There is one pair of A and E for the random initiation reaction and another pair of A and E for Z. These values could be determined by the procedure described in section 3.3. Typical results are shown in Figure 12 with values of kinetic constants derived from our preliminary work. The term $d(W/W_0)/dt$ is calculated by taking the time derivative of the sample weight, which is obtained from the sample volume by multiplying by density. Therefore, this type of result from the degradation model can be directly compared with TGA-type experimental data to augment the understanding of the polymer degradation mechanism with simultaneous studies under the isothermal condition described in the previous sections.

4. Conclusions

1. Simplified approximate analytical expressions describing changes in molecular weight and in sample volume were derived, including the effects of initial polydispersity of the sample. Data calculated from these expressions agree with numerically calculated results better and apply to more flexible initial molecular weight distribution than previously published results.

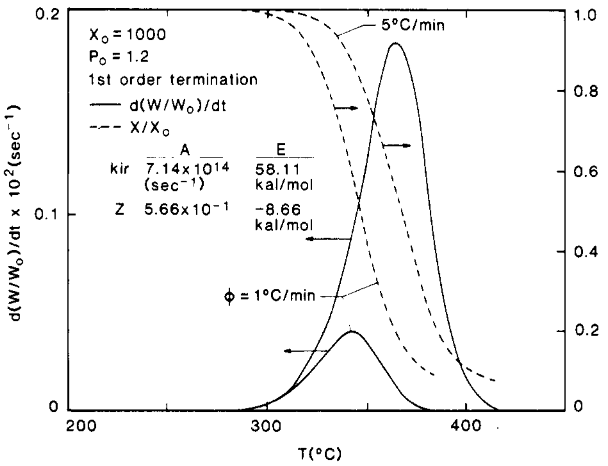

Figure 12. Plots of derivative thermogravimetry (DTG) and of change in molecular weight with temperature at two heating rates of 1 and 5 °C/min.

2. The initial degree of polymerization does not have significant effects on changes in molecular weight and in sample volume during degradation at the isothermal condition as long as the normalized average zip length Z/x_0 is kept at the same value.

3. When Z/x_0 is large, initial polydispersity has significant effects on changes in molecular weight and in polydispersity of the sample. However, when Z/x_0 is small, initial polydispersity and initial molecular weight do not have significant effects on change in molecular weight, but initial molecular weight has significant effects on change in polydispersity of the sample.

4. The order of the disproportionation termination reaction does not have significance for changes in molecular weight and in the sample volume.

5. Values of kinetic constants for random scission initiation and average zip length can be determined by using calculated curves shown in Figures 3 and 8 corresponding to experimentally measured molecular weights and the sample volume under isothermal conditions at different temperatures.

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