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Chain-Length-Dependent Termination for Free Radical Polymerization

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ABSTRACT: On the basis of an analysis of the instantaneous molecular weight distribution for free radical polymerization, it is found that the full form of the bimolecular termination rate constant, $K_t(i,j)$, cannot be found via molecular weight distribution measurements. Therefore, the averages of $K_t(i,j)$ are used for modeling polymerization rate and molecular weight averages. In polymerizations with strong chain-length-dependent termination, a single average K_t is not adequate for modeling high-order molecular weight averages. The use of different K_t averages for comprehensive modeling is recommended. A discussion of the mechanism of polymerization at very high conversion has also been offered. An extraction of kinetic parameters from experimental data shows that the initiator efficiency f falls dramatically when the glassy state transition of the reacting mass is approached. Considering that the propagation rate constant K_p likely falls at very high conversions, we believe that the newly initiated radicals may stay in pairs instead of being uniformly distributed in the reacting mass at this stage of conversion. Such radical pair formation will increase local radical concentration and, in turn, apparent termination rate constant.

Introduction

In free radical polymerizations, bimolecular termination rates of polymer radicals are often diffusion controlled during the whole course of reaction, with segmental diffusion control at low conversions and translational diffusion control at high conversions, often referred to as the Trommsdorff/gel effect. At very high conversions, due to glassy state transition, not only the termination but also initiation and propagation may become strongly diffusion controlled. Molecular diffusion behavior in polymer–monomer mixtures has been studied for several decades. Based on the results of these studies, many models have been proposed recently to give quantitative descriptions of the termination and the propagation rate constants using such concepts as free volume and/or entanglements. Marten and Hamielec[1] and Chiu et al.[2] used a single termination rate constant and demonstrated good fitting of experimental conversion/time history and number-average molecular weight development but underestimated the higher order molecular weight averages at high conversions. Cardenas and O'Driscoll,[3] Ito,[4] Tulig and Tirrell,[5] and Soh and Sundberg[6] proposed specific functions for $K_t(i,j)$, the bimolecular termination rate constant for radicals of chain length i and j, and showed some improvement in fitting higher order molecular weight averages.

Despite such extensive studies, the existing models have not properly accounted for chain-length-dependent termination, nor have these models been tested under severe reaction conditions, such as (1) nonisothermal polymerizations with significant temperature changes, (2) polymerizations in the presence of prepolymer, which has a very different molecular weight than that produced later during polymerization, and (3) reactions run in a continuous stirred-tank reactor (CSTR), nor have any of them considered the possible significant fall in initiator efficiency[7,8] and the effect of radical pair formation at very high conversions. An effort is being made in this work to address these problems. As a first step, in this paper, using experimental data available in the literature, we present a method for accounting for chain-length-dependent termination in a general fashion and discuss the diffusion-controlled behavior of kinetic parameters during the whole course of polymerization. The experimental data for batch bulk polymerization of methyl methacrylate (MMA) initiated by 2,2′-azoisobutyronitrile (AIBN) (initial concentration $[I]_0 = 0.0258$ mol/L) at 70 °C after Balke and Hamielec[9] are used in the analyses.

Termination Rate Constants

An effective starting point is to consider the instantaneous molecular weight distribution formed in a batch reactor. The most general case involves the use of an arbitrary chain-length-dependent model for polymer radical termination. This distribution may be written as follows for linear polymers:

$$w(r,t) = r\Phi^*(r)\left\{\frac{K_{fm}}{K_p} + \frac{K_{fT}[T]}{K_p[M]} + \ldots + \frac{\sum_{i=1}^{\infty} K_{td}(r,i)\ \Phi^*(i)[R^*]}{K_p[M]}\right\} + \frac{r}{2}\sum_{s=1}^{r-1}\frac{K_{tc}(s,r-s)[R^*]}{K_p[M]}\Phi^*(s)\ \Phi^*(r-s) \tag{1}$$

where $w(r,t)$ is the weight fraction of polymers with chain length r, produced in the time interval, t to $t + dt$, $\Phi^*(r)$ is the $(r/2)\sum_{s=1}^{r-1}K_{tc}(s,r-s)[R^*]\Phi^*(s)$ fraction of radicals with chain length r and may be expressed as

$$\Phi^*(r) = \left(\frac{R_I}{R_p} + \frac{K_{fm}}{K_p} + \frac{K_{fT}[T]}{K_p[M]} + \ldots\right) \Big/ \prod_{j=1}^{r}\left\{1 + \frac{K_{fm}}{K_p} + \frac{K_{fT}[T]}{K_p[M]} + \ldots + \frac{\sum_{i=1}^{\infty} K_t(i,j)\ \Phi^*(i)[R^*]}{K_p[M]}\right\} \tag{2}$$

provided that the quasi-steady-state assumption (QSSH) is valid, R_I and R_p are initiation and propagation rates, K_{fm}/K_p represents polymer chains formed by chain transfer to monomer, with K_{fm} and K_p rate constants for chain transfer to monomer and propagation, respectively, $K_{fT}[T]/K_p[M]$ represents polymer chains formed by chain transfer to a small molecule T, where [T] and [M] are the concentrations of T and monomer, K_{fT} is the chain transfer constant, $\sum_{i=1}^{\infty}K_{td}(r,i)\ \Phi^*(i)[R^*]/K_p[M]$ represents polymer chains formed by disproportionation termination with $[R^*]$, the total polymer radical concentration, and $(r/2)\sum_{s=1}^{r-1}K_{tc}(s,r-s)[R^*]\Phi^*(s)\ \Phi^*(r-s)/K_p[M]$ represents polymer chains formed by recombination termination.

$w(r,t)$ and/or $\Phi^*(r)$ are certainly the most dynamic "probes" in a kinetic study. Unfortunately, it is very

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difficult to measure $\Phi^*(r)$. Two of the possible ways to measure $w(r,t)$ are (1) to take derivatives of accumulated molecular weight distributions, which are readily measured by GPC, and (2) direct measurement using radioactive monomer. The former usually requires a very high accuracy in measurement of the accumulated molecular weight distribution, which is difficult. In the latter method, radioactive monomer is well mixed with a required amount of nonradioactive polymer. Then, the mixture is polymerized for a small time interval to produce a small amount of radioactive polymer which may be detected by GPC. But such experimental data are not available in the literature. The measurement of [R*] can be done using modern ESR techniques.

By examination of eq 1 and 2, it is clear that the full form of $K_t(i,j)$ cannot be deduced via measurements of $w(r,t)$ and/or $\Phi^*(r)$. For N species, eq 1 and 2 give $2N$ equations with N^2 unknown K_t's. To note that, $K_t(i,j) = K_t(j,i)$ will reduce the number of unknowns to $^1/_2N^2$, which is still more than $2N$ when $N > 4$. The solution for $K_t(i,j)$ is therefore not unique. One must therefore resort to the use of approximate models with fewer parameters.

In the present study, the use of $K_t(i,j)$ averages is proposed. The use of such averages will permit one, in principle, to calculate the rate of polymerization and the molecular weight averages but not the full molecular weight distribution in all cases.

In the case of chain-length-independent termination, only a single K_t need be used. Therefore, eq 1 can be simplified to where

$$w(r,t) = (\tau + \beta)[\tau + \tfrac{1}{2}\beta(\tau + \beta)(r - 1)]r\frac{1}{(1 + \tau + \beta)^r} \tag{3}$$

where

$$\tau = \frac{K_{fm}}{K_p} + \frac{K_{fT}}{K_p[M]} + \dots + \frac{K_{td}[R^*]}{K_p[M]} \qquad \beta = \frac{K_{tc}[R^*]}{K_p[M]}$$

The instantaneous molecular weight averages can be calculated by using the following equations:

$$\bar{M}_n = \frac{m}{\tau + \tfrac{1}{2}\beta} \tag{4}$$

$$\bar{M}_w = \frac{m(2\tau + 3\beta)}{(\tau + \beta)^2} \tag{5}$$

$$\bar{M}_z = \frac{m(6\tau + 12\beta)}{(\tau + \beta)(2\tau + 3\beta)} \tag{6}$$

etc., where m is the monomer molecular weight. Equation 3 gives a most probable distribution when $\beta = 0$. When termination becomes chain-length dependent, no such simple distribution exists. Equation 1 may produce a complicated multimodal distribution. Thus the calculation of the instantaneous molecular weight averages needs to be done by using numerical integration over $w(r,t)$. Accordingly, the averages of $K_t(i,j)$ are so defined to give correct descriptions for the corresponding instantaneous molecular weight averages:

$$\bar{M}_n = \frac{m}{\tau_n + \tfrac{1}{2}\beta_n} \tag{7}$$

$$\bar{M}_w = \frac{m(2\tau_w + 3\beta_w)}{(\tau_w + \beta_w)^2} \tag{8}$$

$$\bar{M}_z = \frac{m(6\tau_z + 12\beta_z)}{(\tau_z + \beta_z)(2\tau_z + 3\beta_z)} \tag{9}$$

$$\vdots$$

$$\tau_x = \frac{K_{fm}}{K_p} + \frac{K_{fT}[T]}{K_p[M]} + \dots + \frac{\bar{K}_{tdx}[R^*]}{K_p[M]} \tag{10}$$

$$\beta_x = \frac{\bar{K}_{tcx}[R^*]}{K_p[M]} \tag{11}$$

$$x = n, w, z, \dots$$

With these definitions, $\bar{K}_{tn}$ is equivalent to

$$\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} K_t(i,j)\ \Phi^*(i)\ \Phi^*(j)$$

This number-average K_t permits one to calculate not only $\bar{M}_n$ but also the polymerization rate. It can be seen that the high-order average termination rate constants $\bar{K}_{tw}$, $\bar{K}_{tz}$, ... ($\bar{K}_{tn} \geq \bar{K}_{tw} \geq \bar{K}_{tz}$), possess some higher order characteristics in terms of Φ^* but do not have clear physical interpretation as $\bar{K}_{tn}$ does for the most general case which involves both disproportionation and combination termination (see the Appendix).

We now illustrate the empirical extraction of these kinetic parameters from experimental polymerization rate and molecular weight averages. First, fit the conversion (X) vs time (t) data (Figure 1, top) by using the following:

$$dX/dt = K_p(f/\bar{K}_{tn})^{1/2}(2R_d)^{1/2}(1 - X) \tag{12}$$

where f is initiator efficiency, R_d is the initiator decomposition rate which can be expressed as $K_d[I]_0e^{-K_dt}/(1 + \alpha X)$ where K_d (3.12×10^{-5}/sec for AIBN at 70 °C[1]) is the decomposition rate constant and α (−0.197 for PMMA–MMA system at 70 °C[6]) the volumetric expansion factor. Thus, we obtain $K_p(f/\bar{K}_{tn})^{1/2}$ vs X. Second, use eq 7 and assume that K_{fm}/K_p ($=3.4 \times 10^{-5}$ (ref 1)) and K_{td}/K_t ($=0.86$ (ref 16)) are constant to fit the accumulated number-average molecular weight ($\bar{\bar{M}}_n = X/(\int_0^X dX/\bar{M}_n)$, Figure 1, bottom); we have $K_p/(f\bar{K}_{tn})^{1/2}$ vs X. Third, extract f vs X (Figure 2) and $K_p^2/\bar{K}_{tn}$ vs X (Figure 3) from $K_p(f/\bar{K}_{tn})^{1/2}$ and $K_p/(f\bar{K}_{tn})^{1/2}$. As one can see, f shows a relatively small change up to a very high conversion ($X \approx 0.85$) and then falls dramatically. Simultaneously, $K_p^2/\bar{K}_{tn}$ also has a big change at the vicinity of $X \approx 0.85$. Take this X as a critical point and limit our discussions to the conversions <0.85 first. Assuming K_p is constant, we get $\bar{K}_{tn}$ vs X (Figure 4). Finally, use eq 8 and 9 to fit $\bar{\bar{M}}_w$ vs X ($\bar{\bar{M}}_w = (\int_0^X M_w\, dX)/X$) and $\bar{\bar{M}}_z$ vs X ($\bar{\bar{M}}_z = (1/\bar{\bar{M}}_w)(\int_0^X \bar{M}_z\bar{M}_w\, dX)/X$, Figure 1, bottom) and obtain $\bar{K}_{tw}$ and $\bar{K}_{tz}$, respectively (Figure 4).

The characteristic features of the dependence of these K_t's on conversion includes the following: (1) At low conversions, where termination is most likely segmental diffusion controlled, chain-length dependence is negligible, and only a single K_t is required to model molecular weight averages. (2) The onset of translational diffusion-controlled termination is experienced at lower conversions by the higher order $\bar{K}_t$'s. (3) The termination rate constants fall dramatically thereafter, and the termination is chain-length dependent at high conversions where macroradicals are entangled. (4) When polymer radicals are trapped (zero translational diffusion), a single K_t ($=zK_p[M]$, due to "propagation diffusion",[17] where z may be considered a constant) is in effect.

It should be pointed out that when one uses a single K_t in modeling by fitting the polymerization rate as in ref 1 and 2, one is effectively using $\bar{K}_{tn}$; therefore, one underestimates $\bar{M}_x$ ($x \geq w, z, \dots$). Figure 1, bottom, shows such underestimation. The errors are significant. Therefore, the use of different K_t averages for comprehensive modeling is recommended. However, for polymerizations where most of the polymer chains are produced by chain transfer to small molecules, the errors will not be so significant when $\bar{K}_{tn}$ is used to calculate $\bar{M}_w$, $\bar{M}_z$, ...

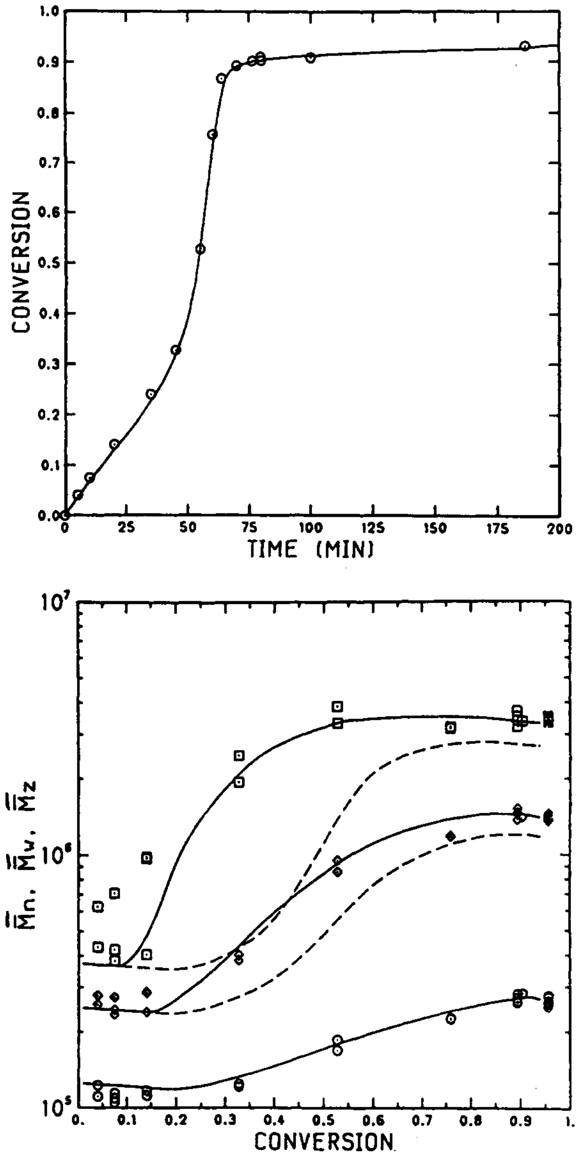

Figure 1. Top: empirical fitting of X vs t to experimental measurements. Bottom: empirical fittings of accumulated molecular weight average measurements (solid lines) and calculations results using $\bar{K}_{tn}$ for higher order molecular weight averages (dotted lines).

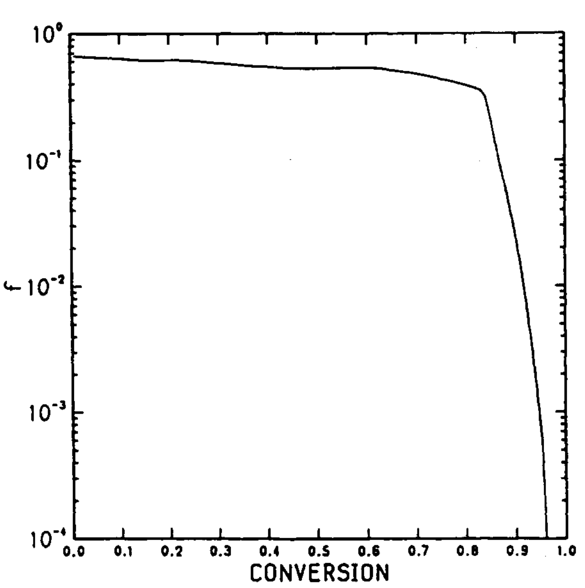

Figure 2. Extracted initiator efficiency, f vs X.

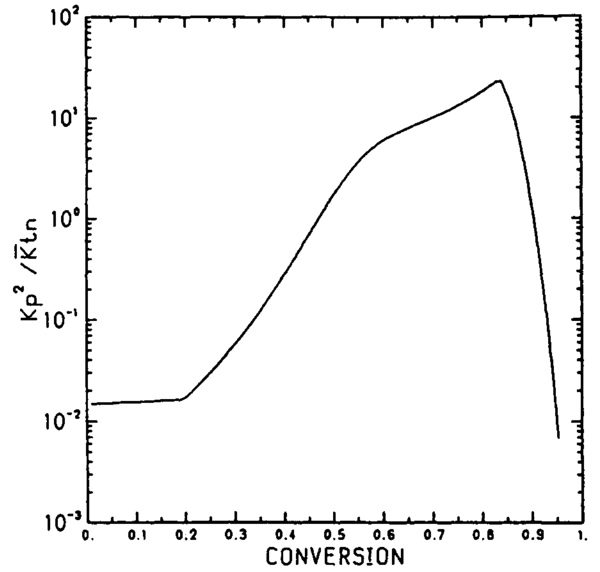

Figure 3. Extracted $K_p^2/\bar{K}_{tn}$ (L/(mol s)) vs X.

Mechanisms at Very High Conversions

In a free radical polymerization below the glass transition temperature T_{gp}, the reaction mechanisms at very high conversions can be very complex and to date remain largely unsolved due to the decrease in the diffusion coefficients of small molecules: primary radical and monomer. This decrease will have one or more of the following consequences: (1) decrease of initiator efficiency as shown in Figure 2; (2) propagation reaction becoming diffusion controlled; (3) radical pair formation. The decrease in initiator efficiency reduces the concentration of primary radicals significantly, and therefore we believe that primary radical termination is negligible.

An experimental phenomenon for such polymerizations is the reduction in conversion rate to almost zero even though appreciable monomer and initiator exist in the reacting mixture. A conventional explanation for this is that the propagation reactions become diffusion controlled. In the corresponding models, K_p is forced to decrease with conversion to reproduce the X vs t history. From Figure 3 and $\bar{K}_{tn} = zK_p[M]$ ($z \approx 28$ L/mol estimated at $X = 0.85$, where $K_p^2/\bar{K}_{tn} = 20$ L/(mol s); [M] = 1.5 mol/L, and K_p = 830 L/(mol s)[14]), K_p vs X (Figure 5) is extracted and shows a simultaneous fall with f. However, recent ESR measurements in corresponding emulsion polymerizations show that K_p falls at higher conversions.[10] Comparing the propagation mechanisms of emulsion polymerization with bulk polymerization at very high conversions, Russell et al.[7] argued that the K_p values for both cases should not be significantly different. In the model aspect, since the propagation reactions involve small monomer molecules, a reasonable model is the Smoluchowski expression:

$$\frac{1}{K_p} = \frac{1}{K_{p0}} + \frac{1}{4\pi N_{av} r_m D_m} \tag{13}$$

where D_m is monomer diffusivity, r_m is the Lennard-Jones diameter of monomer (=5.85 Å[13] for MMA), K_{p0} is the chemically controlled propagation rate constant (=830 L/(mol s)[14] for MMA–PMMA at 70 °C), and N_{av} is Avogadro's number (=6.023 × 10^{23}). Use a free volume model for D_m:[11] $D_m = D_{m0} \exp[-B_m(1/V_f - 1/V_{fm})]$; $V_f = \Phi_m V_{fm} + \Phi_p V_{fp}$, where D_{m0} is the self-diffusion coefficient of pure monomer (set equal to 10^{-5} cm^2/s for MMA at 70 °C), B_m is a critical free volume fraction for diffusion jumping, by using relative jumping segmental size of MMAs over PMMAs at the conversions concerned, 0.53,[12] Φ_m and Φ_p

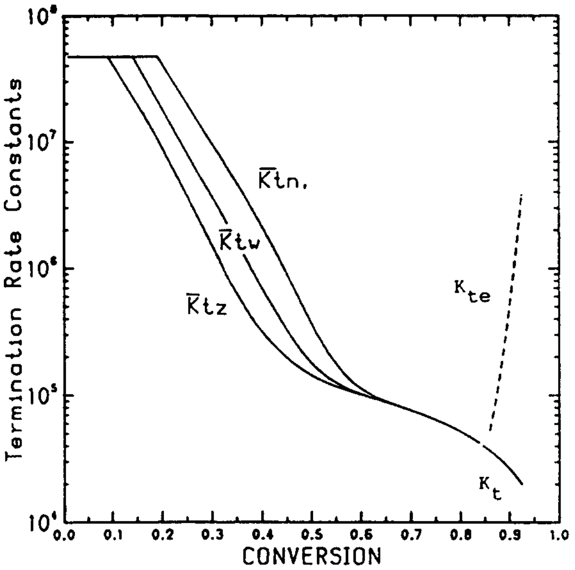

Figure 4. Extracted termination rate constants, $\bar{K}_t$'s (L/(mol s)) vs X. At very high conversions, the apparent termination rate constant K_{te} increases due to the radical pair effect (dotted line).

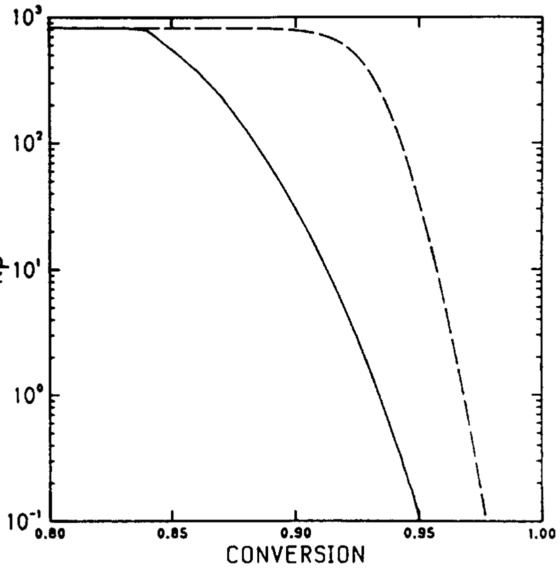

Figure 5. Extracted K_p (L/(mol s), assuming $K_t = zK_p[M]$; solid line) compared with calculated K_p (dotted line).

are monomer and polymer volume fractions, V_{fm} and V_{fp} are monomer and polymer free volumes ($V_{fm} = 0.1693$, $V_{fp} = 0.01485$ (ref 6) for MMA-PMMA at 70 °C) (therefore, $D_m \approx 10^{-20}$ cm^2/s when $X = 1$; this is likely the low limit value for D_m), and K_p is calculated as shown in Figure 5. The fall of the calculated K_p comes later than the experimentally extracted value obtained herein. Using "volume-swept-out" model and assuming that $D_m = D_s$, the polymer segmental diffusion coefficient, Soh and Sundberg[6] conclude that some other phenomena, not K_p, must be contributing to the reduction in polymerization rate at very high conversions.

Whether K_p falls later than or simultaneously with f should be tested by experimental measurement of final conversions, by using initiators with similar decomposition constants but very different molecular sizes (therefore, having very different diffusion coefficients). Since K_p and f involve different small molecules (monomer and primary radical, in general), we cannot expect them to fall simultaneously. In the cases when f falls first as discussed above, the polymers produced in the time interval between the fall in f and the later fall in K_p would have very high molecular weights. This should most affect high-order molecular weight averages. However, this has not been confirmed experimentally in polymerization of MMA. Therefore, either K_p and f fall at the same time, or there is some other phenomenon that accompanies the fall in f to reduce the molecular weights.

Let us examine the molecular processes involved in initiation. Following the decomposition of an initiator molecule, two primary radicals either diffuse apart from each other or recombine to form an inert molecule. Let us focus on the primary radicals which have escaped from the so-called cage. They diffuse further apart via Brownian motion and propagation. In a distance L, the radical chains will become large enough to be entangled with accumulated polymer chains and become trapped. Such trapped radicals then likely terminate with each other via "propagation–diffusion". According to Russell et al.,[7] L can be calculated from the following:

$$L = \left[\frac{6D_m}{K_p[M]}\sum_{n=1}^{j_c}(1/n) + j_c a^2\right]^{1/2} \qquad (14)$$

where a is the root-mean-square end-to-end distance per square root of the number of monomer units of the polymer (0.69 nm for PMMA[15]), j_c is the entanglement spacing of the polymer chains ($=j_{c0}/\Phi_p$, $j_{c0} = 200$ (ref 7) for PMMA). It is clear that at very high conversions when D_m decreases significantly, the two radicals initiated from the same initiator molecule cannot move far apart from each other and they are trapped. Therefore, radicals stay in pairs. Such radical pair formation will cause local radical concentration to increase and leave some reacting mass "black" (without radical centers). Let us define the space with radicals as an effective reaction volume fraction (V_e). As a first approximation

$$V_e = (\tfrac{4}{3}\pi L^3)(N_{av}[R^*]/2) \qquad (15)$$

where $(4\pi L^3/3)$ represents the volume occupied by one radical pair, and $N_{av}[R^*]/2$, the pair numbers in 1 L of reacting mass. It can be easily seen that when $V_e < 1$, the radical centers are not uniformly distributed in the reacting mass but rather stay in pairs though the initiator molecules are uniformly distributed. Therefore, local radical concentration can be written as $[R^*]_{loc} = (2/N_{av})/(4\pi L^3/3)$, which is equivalent to $[R^*]_{loc} = [R^*]/V_e$. To have a consistent termination rate expression ($R_t = K_{te}[R^*][R^*]$, instead of $K_t[R^*]_{loc}[R^*]_{loc}$), the termination rate constant ($K_t = zK_p[M]$, at very high conversions) should be modified as K_t/V_e, the apparent termination rate constant K_{te}. As shown in Figure 4, K_{te} has a dramatic increase while K_t decreases slowly according to $zK_p[M]$. The corresponding V_e is extracted as shown in Figure 6. The dotted line is calculated from eq 15 ($[R^*] = 3.5 \times 10^{-6}$ mol/L was used). As it can be seen, V_e depends on not only monomer but also initiator via radical concentration $[R^*]$.

Radical concentration measurement can play an important role in understanding free radical polymerization mechanisms. A proper model should give a valid prediction of $[R^*]$. Note that both the fall in f and the formation of radical pairs at very high conversions will reduce the radical concentration ($[R^*] = (fR_d/K_{te})^{1/2}$). Recent ESR studies[8] show that the radical concentration remains relatively constant rather than fall significantly with time during the final stages of polymerization. A possible explanation is that the reacting mass may become heterogeneous. Therefore, there exist two radical populations: those in the liquid state (13-line ESR spectra) are still active, and those (9-line spectra) in the solid state are

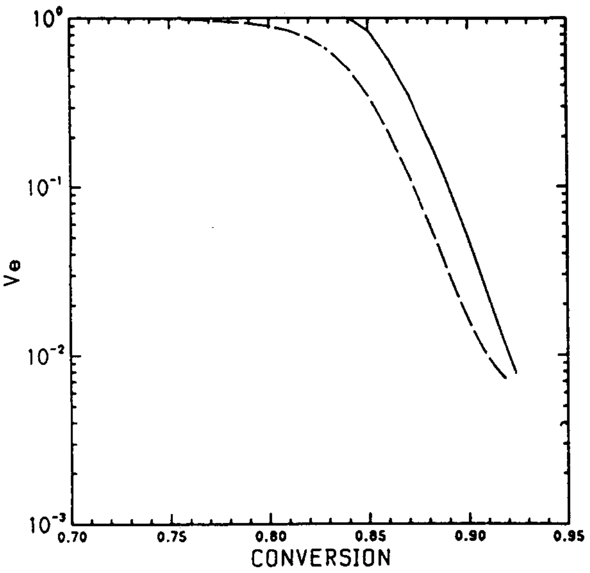

Figure 6. Effective volume fraction (V_e) vs X at high conversions, due to the radical pair effect: solid line, extracted; dotted line, calculated.

largely inactive. Such heterogeneity in the reacting mass will create some difficulties in kinetic analysis. One among the many others is that the propagation rate constant K_p measured by using ESR, i.e., $K_p = (dX/dt)/[R^*](1 - x)$, should be well defined in terms of the radical concentration, either the active radical concentration or the global one (active + inactive). The propagation rate at this stage is $R_p = (K_{p_{act}}[R^*]_{act} + K_{p_{ina}}[R^*]_{ina})[M]$, with $K_{p_{ina}} < K_{p_{act}}$.

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Appendix

The definition of the high-order average termination rate constants ($\bar{K}_{tn}$, $\bar{K}_{tw}$, $\bar{K}_{tz}$, ...) is inspired by the fact that, with no termination by combination, the following relations hold:

$$\bar{K}_{tw} = \sum_{r=1}^{\infty}\{K_t(r)\ r\Phi^*(r)\}/\sum_{r=1}^{\infty}\{r\Phi^*(r)\}$$

$$\bar{K}_{tz} = \sum_{r=1}^{\infty}\{K_t(r)\ r^2\Phi^*(r)\}/\sum_{r=1}^{\infty}\{r^2\Phi^*(r)\}$$

where $K_t(r)$ is the termination rate constant for macroradicals with chain length r:

$$K_t(r) = \sum_{i=1}^{\infty}\{K_t(r,i)\ \Phi^*(i)\}$$

The derivation using the method of moments is as follows:

Radical balances:

$$R^*_1:\quad R_I + K_{fm}[R^*][M] - K_p[M][R^*_1] - K_{fm}[M][R^*_1] - \sum_{i=1}^{\infty}\{K_t(i,1)[R_i][R^*_1]\} = 0$$

$$R^*_r:\quad K_p[M][R^*_{r-1}] - K_p[M][R^*_r] - K_{fm}[M][R^*_r] - \sum_{i=1}^{\infty}\{K_t(i,r)[R^*_i][R^*_r]\} = 0$$

$$r = 2, 3, 4, \ldots$$

Radical moments, $Y_k = \sum_{i=1}^{\infty}\{i^k[R^*_i]\}$:

$$Y_0:\quad R_I = Y_0^2\bar{K}_{tn} \qquad (Y_0 = [R^*] = (R_I/\bar{K}_{tn})^{1/2})$$

$$Y_1:\quad K_p[M]Y_0 = Y_1\{K_{fm}[M] + \bar{K}_{tw}Y_0\} \qquad (K_p[M]Y_0 \gg K_{fm}[M]Y_0, R_I)$$

$$Y_2:\quad 2K_pY_1[M] = Y_2\{K_{fm}[M] + \bar{K}_{tz}Y_0\} \qquad (Y_1 \gg Y_0)$$

$$Y_3:\quad 3K_pY_2[M] = Y_3\{K_{fm}[M] + \bar{K}_{tz+1}Y_0\} \qquad (Y_2 \gg Y_1)$$

Radical molecular weight averages:

$$\bar{M}_n^* = mY_1/Y_0 = m/\{\tau_w + \beta_w\}$$

$$\bar{M}_w^* = mY_2/Y_1 = 2m/\{\tau_z + \beta_z\}$$

$$\vdots$$

Obviously, the type of termination (disproportionation/combination) does not affect the distribution of macroradical chain lengths. But it does affect the distribution of the polymer chain lengths:

Polymer balances:

$$dP_r/dt = K_{fm}[M][R^*_r] + K_t(r)[R^*_r][R^*] + \tfrac{1}{2}\sum_{s=1}^{r=1}\{K_{tc}(s,r-s)[R^*_s][R^*_{r-s}]\} \qquad (r = 1, 2, 3, \ldots)$$

Polymer moments, $Q_k = \sum_{i=1}^{\infty}\{i^k[P_i]\}$:

$$dQ_0/dt = K_{fm}[M]Y_0 + \bar{K}_{tdn}Y_0^2 + \tfrac{1}{2}\bar{K}_{tcn}Y_0^2$$

$$dQ_1/dt = K_{fm}[M]Y_1 + \bar{K}_{tdw}Y_1Y_0 + \bar{K}_{tcw}Y_1Y_0$$

$$dQ_2/dt = K_{fm}[M]Y_2 + \bar{K}_{tdz}Y_2Y_0 + \bar{K}_{tcz}Y_2Y_0 + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\{K_{tc}(i,j)ij[R^*_i][R^*_j]\}$$

$$dQ_3/dt = K_pm[M]Y_3 + \bar{K}_{tdz+1}Y_3Y_0 + \bar{K}_{tcz+1}Y_3Y_0 + 3\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\{K_{tc}(i,j)i^2j[R^*_i][R^*_j]\}$$

Eliminating the moments of the macroradical distribution, one obtains

$$dQ_0/dt = K_{fm}[M]Y_0 + \bar{K}_{tdn}Y_0^2 + \tfrac{1}{2}\bar{K}_{tcn}Y_0^2$$

$$dQ_1/dt = K_p[M]Y_0$$

$$dQ_2/dt = 2K_p[M]Y_1 + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\{K_{tc}(i,j)ij[R^*_i][R^*_j]\}$$

$$dQ_3/dt = 3K_p[M]Y_2 + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\{K_{tc}(i,j)i^2j[R^*_i][R^*_j]\}$$

It is clear that with disproportionation only, i.e., $K_{td} = K_t$ or $K_{tc} = 0$, the above double summation terms disappear. Therefore, the instantaneous molecular weight averages of polymer are

$$\bar{M}_n = (dQ_1/dt)/(dQ_0/dt) = m/\tau_n$$

$$\bar{M}_w = (dQ_2/dt)/(dQ_1/dt) = 2m/\tau_w$$

$$\bar{M}_z = (dQ_3/dt)/(dQ_2/dt) = 3m/\tau_z$$

It is quite clear that the average termination constants defined and used herein are all equivalent to those defined by Boots.[18] However, when termination by combination is significant, $\bar{K}_{tx}$ ($x = w, z, \ldots$) are complex functions of various averages of $K_t(i,j)$.

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Modeling of Network Formation in Free Radical Polymerization†

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ABSTRACT: Kinetic models for network formation in free radical polymerization based on the pseudokinetic rate constant method are proposed for both pre- and postgelation periods. Network formation in free radical polymerization is a nonequilibrium process; namely, it is kinetically controlled and therefore it is necessary to consider the history of the generated network structure. The present kinetic models consider all of the important reactions in free radical polymerization and are therefore quite general and realistic and capable of accounting for reaction types such as primary and secondary cyclization. These kinetic approaches provide greater insight into the phenomena of network formation in free radical polymerization.

Introduction

Though various models have been proposed for polymeric gelation since the pioneering work of Flory[1] and Stockmayer,[2] it is possible to classify these models mainly into two categories. One is called the classical theory, which is based on the Flory/Stockmayer treelike model and includes the cascade theory developed by Gordon[3] and the Macosko–Miller model[4] using conditional probabilities. These models are fully equivalent and enjoy the simplicity of a mean-field theory. Another type is called the percolation theory,[5-9] which is considered to be equivalent to a non-mean-field theory. Though the percolation theory may possess potential universality, it is still too immature to describe the course of network formation and its predictions are just qualitatively acceptable. At present, it is still considered controversial and unclear which theory is more suitable for polymeric gelation.

Generally these statistical theories give rather satisfactory predictions for an *f*-functional polycondensation system, but their predictions are quite often unsatisfactory for a free radical polymerization system. Free radical polymerization is kinetically controlled and involves various elementary reactions. A realistic model for network formation in free radical polymerization must account for the specific reaction mechanism of cross-linking; namely, a cross-linkage is formed only through a radical center whose concentration is very low and whose lifetime is very short. Recently, a new model for gelation in free radical polymerization based on the pseudokinetic rate constant method was proposed.[10] This model considers all of the important reactions in free radical polymerization. In principle, it belongs to the classical theory, but it is more general than the former classical models for free radical polymerization systems. Especially, the concept of pseudokinetic rate constants in which the treatment of a multicomponent polymerization reduces to that of a homopolymerization is useful.

In this paper the pseudokinetic rate constant method is extensively applied and models for both pre- and postgelation period are illustrated.

Pseudokinetic Rate Constant Method

The pseudokinetic rate constant method for multicomponent polymerization has been applied in some copolymerization studies,[11-13] and its derivation and specific approximations have been made clear.[10] In this section let us review the outline of this method.

Linear Copolymer. We now assume that the terminal model for copolymerization is applicable, and let us consider the copolymerization of M_1 and M_2 whose elementary reactions are shown below.

Initiation

$$I \rightarrow 2R^{\bullet}_{in} \qquad (k_d) \tag{1a}$$

$$R^{\bullet}_{in} + M_1 \rightarrow R^{\bullet}_{1,0,1} \qquad (k_1) \tag{1b}$$

$$R^{\bullet}_{in} + M_2 \rightarrow R^{\bullet}_{0,1,2} \qquad (k_2) \tag{1c}$$

Propagation

$$R^{\bullet}_{m,n,1} + M_1 \rightarrow R^{\bullet}_{m+1,n,1} \qquad (k_{11}) \tag{2a}$$

$$R^{\bullet}_{m,n,1} + M_2 \rightarrow R^{\bullet}_{m,n+1,2} \qquad (k_{12}) \tag{2b}$$

$$R^{\bullet}_{m,n,2} + M_1 \rightarrow R^{\bullet}_{m+1,n,1} \qquad (k_{21}) \tag{2c}$$

$$R^{\bullet}_{m,n,2} + M_2 \rightarrow R^{\bullet}_{m,n+1,2} \qquad (k_{22}) \tag{2d}$$

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