Comparison between Polymer Diffusion and Chain Radical Termination Kinetics: The Importance of Polydispersity

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Received January 10, 1994; Revised Manuscript Received May 5, 1994®

ABSTRACT: The diffusion coefficient of labeled poly(methyl methacrylate) (PMMA) has been measured by forced Rayleigh scattering from solutions containing labeled polymer, matrix PMMA, and toluene. Several combinations of the labeled and matrix polymer molecular weights were used. The matrix polymer concentration was varied from 0 to 40% by weight. Under the assumption that the rate of chain termination is controlled by the diffusion of the chain radicals, the diffusion data have been compared with available data for the rate coefficient of termination of PMMA radicals measured over the same polymer concentration range. The comparison shows that the distribution of chain radical molecular weight has a pronounced influence on the kinetics of termination.

Introduction

A vast amount of work has been published on free-radical polymerization,[1,2] but there remain substantial gaps in our understanding of the process. In particular, the bimolecular termination between chain radicals is one of the essential steps of free-radical polymerization, yet its mechanisms and kinetics have not been adequately isolated and quantified throughout the entire span of conversion from monomer to polymer. There are a variety of reasons for this, but they may perhaps be condensed into two broad categories. First, by virtue of being extremely fast, the kinetics of termination are subject to influence by the physical properties of the medium in which the reaction takes place. Consequently, the mechanisms of termination evolve in response to changes in the polymerizing medium with the progress of polymerization. Second, until recently and with few exceptions,[3,4] most investigations of free-radical polymerization over the entire conversion range were concerned only with the measurements of the overall rate of polymerization and the molecular weight averages of the polymer produced. Those quantities depend on many simultaneously changing variables and thus do not easily permit the determination of termination mechanisms or the dependence of the termination rate coefficient, k_t, on the relevant quantities such as polymer concentration, chain radical and formed polymer molecular weight distributions, and temperature. The lack of direct information on k_t has clearly hindered comparisons with theoretical treatments and application to polymerization of the large body of knowledge and techniques concerning the properties of polymer solutions. A number of studies have recently reported measurements of k_t during polymerization using a variety of experimental methods.[5–11]

The experimental situation may be summarized as follows. It is well established that the effect of the polymerization medium on k_t is small in the dilute regime compared to the changes at higher polymer concentrations. We recently discussed polymer–polymer reactions in dilute solutions;[12] here the focus is on termination at much higher polymer concentrations, for which k_t has been shown to decrease markedly with increasing polymer concentration during the polymerization of methyl methacrylate (MMA)[3–9] and other monomers.[10,11] For MMA, although early data[3,4] showed a decrease in k_t which became progressively stronger as the polymer concentration was increased, more recent investigations[5–9] have reported k_t data that displayed the same initial decrease followed by an interval of much slower change—although still generally a decrease—and then another rapid drop. The boundaries between these different regions of behavior are not well established experimentally since they depend on the detailed conditions under which polymerizations are conducted. Broad demarcations do, however, appear in the data: the initial decrease covers from the beginning of polymerization up to 30–50% polymer concentration (by weight), the region of slower change extends to 70–80%, and the final decrease is evident in the last stages of polymerization.

Many theoretical treatments of radical polymerization that contained analyses of chain termination have been proposed;[13–22] they have been critically reviewed.[23–25] A rather disturbing conclusion emerging from these reviews is that although the models are based on different analyses of polymerization kinetics, many of them[13–19] produce very good correlations of conversion versus time and average molecular weight versus conversion data; consequently, no definitive statement can be made about termination mechanisms from these models. Clearly, "global" data such as overall conversion and average molecular weights are not sensitive enough to the details of termination to allow discrimination among the various theoretical ideas. Direct comparison of models with k_t data is more promising. For instance, Russell et al.[20] have shown that the mechanisms of termination in the region of slower change with polymer concentration—beyond the initial rapid decrease—and up to very high concentrations may be rationalized using the idea of residual termination[17,26,27] whereby, as the diffusivities of the chain radicals become increasingly sluggish, the dominant mode of termination will be the encounter of two active chain ends moving about only because of their growth through the propagation reaction.

As stated above, between the dilute regime and the onset of slower change—the so-called "intermediate regime"—k_t

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® Abstract published in *Advance ACS Abstracts*, June 1, 1994.

0024-9297/94/2227-4176$04.50/0

decreases by several orders of magnitude with increasing polymer concentration; the qualitative connection of this observation to the decrease of polymer center-of-mass diffusion with concentration has been made since the first investigations of the course of polymerization. (Segmental rearrangements do not slow down sufficiently with polymer concentration to account for the changes in the kinetics.[28]) A number of polymerization models have incorporated a dependence of k_t on polymer concentration and molecular weight, drawing on theories and experiments in polymer diffusion,[13-19] but no model discrimination has been achieved thus far. It has emerged clearly that a decrease in k_t with polymer concentration and molecular weight is necessary to correlate the rate of polymerization data and that the idea of diffusion-controlled termination provides a suitable framework for the rationalization of such a decrease, but the detailed mechanisms of termination have remained undetermined.

In this paper, we pursue a more basic approach to termination in the intermediate regime: working under the testable assumption that the chain radical center-of-mass diffusion is indeed determining the rate of termination, polymer diffusion measurements in a system very similar to those encountered during polymerization are compared with available k_t data to examine the working hypothesis and to provide more insight into termination. One central issue is the recognition that the measured k_t is an average over the chain radical population of all the individual termination events—k_t monitors the overall radical loss. Thus, the polydispersity inherent to the polymerization medium can be a significant aspect of termination, and particularly for diffusion-controlled termination, since the diffusivities are dependent on the molecular weight of the radicals, the molecular weight of the surrounding polymer, the respective polydispersities, and the overall polymer concentration. O'Shaughnessy and Yu[29] have illustrated the importance of polydispersity in a recent and remarkably detailed analysis of termination.

The polymerization of MMA was selected as the kinetic system with which the diffusion data are compared due to the relative abundance of kinetic studies performed on this monomer. One additional note: the realization that between termination events the chain radicals are not simply diffusing, but also growing in length through propagation steps and the work by O'Shaughnessy and Yu[29] both indicate that the details of termination can be quite complicated.

Experimental Section

Materials. Poly(methyl methacrylate) (PMMA) was obtained from Polymer Laboratories. Two polymer samples of narrow dispersity ($\bar{M}_w/\bar{M}_n < 1.1$) and size exclusion chromatography (SEC) peak molecular weights, M_p, of 9.2×10^3 (PMMA-9) and 3.3×10^5 (PMMA-330) were used in the labeling reactions to be described below as well as matrix polymers in the forced Rayleigh scattering (FRS) measurements of polymer diffusion. A third, nearly-monodisperse ($\bar{M}_w/\bar{M}_n < 1.1$) PMMA sample having $M_p = 1.27 \times 10^5$ (PMMA-127) was also used as a matrix polymer. All polymers were used as received for the labeling reactions, whereas for use as matrix polymers they were dissolved in benzene, filtered, and freeze-dried.

Toluene was obtained from EM Science and used as received. According to the manufacturer's certificate of analysis, it was glass distilled, filtered through a 0.2 μm filter, and had a 0.008% water content.

4-[(4-(Dimethylamino)phenyl)azo]benzoic acid, hereafter referred to as PMR, was prepared from the corresponding sodium salt (Kodak, used as received) by precipitation with HCl from an aqueous solution, followed by repeated water washes, drying, and double reprecipitation from *N,N*-dimethylformamide (DMF). ^{1}H NMR and elemental analysis confirmed that the product obtained was pure PMR.[25]

PMR-Labeled PMMA. The labeling procedure consists of the initial functionalization of PMMA via random reaction (aminolysis) of the ester groups with 2-aminoethanol (EA) following a procedure similar to the one used by Gibson and Bailey;[30] subsequently, the alcohol functionality introduced is reacted with PMR following Hassner and Alexanian.[31]

For aminolysis, a solution of PMMA, freshly distilled EA, and 1,4-diazabicyclo[2.2.2] octane (DABCO) in anhydrous DMF was refluxed for 6 h under a dry nitrogen atmosphere. The reaction conditions for PMMA-330 were 1:40 molar ratio of EA to ester groups, 1:1 molar ratio of DABCO to EA, and 9% total polymer concentration by weight. (Under the above conditions long reaction times eventually led to cross-linking but control was not difficult). After refluxing, the mixture was poured into a 15% (v/v) solution of HCl in methanol/water, washed twice with the same HCl solution, and then washed four times with a 60% (v/v) solution of methanol in water to neutral pH. The polymer was then dried. For the aminolysis of PMMA-9 the ratio of EA to ester groups was doubled and the total polymer concentration was 20%. ^{1}H NMR and SEC of the products showed no significant changes with respect to the precursor polymers.

The labeling reaction was carried out as follows: a solution of the functionalized polymer, dicyclohexylcarbodiimide (DCC), 4-pyrrolidinopyridine (PPY), and PMR in anhydrous tetrahydrofuran (THF) was refluxed for 6 days. The reaction conditions were 3:1 molar ratio of PMR to alcohol functionality (assuming complete conversion in the aminolysis step), 1.2:1 molar ratio of DCC to PMR, 1:6 molar ratio of PPY to PMR, and 4% total polymer concentration by weight. At the end of the reaction the mixture was filtered into hexane to precipitate the polymer. The polymers obtained, PMMA-330-PMR and PMMA-9-PMR, were further purified as follows: PMMA-330-PMR was repeatedly washed with methanol, and PMMA-9-PMR with hexane, until the liquid was colorless and then dried. The polymers were dissolved in THF and precipitated in hexane, dried, dissolved in chloroform (PMMA-330-PMR) or THF (PMMA-9-PMR), eluted through a silica gel column, dried again, and finally freeze-dried from benzene. For both labeled polymers, ^{1}H NMR and SEC results were almost identical to those of the unreacted parent polymers. The use of SEC with on-line UV–vis detection established that the labeled polymers did not contain any residual PMR. The extent of labeling was determined by UV–vis spectroscopy: PMMA-330-PMR had 1 dye molecule per 430 monomers (7.7 per chain) and PMMR-9-PMR had 1 dye molecule per 200 monomers (0.5 per chain).

Sample Preparation. Typically, samples were prepared by dissolving the matrix PMMA in toluene together with a small amount of labeled PMMA. After the components were completely mixed, the solution was directly introduced into a 2-mm path length spectrophotometric cell, which was then cooled to about −30 °C and flame-sealed. To prepare some of the higher-concentration samples with the PMMA-330 matrix, for which direct transfer into the cell was difficult, the matrix polymer was first introduced into the cell and a solution of labeled PMMA in toluene was then added; if necessary, the excess solvent was evaporated to the desired concentration before sealing. Finally, the samples were left to homogenize at 50 °C; the sample homogeneity was ultimately checked by measuring the diffusion coefficient at different locations in the sample. Typically, the labeled polymer concentration was about 0.5 or 0.15% by weight, depending on whether the FRS amplitude or phase protocol, respectively, was used for the measurements; the matrix concentration ranged between 0 and 40% by weight.

Forced Rayleigh Scattering. The basic concepts behind the FRS method have been recently reviewed.[32,33] For this work, two different experimental protocols were used; they will be referred to as phase and amplitude, respectively. In both cases the grating was created by an Ar$^+$ laser operating at $\lambda_0 = 488$ nm. In the phase protocol the decay of the grating was probed with a He–Ne laser operating at $\lambda_0 = 632.8$ nm, whereas in the amplitude protocol the grating was probed using the Ar$^+$ laser, attenuated by a factor of 10^4. The optical configuration of the FRS apparatus and the data acquisition procedure for the phase protocol have been described before.[34,35] The features of the amplitude setup were largely the same as for the phase; the modifications are detailed elsewhere.[25] The diffusion coefficient of PMMA-9-PMR was measured with the phase protocol, whereas

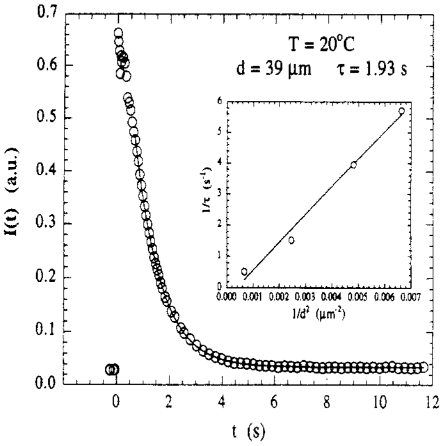

Figure 1. Measured FRS decay curve from a solution of 0.53% PMMA-330-PMR in toluene. The smooth line is a nonlinear fit to eq 1. The linear relationship between the inverse decay time and the inverse square of the grating spacing, according to eq 2, is shown in the inset.

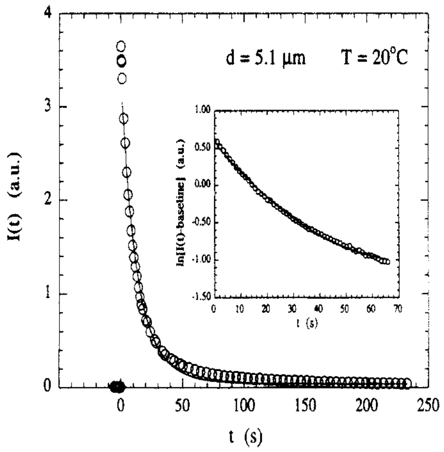

Figure 2. Measured FRS decay curve from a solution of PMMA-330-PMR in 20% PMMA-330 and toluene. The smooth line is a nonlinear fit to eq 1. The inset shows the natural logarithm of the intensity, after baseline subtraction, as a function of time. The smooth line in the inset is a linear fit to eq 3.

the amplitude protocol was used for the measurements of PMMA-330-PMR diffusion. Measurements were made at 20.0 and 0.0 (±0.1) °C.

The FRS decay curves collected from dilute solutions could be fit to a single-exponential function

$$I(t) = (Ae^{-t/\tau} + B)^2 + C^2 \tag{1}$$

where I is the measured intensity, A is a prefactor, t is the time, τ is the characteristic decay time, B is a coherent baseline term, and C is an incoherent baseline term. The diffusion coefficient was determined from values of τ obtained at different spacings according to the following relation:

$$\frac{1}{\tau} = \frac{4\pi^2 D}{d^2} + \frac{1}{\tau_0} \tag{2}$$

where D is the diffusion coefficient, d is the grating spacing, and $1/\tau_0$ is the intercept. A typical decay curve for a sample of 0.53% PMMA-330-PMR in toluene is displayed in Figure 1 together with the dependence of τ on d^2. The linearity of the data in the inset to Figure 1 confirms that a diffusion process is being monitored by the FRS decay.

The dilute solution example of Figure 1 should be compared with Figure 2, which displays the decay curve obtained for a sample containing the same tracer in 20% PMMA-330/toluene. In the latter case the data are not well represented by a single-exponential decay, although the departure is not large. A clearer illustration is presented in the figure inset, which shows the natural logarithm of $I(t)$—after baseline substraction—as a function of time; if the decay were single exponential, the data would fall on a straight line. Decay curves for samples having intermediate concentrations between the two cases illustrated above showed a gradual departure from a single-exponential decay as the concentration was increased. Interestingly, the FRS decay from a sample with 30% PMMA-330 showed a reduction in the departure compared to the 20% sample. No dependence of the degree of deviation from single-exponential behavior on the grating spacing was noticed. Decay curves for the PMMA-330-PMA tracer in a PMMA-9 matrix and the PMMA-9-PMR tracer in PMMA-330 and PMMA-127 matrices also showed a departure from single-exponential behavior as the matrix concentration was increased; for the smaller tracer the deviation was not apparent until the matrix concentration reached 20% and was never very large. Analogous findings have been reported[36] in FRS measurements of labeled polystyrene diffusion in polystyrene/toluene solutions.

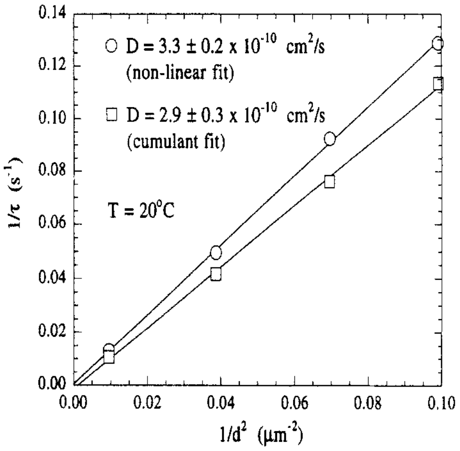

Figure 3. Inverse decay constant of PMMA-330-PMR in a 20% PMMA-330 toluene solution vs the inverse square of the grating spacing.

All the decay curves were also fit to a second-order cumulant function

$$I(t) = [A\exp(-t/\tau + B't^2)]^2 + C^2 \tag{3}$$

without the coherent baseline contribution. The inset to Figure 2 shows the result of this procedure as the solid line through the data. The decay time constants determined by fitting the decay curves with eqs 1 and 3 were always very similar and always linear with d^2, as Figure 3 shows for a particular case. The difference in the diffusion coefficients extracted from the two types of fit was always comparable to, or smaller than, the estimated experimental error (10–30%).

Results

Ideally, to provide as close a comparison as possible with the polymerization system, MMA should be the solvent employed in the polymer diffusion experiments. Unfortunately, no FRS signal was detected using labeled PMMA in MMA. Toluene is a reasonable substitute since its viscosity is within 5% of the viscosity of MMA—at both 20 and 0 °C—and thus the two solvents are expected to be similar in their effect on polymer diffusion. An experimental indication of the dynamic similarity—with respect to polymer diffusion—of solutions containing toluene and MMA was also pursued. By comparing the diffusion coefficients of a photochromic dye in solutions of PMMA in toluene and MMA, an estimate of the similarity or difference in the friction experienced by monomer-sized segments of the polymer in the two different environments may be obtained. The toluene and MMA solutions examined contained 40% PMMA (by weight) with M_p = 7.0 × 10^4. The values of the dye diffusion coefficient in the two systems agree to within 15%, an indication that the toluene and MMA solutions are very similar with respect to PMMA diffusion. The

Table 1. Estimate of the Effect of Temperature on Polymer Diffusion[38]

$r = [D(20\ °C)D_o(0\ °C)]/[D(0\ °C)D_o(20\ °C)]$		
PMMA-330-PMR in PMMA-330	PMMA-330-PMR in PMMA-9	PMMA-9-PMR in PMMA-330
$\omega_p = 11\%, r = 1.14$	$\omega_p = 20\%, r = 1.02$	$\omega_p = 10\%, r = 1.21$
$\omega_p = 30\%, r = 2.47$	$\omega_p = 30\%, r = 1.22$	$\omega_p = 29\%, r = 1.80$
	$\omega_p = 39\%, r = 2.51$	$\omega_p = 40\%, r = 2.69$

polymer concentration of 40% was chosen because it corresponds to the highest concentration used in the polymer diffusion measurements; since toluene and MMA are both good solvents for PMMA, any dynamic dissimilarity between the two should be more evident the higher the polymer concentration. Thus, we conclude that the substitution of toluene for MMA has little effect on PMMA diffusion, and the data presented may be viewed as representative of PMMA/MMA solutions. Details of FRS measurements of dye diffusion in PMMA solutions are given in the subsequent paper.[37]

Another technical point that requires discussion is the temperature, T, dependence of polymer diffusion, as the kinetic data were obtained at different T. In a comparison between the polymer concentration dependence of PMMA diffusion and termination rate, the data must be normalized with respect to a reference concentration; an obvious choice of reference is zero concentration. It is therefore the magnitude of the effect of T on the normalized diffusion data that must be assessed; this will be greater the lower the temperature and the higher the polymer concentration. For these reasons, some polymer diffusion measurements were performed at 0 °C, the lowest T at which appropriate kinetic data are available, whereas the majority of the measurements were made at 20 °C, a temperature close to the ones used in other kinetic studies. Temperatures much higher than 20 °C were precluded since the dye used for the labeling of the polymer undergoes a rapid thermal reconversion after the laser-induced photoisomerization and thus makes FRS measurements impossible.

The importance of T may be assessed by comparing, for each T, the diffusion coefficients normalized with respect to the value obtained at the lowest matrix concentration. This is done in Table 1, where D is the polymer diffusion coefficient, D_0 is the polymer diffusion coefficient at zero matrix concentration, and ω_p is the matrix weight fraction. If T had no contribution beyond its effect on D_0, the quantity r in Table 1 would always have the value of 1, independent of polymer concentration. Overall, the difference between 0 and 20 °C brings about changes in the normalized diffusion coefficient that are less than a factor of 3. It will become evident in the subsequent discussion that such changes do not affect the conclusions of this work in any way. Therefore, in what follows, the polymer diffusion data at 20 and 0 °C are used in all the comparisons with kinetic data, irrespective of the T at which the latter were obtained.

Discussion

The simplest theoretical discussion of diffusion-controlled reactions has been presented by Smoluchowski;[39] when applied to termination, it gives

$$k_t^{n,m} = 4\pi b(D_n + D_m)N_A \qquad (4)$$

where $k_t^{n,m}$ is the rate coefficient for the termination of radicals n and m, D_n and D_m are the diffusion coefficients of the radicals, N_A is Avogadro's number, and b is the so-called capture radius, the distance between the two reactants below which the reaction proceeds instantaneously. Although eq 4 provides a useful qualitative framework for a discussion of chain radical termination, its quantitative use is complicated by the complexity of the system, most notably polydispersity. To obtain the measured k_t, the above expression must be averaged over the chain radical distribution. In the following discussion, the Smoluchowski theory will be used as a qualitative guide to the interpretation of the results. Crudely, eq 4 implies that k_t should display the same features as some representative polymer diffusion coefficient, D, and that there should be some quantitative correspondence between the values of k_t and D for some reasonable value of b; these aspects will be examined by comparing diffusion and kinetic data.

Table 2. Cumulative and Instantaneous Molecular Weights from Kinetic Experiments[a]

ref	ω_p (%)	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w' \times 10^{-5}$	$\bar{M}_n' \times 10^{-5}$
3	0–40		6–10		6–50
4	0–42		0.8		3.5–8.5
5[b]	0–40	2.7–17	1.5–4.6	2.7 to >30	1.5 to >14
5[b]	0–40	1.1–8.3	0.5–1.7	1.1–26	0.5–12
5[b]	0–40	0.5–3.3	0.4–0.7	0.5–14	0.4–7.3
7	0–14		≈0.26		≈0.26
7	20–40		0.4–0.6		7–17
8	0–40		0.2–0.4		0.2–0.6
9	0–29		1–1.5		1–1.5
9	31–43		1–2		1–9

[a] All values except $\bar{M}_w$ and $\bar{M}_n$ from ref 5 are calculated from kinetic equations. [b] Three initiator concentrations were used in ref 5.

It is important to consider the average molecular weights typical of the polymerization experiments; Table 2 shows the cumulative and instantaneous average molecular weights produced in a number of kinetic studies. (The cumulative average molecular weights, $\bar{M}_w$ and $\bar{M}_n$, measured at each level of monomer conversion contain contributions from all polymers formed from the beginning of polymerization up to that conversion. They are to be distinguished from the so-called instantaneous average molecular weights, $\bar{M}_w'$ and $\bar{M}_n'$, which account only for the polymer formed at a specific value of conversion. The cumulative average molecular weight is the quantity usually measured.) The values in Table 2 are obtained from well-known kinetic relationships—with the partial exception of ref 5, which reports measurements of $\bar{M}_w$ and $\bar{M}_n$—and should therefore be regarded only as indicative of the order of magnitude of the various molecular weights. A comparison of the cumulative and instantaneous average molecular weights as given in Table 2—the latter being generally greater than the former—illustrates how the chain radicals have a higher molecular weight than that of the formed polymer except, of course, at low conversion.

First, the dependence of the diffusion coefficient of PMMA-330-PMR on the concentration of the PMMA-330 matrix will be compared to the conversion dependence of k_t from the data of Hayden and Melville[3] and Sack et al.[5] for the bulk polymerization of MMA at 22.5 and 0 °C, respectively. From the values in Table 2 it is apparent that the molecular weight of 3.3×10^5 used in the polymer diffusion experiments is only rather crudely representative of the typical molecular weight of the chain radicals and of the formed polymer found in the polymerization experiments. Of course, an accurate representation of the molecular weight distributions found in radical polymerization would require using many polymers with different molecular weights in many combinations of labeled/matrix pairs: a labor-intensive proposition. Fortunately, it will be shown that the relatively small set of diffusion data

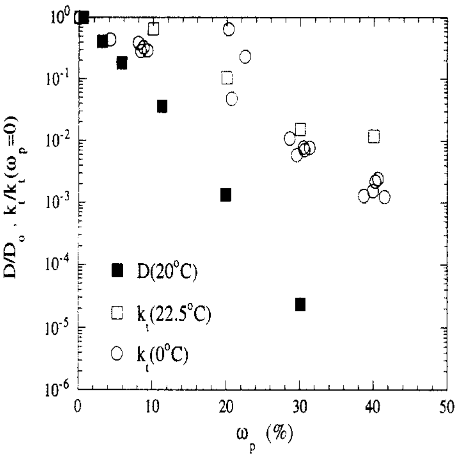

Figure 4. Comparison of the polymer concentration dependence of the diffusion coefficient of PMMA-330-PMR in PMMA-330 with the conversion dependence of k_t. All data are normalized using the zero matrix concentration and zero-conversion data. The kinetic data are from refs 3 and 5.

presented here will suffice to capture some essential and general aspects of the problem.

In Figure 4 the diffusion coefficients of PMMA-330-PMR in the PMMA-330 matrix, normalized by the datum at zero matrix concentration, are compared to the kinetic data of Hayden and Melville[3] and Sack et al.,[5] also normalized using the zero-conversion values.[40] The figure clearly shows that the polymer diffusion coefficient, D, decreases much more rapidly with polymer concentration than does k_t. At 20% polymer the difference between D and k_t is already about 2 orders of magnitude, and it reaches 3 orders of magnitude at 30%. Notice from the estimates in Table 2 that the molecular weights of both the tracer and the matrix in the diffusion experiments are generally lower than the average molecular weights produced in the kinetic studies, especially at high conversion. The differences in the temperatures of the various measurements are of no relevance given the magnitude of the discrepancy between the diffusion and kinetic data. Incidentally, the diffusion data cover a wide range of dynamic conditions, from dilute to fully entangled solutions.

It is evident from the data in Figure 4 that the dependence of the diffusion coefficient of PMMA-330-PMR on the concentration of the PMMA-330 matrix does not represent at all the decrease in k_t measured in the polymerization experiments. It may be argued that a quantitative agreement should not be expected since the labeled polymer and the matrix are only very roughly representative of the average molecular weights of the chain radicals and the formed polymer produced in the polymerization studies. Furthermore, the polymerization medium contains polydisperse polymer whereas the diffusion experiments were carried out with nearly-monodisperse polymers.

Whether the polydispersity of the polymer formed during polymerization is of any consequence in reconciling the difference between the diffusion and kinetic data can be assessed by discussing the effect of the matrix molecular weight on the mobility of the labeled polymer. Increasing the matrix molecular weight in the diffusion experiments—to mimic the effect of the high molecular weight portion of the formed polymer distribution—would only bring the diffusion data in greater disagreement with the kinetic data; the decrease and final plateau of the diffusion coefficient of a probe polymer as a function of the molecular weight of the matrix polymer are experimentally well documented.[42] (The matrix molecular weight necessary to reach the plateau is 3–5 times the probe molecular weight). It can be concluded, therefore, that the presence in the polymerization media of polymers with molecular weight in excess of 3.3 × 10^5 further underscores the discrepancy between diffusion and kinetic data. A decrease in the matrix molecular weight would certainly contribute to a better agreement between the diffusion and kinetic data. Figure 5 shows that using PMMA-9 as the matrix in diffusion measurements—while still using PMMA-330-PMR as the probe—does afford a considerably better agreement between diffusion and kinetic data. But a matrix with a molecular weight of 9.2 × 10^3 is very much smaller than, and therefore not at all representative of, the typical average molecular weight of the polymer formed in the polymerization studies. In other words, the diffusion data of PMMA-330-PMR and the kinetic data could be reconciled if the majority of the polymer formed during polymerization had a molecular weight close to 9 × 10^3; Table 2 shows that this is not the case. It must then be concluded that the concentration dependence of the diffusion coefficient of a polymer with molecular weight of 3.3 × 10^5 grossly overestimates the conversion dependence of k_t as reported by Hayden and Melville[3] and Sack et al.[5] Notice, from Table 2, that the molecular weight of PMMA-330-PMR is generally smaller than that of the average chain radical.

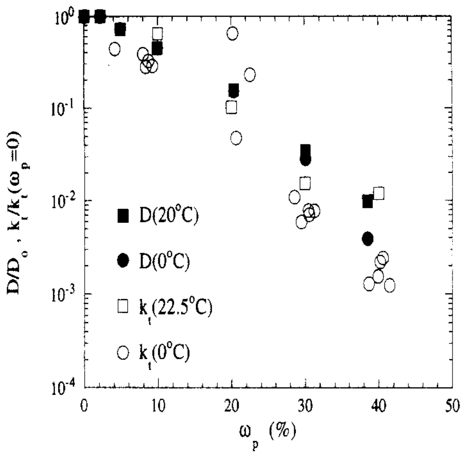

Figure 5. Comparison of the polymer concentration dependence of the diffusion-coefficient of PMMA-330-PMR in PMMA-9 with the conversion dependence of k_t. All data are normalized using the zero matrix concentration and zero-conversion data. The kinetic data are from refs 3 and 5.

The previous comparison between k_t and D implicitly assumed that b did not depend on polymer concentration. This aspect will now be discussed in more detail. For reactions between small molecules, b is on the order of the molecular dimensions, say 5 Å. From the relatively few investigations of reactions between macromolecules in dilute solutions,[43] it appears that b is on the order of the monomer size. Theoretical treatments of macromolecular reactions in melts or concentrated solutions[44] suggest that b should be on the order of the polymer chain dimensions, say 100 Å. Thus, b might increase with polymer concentration, but as yet no experimental information is available on its dependence. Clearly, an increase of b with polymer concentration will tend to lessen the discrepancy between the k_t and D data presented in Figure 4. No attempt will be made here to investigate the issue of the exact dependence of b on polymer concentration. Rather, it will be shown that the previous conclusions are unaffected. The capture radius b can be evaluated from eq 4 using the k_t data of Hayden and Melville[3] at 22.5 °C and the D data for PMMA-330-PMR in PMMA-330 at 20 °C. At zero polymer concentration b = 1.3 Å, a physically reasonable value. At 30% polymer concentration b = 1.3 × 10^3 Å. The latter estimate is unreasonable for the

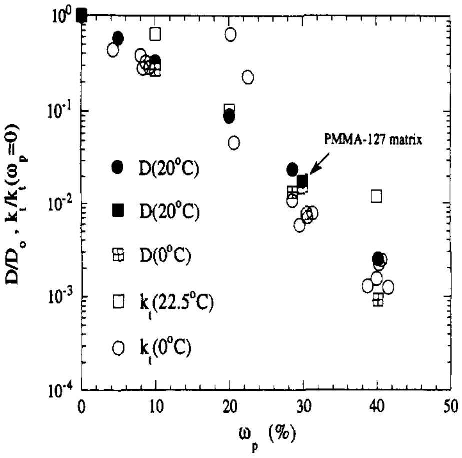

Figure 6. Comparison of the polymer concentration dependence of the diffusion coefficient of PMMA-9-PMR in the PMMA-9 and PMMA-127 matrices with the conversion dependence of k_t. All data are normalized using the zero matrix concentration and zero-conversion data. The kinetic data are from refs 3 and 5.

physical quantity b represents, since it is much larger than the dimension of the polymer chain. Similar results are obtained at 0 °C: $b = 1.4$ Å for 0% polymer and $b = 1.2 \times 10^3$ Å for 30% polymer, using the kinetic data from Sack et al.[5] These estimates imply that no physically reasonable dependence of b on polymer concentration will produce agreement between the k_t and D data displayed in Figure 4. The conclusion is exactly as before: the k_t data cannot be reconciled with the mobility of PMMA-330-PMR in PMMA-330; a much higher polymer diffusion coefficient would be necessary to give reasonable b values.

The other variable that can be manipulated in the diffusion experiments is the molecular weight of the labeled polymer; this directly addresses the effects associated with the distribution of the chain radical molecular weight. Figure 6 displays a comparison between the kinetic data of Hayden and Melville[3] and Sack et al.[5] and the diffusion coefficient data obtained using PMMA-9-PMR as the probe polymer with PMMA-330 and PMMA-127 as the matrix polymers. The diffusion and kinetic data are in remarkably good agreement. As mentioned before, the diffusion coefficient of a probe polymer eventually becomes independent of the matrix molecular weight as the latter quantity is increased.[42] The data presented in Figure 6 conform to expectations in this regard: the diffusion coefficient obtained using the PMMA-127 matrix falls in line with the data for the PMMA-330 matrix. Thus, comparing the diffusion coefficient of PMMA-9-PMR obtained using a nearly-monodisperse matrix with k_t measured in polydisperse media is completely justified given the values of the molecular weights involved in the two sets of data. In other words, the particular choice of the matrix molecular weight has no influence on the quantitative aspects of the comparison made in Figure 6.

The capture radius may again be estimated from eq 4 using the k_t values from Hayden and Melville[3] at 22.5 °C and the diffusion data for PMMA-9-PMR in PMMA-330 at 20 °C. At zero polymer concentration $b = 0.18$ Å. At 20% polymer concentration $b = 0.25$ Å. Finally, at 30% polymer concentration $b = 0.17$ Å. Similarly, at 0 °C $b =$ 0.19, 0.97, and 0.12 Å for 0, 20, and 30% polymer, respectively, using the kinetic data from Sack et al.[5] The b values reported above are somewhat lower than might be expected but are nevertheless reasonable given the coarseness with which eq 4 represents the complexity of termination in a polydisperse polymerization medium. The relative insensitivity of b to changes in polymer concentration is not surprising given the good agreement between the kinetic and diffusion data illustrated in Figure 6. Higher, and therefore more physically reasonable, values of b would have been obtained if the above comparison between k_t and D had been made using diffusion data for a labeled polymer with higher molecular weight (although smaller that PMMA-330-PMR) since smaller diffusion coefficients would have been measured. But, the concentration dependence of D would be more pronounced and therefore less similar to that exhibited by k_t. Other factors should be considered, however. First, any concentration dependence of b could reconcile, at least in part, the different concentration dependences of k_t and D. Furthermore, it should be remembered that k_t represents an average over the distribution of chain radicals with different lengths and particularly that this distribution changes during the course of polymerization. Thus, k_t may not have exactly the same concentration dependence as D for any particular polymer. In summary, given the complex nature of termination during polymerization, as opposed to the comparatively simple diffusion systems examined here, it would be inappropriate to insist on a detailed quantitative comparison between k_t and D.

The conclusion emerging from the previous comparison of diffusion and kinetic data is that the mobility of the average chain radical is not representative of the kinetics of termination, independent of the polydispersity of the formed polymer; the diffusion rate of the average radical grossly underestimates the rate of termination. The decrease of k_t can still be interpreted within the context of diffusion-controlled termination, but the implication is that chain radicals much smaller than the average size dominate the kinetics; the data in Figure 6 are consistent with this interpretation. Although the concentration of small chain radicals is lower—possibly much lower—than the average radical concentration, their much larger mobility enables them to participate in termination more effectively than the more abundant, larger radicals. Thus, the molecular weight distribution of the chain radicals has a determining influence on the kinetics of termination. This influence derives from the dependence of the chain radical mobility on molecular weight. Of course, such an influence will vary in degree as conversion progresses, according to the importance of diffusion in controlling termination; it will be more pronounced the higher the polymer concentration and average molecular weight of both the chain radicals and the formed polymer. These findings are in agreement with the theoretical analysis of O'Shaughnessy and Yu.[29]

The k_t data of Brooks[4] are well suited for a comparison with the diffusion data since their polymerization system was rather well defined in terms of the formed polymer and chain radical molecular weights. Within the framework of diffusion-controlled termination it could be expected from the average values in Table 2 that k_t would fall somewhere between the diffusion data of PMMA-330-PMR in PMMA-330 and in PMMA-9. Figure 7 shows that this is not the case. At least up to 16% polymer, k_t maintains its initial value and then decreases with further increases in polymer concentration. The subsequent decrease may be explained by diffusion-controlled termination, if attention is paid to the distribution of chain radicals. It is clear from Figure 7 that the rate of decrease of k_t cannot be explained by the mobility of PMMA-330-PMR. Again, the PMMA-9 matrix is needed to give a concentration dependence of D similar to the one k_t has, but the unreactive polymer in the kinetic experiments had a molecular weight almost 10 times larger than that of PMMA-9. Notice also that the molecular weight of PMMA-330-PMR is rather well representative of the average molecular weight of the radicals. (The fact that

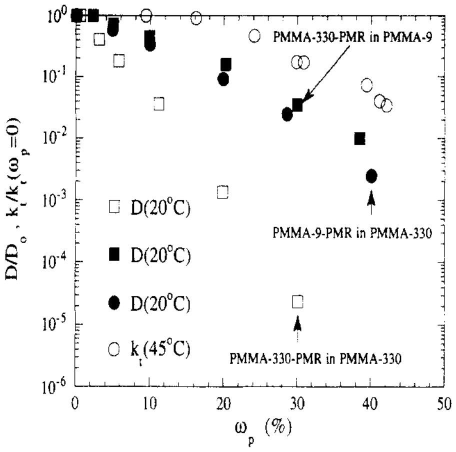

Figure 7. Comparison of the polymer concentration dependence of the diffusion coefficient of PMMA-330-PMR in PMMA-330, PMMA-330-PMR in PMMA-9, and PMMA-9-PMR in PMMA-330 with the conversion dependence of k_t. All data are normalized using the zero matrix concentration and zero-conversion data. The kinetic data are from ref 4.

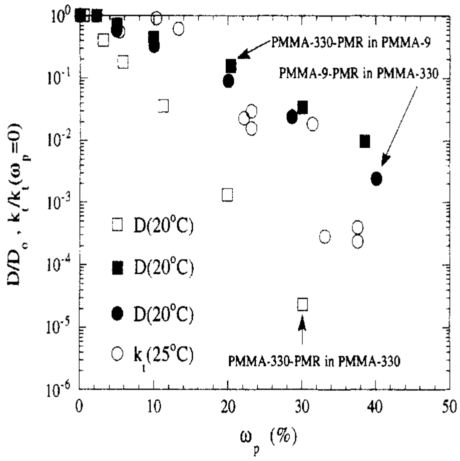

Figure 8. Comparison of the polymer concentration dependence of the diffusion coefficient of PMMA-330-PMR in PMMA-330, PMMA-330-PMR in PMMA-9, and PMMA-9-PMR in PMMA-330 with the conversion dependence of k_t. All data are normalized using the zero matrix concentration and zero-conversion data. The kinetic data are from ref 7.

it is a lower bound only reinforces the point made above.) The diffusion data of PMMA-9-PMR in PMMA-330 have a dependence on matrix concentration very similar to, if somewhat stronger than, the one displayed by k_t. (As before, the difference in molecular weight between the matrix and the unreactive polymer does not matter since the mobility of the probe is independent of matrix molecular weight in this range of values.) Thus, the k_t data of Brooks[4] between 16 and 43% polymer can be interpreted within the diffusion-controlled termination framework but only by assuming, as before, that chain radicals smaller than average are responsible for most termination events. (The difference in temperature between the kinetic study, 45 °C, and the diffusion experiments, 20 °C, is believed to play a minor role.)

In Figure 8, the data of Zhu et al.[7] are compared to the diffusion data. In the 0–14% conversion interval the change in k_t is smaller than the corresponding change in D for each probe/matrix combination. In the 14–40% conversion region the rate of change of k_t with polymer concentration is similar to that of D for PMMA-330-PMR in PMMA-330 and definitely higher than that of the other diffusion pairs; a quantitative comparison between k_t and D is, however, not readily established. The molecular weight of the PMMA-330 matrix is larger than the average molecular weight of the formed polymer—see Table 2—whereas the molecular weight of the PMMA-330-PMR probe is smaller than that of the average chain radical. These differences in the matrix/formed polymer and probe/chain radical molecular weights could reconcile the kinetic and diffusion data in Figure 8 since they have an opposite effect on the concentration dependence of polymer mobility. The above observations are only qualitative in character and are merely intended to point out that the comparison between these last kinetic data and the diffusion data reveals no inconsistency with the assumption of diffusion-controlled termination and the conclusions previously reached on the basis of the data of Hayden and Melville[3] and Sack et al.[5] Interestingly, although they were obtained at a higher temperature, the data of Zhu et al.[7] display a more pronounced decrease with polymer concentration than do the data of Hayden and Melville[3] and Sack et al.[5]

The k_t data of Shen et al.[8] have a weaker dependence on polymer concentration than any of the probe/matrix diffusion pairs. The discrepancy may again be explained by the differences in the molecular weights used in the diffusion and kinetic experiments. It should be noted that under the experimental conditions used by Shen et al.[8]—giving rise to relatively small chain radicals and formed polymer—the kinetics of termination is expected to be less sensitive to the detailed characteristics of the medium—e.g., the size distribution of the chain radicals and of the formed polymer.

Carswell et al.[9] reported k_t data that were independent of polymer concentration up to about 29%; the relatively high temperature used in the polymerization study, 60 °C, may be partly responsible for the reported behavior, although the k_t data of Shen et al.[8] did show a decrease with polymer concentration at the same temperature. From 31 to 43% polymer the data of Carswell et al.[9] show a decrease at a rate intermediate between those displayed by the diffusion data for different probe and matrix molecular weights. On the basis of the differences between the molecular weights used in the diffusion experiments and those that occur during polymerization, the different concentration dependences of k_t and D may be reconciled using arguments entirely similar to those discussed before. Therefore, the data of Carswell et al.[9] show no inconsistency with previous conclusions.

The attempts to analyze the kinetics of diffusion-controlled termination discussed in the Introduction may be re-evaluated in light of the results presented above. No matter how effective they may be at describing some experimental data, models[14,18,19] that use only the average molecular weight of the formed polymer to provide k_t with a molecular weight dependence are to be considered unsound; this point has already been stressed[15] and is certainly confirmed by this investigation. To consider k_t as depending directly on the average molecular weight of the chain radicals—through the dependence of the diffusion coefficient on the size of the diffusing species—and indirectly on the average cumulative formed polymer molecular weight and concentration—which establishes the diffusion mode—follows the current understanding of polymer diffusion in solutions.[15] Such a procedure, however, implies that the mobility of the chain radicals of average size is a reasonable representation of the diffusion rate that controls the kinetics of termination. The findings of this investigation suggest that this approach is in general incorrect, although it might be appropriate under particular polymerization conditions, namely, those that produce low molecular weight polymer. Models that incorporate a sound description of polymer diffusion and the details of the size distribution of both chain radicals and formed polymer[16,17]—especially the former—have the best hope of providing an accurate molecular-level representation of the events determining chain termination; when they are used in the context of a Smoluchowski-type description of k_t from the polymer diffusion coefficients, they automatically eliminate from the accounting all the chain radicals that are too slow to control the kinetics of termination. Other models[13,22] that adopt a distribution of k_t values—with different coarseness—for the termination of radicals of different molecular weights do allow a description of the effect of the size distributions, but their effort is at the phenomenological level and they do not address the origin of the distribution of k_t values, nor can they predict what those different values should be. Finally, the approach of O'Shaughnessy and Yu,[29] based on modern ideas of polymer physics, arguably provides the most basic description yet available of termination; some of its results are confirmed by this work.

Conclusions

The comparison of the polymer diffusion data with the k_t data of Hayden and Melville[3] and Sack et al.[5] clearly shows that the reaction between chain radicals of average size is not representative of the kinetics of termination. To insist on a mechanism of termination controlled by chain radical diffusion requires that reactions involving chain radicals much smaller than those of average size be responsible for most termination events. This underscores that the distribution of chain radical sizes is an essential factor in determining the kinetics of termination under the polymerization conditions used, which produced a polymer having a high average molecular weight. The effect is a direct consequence of the pronounced dependence of the chain radical diffusion coefficient on the radical molecular weight and on that of the surrounding polymer.

In general, it should be expected that the importance of the dispersity in radical sizes would vary according to the characteristics of the polymerization medium: overall polymer concentration, average molecular weight of the chain radicals and the formed polymer, and polydispersity of the formed polymer. For any given set of polymerization conditions, the dependence of the chain radical mobility on the above factors will determine how sensitive the kinetics of termination will be to the chain radical polydispersity. Although other kinetic data[4,7–9] do not lend themselves to as direct a comparison with diffusion data, when such a comparison is made no inconsistency is found with the conclusions already reached.

Finally, modeling of termination kinetics that aims to provide a detailed, molecular-level description of the mechanisms of termination in the intermediate regime should include details of both the chain radical and the formed polymer distributions. As the complications of termination are already demanding the use of numerical solutions of the model equations, the inclusion of polydispersity does not add much to the burden; some examples that followed this course are available.[16,17,21]

Acknowledgment. We would like to thank Professors G. Meyerhoff and D. J. T. Hill for providing us with tables of their data. The financial support of the Shell Companies Foundation is gratefully acknowledged.

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