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Modeling Insight into the Diffusion-Limited Cause of the Gel Effect in Free Radical Polymerization

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ABSTRACT: The molecular-level cause of the gel effect in free radical polymerization, associated with a decrease in the termination rate parameter with increasing conversion, is studied by experimental and modeling approaches. The predictive Vrentas−Duda free volume theory serves as a basis for modeling as it handles quantitatively the temperature and polymer concentration dependencies of monomer diffusion. The polymer concentration (c) dependencies of various diffusional processes fit an expression of the form $[D_m(c)/D_m(0)]^{\xi_{x,m}}$, where D_m is the monomer diffusion coefficient and $\xi_{x,m}$ expresses the power-law dependence of the diffusional process of interest (x) relative to that of monomer (m). Relevant values of $\xi_{x,m}$ vary from ∼ 0.8 for segmental mobility, to ∼1−2 or 3 for oligomeric diffusion, to ∼ 3.0−3.5 for unentangled polymer diffusion, and to ∼ 9.5−10 for entangled polymer diffusion. If the very high conversion regime, where issues unrelated to the origin of the gel effect add unnecessary complications, is avoided, the modeling of conversion−time data requires only that the polymer concentration dependence of the termination reaction, caused by a diffusional process cited above, must be taken into account. Comparison of $\xi_{x,m}$ values needed to fit various methyl methacrylate conversion−time data (values of 1.1−5.0 were required, increasing with increasing molecular weight of the polymer produced) with those needed for different diffusion types indicates that termination is governed by diffusion of the shortest radical chains present in significant number. In contrast to some "short−long" termination theories that commonly distinguish "short" and "long" as unentangled and entangled, this study finds that entanglements are irrelevant in distinguishing "short" from "long". Styrene polymerizations yield $\xi_{x,m}$ values substantially below 1. This is ascribed to chain transfer, supported by the fact that methyl methacrylate systems with chain transfer agent show similar suppressed gel effect behavior. The very low $\xi_{x,m}$ values result in part from the reduced polymer concentration dependence of k_t associated with the highly mobile short radical chains obtained in chain transfer reactions. While systems with significant chain transfer must be studied further, this modeling approach should serve as a robust basis for a more complete description of termination under various conditions.

Introduction

The gel or Trommsdorff[1−4] effect (autoacceleration) in free radical polymerization has been studied for decades. For the past 20−25 years, most attempts to explain this effect have fallen into one of two categories: entanglement pictures and free volume pictures. However, neither is adequate to describe the gel effect completely. The theory that the onset of entanglements[5,6] causes the gel effect is incorrect as it fails to predict trends concerning the effects of temperature, polymer concentration, and molecular weight on the gel effect onset conversion, X_{crit}.[7] The competing free volume theory[8,9] fares better when critically tested;[10] however, it cannot by itself be used to predict accurately conversion−time results for a broad range of conditions and is not a molecular-level theory as it does not account for radical chain length effects in the rate of termination. What is needed is more insight into the molecular-level processes controlling termination.

An approach to this problem is to compare data on the termination rate parameter, k_t, with diffusion data in order to determine which type of diffusion controls termination. Attempts have been made to compare diffusion data with measured k_t values.[11] However, given the difficulties with measuring k_t directly,[12,13] the approach taken here will be to infer the change in k_t with concentration from conversion−time data and compare this to a free volume representation of the concentration dependence of diffusion briefly outlined previously.[14] This method, which entails the modeling of polymerization through intermediate conversion via a free volume framework, provides insight into the process controlling termination under various conditions without employing unnecessary assumptions that lead to the overuse of adjustable curve-fitting parameters.

Preliminary results[14] using this approach show a trend in methyl methacrylate (MMA) polymerization for a stronger concentration dependence for k_t (relative to monomer diffusion) when a higher molecular weight (MW) polymer is formed using low reaction temperature. Thus, either temperature or MW (or some combination) has a serious impact on the process controlling termination. While it is appealing to postulate that molecular weight is the important factor, a study decoupling temperature and molecular weight effects is needed. This work examines this issue and others, offering an in-depth study of the molecular-level cause of the gel effect.

Modeling Explanation

The task is to model the polymerization using various assumptions regarding the physical process controlling k_t and decide, from comparison of predictions with experimental data, which process is most likely to be

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important. Examining the mechanism for free radical polymerization[7,9] consisting of initiation, propagation, and termination and performing species balances on concentrations of monomer, M, initiator, I, radical, R, growing chain of length (degree of polymerization) 1, P_1, and growing chain of length n, P_n, the following equations result (with V as system volume):

$$\frac{1}{V}\frac{\mathrm{d}(MV)}{\mathrm{d}t} = -k_\mathrm{p}M\sum_{n=1}^{\infty}P_n \qquad (1)$$

$$\frac{1}{V}\frac{\mathrm{d}(RV)}{\mathrm{d}t} = 2fk_\mathrm{d}I - k_\mathrm{fast}RM \qquad (2)$$

$$\frac{1}{V}\frac{\mathrm{d}(IV)}{\mathrm{d}t} = -k_\mathrm{d}I \qquad (3)$$

$$\frac{1}{V}\frac{\mathrm{d}(P_1V)}{\mathrm{d}t} = k_\mathrm{fast}RM - k_\mathrm{p}P_1M - P_1\sum_{n=1}^{\infty}k_tP_n \qquad (4)$$

$$\frac{1}{V}\frac{\mathrm{d}(P_nV)}{\mathrm{d}t} = -k_\mathrm{p}M(P_{n-1} - P_n) - P_n\sum_{j=1}^{\infty}k_tP_j \qquad (5)$$

These equations reduce to[9]

$$\frac{\mathrm{d}I}{\mathrm{d}t} = -k_\mathrm{d}I\,\frac{\epsilon I}{1+\epsilon X}\lambda_0(1-X)k_\mathrm{p} \qquad (6)$$

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k_\mathrm{p}(1-X)\lambda_0 \qquad (7)$$

$$\frac{\mathrm{d}\lambda_0}{\mathrm{d}t} = -\frac{{\lambda_0}^2}{1+\epsilon X}(1-X)k_\mathrm{p} + 2fk_\mathrm{d}I - k_\mathrm{t}{\lambda_0}^2 \qquad (8)$$

where t is polymerization time, ϵ is a volume contraction factor defined as $\epsilon = (d_\mathrm{m} - d_\mathrm{p})/d_\mathrm{p}$ (where d_m and d_p are monomer and polymer densities, respectively), X is the fractional monomer conversion, k_d, k_fast, k_p, and k_t are rate parameters for initiator decomposition, fast radical reaction with monomer (completing the initiation step), propagation, and termination, respectively, f is the initiator efficiency, and λ_o is the zeroth moment of the growing radical distribution, equivalent to the total number of active chains in the system:

$$\lambda_0 = \sum_{n=1}^{\infty}P_n \qquad (9)$$

These equations are general, employing no assumptions regarding the physical processes controlling the reactions involved. (However, it must be noted that eq 8 provides only for an "averaged" k_t rather than individual termination rate parameters specifically related to each reaction of radical chains of lengths i and j.) Thus, with appropriate information about the initial values of the rate parameters and their dependencies on system conditions, eqs 6−8 may be solved simultaneously using numerical techniques to provide predicted conversion−time results. The problem is in handling rate parameter variation. However, this is not as difficult as often assumed. In terms of conversion, the parameters act as one combined parameter, $K = k_\mathrm{p}(fk_\mathrm{d}/k_\mathrm{t})^{1/2}$. For the purpose of exploring the cause of the gel effect, the initial value of K may be determined by fitting low conversion data. The parameters k_p, f, and k_d are not significant functions of molecular weight and are thought to remain roughly constant with concentration until rather high conversions where the system begins to exhibit glassy effects.[15−17] (The possible exception, f, may change by a factor of ~2 prior to the onset of the glass effect.[16,17]) Thus, nearly all of the change in K is due to variation in k_t over this conversion range. If modeling is restricted to conversions prior to such glassy effects, the gel effect may still be examined, but only variations in k_t need be considered.

This provides an important contrast with previous models seeking to handle all details of polymerization from low conversion through the gel effect and on to high conversion where glassy effects are important, leading to a complexity requiring the use of many adjustable parameters in order to fit data effectively. Thus, although a number of models[5,9,18−22] obtained some success in fitting a range of polymerization data, often little insight into the molecular-scale cause of the gel effect was gained due to uncertainties in the accuracy or interpretation of the many adjustable parameters. In contrast, the modeling efforts employed here are focused on the *cause* of the gel effect. By avoidance of high conversions where glass and cage effects as well as possible system heterogeneity become important, changes in the polymerization rate can be easily associated with changes in k_t.

This leaves the problem of the MW and concentration dependencies of k_t. Although it is accepted that k_t is related to diffusive polymer motion, it is not clear which type of diffusion is most important. However, while k_t often appears to have a slight dependence on MW,[23−28] this is irrelevant to the *cause of the onset* of the gel effect. If k_t depends on MW, this would certainly affect the initial value of k_t (value at initial conversion), with a higher MW resulting in a lower initial k_t. However, only the *change* in k_t with conversion, not the *magnitude* of k_t, affects the gel effect onset, as the gel effect is simply a result of termination slowing from its initial rate.

This does not mean that MW has no potential effect; in fact, if translational diffusion controls k_t, MW should play a role in determining the gel effect onset, albeit indirectly. This is because the concentration dependence of polymer translational diffusion depends on MW. Diffusion of very long, entangled chains has a stronger concentration dependence than that of unentangled chains. Also, as monomer diffusion has a far weaker concentration dependence than that of polymer diffusion, oligomers must diffuse with a concentration dependence weaker than that of polymers. Thus, formation of higher MW chains may lead to an earlier gel effect, but only because it would cause a stronger concentration dependence of termination controlled by translational diffusion.

This implies that by taking a simple approach of modeling through the gel effect onset but not to very high conversion where other effects are important, one needs only to account for the concentration dependence of k_t. Thus, a function representing the concentration dependence of the various types of diffusion is required. As free volume has been used in the past[9,29−33] to model gel effect systems and as we have shown[10] that free volume reasonably handles the effect of temperature on X_crit, this is a natural framework with which to attempt to handle the concentration dependence of diffusion. We use the Vrentas−Duda predictive free volume theory[34,35] in which the solvent self-diffusion coefficient for a solvent-polymer system is given by

$$D_s = D_{s0} \exp\left\{\frac{-\gamma(\omega_s \hat{V}_s^* + \omega_p \xi_{s,p} \hat{V}_p^*)}{\hat{V}_{FH}}\right\} \tag{10}$$

where $\hat{V}_s^*$ and $\hat{V}_p^*$ are the specific critical hole free volume required for a diffusive jump by solvent and polymer, respectively, ω_s is the weight fraction of solvent, ω_p is the weight fraction of polymer, T is temperature, $\hat{V}_{FH}$ is the average hole free volume per gram of solution, γ is an overlap factor, introduced because the same free volume is available to more than one molecule, and $\xi_{s,p}$ is the ratio of the jumping-unit size of solvent to that of polymer. $\hat{V}_{FH}$ is given by

$$\hat{V}_{FH} = \omega_s K_{1s}(K_{2s} - T_{gs} + T) + \omega_p K_{1p}(K_{2p} - T_{gp} + T) \tag{11}$$

where K_{1s} (K_{1p}) and K_{2s} (K_{2p}) are free-volume parameters for the solvent (polymer), and T_{gs} and T_{gp} are the glass transition temperatures of solvent and polymer, respectively. This expression has been used successfully for various systems,[35−38] and recommended parameter values or estimation procedures based on such data have been tabulated for numerous solvents and polymers.[35]

The starting point to our approach is to recognize that studies[37−41] on ternary polymer−solvent-probe systems have indicated that the polymer concentration dependence of probe diffusion (D_{probe}) relative to that of solvent self-diffusion (D_s) may be represented in the following manner:

$$D_{probe}(c)/D_{probe}(0) = [D_s(c)/D_s(0)]^{\xi_{probe,s}} \tag{12}$$

where $\xi_{probe,s}$ may be interpreted within the Vrentas−Duda theory as the ratio of the "jumping-unit size" of probe to that of solvent. A detailed study[38] on the effect of probe size on probe diffusion in polymer solutions found that diffusion of larger probes has a stronger polymer concentration dependence than that of smaller probes. Quantitatively, variation in molar volume by a factor of ∼7 resulted in a change in $\xi_{probe,s}$ from ∼1 to ∼1.7. In the context of free volume theory, this can be interpreted to indicate that larger molecules require more cooperative motion (or a larger void to form) in order to diffuse, although the relationship is not a 1:1 correspondence with molecular size.

Thus, $\xi_{probe,s}$ expresses the differences in the concentration dependence of diffusion of various species; i.e., by reporting a reference with a known concentration dependence of diffusion and a list of probes and corresponding $\xi_{probe,s}$ values, one defines the concentration dependence of diffusion of all probes listed. If such a method can also define the concentration dependencies of the range of diffusion types that may affect termination, this would facilitate modeling the gel effect, as only one parameter would be needed to handle the concentration dependence of k_t.[42]

Types of diffusion possibly relevant to termination are polymer segmental diffusion[43] and translational diffusion over the range of growing chain lengths in a free radical polymerization: monomer and primary radicals, oligomers, unentangled chains, and entangled chains. As these species are based on repeat unit structures, it is reasonable to expect that the concentration dependence of their diffusion may be related to that of monomer diffusion, with those processes involving greater cooperative motion and hydrodynamic interactions having a stronger dependence on polymer concentration. We postulate that a form similar to eq 12 may fit their concentration dependencies:

$$D_x(c)/D_x(0) = [D_m(c)/D_m(0)]^{\xi_{x,m}} \tag{13}$$

where "m" signifies monomer and "x" refers to the species and process of interest. With this formulation, only the concentration dependence of monomer and the $\xi_{x,m}$ parameter would be required to define the concentration dependence of the process of interest.

It remains to be verified that such an approach is feasible. Data on the concentration dependence of such diffusional processes are scarce, and some may not be reliable at higher concentrations. However, limited reliable data do exist. Figure 1 shows three sets of poly(methyl methacrylate) (PMMA) translational diffusion data[11] in PMMA solutions, an entangled case (330k PMMA diffusing in a matrix of 330k PMMA) and two unentangled cases (9k PMMA diffusing in a matrix of

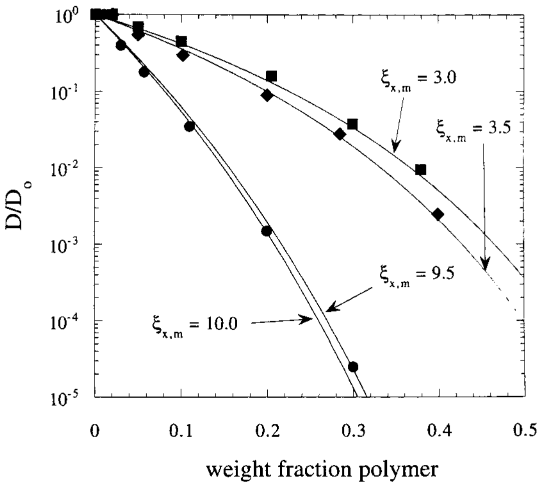

Figure 1. Comparison of experimental[11] concentration dependence of PMMA translational diffusion in solution (D/D_0 is a normalization to the value at zero PMMA concentration) with simulation using different $\xi_{x,m}$ values (see eq 13). Three experimental systems were considered: two unentangled cases, (■) diffusion of 330k PMMA in a 9k PMMA matrix and (◆) diffusion of 9k PMMA in a 330k PMMA matrix, and an entangled case, (●) diffusion of 330k PMMA in a 330k PMMA matrix.

Table 1. Free Volume Parameters for the Model

		ref
	PMMA−MMA System	
$\hat{V}_s^*$ (cm^3/g)	0.87	73
$\hat{V}_p^*$ (cm^3/g)	0.788	35
K_{1s}/γ (cm^3/gK)	7.0×10^{-4}	fit from ref 74
K_{1p}/γ (cm^3/gK)	3.05×10^{-4}	35
$K_{2s} - T_{gs}$ (K)	−32.07	fit from ref 74
$K_{2p} - T_{gp}$ (K)	−301	35
$\xi_{s,p}$	0.59	35
	PS−Styrene System	
$\hat{V}_s^*$ (cm^3/g)	0.846	75
$\hat{V}_s^*$ (cm^3/g)	0.85	32
K_{1s}/γ (cm^3/gK)	8.01×10^{-4}	fit from ref 76
K_{1p}/γ (cm^3/gK)	5.82×10^{-4}	35
$K_{2s} - T_{gs}$ (K)	−41.19	fit from ref 76
$K_{2p} - T_{gp}$ (K)	−327	35
$\xi_{s,p}$	0.634	35

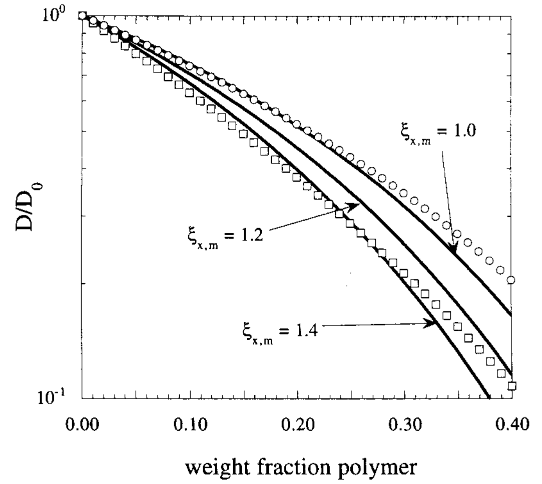

Figure 2. Comparison of experimental[48] concentration dependence of polystyrene oligomer diffusion in solution with benzene at 25 °C (D/D_0 is a normalization to the value at zero polystyrene concentration) with simulation (done as a part of this work, using different $\xi_{x,m}$ values in eq 13). Data for two chain lengths are shown: (○) $N = 2$, and (□) $N = 5$. (Note that the symbols do not represent actual data points, but rather a best fit presented in ref 48.)

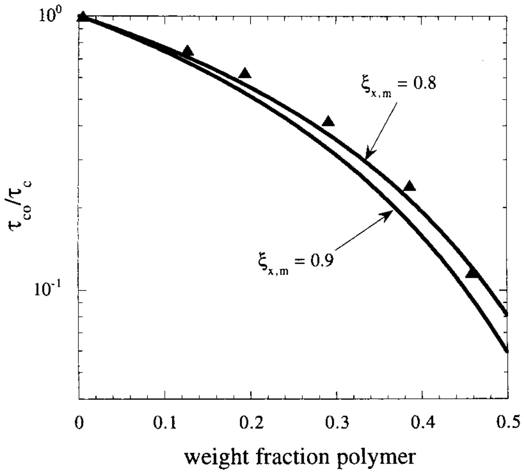

Figure 3. Comparison of experimental[49] concentration dependence of polystyrene segmental diffusion (▲) in solution with THF at 25 °C (τ_{c0}/τ_c is a normalization of the inverse rotational correlation time to its value at zero PS concentration) with simulation (using different $\xi_{x,m}$ values in eq 13).

Table 2. Kinetic Parameters Used in the Free Radical Polymerization Model

		ref
	PMMA	
k_p (L/mol min)	$2.95 \times 10^7 \exp\{-2191/T\ (\mathrm{K})\}$	77
k_d (BPO) (min^{-1})	$3.32 \times 10^{17} \exp\{-16397/T\ (\mathrm{K})\}$	78
k_d (AIBN) (min^{-1})	$6.32 \times 10^{16} \exp\{-15.43 \times 10^3/T\ (\mathrm{K})\}$	9
ρ_m (g/mL)	$0.973 - 1.164 \times 10^{-3}\{T\ (\mathrm{K}) - 273\}$	9
ρ_p (g/mL)	1.20	9
	Polystyrene	
k_p (L/mol min)	$6.54 \times 10^8 \exp\{-3549/T\ (\mathrm{K})\}$	77
k_d (BPO) (min^{-1})	$3.32 \times 10^{17} \exp\{-16397/T(\mathrm{K})\}$	78
ρ_m (g/mL)	$0.9236 - 0.887 \times 10^{-3}\{T\ (°\mathrm{C})\}$	30
ρ_p (g/mL)	$\rho_m(1 + \epsilon)$ where $\epsilon = 0.137 + 4.4 \times 10^{-4}T\ (°\mathrm{C})$[79]	30

330k PMMA, and 330k PMMA diffusing in a matrix of 9k PMMA). To fit these data to eq 13, free volume parameters for the MMA–toluene–PMMA system were obtained. (See Table 1.) Using these parameters, the unentangled chain diffusion data are fit by $\xi_{x,m} = 3.0$–3.5 while the entangled chain diffusion data are fit by $\xi_{x,m} = 9.5$–10. This indicates the strength of the concentration dependence, relative to monomer diffusion, of these types of polymer diffusion.

Another process potentially important to termination is oligomer translational diffusion. The idea of short–long termination[24,44–47] indicates that k_t may be controlled by diffusion of the shortest growing species present in significant number. To test this, the concentration dependence of such diffusion data must be examined or inferred. The concentration dependence of oligomer diffusion may be expected to be intermediate between that of monomer diffusion and that of unentangled chain diffusion, leading to a predicted $\xi_{x,m}$ value in the range of ~1 to ~3. Although oligomer diffusion data are very rare, Figure 2 shows such data[48] for two styrene oligomers. (The symbols are not actual data but calculations based on the reported best fit to the data.) These data are represented fairly well by $\xi_{x,m}$ values of ~1.0 and ~1.4, within the expected range.

The final process to examine is segmental diffusion. Figure 3 shows data[49] on the concentration dependence of polystyrene segmental mobility in polystyrene-tetrahydrofuran (THF) solutions. These data are fit fairly well by $\xi_{x,m} \approx 0.8$, indicating a concentration dependence close to that of monomer diffusion and much weaker than that of polymer diffusion. While this result is strictly for interior chain segmental mobility rather than chain end segmental mobility,[43] the two are expected to be similar and to have concentration dependencies close to that of monomer diffusion.

These results show that eq 13 is an effective form with which to express the concentration dependencies of the types of diffusion thought relevant to termination. Moreover, as termination is diffusion-limited, k_t should be proportional to the diffusion coefficient of the process controlling termination, meaning the concentration dependence of k_t may be modeled in this manner:

$$k_t(c)/k_t(0) = D_x(c)/D_x(0) = [D_m(c)/D_m(0)]^{\xi_{x,m}} \qquad (14)$$

With this formulation, $\xi_{x,m}$ may be varied according to the diffusional process of interest to represent the concentration dependence of k_t, assuming that termination is controlled by that process. The $\xi_{x,m}$ value yielding the best fit to conversion–time data then indicates the process relevant to termination for that system, as the various processes have different concentration dependencies.

To summarize, eqs 6–8 are solved simultaneously via a Runga–Kutta method, with only a concentration dependence of k_t. Initial values of the effective rate parameter, $K = k_p(k_d f/k_t)^{1/2}$, are fit from low conversion data (fractional conversion < 0.10). (Literature values of all parameters except k_t are used in the model, and the initial value of k_t is fit from low conversion data; this is equivalent to fitting for an initial value of K. See Table 2 for parameter values.) With K values found, simulations are done for various $\xi_{x,m}$ values, using eq 14 for the concentration dependence of k_t and eqs 10 and 11 for the concentration dependence of monomer diffusion. (See Table 1 for values of free volume parameters.) The simulations providing the best observed fits are reported.

The key to this procedure is comparing the value of $\xi_{x,m}$ needed to give the best fit to the conversion–time data with the analogous value needed to fit the concen-

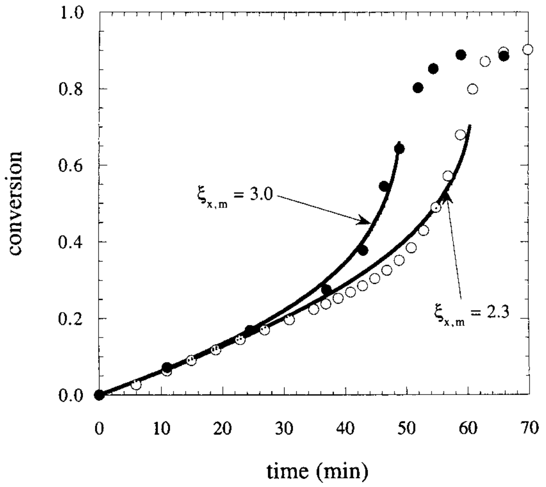

Figure 4. Comparison of simulation with experiment for the same MMA polymerization (70 °C, 0.50 wt % AIBN) carried out via two methods having different heat transfer characteristics: (●) polymerization done via the "ampule" method, which results in a temperature rise during the gel effect, and (○) polymerization done via DSC, which results in an isothermal experiment. Modeling results are represented by the solid lines, with the arrows indicating the $\xi_{x,m}$ values used in each simulation. The initial k_t value used is 4.42 × 10^9 L/mol min.[81]

tration dependence of the various types of diffusion. For instance, $\xi_{x,m} = 1.0$ would suggest that either segmental diffusion or translational diffusion of small molecules or very short oligomers likely controls termination, as these processes have roughly this concentration dependence. If $\xi_{x,m} \approx 3.0$ provides the best fit, then this would suggest that translational diffusion of unentangled (but not oligomeric) chains likely controls termination. Finally, if $\xi_{x,m} \approx 6.0$ or higher fits the conversion–time data, then entangled chain translational diffusion is likely becoming important.

Experimental Section

Styrene and MMA (99% purity, Aldrich) were purified and dried by mixing with commercial inhibitor remover replacement packing and calcium hydride for several hours, and then filtering. The initiators 2,2-azobisisobutyronitrile (AIBN) (Pfaltz and Bauer) and benzoyl peroxide (BPO) (97% purity, Aldrich) were used as received. Free radical polymerization was performed using differential scanning calorimetry (DSC)[10,50,51] or the "ampule"[7,52] method. In the ampule reactions, 15 mL test tubes were used, with about 5 mL of monomer in each. Molecular weight characterization was done by gel permeation chromatography (GPC) using tetrahydrofuran as solvent and monodisperse polystyrene (PS) and PMMA standards for calibration.

Results and Discussion

A. Methyl Methacrylate Polymerization. With the model established and justified, it may now be used to explore how well it can fit conversion–time data and what information may be gained about the molecular-scale process likely controlling termination for a range of systems. Figure 4 shows two important points related to the modeling: the accuracy of the fit, and the importance of using data taken isothermally. The data are for MMA polymerization at 70 °C with 0.50 wt % AIBN as initiator, using the ampule and DSC methods. (The DSC data were taken under essentially isothermal conditions, but the ampule reaction had a significant temperature rise[53] during the gel effect.) Included in this plot are the best-fit simulations for each data set using the model described above. (The initial k_t values used in this and all other simulations herein are given in the respective figure captions.[54]) An important point arising from inspection of Figure 4 is that, despite the simplicity of the model, it indeed provides a respectable fit to the conversion–time data (through intermediate conversions), given an appropriate choice of $\xi_{x,m}$. A second point is that the effect of using nonisothermal data[50,53] (and assuming the data are from an isothermal reaction) is to overestimate the $\xi_{x,m}$ value needed to fit data. Here, isothermal data are fit with $\xi_{x,m} \approx 2.3$ while nonisothermal data are fit with $\xi_{x,m} \approx 3.0$. This illustrates that modeling of nonisothermal data inevitably results in the conclusion that k_t has a stronger concentration dependence than is truly the case. Unfortunately, this problem has affected some of the modeling literature in this area.

It should be noted that the $\xi_{x,m}$ values reported herein as providing the best fit are really estimates to some degree. A range of values can approximately fit the data, and no attempt is made to provide any least-squares analysis of the relative quality of the fits. This is beyond the scope of the present study as all that is sought is an indication of the process controlling termination. As diffusion data may also be fit by a range of $\xi_{x,m}$ values, and the fits to the conversion–time or the diffusion data are by no means perfect, an estimate of the range of $\xi_{x,m}$ values needed in each case is all that is needed to accomplish the present goal. Figure 4 provides an indication of the effect on the simulations of the variation of $\xi_{x,m}$ from 2.3 to 3.0, showing that the fitting procedure is sensitive to these types of variations; certainly the ampule data could not be fit by $\xi_{x,m} = 2.3$. Subsequent MMA modeling results will show simulations for three $\xi_{x,m}$ values per system to provide an indication of the range of values that may fit the data. Given this and the fact that there is also a degree of uncertainty in the appropriate initial k_t value to employ, the $\xi_{x,m}$ values providing the best fit to the data should be considered to have a maximum uncertainty of ±0.2.

As indicated before, previous work has dealt with a range of systems for which both molecular weight and temperature were varied. However, these effects must be decoupled. Two issues will be explored, the effect of temperature independent of molecular weight, and the effect of molecular weight independent of temperature. The first is the more difficult of the two, as varying temperature while maintaining a constant molecular weight is only possible over a certain range of conditions. Fortunately, this has already been done[10] for MMA over a temperature range from 40 to 85 °C by varying the initiator concentration with the temperature. Modeling these cases provides a test of whether temperature alone has a significant impact on the $\xi_{x,m}$ value needed to fit the data. Two of the five cases considered are shown in Figures 5 and 6, and the conditions, molecular weight values, and $\xi_{x,m}$ values needed to fit the data for these systems with BPO as the initiator are summarized in Table 3, along with subsequent MMA results. At the lowest temperature considered, 40 °C (using 2.8 wt % BPO as initiator), $\xi_{x,m} \approx 2.9$ provides the best fit to the data. At 50 °C with 1.1 wt % BPO, a value of $\xi_{x,m} \approx 2.7$ offers the best fit. The 60 °C results using 0.55 wt % BPO are modeled in Figure 5, with the best fit given by $\xi_{x,m} \approx 3.0$. Figure 6 indicates that $\xi_{x,m} \approx 3.3$ fits the 75 °C, 0.10 wt % BPO data. Finally, the results at the highest temperature, 85 °C with 0.030 wt % BPO, are fit by $\xi_{x,m} \approx 3.5$.

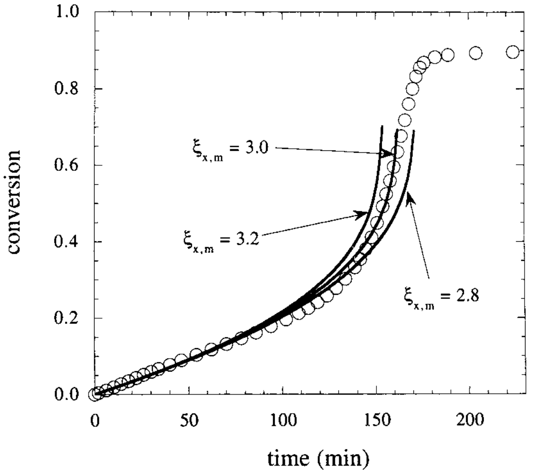

Figure 5. Comparison of simulation with experiment for MMA polymerization at 60 °C with 0.55 wt % BPO (DSC method). Open circles represent experimental data while solid lines represent modeling results. Simulations were carried out with the $\xi_{x,m}$ values indicated by the arrows and an initial k_t value of 2.14×10^9 L/mol min.[81]

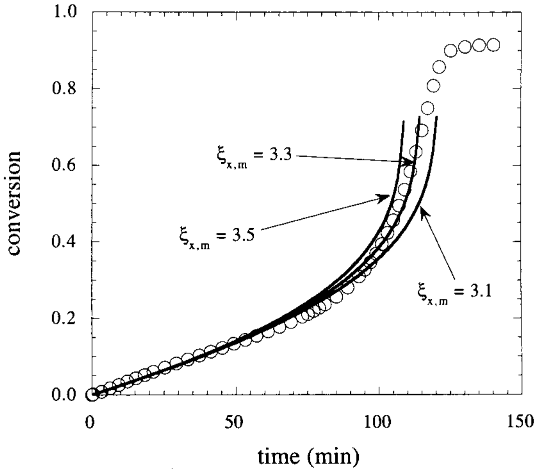

Figure 6. Comparison of simulation with experiment for MMA polymerization at 75 °C with 0.10 wt % BPO (DSC method). Open circles represent experimental data while solid lines represent modeling results. Simulations were carried out with the $\xi_{x,m}$ values indicated by the arrows and an initial k_t value of 2.67×10^9 L/mol min.[81]

These results show that temperature has little or no intrinsic effect on the concentration dependence of k_t, beyond the temperature dependence of monomer diffusion,[56] at the temperature of interest. (The concentration dependence of k_t *will* depend on polymerization temperature, given that monomer diffusion itself is a strong function of temperature.[56] However, by comparison of $\xi_{x,m}$ values needed to fit data, the concentration dependence of k_t is inherently being compared *relative to monomer diffusion*.) While there is some variation among the five cases, this may be attributed to experimental scatter or the fact that the molecular weights for the different temperatures are not exactly the same. Inspection of Table 3 reveals that the molecular weight distribution is slightly narrower at the higher temperatures, with higher M_n values and fewer shorter chains present. While not a big effect, this may account for the minor variation in $\xi_{x,m}$ with polymerization temperature. Thus, it seems that temperature is not a significant factor in determining the $\xi_{x,m}$ value of relevance, and that the variation seen in these cases in $\xi_{x,m}$ was likely due to molecular weight differences. This is actually a further verification of the appropriateness of the free volume framework *for handling temperature effects* (as in the effect of temperature on the monomeric friction coefficient), as it seems that any potential temperature issues related to the diffusional processes important to termination can be accounted for by including the free volume dependence of monomer diffusion.

Table 3

A. Conditions, Molecular Weight Data,[a] and $\xi_{x,m}$ Values[b] Providing the Best Fit to Conversion Data for MMA Systems Considered

temp (°C)	[*I*] (wt % BPO)	M_n	M_w	$\xi_{x,m}$ (best fit)
40	0.55	587 100	1 105 000	3.1
40	2.8	321 000	640 000	2.9
40	7.0	139 300	303 300	2.5
50	1.1	316 000	644 000	2.7
60	0.10	403 500	712 800	3.2
60	0.55	346 000	614 000	3.0
60	2.0	166 300	294 100	2.7
60	7.0	74 100	163 400	2.2
75	0.10	345 000	608 000	3.3
75	0.55	143 200	265 500	2.7
75	2.0	76 000	134 200	2.2
75	7.0	35 400	65 600	1.8
85	0.030	413 000	676 000	3.5

B. Conditions, Molecular Weight Data,[a] and $\xi_{x,m}$ Values[b] Providing the Best Fit to Conversion Data for MMA Systems with AIBN as Initiator

temp (°C)	[*I*] (wt % AIBN)	M_n	M_w	$\xi_{x,m}$ (best fit)
20	4.0	910 000	1 650 000	5.0
50	0.30	420 000	1 000 000	3.2
70	0.50	77 300	139 000	2.3
70	1.26	59 300	109 000	1.9
75	5.0	22 100	40 400	1.1

[a] Average molecular weight values at low conversion (prior to the gel effect). [b] In addition to the figures in this manuscript, refs 14, 60, and 80 also shows fits of the model proposed here (with various $\xi_{x,m}$ values) to a number of other MMA polymerization systems.

The effect of molecular weight on the process controlling termination can be further examined by modeling a series of polymerizations for which the temperature is held constant while the molecular weight is varied. Such a variation is easily achieved by changing the initiator concentration, and we have done this for three temperatures: 40, 60, and 75 °C. Table 3A shows the $\xi_{x,m}$ values used at all the conditions, while Figures 7 and 8 show representative graphical modeling results. Inspecting Table 3A, it is clear that molecular weight plays the key role in the concentration dependence of termination (relative to that of monomer diffusion); at these three temperatures, $\xi_{x,m}$ increases substantially and smoothly with increases in M_n. Upon a broader inspection of parts A and B of Table 3, several conclusions may be reached. First, termination is not controlled by segmental diffusion as the $\xi_{x,m}$ values are too large and strongly dependent on molecular weight. (Recall that $\xi_{x,m} \approx 0.8-1.0$ is expected to fit segmental diffusion control, a result that should be largely independent of molecular weight. In only one case, the lowest molecular weight produced with $M_n = 22\ 100$, is the apparent concentration dependence of k_t close to that of segmental mobility. However, this result is simply an indication that primary and short oligomeric radical diffusion play key roles in the production of these

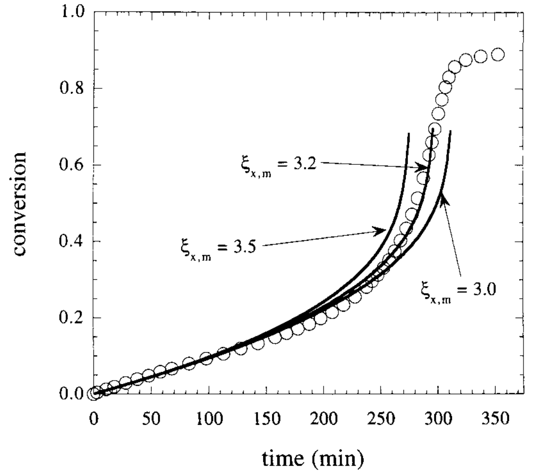

Figure 7. Comparison of simulation with experiment for MMA polymerization at 60 °C with 0.10 wt % BPO (DSC method). Open circles represent experimental data while solid lines represent modeling results. Simulations were carried out with the $\xi_{x,m}$ values indicated by the arrows and an initial k_t value of 1.43×10^9 L/mol min.[81]

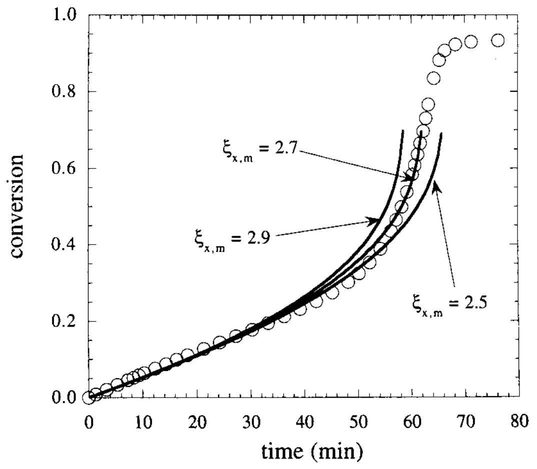

Figure 8. Comparison of simulation with experiment for MMA polymerization at 75 °C with 0.55 wt % BPO (DSC method). Open circles represent experimental data while solid lines represent modeling results. Simulations were carried out with the $\xi_{x,m}$ values indicated by the arrows and an initial k_t value of 3.31×10^9 L/mol min.[81]

very short PMMA chains.) Second, the concentration dependence of the apparent termination process is not sensitive to initiator type (BPO vs AIBN) as similar $\xi_{x,m}$ values are obtained for the two initiators when similar molecular weights of PMMA are produced. Finally, there is a clear trend for a stronger concentration dependence (relative to monomer diffusion) for k_t when higher MW polymer is formed, independent of temperature. When very low molecular weight PMMA is produced, $\xi_{x,m}$ values close to that of monomer diffusion are obtained. These values increase rapidly, from 1.1 for $M_n = 22\,100$, to 1.8−1.9 for M_n = 35k−59k, to 2.2−2.3 for M_n = 74k−77k, to 2.5−2.7 for M_n = 139k−166k. Values of 2.9−3.5 are typically observed for M_n in the range 300k−600k. When M_n approaches 10^6, the value increases to 5.0, indicating that control of the termination process may include effects of entangled polymer radical diffusion only with production of unusually high molecular weight polymer.

These data support a picture of termination where the shortest chains present in reasonable number dominate the reaction. When the molecular weight distribution is skewed to lower values, many highly mobile oligomeric chains are present. As these are the fastest diffusing species, they should be preferentially involved in termination. Thus, k_t has a weak concentration dependence, like oligomeric translational diffusion. At somewhat higher molecular weights, such oligomeric species are still present, but not in great enough number to dominate termination, so the system must rely on diffusion of longer chains for termination, leading to a stronger concentration dependence for k_t. Finally, at extremely high molecular weights, there may be so few unentangled chains present that the termination process must begin to involve diffusion of entangled chains, leading to a very strong concentration dependence for k_t. Thus, while entanglements may play an identifiable role in some termination reactions, this would be the exception rather than the rule.

This description of termination is somewhat related to pictures of "short−long" termination presented previously.[44−47] A common feature is the importance of short, highly mobile chains on the termination reaction. Instead of representing the global k_t value as arising from a series of termination events between chains all having some average molecular weight, it is clear that the details of individual termination reactions are important. Considering three broad classes of termination reactions, those between two "short" chains, those between a "short" and a "long" chain, and those between two "long" chains, it appears likely that the reaction between two "long" chains should be rare. The dominant mode of termination for a "long" chain should be for a short, highly mobile chain to diffuse into its vicinity and react with it. Thus, diffusion of very long chains should not be particularly important in determining k_t. However, the description presented herein and more traditional "short−long" pictures differ significantly in the definitions of "short" and "long". Generally, in the more traditional pictures,[44−47] "short" is taken to be "unentangled" while "long" has been defined as "entangled". This work shows that this distinction is incorrect; a chain does not have to be entangled to diffuse substantially more slowly than a primary radical or short oligomer. The shortest chains present in significant number, however short or long they may be, dominate the termination reaction, whether any chains are entangled.

B. Styrene Polymerization and Polymerization of Methyl Methacrylate in the Presence of Chain Transfer Agent. While this picture is robust for MMA, the situation is not so simple for styrene. Figure 9 shows the problem in modeling styrene polymerization at 60 °C with 3.2 wt % BPO; here a value of even $\xi_{x,m} = 1.0$ is *too high* to fit the experimental data.[58] Similar results are given in ref 14. In particular, conversion−time data are provided in ref 14 for two additional circumstances of bulk styrene polymerization, run with 0.05 M AIBN at 60 and 80 °C; both cases clearly show that even $\xi_{x,m} = 1.0$ is too high to fit the conversion−time data into the gel effect regime. Such an apparently weak gel effect has the general response we have observed[59,60] for isothermal, bulk styrene polymerization via free radical methods. This potentially suggests that k_t varies less strongly with concentration than even styrene monomer diffusion or segmental diffusion.[61] Thus, models imposing strong scaling for the concentration and molecular weight dependencies of k_t for styrene polymerization should be greatly in error[62] if adjustable parameters

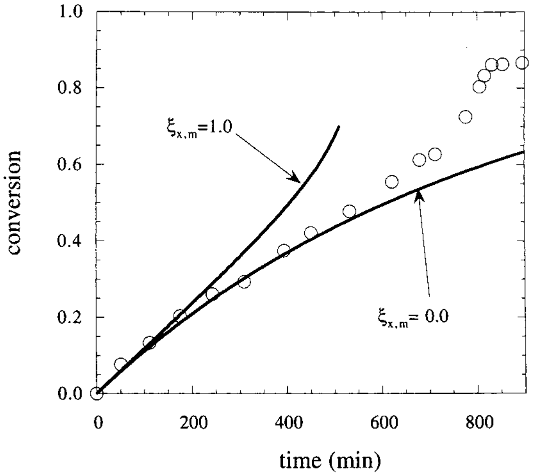

Figure 9. Comparison of simulation with experiment for styrene polymerization at 60 °C with 3.2 wt % BPO (ampule method). Open circles represent experimental data while solid lines represent modeling results. Simulations were carried out with the $\xi_{x,m}$ values indicated by the arrows and an initial k_t value of 3.32×10^9 L/mol min.[81]

are eliminated to avoid or reduce any aspect of curve fitting of experimental data.

One explanation for this result is to postulate that k_t is chemically controlled up to moderate styrene conversion, supported by classical kinetics ($\xi_{x,m} = 0.0$, i.e., k_t independent of conversion) fitting data up to 20−30% conversion. However, styrene is known to have a diffusion-controlled k_t, as at very low conversion k_t scales with fluidity.[63] Another possible explanation is that the assumption that rate parameters other than k_t remain constant is in error. As stated earlier, there is uncertainty in the measurement of rate constants. While f, k_d, and k_p do not appear to change appreciably until very high conversions where the systems turns glassy, this case has been made more fully in the literature for MMA than for styrene. Although not likely, it is not inconceivable that the effective rate parameter, $K = k_p(k_d f/k_t)^{1/2}$, could be nearly invariant as long as a reduction in $k_t^{1/2}$ with conversion is offset by a reduction in $k_p(k_d f)^{1/2}$. More study of the effect of conversion on rate parameters is warranted, especially for systems other than MMA.

Despite this, there is no reason to expect that styrene rate parameters other than k_t should depend on concentration much differently than the MMA parameters. A more appealing explanation of the weak concentration dependence of k_t for styrene is that a mitigating factor is present that apparently enhances termination relative to expectations from simple diffusion control. Does this imply that one set of physical assumptions is applicable with one monomer type but inapplicable with a second? While not impossible, this is unlikely. Instead, it implies that circumstances that slow the gel effect in styrene must be much less important in MMA.

A significant possibility is related to chain transfer and its effect on short−long termination processes thought to be of importance in the gel effect regime. It is known that in free radical polymerization styrene exhibits greater chain transfer than does MMA.[64,65] This may result in suppression of the gel effect relative to MMA. One reason is that shorter growing chains are produced than when chain transfer is absent. As diffusion of shorter chains is faster and less dependent on polymer concentration than that of longer chains, then k_t should be enhanced if these short chains control termination. In other words, chain transfer acts to provide more very short, oligomeric radicals, enhancing termination for the same reason that lower $\xi_{x,m}$ values were needed to fit the conversion−time data for MMA systems with lower molecular weights.

This is within the bounds of the previous MMA discussion and is the most obvious effect that chain transfer may impose to enhance k_t. However, while this may help to explain why a later gel effect occurs for styrene systems, it does not fully account for the fact that k_t in the styrene systems has a weaker concentration dependence than monomer diffusion. While chain transfer certainly leads to shorter growing chains, these chains cannot be shorter than one unit (monomer) and so should not diffuse with a much weaker concentration dependence than monomer diffusion. If k_t in styrene systems is controlled trivially by the diffusion of a fixed population of the shortest chains present, then this effect of chain transfer should not lead to a situation where conversion−time data are fit by $\xi_{x,m}$ values much less than 1.0. Thus, the $\xi_{x,m} \ll 1$ values remain to be explained.

There are subtler reasons why chain transfer may enhance termination beyond the effects of having a lower molecular weight distribution. At conversions where termination of fairly long chains is greatly inhibited due to their relative immobility, transfer allows for a separate means by which chains may form dead polymer, via transfer of the active radical to the transfer agent. Instead of having to find (or be found by) another growing chain which may itself have diffusional limitations, the live chain may be terminated by another abundant molecule which forms a new, short chain that is easily terminated by virtue of being highly mobile. In cases of significant chain transfer to monomer, initiator, or added chain transfer agent, there are far more molecules available from which to abstract a hydrogen atom than there are active growing chains. This may prove a significant means of terminating chains which otherwise would have difficulty in this regard.

Along these lines, chain transfer may have an increasing relative importance to the overall termination reaction as conversion increases. The formation of dead chains may be thought of as a competition between conventional termination, where growing chains diffuse together and react, and chain transfer, where a relatively abundant molecule near a growing chain forms a new, short radical chain via transfer. The former reaction is affected greatly by polymer concentration, with diffusion more severely limited at higher conversion. Therefore, this reaction becomes slower as monomer is converted to polymer. However, the transfer reaction is much more analogous to propagation than termination, as the chemical reaction involved, typically a hydrogen abstraction, occurs far less rapidly than the radical−radical reactions of conventional termination.[66] Like propagation, transfer is not generally considered to be diffusion-controlled until very high concentrations. Thus, changes in polymer concentration do not affect transfer nearly to the degree that they affect termination. (The exception is transfer to polymer which would increase as polymer concentration increases.) As a result, transfer may become more important relative to conventional termination (combination and/or disproportionation) as conversion increases.

This effect may seem trivial at first in terms of k_t, as the newly initiated chains formed in the transfer reaction must still undergo combination or disproportionation eventually unless they themselves also die due to transfer. However, if the increasing importance of transfer results in shorter chains being involved in termination as conversion increases, then the concentration dependence of k_t will be lower than if the exact same chain lengths are always involved in termination. Thus, a significantly increasing level of very short radicals with conversion in styrene polymerizations may result in an apparently higher k_t value at intermediate conversion than would be expected in the absence of significant chain transfer, suppressing the gel effect.

Another option is that imperfect reinitiation of new chains could enhance the apparent k_t. Chain transfer is related to retardation and inhibition.[67] When an active radical is transferred from a growing chain, several outcomes may occur. If the newly formed radical is roughly as reactive as the old growing chain, it will likely react with monomer and reinitiate; this is ideal chain transfer. If the new species is less reactive, it may never react or react slowly with monomer.[67] The former is inhibition, the latter retardation. If either occurs, the new radical molecule may be effectively terminated, although not in the classic sense, leading to an apparent enhancement of k_t.

Finally, significant chain transfer would increase primary radical termination where newly formed radicals terminate with growing chains. This would effectively enhance k_t because, whenever this process occurs, the transfer event that forms the primary radical is essentially a termination event, leading directly to the termination of the original chain and another chain with which the primary radical reacts immediately. This increases the frequency of termination and the apparent k_t and decreases the rate of polymerization. Also, as this effect may become increasingly prevalent at higher conversion, this would lower the observed concentration dependence of k_t.

This discussion attempts to justify the styrene results within the framework of the previous explanation of the MMA results. While it is difficult to quantify chain transfer effects in terms of a prediction for its effect on the measured concentration dependence of k_t, what can be done is to determine whether increasing the amount of chain transfer in MMA polymerizations results in similar effects. Simply put, if chain transfer is the origin of the differences between MMA and styrene polymerization, then increasing the level of chain transfer in MMA reactions should cause them to act more like styrene systems, at least regarding the concentration dependence of k_t.

A simple means of increasing transfer in MMA systems is to add dodecanethiol, a transfer agent. Figures 10 and 11 compare modeling and experiments for MMA at 70 °C with 3.0 vol % dodecanethiol at two AIBN concentrations. As with styrene, even an $\xi_{x,m}$ value of 1.0 predicts a far earlier gel effect than seen experimentally.[68] The decreased concentration dependence of k_t may be accounted for in part by increased primary radical termination, as molecules to which radicals have been transferred may terminate some of the other growing chains. Here these species are dodecanethiol radicals, which may diffuse with a weaker concentration dependence than monomeric/oligomeric chains because of their flexibility. (Such effects of flexibility have been noted in the literature.[38,69]) At any rate, addition of transfer agent causes MMA systems to resemble styrene systems in the context of the apparent concentration dependence of k_t.

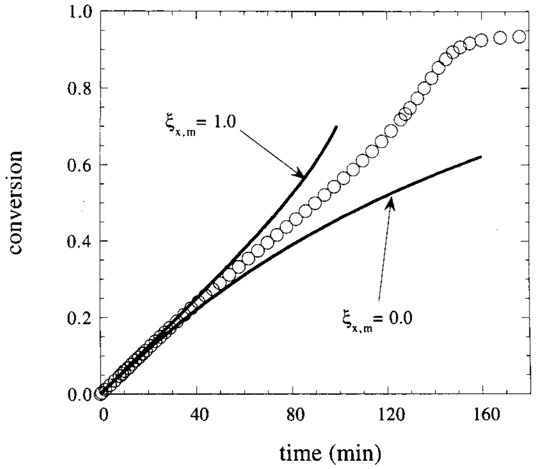

Figure 10. Comparison of simulation with experiment for MMA polymerization at 70 °C with 0.50 wt % AIBN and 3.0 vol % chain transfer agent (dodecanethiol) (DSC method). Open circles represent experimental data while solid lines represent modeling results. Simulations were carried out with the $\xi_{x,m}$ values indicated by the arrows and an initial k_t value of 3.79 × 10^9 L/mol min.[81]

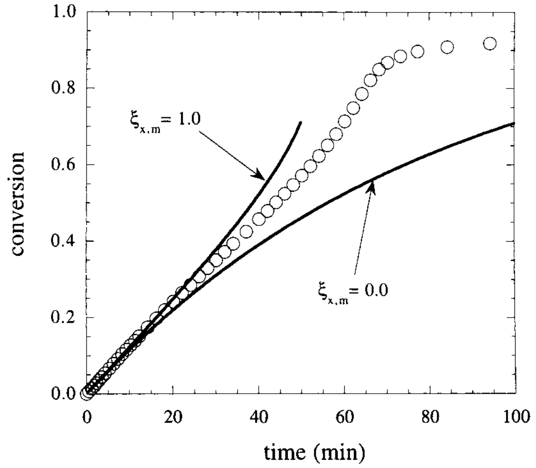

Figure 11. Comparison of simulation with experiment for MMA polymerization at 70 °C with 2.0 wt % AIBN and 3.0 vol % chain transfer agent (dodecanethiol) (DSC method). Open circles represent experimental data while solid lines represent modeling results. Simulations were carried out with the $\xi_{x,m}$ values indicated by the arrows and an initial k_t value of 4.00 × 10^9 L/mol min.[81]

The results for MMA systems with transfer agent significantly support the arguments given above to explain the MMA and styrene results.[70,71] MMA without added agent may be ideal, as chain transfer is small compared to many other systems. In the absence of complications associated with chain transfer, it may be argued that the picture outlined previously, whereby k_t is controlled by diffusion of the shortest chains present in significant number, is quantitatively correct, or nearly so.[72] The molecular-level cause of the gel effect is then associated with the polymer concentration dependence of the diffusion of the short radicals controlling termination which in turn is dependent on the molecular weight of the polymer being produced. Of course, a complete description must account for any effect that can influence termination, including the many issues associated with chain transfer. While a quantitative understanding is now possible in systems without significant transfer effects, e.g. in MMA, only a qualitative understanding has been achieved in systems with substantial transfer; a quantitative understanding of systems with substantial transfer requires further study.

Conclusion

With a combination of experimental polymerization studies and computer modeling, this work has provided insight into the molecular processes controlling termination and resulting in the gel effect under various circumstances. To achieve this, the modeling efforts focused on the cause of the gel effect and not on fitting data over the whole range of conversion. If the complex, very high conversion regime where the glass and cage effects as well as system heterogeneity may be important is avoided, any change in the polymerization rate can be associated essentially with changes in k_t. The model handles temperature effects (related to the temperature dependence of the monomeric friction coefficient) via the Vrentas−Duda predictive free volume picture.[35] The conversion dependence of k_t is handled by one fitting parameter, $\xi_{x,m}$, which relates the polymer concentration dependence of the diffusion process of interest (controlling the termination process) to that of monomer diffusion. Thus, not only is the value of $\xi_{x,m}$ tied quantitatively to the concentration dependence of the diffusing species controlling termination, obtainable from conversion−time data, but also it is easily related to the concentration dependencies of segmental mobility (low $\xi_{x,m}$ values), monomer and oligomer diffusion (low $\xi_{x,m}$ values growing with chain length), and diffusion of unentangled (moderate $\xi_{x,m}$ values) and entangled (very high $\xi_{x,m}$ values) polymer chains, obtainable by comparison with experimental diffusion data. Thus, much insight about the concentration dependence of termination and the molecular processes controlling termination (and hence the gel effect) can be inferred from this modeling procedure.

Using this procedure, examination of MMA conversion−time data indicates that termination related to the gel effect is not controlled by chain-end segmental mobility but instead is controlled by diffusion of the shortest radical chains present in reasonable number. This gives credence to the general idea of "short−long" termination processes[44−47] in which short radicals chains control the termination reaction. This conclusion is derived from the fact that, in the absence of significant chain transfer, systems with a lower overall molecular weight distribution have a characteristic k_t with a weaker concentration dependence relative to monomer diffusion, i.e., can be modeled with lower $\xi_{x,m}$ values, than systems with higher overall molecular weights. This trend holds at multiple temperatures and is quantitatively described by the model employing the single $\xi_{x,m}$ parameter. The $\xi_{x,m}$ values required to fit the various conversion−time data indicate that the length of the short chains controlling the termination process may be considerably smaller than have been imagined. For example, very short oligomeric chains apparently control termination in the production of PMMA with M_n = 22k, and unentangled PMMA radicals control termination in the production of polymer with M_n as high as 300k−600k. It is not until M_n approaches 1000k that entangled radical chains apparently play a discernible contributory role in controlling termination, consistent with recent studies[7] showing that entanglements cannot in general cause the gel effect.

The model provides quantitative agreement with conversion−time data for MMA polymerizations in the absence of substantial chain transfer effects. However, chain transfer, resulting in lower overall molecular weights as well as a separate means for long chains to cease propagation, may enhance termination in several ways, resulting in an apparent reduction in the strength of the gel effect. For systems with significant chain transfer, such as normal styrene systems or MMA systems with added chain transfer agent, the apparent concentration dependence of k_t is very weak, even weaker than segmental or monomer translational diffusion. While this result can be understood qualitatively, it is yet to be explained quantitatively, as the effects of chain transfer on termination are complex and not fully understood. Further investigations into the effects of chain transfer on modifying the gel effect, as well as study of other monomer systems besides MMA and styrene, will be needed in order to obtain a complete understanding of the gel effect in free radical polymerization. Such studies are ongoing in our laboratory.

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(8) Some free volume theories provide a basis (related to relative amounts of polymer and solvent or monomer) for handling, directly or indirectly, the temperature and polymer concentration dependencies of the monomeric friction coefficient, which in turn are related to the temperature and concentration dependencies of diffusion in polymer solutions such as those found in free radical polymerizations. Thus, in the more sophisticated forms, free volume theories can be more than fitting functions as they can address, with the use of meaningful physical parameters, issues of broad ranging importance in polymer physics in addition to phenomena in polymerization processes.

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(53) While the phenomenon of a temperature rise accompanying the gel effect in systems without absolutely optimal heat transfer has been known for over 50 years (for examples, see ref 1 and see: Schulz, G. V.; Blaschke, F. *Z. Phys. Chem.* **1942**, *B51*, 75.), this point was seemingly lost in some of the important litertature that followed, leading some researchers to model nonisothermal experimental data as if they were isothermal. Work published in 1987 (ref 50) and 1990 (O'Driscoll, K. F.; Huang, J. *Eur. Polym. J.* **1990,** 25, 629) made clear that normal ampule polymerizations would often suffer from the effects of nonisothermality near and in the gel effect regime.

(54) While the point of the model is not to extract initial k_t values, we note that the values used in the MMA simulations scale as, at initial conversion, $k_t \sim M_n^{-0.22}$ after being normalized with respect to temperature using an activation energy derived from the cases at constant M. This dependence on M_n is similar to previous observations on experimentally determined k_t values. See, for example, refs 26 and 27 and the following: Mahabadi, H. K. *Macromolecules* **1985**, 18, 1319; Mahabadi, H. K. *Macromolecules* **1991**, 24, 606. Matsumoto, A.; Mizuta, K. *Macromolecules* **1994**, *27*, 1657. Wisnudel, M. B. Ph.D. Dissertation, Northwestern University, 1996.

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(56) The temperature dependence of monomer diffusion in polymer-monomer solutions has received little study. However, ref 66 provides limited data for MMA diffusion as a function of PMMA concentration at −10 and +50 °C. Additionally, detailed information regarding the quantitative effects of temperature on small-molecule probe diffusion in polymer solutions is found in ref 38.

(57) It must be noted that both temperature and molecular weight play key roles in the polymerconcentration dependence of k_t. While the role of temperature can be handled directly using a free volume model, the role of molecular weight cannot, as free volume does not suggest anything about its role. While our discovery of an approximate relationship between the polymer concentration dependence of the polymer diffusion coefficent and that of the monomer diffusion coefficient (through the parameter $\xi_{x,m}$ that depends on polymer molecular weight) is both reasonable and useful, this does *not* mean that the polymer concentration dependence of k_t at any given temperature is fundamentally and only due to free volume effects.

(58) A "best fit" to the conversion−time data in Figure 9, up to fractional conversion of 0.6−0.7, is achieved with an $\xi_{x,m}$ value of about 0.2. However, the significance of this fit is not that the polymer concentration dependence of k_t is only a small fraction of that of monomer diffusion. (It is physically unreasonable for the true polymer concentration dependence of k_t to be significantly weaker than that of monomer diffusion.) Instead, it is that the simple model described here, which does not account for effects of chain transfer in slowing the rate of polymerization through behavior akin to retardation or inhibition, is inadequate to model quantitatively the early to middle stages of the gel effect in bulk styrene free radical polymerization.

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(61) This point implicitly assumes that the models do not account quantitatively for chain transfer effects, especially concerning how k_t may be increased (relative to the case of no chain transfer) due to the presence of a significantly higher level of short oligomeric radical chains deriving from chain transfer reactions.

(62) A significantly more complex model postulating an entanglement-based reptation scaling for the molecular weight dependence of the polymer diffusion coefficient controlling k_t ($D \sim M_w^{-2}$) and employing a Vrentas−Duda free volume approach for the polymer concentration dependence of the diffusion-controlled nature of k_t has reportedly allowed for approximate fitting of several sets of conversion−time curves for MMA and styrene polymerizations (see Achilias, D. S.; Kiparassides, C. *Macromolecules* **1992**, *25*, 3739). However, the simulation of data sets for a broad range of molecular weights was not reported; the very strong molecular weight scaling of D certainly would not allow for quantitative agreement of the model over the range of molecular weight studied here for MMA polymerization. (See ref 54.) Additionally, the polymer concentration dependence of D was assumed to be characterized by the equivalent of our $\xi_{x,m}$ parameter (it is expressed somewhat differently in the 1992 reference) having a molecular weight *independent* value of 1.50 for MMA and 1.57 for styrene, an assumption not supported by the results presented in this paper. To provide approximate fits under these circumstances, the simulations from this complex model consistently overestimated MMA conversions up to fractional conversions of 0.4, in some cases significantly overestimating the onset conversion of the gel effect.

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(68) "Best fits" to the conversion−time data in Figures 10 and 11, up to fractional conversions of 0.6−0.7, may be achieved with $\xi_{x,m}$ values of 0.5−0.6. However, the significance of these fits is not that the polymer concentration dependence of k_t is only a small fraction of that of monomer diffusion. (It is physically unreasonable for the true polymer concentration dependence of k_t to be significantly weaker than that of monomer diffusion.) Instead, it is that the simple model described here, which does not account for effects of chain transfer (in these cases due to addition of dodecanethiol) in slowing the rate of polymerization through behavior akin to retardation or inhibition, is inadequate to model quantitatively the early to middle stages of the gel effect in bulk MMA free radical polymerization when substantial amounts of chain transfer agent are present.

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(71) We do not discount that other reasons besides chain transfer (with some related retardation and inhibition effects) contribute to the apparently mild gel effect observed in isothermal, bulk styrene polymerization. However, we as yet have no support for other causes.

(72) A criticism that could be leveled at the approach outlined here is that the single $\xi_{x,m}$ parameter used in the fitting to experimental data does not account for increases in the average molecular weight of the polymer produced during the gel effect, a phenomenon often although not always accompanying the gel effect. In many cases, this issue will lead to only very small increases in the concentration dependence of k_t in the gel effect regime. This is evidenced by the fact that with a factor of 4 increase in PMMA molecular weight (M_n roughly 143k−590k) the parameter $\xi_{x,m}$ increases only slightly. (See Table 3.) Nevertheless, further study will be needed to determine conditions where this issue may be of some quantitative importance, well outside the range of experimental error.

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(79) Note that due to a typographical error the value of ϵ was listed as $1.37 + 4.4 \times 10^{-4}T$ (°C) in ref 14. The results in ref 14 were in fact determined using the correct value of ϵ listed here in Table 2.

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(81) The values of k_t in the captions of Figures 4−11 are provided for completeness so that readers may be able to reproduce the plots provided in these figures. It must be noted that the k_t values listed in the captions are a function of the values of k_d and k_p from other sources as we have fit low conversion data to obtain the initial k_t values. (See Tables 1 and 2.) If the k_d and k_p values are in error, this would affect the validity of the values of k_t provided in the figure captions. However, the initial value of combined parameter $k_p(fk_d/k_t)^{1/2}$ should be approximately correct in each case. It must be remembered that only the initial value of this combined parameter and the polymer concentration dependence of k_t are of key importance in the analysis provided in this manuscript.

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