Gel Effect in Free Radical Polymerization: Model Discrimination of Its Cause

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Autoacceleration at intermediate conversion in free radical polymerization, known as the gel effect, is of practical and scientific interest (O'Neil et al., 1996; O'Neil and Torkelson, 1997). While its molecular cause is the subject of active research, it is known to be associated with a slowing of the rate of termination between active growing chains due to decreasing chain mobility which results from conversion of monomer to polymer. Previous models (Cardenas and O'Driscoll, 1976; Marten and Hamielec, 1979; Tulig and Tirrell, 1981; Soh and Sundberg, 1982; Chiu et al., 1983; Achilias and Kiparissides, 1992; Gao and Penlidis, 1996; Tefera et al., 1997) which have attempted to quantitatively describe the gel effect have suffered from two key difficulties: (1) the use of adjustable model parameters which cannot be estimated independently; and (2) the modeling of polymerization data taken under nonisothermal conditions (Armitage et al., 1988; Zhu and Hamielec, 1991). While the former is well documented, the latter is often overlooked; both can lead to misjudgments regarding the molecular-scale process controlling the termination rate parameter k_t. In particular, the use of adjustable parameters may lead to models which include significant curve fitting, while modeling nonisothermal data assuming isothermality leads to a large overestimation of the concentration dependence of k_t, as experimental trends that result from a temperature rise are misinterpreted as being due to diffusional properties. These difficulties have hindered understanding of basic mechanistic issues associated with free radical polymerization, such as whether termination is controlled by segmental or translational diffusion. Here we eliminate these difficulties while modeling well into the gel effect region in order to gain critical insight into and discrimination of the molecular process underlying termination.

Explanation of the Model

In order to minimize the use of adjustable parameters, our model does not account for complexities occurring at high conversion beyond the gel effect regime, such as the glass effect, diffusion-controlled propagation, and residual termination. Thus, our model is not designed to be accurate at very high conversion. Our objective is only to model polymerization through the onset of the gel effect as simply as possible and determine what molecular process likely controls termination. We employ the classical kinetic equations (Chiu et al., 1983) with all rate parameters except k_t assumed independent of molecular weight M and concentration C. (Evidence (Parker et al., 1996; Russell et al., 1988) indicates that k_p, the propagation rate parameter, k_d, the initiator decay parameter, and f, the fractional initiator efficiency, depend little on conversion at conversions of interest.) The governing equations are

$$dI/dt = -k_dI - k_p(1-X)\{\epsilon I/(1+\epsilon X)\}\lambda_0 \tag{1}$$

$$dX/dt = k_p(1-X)\lambda_0 \tag{2}$$

$$d\lambda_0/dt = -k_p(1-X)\{\epsilon\lambda_0^2/(1+\epsilon X)\} + 2fk_dI - k_t\lambda_0^2 \tag{3}$$

where I is the initiator concentration, t is the time, ϵ is a volume contraction factor defined as $\epsilon = (d_m - d_p)/d_p$ (where d_m and d_p are the densities of monomer and polymer, respectively), X is the fractional monomer conversion, and λ_0 is the zeroth moment of the growing radical distribution. Parameter variation with temperature has been taken from the literature (see Table 1).

The key to our model (and to exploring the cause of the gel effect) is handling the $M-$ and C-dependencies of k_t. This presents a challenge because, although it is accepted that k_t is related to diffusive polymer motion, it is not clear which type of diffusion is most important. While it is uncertain whether (or to what degree) k_t scales with M, what is often

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Table 1. Kinetic Parameters Used in the Free Radical Polymerization Model

	PMMA	Reference
k_p(L/mol·min)	$2.95\times10^{7}\exp\{-2{,}191/T(\mathrm{K})\}$	Mahabadi and O'Driscoll (1977)
k_d(AIBN)(min^{-1})	$6.32\times10^{16}\exp\{-15.43\times10^{3}/\mathrm{T(K)}\}$	Chiu et al. (1983)
ρ_m (g/mL)	$0.973-1.164\times10^{-3}\{T(\mathrm{K})-273\}$	Chiu et al. (1983)
ρ_p (g/mL)	1.20	Chiu et al. (1983)
	PS	
k_p(L/mol·min)	$6.54\times10^{8}\exp\{-3{,}549/T(\mathrm{K})\}$	Mahabadi and O'Driscoll (1977)
k_d (AIBN) (min^{-1})	$6.32\times10^{16}\exp\{-15.43\times10^{3}/T(\mathrm{K})\}$	Chiu et al. (1983)
ρ_m (g/mL)	$0.9236-0.887\times10^{-3}\{T(^\circ\mathrm{C})\}$	Soh and Sundberg (1982)
ρ_p (g/mL)	$\rho_m(1+\epsilon)$ where $\epsilon=1.37+4.4\times10^{-4}T(^\circ\mathrm{C})$	Soh and Sundberg (1982)

not recognized is that this issue is in a sense irrelevant if the focus is limited to the *cause of the onset* of the gel effect. If k_t depends on M, this would certainly affect the initial value of k_t (value at zero concentration) with higher M resulting in lower initial k_t values. 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 falling out of balance with initiation, that is, only the relative change in kinetics matters. Since M does not change appreciably with conversion prior to autoacceleration, any potential M-dependence of k_t should not influence the gel effect onset.

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

This discussion indicates that by taking a simple approach of modeling through the gel effect onset, but not to high enough conversions where other complexities are important, we need only account for the C-dependence of k_t. To gain insight about the gel effect onset, we compare this C-dependence with expectations from various pictures (such as segmental and translational diffusion), providing information about the molecular process controlling k_t. Vrentas-Duda free volume theory (Vrentas and Duda, 1977; Zielinski and Duda, 1992) is used for the C-dependence, as we have shown (O'Neil et al., 1998) that free volume accurately handles temperature effects related to the gel effect onset and that free volume–related expressions fit various diffusion data. In order to describe the C-dependence of k_t, one must describe the C-dependence of the diffusive process controlling k_t. We relate this to the C-dependence of monomer diffusion

$$\frac{k_t(c)}{k_t(0)}=\frac{D_x(c)}{D_x(0)}=\left(\frac{D_m(c)}{D_m(0)}\right)^{\xi_{x,m}} \tag{4}$$

where m refers to monomer and x refers to the species and process controlling k_t. This formulation, which has its origin in the description of the effect of diffusant size on diffusion coefficient for small molecules (Wisnudel and Torkelson, 1996), is convenient because it represents the differences in C-dependence for diffusion in one accessible parameter $\xi_{x,m}$. Specifically, a high $\xi_{x,m}$ value indicates a strong C-dependence while a low $\xi_{x,m}$ indicates a weak C-dependence (relative to monomer diffusion). (In the description of small molecule diffusion, $\xi_{x,m}$ may be interpreted as a ratio of the "jumping unit size" of species "x" to that of the monomer.) D_m is calculated from the Vrentas-Duda model (Zielinski and Duda, 1992)

$$D_m=D_0\exp\left\{-\gamma\left(\omega_1\hat{V}_1^*+\omega_2\xi_{1,2}\hat{V}_2^*\right)/\hat{V}_{\mathrm{FH}}\right\} \tag{5}$$

where $\hat{V}_1^*$ and $\hat{V}_2^*$ are the specific critical hole free volume required for a diffusive jump by monomer and polymer, respectively, ω_1 (ω_2) is the weight fraction of monomer (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 $\xi_{1,2}$ is the ratio of the jumping-unit size of monomer to that of polymer. $\hat{V}_{\mathrm{FH}}$ is given by

$$\hat{V}_{\mathrm{FH}}=\omega_1K_{11}(K_{21}-T_{g1}+T)+\omega_2K_{12}(K_{22}-T_{g2}+T) \tag{6}$$

where K_{1i} and K_{21} are free-volume parameters for component i, and T_{g1} is its glass transition temperature. Values used in the calculations are given for both MMA and styrene in Table 2.

Our approach uses $\xi_{x,m}$ as a fitting parameter and then compares the value needed to fit polymerization data to $\xi_{x,m}$ values expected if k_t were controlled by various processes. (Initial k_t values are determined by fitting the low-conversion data using $\xi_{x,m}=0$, that is, classical kinetics.) Thus, we directly compare the C-dependence of k_t (as represented by $\xi_{x,m}$) with that of any physical process deemed likely to control termination.

Results and Discussion

The first step that must be taken is to establish what $\xi_{x,m}$ values would be expected on the basis of the various molecular processes potentially controlling k_t. For example, if monomer diffusion controlled the termination reaction, then $\xi_{x,m}=1.0$ should offer the best fit to polymerization data.

Table 2. Free Volume Parameters for the Vrentas-Duda Model

MMA-PMMA		Reference
$\hat{V}_1^*$ (cm^3/g)	0.87	Faldi et al. (1994)
$\hat{V}_2^*$ (cm^3/g)	0.788	Zielinski and Duda (1992)
K_{11}/γ (cm^3/g·K)	7.0×10^{-4}	Fit from data in Waggoner et al. (1993)
K_{12}/γ (cm^3/g·K)	3.05×10^{-4}	Zielinski and Duda (1992)
$K_{21}-T_{gl}$ (K)	-32.07	Fit from data in Waggoner et al. (1993)
$K_{22}-T_{g2}$ (K)	-301	Zielinksi and Duda (1992)
$\xi_{1,2}$	0.59	Zielinski and Duda (1992)
Styrene-PS		
$\hat{V}_1^*$ (cm^3/g)	0.846	Achilias and Kiparissides (1992)
$\hat{V}_2^*$ (cm^3/g)	0.85	Zielinski and Duda (1992)
K_{11}/γ (cm^3/g·K)	8.01×10^{-4}	Fit from data in Mark (1989)
K_{12}/γ (cm^3/g·K)	5.82×10^{-4}	Zielinski and Duda (1992)
$K_{21}-T_{g1}$ (K)	-41.19	Fit from data in Mark (1989)
$K_{22}-T_{g2}$ (K)	-327	Zielinski and Duda (1992)
$\xi_{1,2}$	0.634	Zielinski and Duda (1992)

Likewise, since it has been established (Ediger, 1991) that segmental mobility has roughly the same C-dependence as small molecule diffusion, a segmental diffusion-controlled termination reaction should lead to a polymerization that can be fit with $\xi_{x,m} \approx 1.0$–1.2. (A maximum $\xi_{x,m}$ value for segmental mobility can be derived from Vrentas-Duda theory as 1.69 for poly(methyl methacrylate) (PMMA) and 1.58 for polystyrene, the inverse of the $\xi_{1,2}$ values in Table 2). For translational diffusion, the result is not so obvious; one must fit diffusion data directly. Figure 1 shows data (Faldi et al., 1994) on the C-dependence of PMMA self-diffusion in solution along with predictions by our model (Eq. 4) for different values of $\xi_{x,m}$. For unentangled chains (9 k PMMA diffusion in a 330 k PMMA matrix and 330 k PMMA diffusion in a 9 k PMMA matrix), an $\xi_{x,m}$ value of roughly 3.0–3.5 is effective in fitting the C-dependence. For entangled chains (330 k PMMA diffusion in a 330 k PMMA matrix), an $\xi_{x,m}$ value of 9.5–10 is needed. Finally, as oligomers are intermediate between monomer and unentangled chains, the C-dependence of oligomer diffusion should be represented by an $\xi_{x,m}$ value between 1.0 and ~ 3.0.

The task now is to fit conversion-time data to our model and compare the $\xi_{x,m}$ value needed to fit the data with the values discussed above. The normal modeling approach is to simulate experimental conversion-time data taken via "ampoule" polymerizations. In such an experiment (Balke and Hamielec, 1973; O'Neil et al., 1996, 1998) ampoules containing monomer and initiator are placed into a constant temperature medium, with fractional conversion determined by precipitating, drying, and weighing the resultant polymer or by other means such as dilatometry. The advantage of this technique is its simplicity. The disadvantage in using this experimental setup (Zhu and Hamielec, 1991) is the difficulty in avoiding an often dramatic temperature rise during the gel effect for monomers with fairly fast kinetics, such as methyl methacrylate (MMA), which can cause an earlier gel effect than when the polymerization is done isothermally (O'Neil et al., 1998; Zhu and Hamielec, 1991). This can lead to spurious conclusions about the strength of the C-dependence of termination.

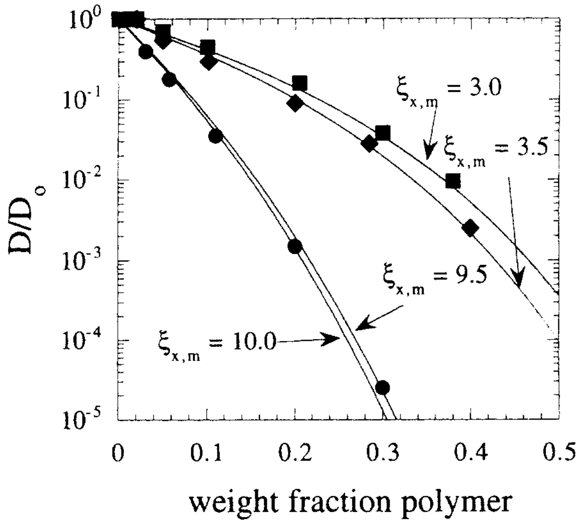

Figure 1. Comparison of experimental (Faldi et al., 1994) concentration dependence of PMMA translational diffusion in solution.

(D/D_0 is a normalization to the value at zero PMMA concentration) with simulation (using different $\xi_{x,m}$ values). Three different experimental sytems were considered by Faldi et al.: two unentagled cases, (■) diffusion of 330 k PMMA in a 9 k PMMA matrix and (◆) diffusion of 9 k PMMA in a 330 k PMMA matrix, and an entangled case, (●) diffusion of 330 k PMMA in a 330 k PMMA matrix.

To avoid this complication, there is a need for isothermal conversion-time data in order to test the model adequately. With the ampoule method, reactions must be done slowly and/or in very narrow ampoules (high surface area to volume ratio). Figure 2 shows results of such polymerizations. The data in Figure 2a, MMA at 50°C with 0.3 wt. % (2,2-azobisisobutyronitrile) (AIBN) as initiator, are taken from the literature (Balke and Hamielec, 1973); this case has been shown (Zhu and Hamielec, 1991) to be approximately isothermal, owing to the use of narrow ampoules and slow kinetics. Here, three $\xi_{x,m}$ values are used to show the sensitivity of this parameter. For all three cases, the qualitative "look" of the gel effect is predicted, while $\xi_{x,m} \approx 3.2$ provides the most reasonable fit to the data through intermediate conversion, beyond which the model is not designed to work. Since $\xi_{x,m} \approx 3.2$ falls into the range of the C-dependence of unentangled chain polymer diffusion, it is reasonable to postulate that termination in this case may be controlled by this process. Figure 2b shows one of our isothermal ampoule polymerizations, MMA at 20°C using 4 wt. % AIBN as initiator; here the very slow kinetics assure isothermality. A value of $\xi_{x,m} \approx 5.0$ offers the best fit to the data, meaning that k_t seems to have a C-dependence intermediate between that of unentangled and entangled polymer diffusion.

Because MMA ampoule polymerizations must be done very slowly in order to maintain isothermality, and slow kinetics lead to high M values, the data in Figure 2 offer only a limited range of conditions. For Figure 2a, $M_n \approx 420{,}000$ and $M_w \approx 1{,}000{,}000$ prior to the gel effect (Balke and Hamielec, 1973); for Figure 2b, $M_n \approx 910{,}000$ and $M_w \approx 1{,}650{,}000$. Since the previous discussion indicates that M could be a key fac-

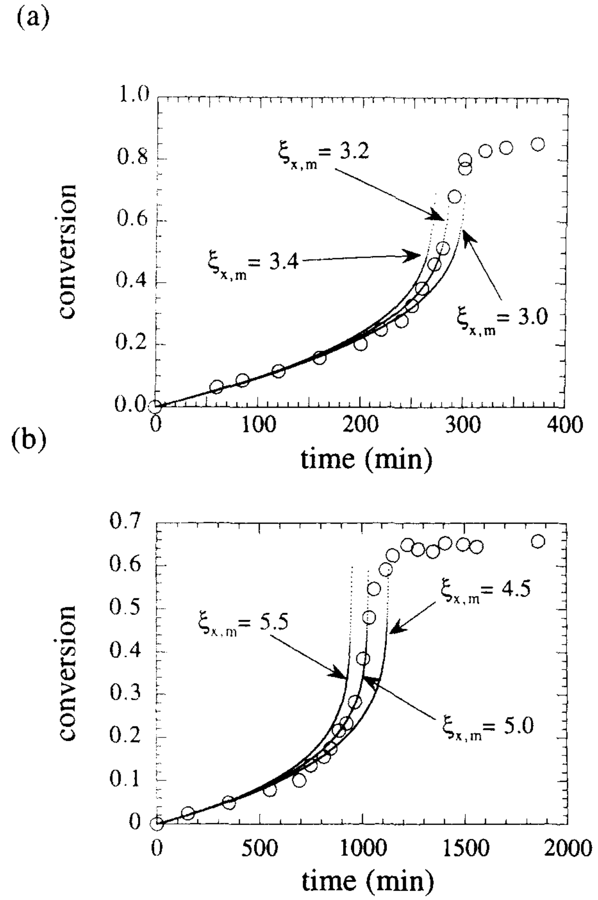

Figure 2. Comparison of simulation to approximately isothermal MMA experiments in which high molecular weights are formed.

Figure 2a uses data from the literature (Balke and Hamielec, 1973) at 50°C with 0.3 wt. % AIBN as initiator; Figure 2b uses data gathered for this study at 20°C with 4 wt. % AIBN. Experimental points (○) are compared with simulated results using three different $\xi_{x,m}$ values in each case. (The relatively low limiting conversion observed in Figure 2b is due to the very low polymerization temperature, resulting in the glass effect at fractional conversion < 0.7.)

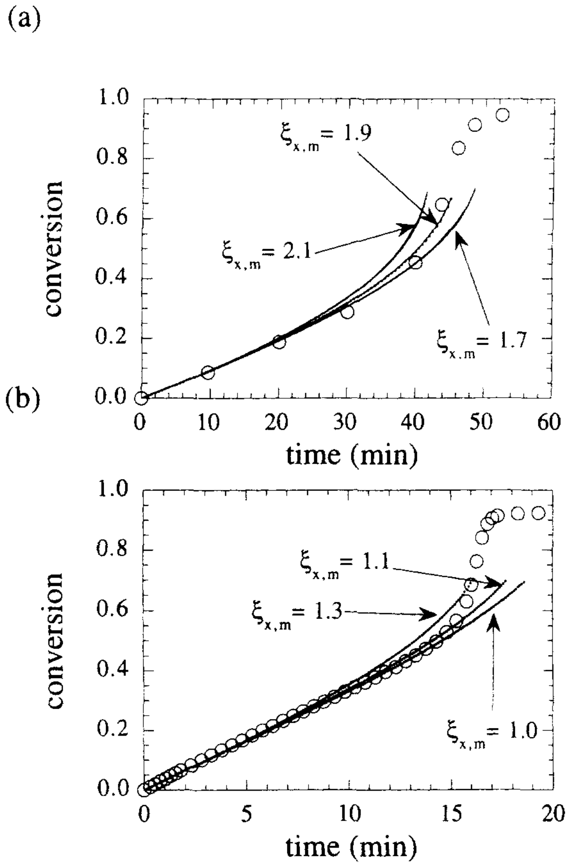

Figure 3. Comparison of simulation to approximately isothermal MMA experiments in which fairly low molecular weights are formed.

Figure 3a uses data from the literature (Armitage et al., 1988) at 70°C with 0.073M (1.26 wt. %) AIBN as initiator; Figure 3b uses data gathered for this study at 75°C with 5 wt. % AIBN. Experimental points (○) are compared with simulated results using three different $\xi_{x,m}$ values in each case.

tor in the gel effect, we must examine cases where lower M polymer is formed. As this requires faster kinetics, we use reactions done via differential scanning calorimetry (DSC), which offers extremely small sample sizes and excellent heat transfer, allowing for isothermality on even short time scales. Figure 3a shows DSC conversion data from Armitage et al. (1988) using MMA at 70°C with 0.073 M (1.26 wt. %) AIBN. This system, resulting in $M_n \approx 59{,}300$ and $M_w \approx 109{,}000$ prior to the gel effect (our results, not reported by Armitage et al.), is best fit with $\xi_{x,m} \approx 1.9$, a weaker C-dependence than the cases at higher M. Figure 3b shows one of our DSC polymerizations, MMA at 75°C using 5 wt. % AIBN. Here, with $M_n \approx 22{,}100$ and $M_w \approx 40{,}400$ prior to the gel effect, $\xi_{x,m} \approx 1.1$-1.3 offers the best fit, indicating a yet weaker C-dependence for k_t.

In the cases shown, there is a clear trend for a stronger C-dependence for k_t when higher M polymer is formed. For low M, the low $\xi_{x,m}$ values needed to fit the conversion-time data are in the range of translational diffusion of oligomeric chains, while the cases with high M are in line with the C-dependence of polymeric translational diffusion. Two 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 M. Second, the data indicate that translational diffusion of the shortest chains present (the most mobile chains) dominates termination. For instance, when low M polymer is formed, many very short, oligomeric growing chains are present. Since they are the most mobile species and are present in great number, it makes sense that they would dominate k_t, leading to a weak C-dependence. On the other hand, if much higher M polymer is formed, then the system has many fewer very mobile oligomeric chains and so would rely more on longer chains for termination, resulting in k_t having a stronger C-dependence. These results indicate that the termination process in MMA systems is dominated by the fast diffusing, "short" radical chains, with the definition of "short" depending on the M values of the chains formed in the reaction.

As a further exploration of this issue, we report results for the second-most studied gel effect monomer, styrene. Figure 4 compares simulation to experiments, both via ampoule (Nishimura, 1966) and DSC (our results) methods, for styrene

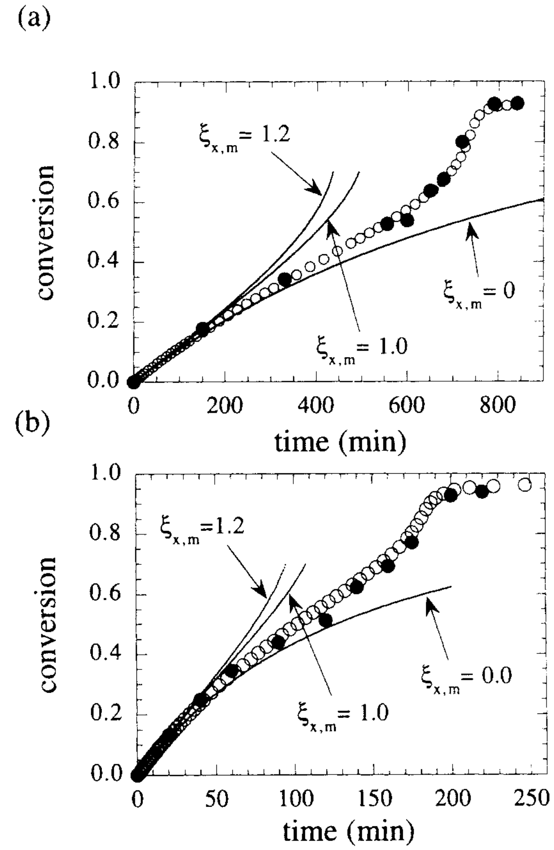

Figure 4. Comparison of simulation to polymerization experiments done via the ampoule (●) (Nishimura, 1996) and DSC (○) methods, using styrene with 0.05 M AIBN as initiator at 60°C (Figure 4a), and 80°C (Figure 4b).

Experimental points are compared with three different simulated results, using the following values for $\xi_{x,m}$: 0.0, 1.0, and 1.2.

with 0.5 M (0.9 wt. %) AIBN at 60°C and 80°C. (The match between ampoule and DSC results indicates that heat transfer was not a problem in the ampoule studies). In contrast to the MMA simulations, a value of even $\xi_{x,m} = 1.0$ is *too high* to fit experimental data. This is a suprising result, apparently suggesting that k_t varies less strongly with concentration than either styrene monomer diffusion or segmental diffusion. Other means of describing the diffusion-controlled termination reaction, such as entanglement control, would be even more in error. Thus, models which impose strong scaling for the *C*- and *M*-dependencies of k_t for styrene polymerization should be greatly in error if all adjustable parameters are eliminated to avoid any aspect of curve fitting of the experimental data.

One explanation is to postulate that k_t may be chemically controlled, rather than diffusion-controlled, up to moderate styrene conversion, supported by the fact that classical kinetics ($\xi_{x,m} = 0$, that is, k_t independent of conversion) fit data up to a 20–30% conversion. However, the magnitude of k_t consistent with the polymerization rate R_p, fits expectations based on diffusion control (Wisnudel, 1996), and at very low styrene conversion Burnett et al. (1973) show proportionality between k_t and medium fluidity. A more appealing explanation is that a mitigating factor is present that apparently enhances termination relative to expectations based on simple diffusion control. Our model assumes that propagation and initiation rate parameters depend little on conversion for the range of conversion of interest, which is operative for MMA. R_p is given by

$$R_p = k_p(k_d f/k_t)^{1/2}[\mathrm{M}][\mathrm{I}]^{1/2} \qquad (7)$$

where $[M]$ and $[I]$ are monomer and initiator concentrations, respectively. The effective rate parameter $k_p(k_d f/k_t)^{1/2}$ could remain nearly constant 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 all rate parameters is warranted (Buback et al., 1988). A second possibility is that a substantial population of short, mobile active chains is maintained during much of a typical styrene polymerization. This is somewhat related to recent explanations of "short-long" termination (O'Shaughnessy and Yu, 1994; Russell et al., 1993). As styrene systems are more susceptible to chain transfer (Odian, 1991) than MMA systems, the population of short chains needed to mitigate the gel effect is more likely to exist in a styrene system. It may be possible for k_t to remain nearly constant over a range of conversion due to an increasing contribution of short chains participating in termination. Consistent with this explanation is that, in the presence of chain transfer agent, the gel effect occurs at higher conversion in MMA systems (Flory, 1953; O'Neil et al., 1996). (Chain transfer to initiator may contribute to the low *C*-dependence of k_t indicated in Figure 3b where a high initiator concentration was used.) Greater study of these issues is underway.

Conclusion

A model has been developed to compare experimental free radical polymerization conversion-time data to predictions based on various physical processes likely controlling termination. By modeling only through intermediate conversion (including the gel effect onset), many of the difficulties associated with other models, which have in the past hindered progress in determining the cause of autoacceleration, were eliminated. Comparison to isothermal experiments reveals that, for MMA, formation of higher *M* polymer leads to a stronger *C*-dependence for k_t, consistent with the interpretation that translational diffusion of the shortest active chains present will dominate termination and be related to "short-long termination" theories presented recently. For styrene, the *C*-dependence of k_t appears far too weak to be described even by monomeric radical or segmental diffusion, a result which, at first, appears puzzling. This may be associated, at least in part, with short-long termination, as substantial chain transfer in styrene polymerization may result in a population of short, very mobile chains, enhancing termination and lowering its *C*-dependence.

Acknowledgment

We gratefully acknowledge helpful comments from a reviewer as well as support from an NSF Graduate Research Fellowship and a Terminal-Year Cabell Fellowship (both to GAO).

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Manuscript received Sept. 19, 1997, and revision received Mar. 6, 1998.