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Toward a Molecular Theory of the Trommsdorff Effect

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ABSTRACT: A theory for the kinetics of high-conversion autoaccelerating free radical polymerization, incorporating the reptation model of de Gennes for polymer diffusion, is presented. Earlier models of various aspects of the Trommsdorff effect are reviewed and several weaknesses pointed out. These approaches have been empirical in the sense that diffusion behavior has usually been put in in an ad hoc manner flexible enough so that it could be adjusted to fit experimental data. The present model uses classical diffusion-controlled reaction kinetics (the Smoluchowski equation) to relate the termination rate constant to the diffusion constant of the growing radical. The best current theory for polymer diffusion is then included in the kinetic model. The model is shown to fit data on conversion vs. time and molecular weight vs. conversion up to 70 or 75% conversion. Examination of some data due to Brooks shows that the dependence of the termination rate constant on molecular weight is consistent, at high molecular weight, with the inverse square chain length dependence expected from this reptation-based kinetic model. The model suggests several new experimental approaches to a better understanding of the molecular dynamics of polymerizing media.

Introduction

The course of free radical polymerization carried out in both concentrated solution and bulk monomer has been a matter of study for over 3 decades. From the vast array of published experimental data[1-17] it is well-known that classical low-conversion free radical kinetics[18,19] do not apply over the entire conversion range in concentrated polymerizing systems. In particular, many such polymerizations exhibit a large autoacceleration of the rate of polymerization with an associated increase in the molecular weight of the polymer produced in media on the order of 20–30% in polymer content, even under isothermal conditions. This autoacceleration, known as the Trommsdorff[1] or "gel" effect, is the result of a drastic decrease in the rate of chain termination steps due to severe diffusional limitations.

Diffusion theory of polymers has advanced considerably in the past 10 years. The purpose of the present work is to use some of these advances to put the molecular understanding of the Trommsdorff effect on a more solid footing. Simple empirical methods have been used to describe such polymerization kinetics by correlating an "apparent" termination constant with various system parameters, such as conversion, temperature, and free volume.[20-22] More recently, two approaches have evolved which attempt to relate high-conversion polymerization and the "gel" effect to some feature of the underlying physics of the problem. One approach, used by Turner and co-workers,[23-28] deals only with the onset of the autoacceleration. A point of departure of experimental data from classical dilute-solution kinetics (there is a certain arbitrariness here) is identified with a "critical" polymer concentration, $C_{\rm crit}$, at which the onset of the gel effect is defined to occur. Theories of polymer dynamics and extensive rheological data due to Graessley, Bueche, Onogi, and others[29-32] have attributed observed changes in the concentration and molecular weight dependence of polymer dynamic properties such as viscosity, modulus, and compliance when crossing from dilute to more concentrated solution to the onset of "entanglements"; moreover, they have established that the onset of such "entangled" behavior obeys an equation of the form

$$K = C_{\rm crit}\bar{M}_{\rm crit}{}^{a} \qquad (1)$$

where $C_{\rm crit}$ is the polymer concentration, $\bar{M}_{\rm crit}$ is some average molecular weight, and a and K are constants, with $0.5 \lesssim a \lesssim 1$. Turner et al.[23-28] suggest that the onset of the gel effect be identified with either the onset of molecular overlap ($a = 0.5$) or the onset of "entanglement" ($a = 1$) in the polymerizing mixture, and the dependence of $C_{\rm crit}$ on the molecular weight of the polymer produced is fit to the form of eq 1.

The most systematic experimental studies of this dependence are those of O'Driscoll, Wertz, and Husar,[33] Abuin and Lissi,[34] Lachinov et al.,[35] and Lee and Turner.[24-28] O'Driscoll et al.[33] studied the polymerization of styrene and found that their data fit eq 1 with $a = 1$, using the number-average molecular weight of the polymer produced for $\bar{M}$ ($\bar{M} = \bar{M}_{\rm n}$). They also observed that the value of K obtained was lower than that observed in rheological measurements on the same system. Abuin and Lissi[34] used their own data as well as data due to Naylor and Billmeyer,[14] Schulz,[9] and Balke and Hamielec[2] on MMA polymerization and found that $a \approx 0.5$ for high number-average degrees of polymerization, while for low degrees of polymerization the data did not fit eq 1. Lachinov et al.[35] studied methyl methacrylate (MMA) and butyl methacrylate (BMA) and found $a = 0.53$ for MMA and $a = 0.25$ for BMA. Lee and Turner[24-28] studied MMA, styrene, and vinyl acetate and found $a = 0.4$, 0.35, and 0.34, respectively.

The major conclusion which can be drawn from this work is that the onset of the gel effect does correlate with some change in the character of polymer solution prop-

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erties. The exact dependence on concentration and molecular weight, however, and the relationship between the gel effect onset and the onset of "entangled" behavior in rheological properties are still unclear.

The second approach applied to the gel effect has been to make some empirical statements about the molecular weight and conversion dependence of the termination rate constant, k_t, sometimes using qualitative analogies with theories and experimental results on polymer transport phenomena. Two recent attempts of this nature have been made. One, by Cardenas and O'Driscoll (COD), is based on entanglement ideas;[36-38] the second, by Marten and Hamielec (MH)[39] also treats the very high conversion regime where propagation steps become constrained by diffusion control and is based on free volume ideas.

In the COD model the polymer species are divided into two populations, those with degree of polymerization greater or less than a critical value N_c. The critical chain length is identified with the degree of polymerization at the break in a double log plot of viscosity vs. chain length. Entanglement theories of polymer dynamics have identified this break with the critical product of polymer concentration and chain length as in eq 1, with $a = {}^1/_2$ or $a = 1$, depending upon the particular theory involved.[29-32] Termination of radicals A and B with $N_A < N_c$ and $N_B < N_c$ is given a termination rate constant k_{t0}, which is the dilute-solution value. Termination of two "entangled" radicals, $N_A > N_c$ and $N_B > N_c$, is given a termination constant k_{te}, while termination of a radical pair in which $N_A > N_c$ and $N_B < N_c$ is given a termination constant k_{tc}, which is postulated to be the geometric mean of k_{t0} and k_{te}:

$$k_{tc} = (k_{t0}k_{te})^{1/2} \tag{2}$$

Then, as a first-order approximation, it is asserted that k_{te} is inversely proportional to the entanglement density. This leads to a functional dependence of

$$k_{te} \sim 1/\phi_p\bar{N} \tag{3}$$

where ϕ_p is the polymer volume fraction and $\bar{N}$ is the number-average degree of polymerization of the dead polymer chains.

In the MH model, qualitative physical arguments regarding the relationship between viscosity, diffusion coefficients, and free volume theory are used to justify an assumption about the dependence of k_t on polymer concentration and molecular weight. It is asserted that k_t is proportional to a diffusion coefficient, which in turn depends upon the viscosity of the medium. Since viscosity, in general, has been found to depend upon the weight-average molecular weight,[32] k_t is given the form

$$k_t \sim \frac{1}{\bar{M}_w{}^n} e^{-A/V_f} \tag{4}$$

where $\bar{M}_w$ is the weight-average molecular weight of the dead polymer chains, n is a parameter which is arbitrarily chosen to be 1.75, and A is a constant. The concentration dependence of k_t enters in the exponential term through the dependence of free volume, V_f, on the concentration.

A review of ref 36–39 demonstrates that both of these models are quantitatively quite good in fitting experimental conversion vs. time and molecular weight vs. conversion data for a variety of experimental conditions. The success of these models demonstrates that introduction of a concentration and molecular weight dependent termination constant into the kinetic equations allows good quantitative fit to experimental data to be made. However, the fact that two models based on totally different and nonequivalent physical assumptions and using different dependences of k_t upon concentration and molecular weight fit the same data equally well indicates that this success cannot verify the correctness of either model in its physical assumptions.

The major difficulty associated with the work described lies in the degree of empiricism involved in each formulation. In all the work described above an isolated aspect or prediction of a theory of polymer solution physics is singularly extracted, suitably modified with various assumptions, and used to make predictions regarding kinetic behavior. Neither the accuracy of the physical theory nor that of the assumptions made is tested against other solution properties of the system over the range of conditions occurring in the polymerization experiment. Recent advances in molecular diffusion theory and new experimental techniques, particularly various static and dynamic scattering methods, have provided a new understanding of the physics of polymer solutions over a wide range of polymer concentration.[40] In this paper we focus on the diffusive nature of termination in these polymerizing systems and demonstrate how the best available molecular theories and experimental results regarding polymer diffusion can be used to model several aspects of polymerization reaction kinetics. In the next section a review of the current theoretical understanding of transport in polymer solutions is presented. Subsequent sections describe the application of these theories to the polymerization problem and the kinetic model arising from this application.

Polymer Diffusion Theory

The understanding of static and dynamic properties of flexible polymers in "good" solvent has been advanced quite remarkably by use of scaling concepts and renormalization group techniques together with the idea of reptation due to de Gennes.[41] The literature in this area is quite substantial; the interested reader is directed to ref 40–45 and references contained therein.

The properties of a polymer–solvent system depend to a great extent upon the relative importance of polymer–polymer and polymer–solvent interactions. In the dilute limit individual polymer coils are well separated; thus solution properties reflect the hydrodynamic and frictional interactions between the deformable polymer coil and a continuum of low molecular weight solvent. In this regime the chains behave as hydrodynamic spheres with an effective radius, R, which is approximately proportional to the root-mean-square radius of gyration:

$$R \sim R_G \sim N^{\nu} \tag{5}$$

Here N is the number of monomers per chain and ν is the excluded volume exponent. According to Flory[18] $\nu = {}^3/_5$ for asymptotically "good" solvents, while $\nu = {}^1/_2$ for a Θ solvent. At infinite dilution the translational diffusion coefficient, D_0, and the intrinsic viscosity, $[\eta]$, are expected to obey the following relations, based on the theory of Kirkwood and Riseman:[46]

$$D_0 = k_BT/6\pi\eta_0R \sim 1/N^{0.6} \tag{6}$$

$$[\eta] = \phi R_G{}^3/(M_{mon}N) \sim N^{0.8} \tag{7}$$

η_0 is the solvent viscosity, T the absolute temperature, k_B Boltzmann's constant, M_{mon} the molecular weight of a monomer unit, and ϕ a constant. Experimentally, it is found that $D_0 \sim N^{-x}$, where $0.53 \lesssim x \lesssim 0.56$[47-54] and $[\eta] \sim N^y$, with $0.70 \lesssim y \lesssim 0.75$[55] in good solvent. A possible explanation for these small discrepancies between theory and experiment has been proposed by Weill and des Cloizeaux;[56] however, no experimental evidence has either

Table I
Comparison of Predictions of the Scaling Law Based Reptation Theory with Experimental Results

quantity	prediction	ref	experiment	ref
bulk viscosity	$\eta \sim N^3c^{3.75}$	43	$\eta \sim N^{3.4}c^3$ to $\eta \sim N^{3.4}c^4$	67
self-diffusion coefficient				
bulk polymer	$D_s \sim N^{-2}$	41-44	$D_s \sim N^{-2.0\pm0.1}$	68
polymer solution	$D_s \sim N^{-2}c^{-7/4}$	43	$D_s \sim c^{-1.7\pm0.1}$	69, 70
cooperative diffusion coefficient	$D_s \sim N^0c^{3/4}$	43	$D_c \sim N^0c^{0.67}$	51
			$D_c \sim N^0c^{0.81\pm0.05}$	71, 72
correlation length	$\xi \sim N^0c^{-3/4}$	45	$\xi \sim N^0c^{-0.72\pm0.06}$	45
radius of gyration	$R_G{}^2 \sim Nc^{-1/4}$	45	$R_G{}^2 \sim Nc^{-0.25\pm0.02}$	45

supported or conflicted with their hypothesis.

While polymer–solvent interaction in dilute solution may be simply described by a polymer–solvent friction coefficient and intramolecular hydrodynamic interactions, analysis of higher concentrations where intermolecular polymer–polymer interactions are important is more complex. These intermolecular interactions may take three forms. First, intermolecular hydrodynamics may "screen" the intramolecular hydrodynamic interaction which dominates dilute-solution behavior. Second, due to their long chain nature, polymer chains may impose topological constraints upon the motions of surrounding polymer molecules. Finally, polymer chains may exert direct friction upon one another at very high polymer concentration.

The effect of hydrodynamic screening of intramolecular hydrodynamic interaction in the absence of topological constraints has been described by Freed and co-workers.[57-64] Their results indicate a transition in the molecular weight dependence of the specific viscosity, η_s, and self-diffusion coefficient, D_s, from dilute behavior (eq 6 and 7) to a Rouse-like[65] behavior

$$\eta_s \sim N \tag{8}$$

$$D_s \sim 1/N \tag{9}$$

as hydrodynamic and excluded volume effects within a chain become screened with increasing concentration. The concentration dependence of the self-diffusion coefficient and specific viscosity are shown to be expandable in a virial series at low concentration (the dilute regime)

$$D_s = D_0[1 - K_dc + O(c^2)] \tag{10}$$

$$\eta_s = c[\eta][1 + c[\eta]k_H + O(c^2)] \tag{11}$$

while at higher concentration, in what has been called the semidilute regime, a dependence of

$$D_s \propto k_BTg(c)/N\eta_0\xi(c) \sim 1/Nc^{0.5} \tag{12}$$

$$\eta_s \propto cN\xi^3(c)N_{av}/M_{mon}g^2(c) \sim Nc^{1.25} \tag{13}$$

is predicted.[61] In eq 12 and 13 the quantity ξ is a concentration-dependent screening or correlation length. On length scales smaller than ξ intramolecular excluded volume and hydrodynamic interaction are dominant, while on length scales greater than ξ such effects are effectively screened. $g(c)$ is the effective number of monomers experiencing these interactions; i.e., g is the number of monomers contained within a screening element of size ξ. In good solvent the concentration dependences of ξ and g are[45,61]

$$\xi \sim c^{-0.75} \tag{14a}$$

$$g \sim c^{-1.25} \tag{14b}$$

The predictions in eq 12 and 13 have not yet been tested experimentally, since the influence of "entanglement" effects is important over much of the semidilute regime. The work described[57-64] explicitly excludes the effects of such polymer "entanglement" resulting from the constraints imposed upon chain motions by neighboring polymer chains; thus these results are restricted to a limited range of concentration and molecular weight where the influence of such constraints is small.

In 1971 de Gennes considered the effect of topological constraints imposed upon the motion of a polymer molecule by its neighbors.[41] In his view the motion of a given macromolecule is confined within a virtual "tube" defined by the locus of its intersections (or points of "entanglement") with adjacent molecules. The molecule is constrained to wriggle, snakelike along its own length, by curvilinear propagation of length defects such as kinks or twists along the tube. This mode of motion was termed reptation. A consequence of confining a polymer molecule to move along a curvilinear tube is that the molecular weight dependence of the self-diffusion coefficient becomes

$$D_s \sim N^{-2} \tag{15}$$

while the corresponding molecular weight dependence of the viscosity is

$$\eta \sim N^3 \tag{16}$$

The idea of reptation may be extended to polymer–solvent systems to describe the concentration dependence of dynamic properties in those systems also. de Gennes describes the properties of a reptation-dominated polymer–solvent system in terms of a swollen pseudogel containing temporary "cross-links" of finite lifetimes.[42,43] Concentration becomes an important variable in defining the effective tube size (i.e., the mean interentanglement separation or average mesh size of the gel) and the extent of polymer–polymer friction a reptating macromolecule experiences. In the absence of significant polymer–polymer friction (the semidilute regime), application of scaling analysis in the context of the reptation model leads to

$$D_s \sim N^{-2}c^{-7/4} \tag{17}$$

$$\eta_s \sim N^3c^{3.75} \tag{18}$$

for the concentration and molecular weight dependence of the self-diffusion coefficient and specific viscosity, respectively. In the same regime cooperative polymer–solvent motions on time scales shorter than the entanglement lifetime may be described by a cooperative diffusion coefficient, D_c, which de Gennes predicts to be independent of molecular weight and to scale as

$$D_c \sim c^{0.75} \tag{19}$$

This quantity may be probed directly by quasi-elastic light scattering, which measures cooperative polymer–solvent concentration fluctuations.

A summary of the major predictions of the scaling law based reptation theory as compared with experimental results, chiefly in the semidilute regime, is presented in Table I. This comparison indicates that the theory is substantially correct in most respects. The weakest point is the molecular weight dependence of viscosity (third

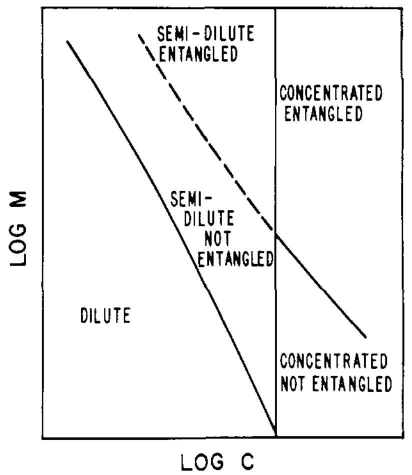

Figure 1. Molecular weight–concentration diagram illustrating the regimes of dynamic behavior available to a polymer–solvent system. Graessley[73] shows plots of this type for polystyrene and polybutadiene.

power for reptation vs. 3.4 power experimentally). Very recently Doi[66] has presented a reptation-based theory which predicts the apparent 3.4 power dependence of viscosity on molecular weight. Doi's model may reconcile this important discrepancy between reptation theory predictions and experiment.

A summary of the concentration regimes available to a polymer–solvent system is seen in Figure 1. As the polymer concentration increases from the dilute regime, a concentration c^* is reached, above which the polymer coils interpenetrate to achieve uniform monomer segment concentration throughout the medium. Above c^* the regime known as the "semidilute" regime is defined. In this regime polymer–polymer friction is still negligible; however, due to the constant monomer segment density, intramolecular excluded volume and hydrodynamic interactions are screened on length scales greater than the correlation length ξ. As concentration increases still further, a second transition occurs at c^{**}. Here reptative (pseudogel) behavior becomes dominant due to constraints imposed upon polymer chains by their slow-moving neighbors. Finally, a third transition occurs at c^{***}, where polymer–polymer friction becomes important, the concentrated regime. These regimes have been summarized in a form similar to Figure 1 by Graessley,[73] based on available rheological data for polystyrene and polybutadiene.

The transitions between regimes have been studied both theoretically and experimentally. Daoud et al.[45] demonstrate that c^* should depend upon molecular weight in a form

$$c^* = KN^{-b} \qquad (20)$$

where for very long chains in good solvent $b = 0.8$ while for poorer solvents $b < 0.8$. Klein[74] has analyzed the interactions between the motion of a reptating species and its neighbors. His work indicates that

$$c^{**} = K'N^{-0.8} \qquad (21)$$

theoretically for long chains in good solvent. Equation 21 is found to be consistent with data of Schurz and Hochberger[75] on the onset of "entangled" viscosity behavior of polyisobutylene in the semidilute regime. Finally, dynamic light scattering experiments by Jamieson et al.[71,72] have experimentally demonstrated that two transitions, c^* and c^{**}, in dynamic behavior are observed; moreover, the values are consistent with estimates from Daoud et al.[45] and Klein.[74] These data indicate, however, that a different dependence of c^* and c^{**} on molecular weight is found at high and low molecular weight in the same solvent.

Theoretical description of polymer–polymer friction in the concentrated regime and the transition to concentrated-solution behavior is not well developed. The more effective theories are semiempirical in nature, for they attempt to correlate data on various physical properties in terms of an effective, concentration-dependent, polymer–polymer friction factor, which may then be used to extrapolate the available information to different conditions or different physical properties. At high polymer concentration, particularly near the glass transition, the free volume theory of Vrentas and Duda[76-78] has proved effective.

Complete experimental determination of the transition between regimes of dynamic behavior as illustrated in Figure 1 has not been accomplished for any polymer–solvent system over the complete range of concentration and molecular weight; however, the previous discussion indicates how measurement of a variety of solution properties by various experimental techniques may be used to determine the changing character of polymer solution dynamics. The nature of interactions evident in these measurements may then be used in relation to understanding the physical nature of kinetic phenomena.

Diffusive Nature of Termination in Polymerization

During the course of a free radical polymerization from bulk monomer to complete or limiting conversion, the polymerizing system crosses between several regimes of dynamic behavior. It has been shown[7,79,80] that the effect of the polymerizing medium on initiation and propagation is small except at very high conversion; however, radical termination, which involves diffusion together of two polymer chains, is a strong function of the polymerizing medium over the entire conversion range. The dependence of k_t upon relevant system parameters—concentration, radical and dead polymer size, temperature, and solvent quality—over a range of conditions is unknown, for in a typical polymerization experiment many variables change simultaneously; thus the experimental data do not uniquely determine the termination mechanism. Under limited conditions some direct knowledge of the dependence of k_t on concentration, molecular weight, and solvent is available. At very low polymer concentration ($c \lesssim 10$ wt %) North and Reed[81] have demonstrated for poly(methyl methacrylate) (PMMA) that (1) termination is diffusion controlled from the beginning of the reaction and both k_t and the polymer diffusion coefficient depend inversely upon the solvent viscosity, η_0, at zero conversion (infinite dilution), (2) at finite concentration k_t is an increasing function of concentration in good solvent, $k_t/k_{t0} = 1 + \delta c$, where δ is proportional to the polymer degree of polymerization, while in poor solvent k_t is a decreasing function of concentration, (3) over the same concentration range in good solvent the mutual diffusion coefficient, D_{mut}, increases with concentration, while the self-diffusion coefficient, D_s, decreases with concentration, (4) neither k_t, D_s, nor D_{mut} depends inversely upon the bulk solution viscosity at finite polymer concentration, and (5) k_t goes through a maximum and begins to decrease at a concentration which depends upon the molecular weight of the polymer produced. The observed relationship between the mutual diffusion coefficient and termination at low polymer concentration has been qualitatively explained by North and Reed[81] and more quantitatively by Mahabadi and O'Driscoll[82] as control of termination by segmental diffusion of radical ends together after the terminating coils

Table II
Variation of the Termination Rate Constant, k_t, Bulk Viscosity, η, and Radical Number-Average Degree of Polymerization, $\overline{N}'$, with Added Polymer Concentration As Calculated from the Data of Brooks[80]

wt % polymer	c, g/cm^3	$\overline{N}'$	η, Pa s	$k_t \times 10^{-7}$, L/(mol s)
0	0	3660	5.07×10^{-4}	5.94
0	0	3880	5.07×10^{-4}	5.93
9.36	0.0869	3340	3.70×10^{-3}	6.35
16.18	0.1528	3230	1.50×10^{-2}	5.40
24.13	0.2326	4180	7.00×10^{-2}	2.73
29.93	0.2928	6770	2.80×10^{-1}	1.01
30.89	0.3030	6940	3.70×10^{-1}	1.00
39.47	0.3960	8860	4.20	0.427
41.21	0.4154	11060	9.93	0.236
42.16	0.4531	11590	13.33	0.201

have translationally diffused into close proximity. The maximum in k_t and subsequent decrease has been described[83] as a transition to translational (self) diffusion control as the polymer self-diffusion coefficient decreases.

Ludwico and Rosen[84] have performed styrene polymerization in the presence of known concentrations of predissolved polystyrene of well-defined molecular weight at concentrations up to ~20%. In these experiments the effects of concentration, radical, and environment polymer size may be varied independently. Over the range of concentration considered (which is still in the dilute regime at the molecular weights of added polymer used) k_t shows an initial increase followed by an approximately linear decrease. The effect of both radical and added polymer molecular weight in the decreasing region is small.

Brooks[80] has performed MMA polymerization in the presence of predissolved PMMA at concentrations up to 42 wt %. His analysis, however, attempts to correlate k_t as being inversely proportional to the bulk viscosity of the medium. The data of North and Reed and discussion of diffusion behavior in the previous section indicate that termination should not depend inversely upon the bulk viscosity in any concentration regime. With values for the propagation and initiation rate constants as given by Brooks and monomer and polymer specific volumes due to Schulz and Harborth,[17] the termination constant, average radical degree of polymerization, and added polymer concentration can be calculated as

$$k_t = 2fk_dI_0(k_pM_0/R_p)^2 \qquad (22)$$

$$\overline{N}' = k_pM_0/(2fk_dI_0k_t)^{1/2} \qquad (23)$$

$$c = \frac{Z}{V_M + Z(V_p - V_M)} \qquad (24)$$

$Z \equiv$ weight fraction polymer

These data are presented in Table II. A plot of log η_s vs. log c (Figure 2) from the data of Brooks indicates that for the predissolved polymer used in these experiments ($\overline{M}_v$ = 79 000, $\overline{M}_n$ = 68 000) the onset of "entangled" viscosity behavior occurs at c_η^{**} = 0.24 g/cm^3. In Figure 3A the data of Table II are plotted on log coordinates. It is apparent that k_t is a strong function of the polymer medium over the entire concentration range. In Figure 3B the same data are replotted as log k_t/k_{t0} + 1.75 log c vs. log $\overline{N}'$. (Where it is necessary to distinguish between growing and dead chains, we use primed variables to denote growing chains and unprimed variables to denote dead chains.) On such a plot, for reptating species a slope of −2 is expected if the termination constant is proportional to the self-diffusion coefficient (as it should be for translational diffusion control). The strong dependence of k_t on concentration and radical molecular weight at high polymer concentration is obvious. At the very highest concentrations the data are definitely consistent with a reptative picture; however, the sparsity of data precludes making any strong conclusions.

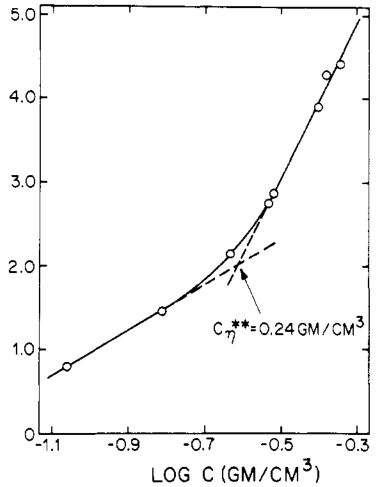

Figure 2. Specific viscosity–concentration diagram indicating the "critical" concentration for onset of entangled behavior, c_η^{**}, and the fit of viscosity data by behavior extrapolated from the entangled and unentangled regimes. Experimental data from Brooks.[80]

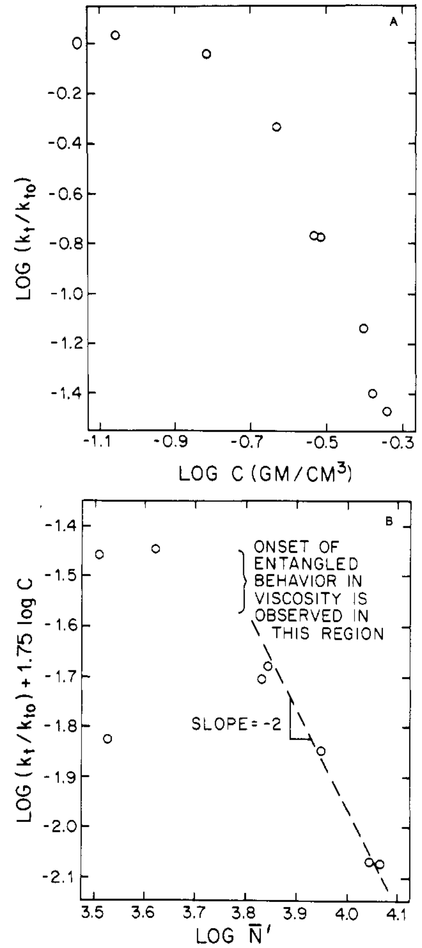

Figure 3. (A) Apparent dependence of the termination rate constant on polymer concentration. Data from Brooks.[80] (B) Same data plotted according to a reptative dependence of termination on polymer concentration and radical size.

The three sets of data described indicate that the termination rate constant is a complex function of system

Scheme I
Kinetic Scheme for Free Radical Chain Growth Polymerization in the Presence of an Initiator[a]

initiation $\mathrm{I} \xrightarrow[k_{\mathrm{d}}]{} 2\mathrm{R}\cdot$

$\mathrm{R}\cdot + \mathrm{M} \xrightarrow[k_{\mathrm{i}}]{} \mathrm{P}_1\cdot$

propagation $\mathrm{P}_n\cdot + \mathrm{M} \xrightarrow[k_{\mathrm{p}}]{} \mathrm{P}_{n+1}\cdot$

transfer $\mathrm{P}_n\cdot + \mathrm{M} \xrightarrow[k_{\mathrm{tr}}]{} \mathrm{D}_n + \mathrm{P}_1\cdot$

termination $\mathrm{P}_n\cdot + \mathrm{P}_m\cdot \xrightarrow[k_{\mathrm{t}}]{} \mathrm{D}_n + \mathrm{D}_m$

[a] I = initiator, R = initiated radicals, P_n = growing polymer chain of length n, D_n = dead polymer of length n, M = monomer.

variables due to its control by diffusive processes and the changing nature of these diffusive processes as conversion proceeds. While the exact dependence of k_{t} on concentration and radical and dead polymer sizes may not be extracted from the limited available data, the following points must be made: First, both the previous kinetic models (COD and MH) and the work which identifies the gel effect onset (Lee and Turner, etc.) have assumed that a constant k_{t} may be used to describe termination prior to the gel effect onset. While the dependence of k_{t} on concentration and polymer size in the dilute regime may be small in some cases, this dependence must be recognized. Second, Lee and Turner[24-28] define what they call the gel effect onset as the departure from linearity of a plot of ln $(1 - x)$ vs. time. Such a plot is expected to be linear for constant k_{t}. While the strong dependence of k_{t} on concentration and polymer size in entangled solution will certainly give a departure from linearity in such a plot, the critical concentration defined in this way may very well reflect the pregel effect variation of k_{t} with concentration. This is totally unrelated to the onset of entanglement, since k_{t} is a function of concentration throughout the conversion regime. This definition of the gel effect onset, therefore, is imprecise (and cannot be expected to correlate with the onset of entanglement) since a truly constant k_{t} never exists. Finally, the models of COD and MH have used a termination constant during acceleration which depends upon concentration and a dead polymer molecular weight average. The models of diffusion previously described indicate that the *mode* of polymer diffusion is primarily determined by the cumulative dead polymer concentration and molecular weight distribution, which specifies the expected regime of dynamic behavior as illustrated in Figure 1. *However, the self-diffusion coefficient of a particular tagged species is dependent upon the molecular weight of that species itself.* In a kinetic model, therefore, the transitions between forms of termination should be influenced most strongly by the concentration and molecular weight distribution of the dead polymer, while the termination constant should depend upon the molecular weight distribution of the diffusing species, i.e., the radicals. This has never been properly accounted for in other gel effect models.

Reptation-Based Kinetic Description

Having briefly described the current understanding of polymer solution physics and the best available data regarding free radical kinetics, we now formulate a kinetic model which incorporates the best available representations of both fields.

Given kinetic Scheme I, the species balance equations incorporating a concentration- and chain-length-dependent termination constant are

$$\mathrm{d}M/\mathrm{d}t = -k_{\mathrm{i}}RM - (k_{\mathrm{p}} + k_{\mathrm{tr}})M\sum_{n=1}^{\infty}P_n \tag{25}$$

$$\mathrm{d}R/\mathrm{d}t = 2fk_{\mathrm{d}}I - k_{\mathrm{i}}RM \tag{26}$$

$$\mathrm{d}I/\mathrm{d}t = -k_{\mathrm{d}}I \tag{27}$$

$$\mathrm{d}P_1/\mathrm{d}t = k_{\mathrm{i}}RM - k_{\mathrm{p}}P_1M + k_{\mathrm{tr}}M[\sum_{n=1}^{\infty}P_n - P_1] - P_1\sum_{n=1}^{\infty}k_{\mathrm{t}}(1,n)P_n \tag{28}$$

$$\mathrm{d}P_n/\mathrm{d}t = k_{\mathrm{p}}M(P_{n-1} - P_n) - k_{\mathrm{tr}}MP_n - P_n\sum_{m=1}^{\infty}k_{\mathrm{t}}(m,n)P_m \tag{29}$$

$$\mathrm{d}D_n/\mathrm{d}t = k_{\mathrm{tr}}MP_n + P_n\sum_{m=1}^{\infty}k_{\mathrm{t}}(n,m)P_m \tag{30}$$

From the Smoluchowski equation[85] for a diffusion-controlled chemical reaction between species A and B the rate constant is

$$k = 4\pi\rho(D_{\mathrm{A}} + D_{\mathrm{B}}) \tag{31}$$

where D_{A} and D_{B} are the self-diffusion coefficients of species A and B and ρ is the intermolecular separation required for reaction. Since it has been shown that termination is diffusion controlled, the rate constant for termination between species P_n and P_m under translational diffusion control is, in general

$$k_{\mathrm{t}}(n,m) = 4\pi\rho(n,m,c)[D_{\mathrm{s}}(n,c,Q(i)) + D_{\mathrm{s}}(m,c,Q(i))] \tag{32}$$

where the self-diffusion coefficient of a species n may be a function of its length, n, as well as the total concentration, c, and size distribution, $Q(i)$, of the dead polymer chains in whose environment it moves.

The solution of the mass balance equations for particular functional forms of a chain-length-dependent termination constant has been considered by Benson and North.[86] However, the solution for a general function $k_{\mathrm{t}}(n,m)$ is quite difficult. Additionally, diffusion theories in semidilute and concentrated solution have not yet been extended to include polydisperse systems. As a first approximation, therefore, we neglect the dependence of termination constants on individual chain length and consider k_{t} to be a function of concentration and the moments of the radical and dead polymer distribution only. In future work, as molecular theories of diffusion are extended to polydisperse systems, this assumption may be modified. With this assumption, the long-chain hypothesis (zero consumption of monomer by initiation), and the quasi-steady-state approximation (QSSA) for the initiator fragment balance (eq 26), the kinetic equations for the moments of the polymer distribution become

$$\frac{\mathrm{d}I}{\mathrm{d}t} = -k_{\mathrm{d}}I + I\,\frac{\epsilon(1 - x)}{1 - \epsilon x}\lambda_0(k_{\mathrm{p}} + k_{\mathrm{tr}}) \tag{33}$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \lambda_0(1 - x)(k_{\mathrm{p}} + k_{\mathrm{tr}}) \tag{34}$$

$$\frac{\mathrm{d}\lambda_0}{\mathrm{d}t} = 2fk_{\mathrm{d}}I - k_{\mathrm{t}}\lambda_0^2 + \lambda_0^2\frac{\epsilon(1 - x)}{1 - \epsilon x}(k_{\mathrm{p}} + k_{\mathrm{tr}}) \tag{35}$$

$$\frac{\mathrm{d}\lambda_1}{\mathrm{d}t} = k_{\mathrm{p}}\frac{M_0(1 - x)}{1 - \epsilon x}\lambda_0 - k_{\mathrm{t}}\lambda_1\lambda_0 - k_{\mathrm{tr}}\frac{M_0(1 - x)}{1 - \epsilon x}(\lambda_1 - \lambda_0) + \lambda_0\lambda_1\frac{\epsilon(1 - x)}{1 - \epsilon x}(k_{\mathrm{p}} + k_{\mathrm{tr}}) \tag{36}$$

$$\frac{\mathrm{d}\lambda_2}{\mathrm{d}t} = k_{\mathrm{p}}\frac{M_0(1 - x)}{1 - \epsilon x}(2\lambda_1 + \lambda_0) - k_{\mathrm{t}}\lambda_0\lambda_2 - k_{\mathrm{tr}}\frac{M_0(1 - x)}{1 - \epsilon x}(\lambda_2 - \lambda_0) + \lambda_2\lambda_0\frac{\epsilon(1 - x)}{1 - \epsilon x}(k_{\mathrm{p}} + k_{\mathrm{tr}}) \tag{37}$$

$$\frac{\mathrm{d}\mu_0}{\mathrm{d}t} = k_\mathrm{t}\lambda_0{}^2 + k_\mathrm{tr}\frac{M_0(1-x)}{1-\epsilon x}\lambda_0 + \mu_0\lambda_0\frac{\epsilon(1-x)}{1-\epsilon x}(k_\mathrm{p} + k_\mathrm{tr}) \tag{38}$$

$$\frac{\mathrm{d}\mu_1}{\mathrm{d}t} = k_\mathrm{t}\lambda_0\lambda_1 + k_\mathrm{tr}\frac{M_0(1-x)}{1-\epsilon x}\lambda_1 + \mu_1\lambda_0\frac{\epsilon(1-x)}{1-\epsilon x}(k_\mathrm{p} + k_\mathrm{tr}) \tag{39}$$

$$\frac{\mathrm{d}\mu_2}{\mathrm{d}t} = k_\mathrm{t}\lambda_0\lambda_2 + k_\mathrm{tr}\frac{M_0(1-x)}{1-\epsilon x}\lambda_2 + \mu_2\lambda_0\frac{\epsilon(1-x)}{1-\epsilon x}(k_\mathrm{p} + k_\mathrm{tr}) \tag{40}$$

where λ_i and μ_i are the moments of the radical and dead polymer distributions, respectively. In eq 34–40 a volume contraction parameter ϵ [$\epsilon = [V(x = 0) - V(x = 1)]/V(x = 0)$] has been included to account for any volume changes accompanying polymerization. This factor is not essential to the model development.

Except at very high conversion the values of k_d, f, k_p, and k_tr may be taken to be constant. Appropriate values for PMMA taken from the literature are listed in Table III. The data of North and Reed[81] and theoretical description of Mahabadi and O'Driscoll[82] indicate that for MMA polymerization the initial increase in k_t follows a form

$$k_\mathrm{t}/k_\mathrm{t0} = k_\mathrm{t\,seg}/k_\mathrm{t0} = 1 + K_1\bar{N}C \tag{41}$$

due to segmental diffusion control of termination. As translational diffusion becomes controlling, k_t becomes a decreasing function of concentration. Since the data of Ludwico and Rosen[84] and Brooks[80] give only limited information in this regime, we approximate this translational control in the dilute regime by

$$k_\mathrm{t\,trans}/k_\mathrm{t0} = k'(1 - K_2C) \tag{42}$$

At higher concentration the polymer solution will pass into the semidilute regime at c^*, and at high enough molecular weight to the entangled semidilute regime at c^{**}. At concentrations above c^{**}, but still in the semidilute regime, the self-diffusion coefficient of a radical is governed by reptation; i.e.

$$D_\mathrm{s} \sim 1/N^2C^{1.75} \tag{43}$$

Thus, from the Smoluchowski equation

$$k_\mathrm{t} \sim 1/\bar{N}'^2C^{1.75} \tag{44}$$

provided that ρ, the interradical separation at reaction, is constant. Here $\bar{N}'$ is the number-average degree of polymerization of the radicals. At still higher concentrations (above c^{***}) polymer–polymer friction will result in a stronger concentration dependence; however, as previously noted, the details of this dependence are not well understood.

The functional form of k_t used in eq 33–40 is then

$$k_\mathrm{t} = k_\mathrm{t\,seg} + k_\mathrm{t\,min} \qquad 0 \le C \le C_1 \tag{45a}$$

$$k_\mathrm{t} = k_\mathrm{t\,trans} + k_\mathrm{t\,min} \qquad C_1 \le C \le C^{**} \tag{45b}$$

$$k_\mathrm{t\,rept} = k_\mathrm{t\,trans}(c^{**})\frac{N'^{**2}}{\bar{N}'^2C^{1.75}}c^{**1.75} + k_\mathrm{t\,min} \qquad c^{**} < c \tag{45c}$$

where

$$c^{**} = K_\mathrm{c}/\bar{N}^{0.5} \tag{46}$$

c_1 is the concentration at which $k_\mathrm{t\,seg} = k_\mathrm{t\,trans}$

$$c_1 = \frac{k' - 1}{K_1\bar{N} + K_2k'} \tag{47}$$

and $\bar{N}'^{**}$ is the number-average degree of polymerization of the growing chains when $c = c^{**}$. An exponent of 0.5 has been used in eq 46 on the basis of light scattering data due to Jamieson et al.[71] on polystyrene in good solvent. They find that for polymers of the size formed in the experiments considered in this study, a transition to a "Θ" pseudogel is observed. Further investigation of the correct value for this exponent is in progress. $k_\mathrm{t\,min}$ (eq 45a–c) is a parameter which has been introduced to account for the fact that in any molecular weight distribution of radicals a few radicals have very small chain length (on the order of a few monomer units). The motion of such radicals will be similar to that of the solvent, rather than being governed by any polymer diffusion model. The contribution of such radicals will be negligible at high termination rates. However, since the termination constant may decrease by 4–5 orders of magnitude during acceleration, this small contribution becomes important in some cases. In the present model, this parameter is taken to be constant and a single value of 2 × 10^4 L/(mol s) has been used at all temperatures and for all polymerization conditions. It should be noted that between c^* and c^{**}, neither eq 42 nor eq 43 is expected to be strictly valid. By analogy with viscosity data (see Figure 2) the dependence of k_t in this regime is fit by extrapolation of the dilute and entangled equations to c^{**}. This effectively defines c^{**} for the gel effect. In the unentangled semidilute regime, the theory of Adler and Freed[61] (eq 12) could be used; however, these predictions have not been experimentally verified. When the correct dependence of self-diffusion on concentration and molecular weight in this regime is determined, more detailed extensions of this model may incorporate the effect of transitions at both c^* and c^{**}.

The simple description of termination as formulated in eq 41–47 (hopefully) incorporates the most important physics behind the gel effect in the semidilute regime. Equation 45c is a major feature of this model which distinguishes it from previous efforts in that reptation has now been included in the kinetic scheme. Several limitations, however, are immediately evident. First, due to the use of a single critical concentration to describe the transition to reptative behavior, the model will lose some ability to fit data near the onset of reptation. Second, the higher polymer–polymer friction occurring in the concentrated regime and eventual diffusion control of propagation as the glass transition is approached in polymerizations carried out at temperatures below T_g are not included. Third, the details of the individual chain length dependence of termination are lumped in a single k_t dependent upon an average radical molecular weight.

In eq 41–47 several parameters have been introduced to describe the dependence of termination on concentration and molecular weight. Of these, k_t0, k_1, k_2, and k' pertain only to the dilute regime, while K_c is important in describing the onset of reptative diffusion and, consequently, the course of the gel effect rate acceleration. Approximate values of k_t0 and K_1 are available from dilute-solution experiments[81,87,24] while K_2 and k' have been estimated by applying the model to the initial stages of bulk polymerization. The exact values of these parameters are not crucial in describing the conversion vs. time and molecular weight vs. conversion behavior of polymerization. This is to be expected since most descriptions of free radical kinetics in the absence of the gel effect use a single average termination constant to describe kinetics in this regime. Correct values for these parameters may be gotten

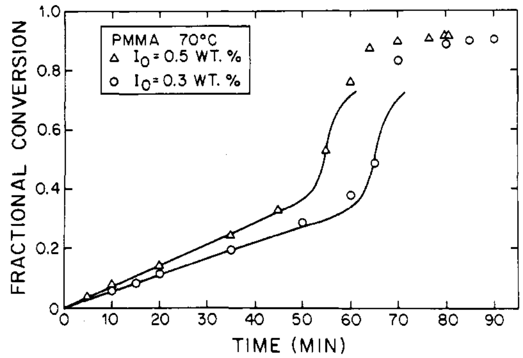

Figure 4. Conversion–time curves for PMMA at 70 °C. Experimental data from Balke and Hamielec.[2]

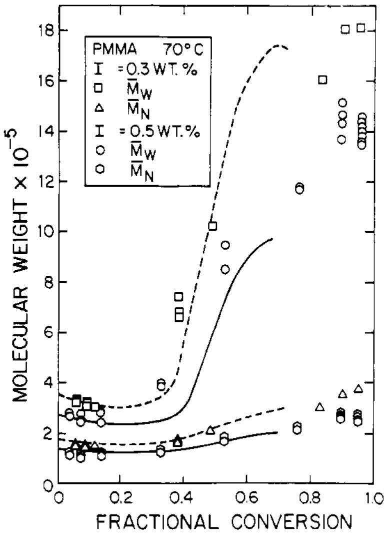

Figure 5. Experimental and predicted molecular weight averages for PMMA at 70 °C: (---) for $I_0 = 0.3$ wt %; (—) for $I_0 = 0.5$ wt %. Experimental data from Balke and Hamielec.[2]

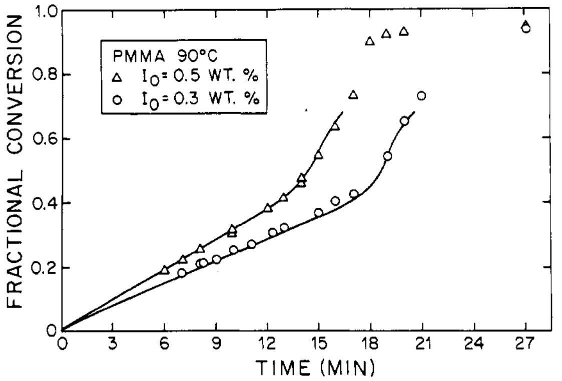

Figure 6. Conversion–time curves for PMMA at 90 °C. Experimental data from Balke and Hamielec.[2]

by a more complete series of experiments modeled after those of Brooks[80] and Ludwico and Rosen.[84] The actual values used in eq 42 are summarized in Table III.

Results and Discussion

Equations 33–40 were integrated by using a fourth-order Runge–Kutta technique on a Control Data Cyber 74 computer system. At the present level of the model development no attempt was made to fit experimental data by regression analysis; rather, values of K_c at each temperature were estimated from a visual fit of the model curves to conversion vs. time data. It should be emphasized that $k_{t\,\mathrm{min}}$ did not serve as an adjustable parameter; rather, the same value was used under all conditions. Also, the same value of K_c was used for all initiator concentrations at a single temperature. In this model, therefore, a single parameter, K_c, is used to characterize the changing kinetics associated with the gel effect. The sensitivity of the model predictions to the various parameters has been studied. A small percent change (e.g., less than 5%) in K_c causes the onset of the acceleration and subsequent conversion data to be missed completely. Comparable changes in any

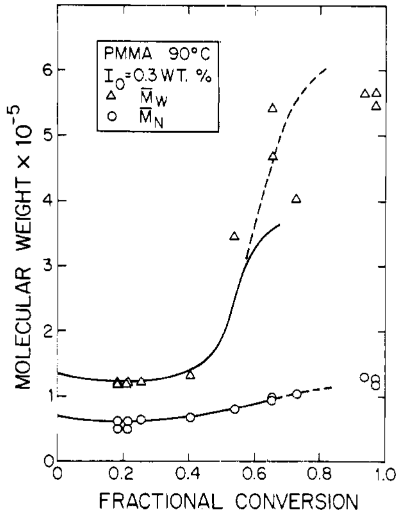

Figure 7. Experimental and predicted molecular weight averages for PMMA at 90 °C: (—) using eq 43; (---) using eq 47 for reptative termination. Experimental data from Balke and Hamielec.[2]

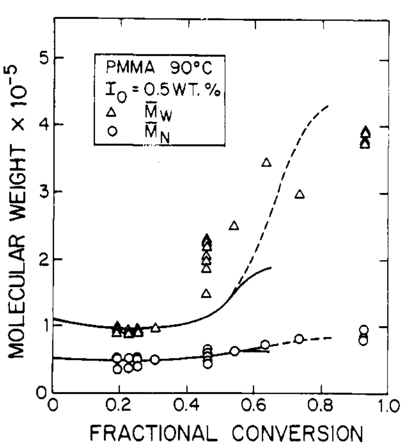

Figure 8. Experimental and predicted molecular weight averages for PMMA at 90 °C: (—) using eq 43; (---) using eq 47 for reptative termination. Experimental data from Balke and Hamielec.[2]

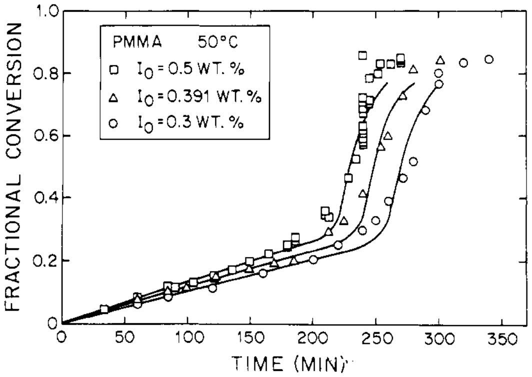

Figure 9. Conversion–time curves for PMMA at 50 °C. Experimental data from Balke and Hamielec.[2]

Table III
Parameters for MMA Polymerization

quantity	symbol	temp, °C 50	70	90	ref
propagation rate constant, L/(mol s)	k_p	558	828	1178	87
initiator dissociation constant, s^{-1}	k_d	2.07×10^{-6}	3.33×10^{-5}	3.94×10^{-4}	88, 89
initiator efficiency	f	0.5	0.5	0.5	88
volume contraction parameter	ϵ	0.242	0.251	0.259	17
bulk monomer concentration, mol/L	M_0	9.07	8.83	8.58	11
zero-conversion termination rate constant, L/(mol s)	k_{t0}	2.65×10^7	3.16×10^7	3.56×10^7	24, 87
coefficient in concentration dependence of segmentally controlled termination, cm^3/g	K_1	4.15×10^{-3}	4.61×10^{-3}	5.06×10^{-3}	81
coefficient in concentration dependence of translationally controlled termination, cm^3/g	K_2	2	2	2	
proportionality constant for translationally controlled termination	k'	1.45	1.45	1.45	
critical constant for onset of reptation	K_c	16.4	12.7	11.0	
minimum termination rate constant, L/(mol s)	$k_{t\,min}$	2×10^4	2×10^4	2×10^4	

other parameters produce only relatively minor effects.

In Figures 4–9 the model is compared to experimental conversion vs. time and average molecular weight vs. conversion data for PMMA over a range of polymerization conditions. In all cases, over the conversion range from 0 to 70% conversion the fit of x vs. t is quite good. Above 70% conversion, however, the model quickly decelerates, predicting a virtually zero polymerization rate if the semidilute concentration dependence for reptative termination k_t in eq 45c is used. If a higher concentration dependence for k_t is included in eq 45c at high polymer concentration, however, the model does not decelerate but continues to complete conversion. The range of applicability of the model, therefore, may be extended by introduction of a theory for polymer–polymer friction effects in the concentrated regime.[76–78]

For the data of Balke and Hamielec[2] at 70 °C (Figure 5) the model is successful in predicting the variation in average molecular weight with conversion using the semidilute concentration dependence of reptation. For data at 90 °C (Figures 7 and 8), where a much lower molecular weight polymer is produced, the fit is not as good. If, however, a higher concentration dependence is given to the reptative termination term at high polymer concentration, the fit becomes considerably better. This is to be expected since for low molecular weight polymer the entangled semidilute concentration regime is much narrower, the range of concentration where eq 45c should be valid is more restricted, and the inclusion of polymer–polymer friction is more important. The effects of polymer–polymer friction were simulated by using a termination rate constant which depends more strongly on concentration

$$k_t \sim 1/\bar{N}'^2 c^3 \qquad (48)$$

in place of eq 44 for conversions greater than 50%. This form has no theoretical justification; it is intended only to demonstrate that inclusion of a stronger concentration dependence for reptative termination produces qualitatively accurate corrections to the model in the concentrated polymer concentration regime.

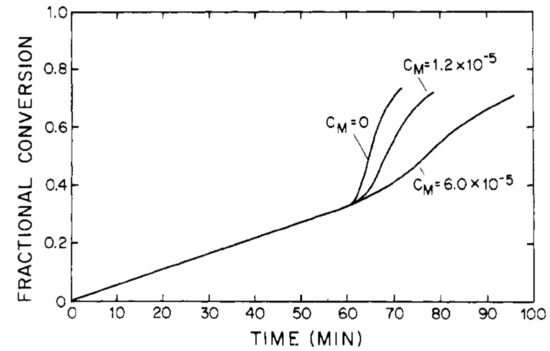

Figure 10. Effect of C_M on conversion–time predictions, using kinetic parameters for PMMA at 70 °C.

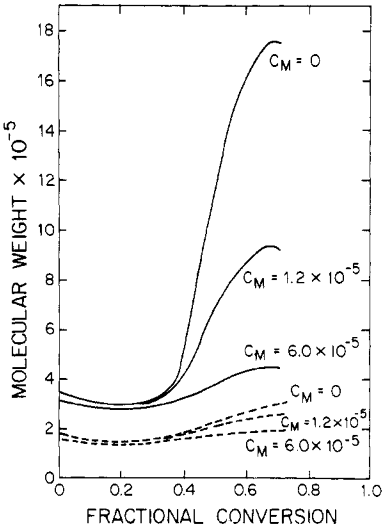

Figure 11. Effect of C_M on predicted number-average (---) and weight-average (—) molecular weight, using kinetic parameters for PMMA at 70 °C.

The effect of chain transfer on the predicted increase of rate and molecular weight is illustrated in Figures 10 and 11 with parameters for PMMA at 70 °C and an initial initiator concentration of 0.3 wt %. Even small values of C_M ($C_M = k_{tr}/k_p$) have a profound effect due to the strong dependence of k_t on radical size in the reptative regime. This effect may explain the greatly reduced gel effect seen in polymerizations where chain transfer is a significant dead polymer forming mechanism, such as high-temperature styrene polymerization.[39]

As was expected, from the good fit of data prior to c^{**} the variation of k_t with concentration and molecular weight given in eq 41 and 42 in the dilute regime is consistent with the experimental data. Since the data in this regime can be fit by a single average termination constant,[36–39] the exact choice of the various parameters is not important

Table IV
Dependence of Critical Concentration As Defined by Lee and Turner[23-25] on Number-Average Degree of Polymerization[a]

X_{crit}	C_{crit}, g/cm^3	$\bar{N}$	$C_{\mathrm{crit}}\bar{N}^{0.5}$
0.196	0.182	6160	14.3
0.206	0.192	5260	13.9
0.219	0.206	4250	13.4
0.229	0.215	3250	12.3
0.239	0.225	2260	10.7
0.254	0.240	1810	10.2
0.261	0.248	1370	9.2
0.277	0.264	950	8.1
0.284	0.271	770	7.5

[a] Data simulated from present model using parameters for PMMA at 70 °C.

in an engineering model whose sole purpose is to predict conversion vs. time and average molecular weight vs. conversion. The importance of recognizing that termination is a medium-dependent diffusion-controlled process from zero conversion, however, becomes evident in mechanistic description of the termination process. Using the model parameters for PMMA at 70 °C in Table III, a series of $\ln(1-x)$ vs. time curves were generated from the model for various initiator concentrations, and the apparent "onset" of the gel effect as defined from departure from linearity on these plots was determined. The simulated experimental data were analyzed according to the procedure of Lee and Turner[24] for defining the onset of the gel effect and the dependence of the onset conversion on the average molecular weight of the polymer produced. The simulated data are presented in Table IV. A least-squares fit of these data to an expression $K = C_{\mathrm{crit}}\bar{N}_{\mathrm{crit}}{}^{a}$ gives an apparent exponent of $a = 0.19$, though an exponent of 0.5 was used in eq 46 to describe the onset of reptation for the simulated data. Thus, in attempting to correlate such data with a theory of polymer entanglement, an anomalous result is obtained due to the effects of concentration-dependent termination in the preaccelerative regime. This effect is likely behind the inconsistent results obtained by workers who have used this definition in correlating the gel effect onset.[23-28,33-35]

Conclusions and Outlook

In this paper we have attempted to bring a new perspective to understanding the physical rate processes of free radical polymerization. The model described may be used as a starting point for including further aspects and regimes of diffusion behavior as well as for providing a guide to the design of future experiments. The major areas requiring investigation include (1) study of the dependence of the transition concentrations c^* and c^{**} on molecular weight for both free radical termination and polymer solution properties in order to determine the relationship between transitions in the different properties (For example, from Figure 2 and Brooks' data on molecular weight[80] a value of $\bar{K}_c = 6.3$ may be calculated for the onset of entangled viscosity behavior in these experiments. This may be compared qualitatively with the K_c values for polymerization reported in Table III; however, more data of this type are needed in order to decide upon the correct relationship between the rheological and kinetic manifestations of polymer entanglement.), (2) direct experimental determination of the dependence of termination rate on polymer concentration and the dead polymer and radical chain length distributions over the entire concentration range, (3) study of the dependence of polymer–polymer friction on the properties of the polymerizing medium and possible diffusion control of small-molecule reactions, such as initiation, propagation, and transfer in the concentrated-solution regime, particularly near the glass transition temperature, and (4) theoretical consideration of the effects of both dead polymer and radical polydispersity.

In the first two areas a systematic experimental study of radical termination in the presence of predissolved polymer of a well-defined narrow molecular weight distribution at known concentrations will uncouple the various factors upon which k_t depends. When combined with a study of the dependence of solution properties, perhaps zero shear viscosity and cooperative diffusion as probed by dynamic light scattering, of the same polymer over the same concentration ranges, these experiments will provide the experimental link between free radical kinetics and polymer solution physics. Theoretically, the inclusion of a theory of polymer–polymer friction in the concentrated regime presents no major difficulty. The available theories are semiempirical, however, and thus require evaluation of several parameters on the basis of experimental data on polymer physical properties. Finally, some progress has been made[73,90,91] toward extending the idea of reptation to polydisperse systems. As these extensions become more fully developed, they too may be incorporated into the kinetic model. Work is continuing in this laboratory toward establishing the connections between the transitions observed in rheological and dynamic scattering behavior and those observed in the kinetics of free radical polymerization.

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Ring-Opening Polymerization of Heterocycles: Statistical Properties of the Polymer Derived from 1-Oxa-3-thiacyclopentane

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ABSTRACT: 1-Oxa-3-thiacyclopentane was polymerized in bulk with boron trifluoride etherate as initiator. Dielectric measurements were carried out on $\langle \mu^2 \rangle / nm^2$ of the polymer in benzene at several temperatures in the interval 30–60 °C. The measurements yielded dipole moment ratios $\langle \mu^2 \rangle / nm^2$ of 0.255–0.288 and a temperature coefficient $d \ln \langle \mu^2 \rangle / dT$ of 4.2×10^{-3} K^{-1}. The experimental results were found to be in very good agreement with theoretical results based on a rotational isomeric state model which assumed perfect alternation of 1,3-dioxolane and 1,3-dithiolane, rather than a more irregular distribution which could conceivably occur in the type of ring-opening polymerization used to prepare the polymer.

Introduction

Ever-increasing emphasis is being placed in the cationic ring-opening polymerization of heterocycles.[1-4] The process involves an equilibrium between monomer and polymer, the equilibrium being governed by the ring size of the monomer, the nature of the heteroatoms, and the kind, number, and position of the substituents attached to the ring. The structure of the resulting polymer is determined by the place or places where bond scission occurs.

Recently, the ring-opening polymerization of 1-oxa-3-thiacyclopentane (OTC)[5,6] was reported. Although the polymerization seems to be initiated by quantitative formation of ethyl sulfonium, the propagation is not the simple repeating formation of sulfonium ions, as occurs

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