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Concentration Dependence of the Rate of Polymer–Polymer Reactions in the Dilute Regime

Michael S. Kent,[†] Alessandro Faldi, and Matthew Tirrell*

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

Timothy P. Lodge*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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ABSTRACT: The effects of a background polymer on the solution properties of a dilute probe polymer have been studied in detail and reported in a previous paper. In this work, those results are applied toward interpreting the kinetics of bimolecular reactions between macromolecules containing reactive ends. Initial increases in the rates of bimacromolecular reactions with increasing concentration of unreactive polymer have been well established but poorly understood. Specific application is made to the termination reaction in free-radical polymerization at low conversion. We emphasize the ternary character of the solution: reactive chains, unreactive chains, and solvent. Our earlier results showed that the dominant effect of the background polymer in the dilute regime is a decrease in the apparent second virial coefficient of the probe. The background polymer acts to reduce the repulsive potential of interaction between two probe molecules. This effect is evident before there is any significant contraction of the probe coils or decrease in their mobility. In this paper, we argue that this effect leads to an increase in the rate of termination by increasing the probability of reaction between chain ends during a binary encounter, in a manner similar, but not exactly analogous, to that observed experimentally with decreasing quality of a small-molecule solvent.

Introduction

It has been observed experimentally for several systems that the rate of free-radical polymerization initially decreases with conversion to polymer more than can be attributed to monomer or initiator consumption. The interpretation of this effect has not, in our opinion, been clearly established. While this initial decrease is small compared to the variations in the rate of polymerization that occur during later stages of conversion, it is important because kinetic parameters are often estimated from measurements at low conversions.

The decrease in the polymerization rate has been observed for the polymerization of methyl methacrylate,[1,2] styrene,[3,4] and styrene in the presence of either predissolved, unreactive polystyrene or polybutadiene chains.[4] The phenomenon has been shown to be a direct consequence of an increase in the termination rate of the growing radical chains.[2] Also, at fixed concentration, the polymerization rate reduction increased with both the molecular weight of the growing chains and the molecular weight of the surrounding, unreactive polymer.

A similar effect has also been observed in model polymer–polymer reactions. In a study of phosphorescence quenching of end-labeled, monodisperse polystyrene chains, Mita and Horie[5,6] found that the rate of quenching initially increased with the concentration of dissolved, unlabeled polymer in a good solvent; the increase was greater for larger molecular weights. The polymerization and model reaction studies cited above are closely related, in that the rate of a bimolecular reaction between polymers with reactive ends is studied as a function of the concentration of unreactive, background chains. In the polymerization rate studies, the reactive species are the growing radical chains and the background chains are either the "dead" chains formed earlier in the reaction or the predissolved polymer. In the model polymer–polymer reactions, the reactive species are the end-labeled polystyrene chains and the background chains are the unlabeled chains.

To understand the initial increase in the termination rate with concentration and its molecular weight dependence, a comprehensive characterization of the effects of the changing environment on the properties of the reactive chains is needed. In a previous paper,[7] measurements of the radius of gyration, apparent second virial coefficient, and self- and mutual-diffusion coefficients of a dilute probe polymer [polystyrene (PS)] were reported as a function of the concentration of a background polymer [poly(methyl methacrylate) (PMMA)] in a solvent which was good for both polymers. Although this was a model study involving monodisperse, unreactive polymers, conclusions regarding the effects of the background polymer on the physical properties of the probe should give insight into the kinetics of the reacting systems. In this paper, our previous results are applied to the problem described above, with the probe and background chains corresponding to the reactive and unreactive chains, respectively. The initial increase in the termination rate is interpreted in light of the changes that were observed in the properties of the probe chains with increasing concentration of background polymer.

Results

In this section we summarize the results of refs 7 and 8 that are relevant to the present discussion.

The radius of gyration and the apparent second virial coefficient of a dilute probe polymer (PS) as a function of the concentration of a background polymer (PMMA) in ethyl benzoate were measured by total intensity light scattering at 15 °C. The solvent is good for both polymers, and the polymer concentrations were such that no phase separation occurred. The background polymer and the solvent were exactly optically matched in order to study the properties of the probe in the presence of the background polymer. The results are presented in Figures 1 and 2 for the radius of gyration and apparent second virial coefficient, respectively, of a PS probe ($M_w = 9.3 \times 10^5$) as a function of PMMA concentration for three values of the PMMA molecular weight ($M_w = 1.3 \times 10^6$, 7.0×10^4,

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[†] Sandia National Laboratories, Albuquerque, NM 87185.

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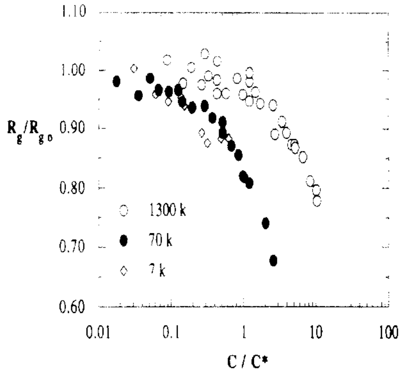

Figure 1. Behavior of the radius of gyration of a PS probe (M_w = 9.3 × 10^5) with PMMA concentration scaled by the overlap concentration C^* for the latter, for three PMMA molecular weights.

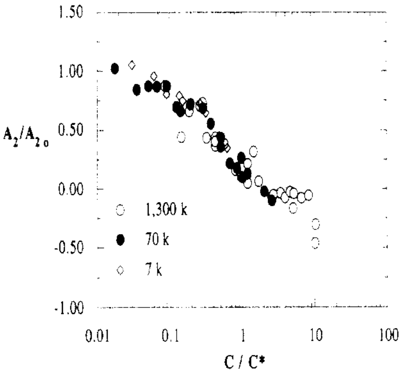

Figure 2. Behavior of the apparent second virial coefficient of a PS probe (M_w = 9.3 × 10^5) with PMMA concentration scaled by the overlap concentration C^* for the latter, for three PMMA molecular weights.

and 7.0 × 10^3). In Figures 1 and 2, the ordinate values are normalized by the values obtained with no background polymer present. The background polymer concentration is normalized by the overlap concentration, C^*, for that molecular weight.

The PS mutual diffusion coefficient as a function of PMMA concentration was measured by dynamic light scattering in toluene at 18 °C. Again, the solvent is good for both polymers and is almost index-matched with the PMMA. The range of concentration was such that no phase separation occurred. The initial dependence of the probe mutual diffusion coefficient on probe concentration, k_D(app), was determined experimentally as a function of background polymer concentration:

$$k_D(\text{app}) = \left[\frac{\partial(D_P/D_0)}{\partial c_P}\right]_{c_P=\bar{c}_P} \qquad (1)$$

where D_P is the probe diffusion coefficient, D_0 is the extrapolated value of the diffusion coefficient at zero probe concentration, c_P is the probe concentration, and $\bar{c}_P$ is the mean of the range of the probe concentration used to determine the initial slope. Figure 3 shows the experimental results for a pair of molecular weights of the probe and background polymer (M_w = 9.3 × 10^5/8.4 × 10^5).

Discussion

The termination rate in free-radical polymerization is often[9-11] written as the product of a collision rate between growing radical chains and the probability that a reaction between chain ends occurs during such a collision. The former is related to the single-chain mobility (center-of-mass diffusion) in its environment. The latter is presumably determined by several factors: the rate of intramolecular segmental diffusion, which must occur for the two reactive ends to meet; the degree of overlap, which dramatically affects the probability per unit time that the two reactive ends will encounter each other; and the duration of a collision or the length of time over which the coils are in close proximity. Each of these factors can be affected by changes in the environment. Variations in chain mobility, resulting from changes in the viscosity of the medium or from changes in the radius of gyration, may affect the collision rate. The rate of intramolecular segmental diffusion will depend upon chain stiffness, solvent viscosity, and possibly coil dimensions. The degree of overlap and the duration of a collision have been shown theoretically[9,10] to increase with decreasing solvent quality, due to a reduction in the effective repulsion between coils; experimental results of Mita and Horie[5,12] have supported this conclusion.

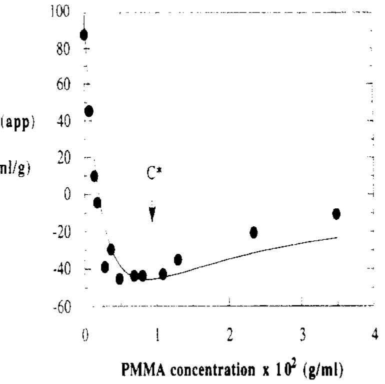

Figure 3. k_D(app), defined in eq 1, versus background polymer concentration. The k_D(app) values are obtained as the slope of a plot of the probe mutual diffusion coefficient vs probe concentration for each value of the background polymer concentration. The molecular weights of the probe and background polymer are 9.3 × 10^5 and 8.4 × 10^5, respectively.

Several theories have been proposed to account for the initial increases in the termination rate. They are based on either the contraction of the reactive coils or an increase in mutual diffusion with increasing polymer concentration. The first suggestion, put forth by North and Reed,[2] is that a reduction in coil size increases the segment density in the coil and thus increases the concentration gradient from the center to the outside of the coil. The larger gradient leads to an increased rate of diffusion of a chain end from the interior of the coil to the outside where it can react with another radical. The basis for this idea was the observation that both the termination rate and the measured rate of macroscopic mutual diffusion increased with polymer concentration. This fact was combined with evidence which suggested that chain flexibility, and therefore segmental diffusion, limits the rate of reaction rather than center-of-mass diffusion.[13] The above explanation attempts to unite the observations regarding macroscopic mutual diffusion and the importance of segmental mobility. These ideas were also elaborated by Mahabadi and O'Driscoll.[10,11] Another idea, offered by Rosen et al.,[3,4,14,15] is that a decrease in coil size should lead to an increase in chain mobility, thereby increasing the collision rate between coils. A third explanation for the initial increase in the rate of bimacromolecular reactions with polymer concentration has been offered by Mita and Horie.[5] They regarded the reaction as being diffusion-controlled and related its rate to the mutual diffusion coefficient of the polymer in a binary solution; the latter is known to display an initial increase with polymer concentration.

Although several interpretations for the initial increase in the termination rate have been offered, accompanying experimental measurements of the changes in the properties of a probe polymer as a function of the concentration of a background polymer have been rather limited. As mentioned above, North and Reed reported measurements which showed that macroscopic mutual diffusion increases with the total polymer concentration in a good solvent, now a well-understood phenomenon.[16] Lin and Rosen[15] measured the coil contraction of a probe polymer as a function of the concentration of a background polymer by total intensity light scattering. Several other studies[7,8,17–26] of this type have been reported in the literature. While there is some disagreement in the quantitative aspects of these studies, it is clear that, for polymers of similar molecular weight, very little contraction occurs in the dilute regime and a gradual contraction occurs in the semidilute regime. In view of Lin and Rosen, coil contraction leads to increased mobility of the growing radical chains; however, they presented only measurements of coil dimensions and none of mobility over the same concentration range.

Figures 1 and 2 show that the apparent second virial coefficient A_2(app) of the probe decreases more strongly with background polymer concentration than does the radius of gyration R_g; when the molecular weights of the probe and background polymers are similar, the onset of the decrease occurs at much lower background polymer concentrations for A_2(app) than for R_g. The dynamic light scattering experiments showed that the mutual diffusion coefficient, describing the rate of dissipation of fluctuations in the concentration of the probe, decreases significantly upon addition of a small amount of background polymer; this effect is displayed in Figure 3, recast in terms of k_D(app). The initial decrease is related to the decrease in the apparent second virial coefficient, as measured in the total intensity experiment.[7] At low background polymer concentrations, the initial decrease in the mutual diffusion coefficient can be greater, in fact much greater, than the decrease in the basic mobility of the probe.[7] Thus, when the molecular weights of the probe and background polymers are similar, there is virtually no change in R_g of the probe in the dilute regime and only a small decrease in its mobility, but there is a substantial decrease in A_2(app) and the mutual diffusion coefficient. When the molecular weight of the background polymer is smaller, there is a somewhat greater contraction of the probe polymer (see Figure 1) before the system reaches C^* of the background polymer. Thus, we conclude that the thermodynamic effect, reflected in the decrease of both A_2(app) and the mutual diffusion coefficient, is the dominant effect of the background polymer at low concentrations. This view has not previously been considered in the context of the termination reaction.

In light of the results in Figures 1–3, the previous theories for the initial increase in the termination rate may be examined more closely. Results from the work of Mita et al.[5,6] have shown an *initial increase of up to a factor of 3* in the quenching rate with increasing concentration of unreactive polymer. The quenching rate seems to reach a maximum around C^* (estimated as $C^* = M/(N_A R_g^3)$). Therefore, explanations based on the contraction of the reactive chains in the presence of background chains appear to be inadequate, given the low degree of contraction observed in our measurements for similar molecular weights (<5% when the concentration of background polymer has reached C^*). For background polymer chains smaller than the probe, the amount of contraction increases but this effect cannot be invoked to explain the increase in termination rate, since the latter is more pronounced for larger values of the background polymer molecular weight. Lin and Rosen postulated that coil contraction leads to an initial increase in the mobility. As mentioned before, our results showed that there is no appreciable increase in mobility at low concentrations but rather a monotonic decrease,[7] which can only lead to a reduction in the termination rate.

The fact that mutual diffusion increases with concentration in binary solutions (good solvent), cited both by North and Reed[2] and by Mita and Horie,[5,6] is not a sufficient explanation for the initial increase in the termination rate, as it fails to recognize the ternary nature of the solution, i.e., that the unreactive chains form part of the background for the growing radical chains. This is the main point of this work. The reaction rate is determined by the dynamics of the reactive chains: the collision rate between reactive chains and the probability of reaction during a collision. Therefore, it is relevant to study the rate of fluctuations in the concentration of the reactive chains only, rather than the rate of fluctuations in the concentration of the total polymer. Dynamic light scattering from ternary solutions in which the background polymer is isorefractive with the solvent examines the rate of fluctuations in the concentration of the probe, and our results have shown that the presence of the background polymer actually leads to a decrease in the rate of dissipation of concentration fluctuations of the probe chains as implied by the smaller values of the probe mutual diffusion coefficient. The effect is of opposite sign to that observed for binary solutions. In a good solvent, with no background polymer present, there is a strong effective repulsion between probe coils that is reflected in a large second virial coefficient and an increase in the mutual diffusion coefficient with concentration. This occurs because the polymers interact more favorably with the solvent than with other polymers, resulting in a strong tendency for concentration fluctuations to dissipate. In a ternary solution, however, the environment of the probe chains is composed of the small-molecule solvent *plus* the background polymer. The thermodynamic driving force for the dissipation of concentration fluctuations of the probe polymer decreases with background polymer concentration since the probe polymer experiences interactions with the background polymer. This is reflected in the decrease in the apparent second virial coefficient and the mutual diffusion coefficient with background polymer concentration. In our experiments[7] involving probe and background polymers with similar molecular weights (9.3 × 10^5 and 8.4 × 10^5, respectively) and a probe concentration half its own overlap concentration, the mutual diffusion coefficient had decreased by roughly a factor of 3 when the total concentration reached C^* of the background polymer.

The above effect runs counter to those postulated by North and Reed[2] and Mita and Horie,[5,6] who suggest that the increase in the termination rate is related to the fact that mutual diffusion *increases* with concentration in binary solutions. Here, we point out that the rate of mutual diffusion of the probe in a ternary polymer–polymer–solvent solution *decreases* with increasing concentration of background chains (unreactive polymer). Mita and Horie[5,6] have cited the following equation as the source for the initial increase in the quenching rate observed in their experiments:

$$D = \frac{k_B T}{f(c)} cM\left(\frac{\partial \mu}{\partial c}\right) \cong \frac{k_B T}{f(c)} (1 + 2A_2Mc + ...) \qquad (2)$$

where μ is the chemical potential of the polymer, c is its concentration, M is its molecular weight, k_B is Boltzmann's constant, T is the temperature, $f(c)$ describes the friction felt by the diffusing polymer, and A_2 is the second virial coefficient. This is the well-known[16] expression for the mutual diffusion coefficient in *binary* solutions. Strukelj et al.[27] have studied the kinetics of excimer formation of pyrene-end-labeled polystyrene in toluene and cyclohexane in the absence of unreactive polystyrene in solution. The system investigated was then a binary reactive polymer/solvent system, and the use of eq 2 was shown to be appropriate. The work of Strukelj et al.[27] is related but does not apply directly to the present discussion; we aim to describe the changes in the kinetics of polymer–polymer reactions in solutions which are due to the presence of an unreactive polymer and thus we are concerned with a ternary, reactive polymer/unreactive polymer/solvent system.

In our earlier paper,[7] the expression for the ternary solution mutual diffusion coefficient that describes the rate of dissipation of concentration fluctuations of the probe as a function of the concentration of the matrix chains was shown to be

$$D_P^{\,T} \cong \frac{k_B T}{f(c_P,c_M)} c_P M_M \left[\frac{\left(\frac{\partial \mu_P}{\partial c_P}\right)\left(\frac{\partial \mu_M}{\partial c_M}\right) - \left(\frac{\partial \mu_P}{\partial c_M}\right)\left(\frac{\partial \mu_M}{\partial c_P}\right)}{\left(\frac{\partial \mu_M}{\partial c_M}\right)} \right] \tag{3}$$

where the subscripts P and M refer to probe and background polymers, respectively, and the superscript T indicates that the probe is present in trace amounts. We suggest that eq 3 describes the physical effects relevant to the kinetics of reactions between dilute (tracer) polymers in the presence of unreactive background polymers, rather than eq 2. The function of chemical potential derivatives in square brackets in eq 3 is the same function that appears in the description of the total intensity of light scattered by the isorefractive ternary solution.[7] It is the effect described by this factor which we believe is responsible for the initial increase of the reaction rate with the concentration of unreactive polymer.

In our earlier work,[7] we showed that A_2(app) and $D_P^{\,T}$ decrease with the background polymer concentration primarily because certain chains are viewed as probe chains and the other chains form part of the background. It was shown that the strong decrease in A_2(app) and $D_P^{\,T}$ with background polymer concentration occurs even when the binary interaction parameter between probe and background coils, χ_{PM}, is zero but is enhanced somewhat when the polymers are incompatible ($\chi_{PM} > 0$). In other words, the most important factor is that the environment of the reactive chains contains a polymer. Thus, the initial increase in the reaction rate is observed for labeled and unlabeled PS chains in the work of Mita et al. and in the polymerization of styrene and methyl methacrylate, even though $\chi_{PM} = 0$ for the reactive and unreactive chains.

What remains, then, is to understand how the described thermodynamic effect of the background chains leads to an increase in the termination rate. Previously, it was mentioned that the reaction rate can be viewed as the product of a collision rate between coils, containing a reactive end group, and the probability that an intermolecular reaction between chain ends will occur during a collision. The probability that a reaction occurs depends on whether the coils remain in contact long enough for the reactive chain ends to encounter one another. The probability that two chain ends encounter each other per unit time is a strong function of the extent of overlap between the coils. The degree of overlap and the duration of an encounter should both increase as the effective repulsion between reactive coils decreases. In a good solvent, there is a strong effective repulsion between the coils, causing them to tend to move away from one another. In a ternary solution, however, interactions with the unreactive background polymers reduce the effective repulsion between reactive coils and thus increase the probability that a reaction will occur during an encounter. Support for the above interpretation is offered by the data in Figure 2; the decrease in A_2(app) reflects a softening of the repulsive interaction between probe coils. Notice also from Figure 2 that the decrease in A_2(app) with concentration is more pronounced for higher molecular weights of the background polymer, since C^* is smaller. This effect of molecular weight on A_2(app) is in the same direction as that observed for the increase in the termination rate.

Support for the idea that the termination rate in the initial stages of free-radical polymerization is limited by the probability of reaction during a collision, rather than the collision rate, was obtained many years ago by North and Reed.[13] In their work, the ratio of the termination rate constant to the propagation rate constant, k_t/k_p, was measured for several alkyl methacrylates. It was found that k_t/k_p decreases markedly with an increase in the size of the alkyl group. Since the translational diffusion coefficients do not change much with the size of the alkyl group, it was concluded that segmental diffusion of the radical chain end is the rate-determining step. This conclusion was later supported by measurements of the molecular weight dependence of the reaction rate in model polymer–polymer reactions.[6,12,28,29] The rate constant was found to go with the −0.3 power of molecular weight, rather than −0.5 to −0.6 power which is observed for the translational diffusion coefficient. Therefore, assuming that the rate-limiting step is the diffusion of chain ends to within a reactive cross-section of one another, the reaction rate can be affected either by altering the rate of intramolecular segmental diffusion, as in the work of North and Reed,[13] or by increasing the duration of the collision and the degree of overlap, as when a matrix polymer is added.

This interpretation implies that the rate of bimolecular reactions of macromolecules should also increase as the quality of the small-molecule solvent decreases, if all other variables, such as viscosity and temperature, remain the same. An increase of the reaction rate with decreasing solvent quality has been predicted theoretically[9] and observed experimentally in the study of model polymer–polymer reactions by Horie and Mita.[12] They showed that when the effects of solvent viscosity and of temperature were removed, the rate of reaction between end-labeled PS chains was greater in a poorer solvent for degrees of polymerization N smaller than 1000. Above $N = 1000$, there was a reversal in the solvent dependence; the latter effect was attributed to the higher number of intrachain contacts that are formed with increasing N, which should result in a decreased rate of segmental diffusion. The effect of intrachain contacts is more important in a poor solvent than in a good one since the chain is more compact in the former. In a good solvent, the chain is much swollen and makes very few contacts on itself. The effect of intrachain contacts is not nearly so important in a good solvent when the effective repulsion between reactive coils is reduced by adding a background polymer since A_2(app) is reduced, but the coil size decreases only slightly when the molecular weights of the polymers are similar. Thus, the behavior in the presence of a background polymer should be similar to that observed for degrees of polymerization less than 1000. Therefore, the interpretation that the increase in the rate of reaction can result from a reduction in the effective repulsion between reactive chains is not new. However, in this work it is shown that the effect can result from the presence of a background polymer.

Conclusions

The effects of a background polymer on the properties of a dilute probe polymer have been studied in detail and reported in previous papers. In this work, those results have been applied toward interpreting the initial increase in the rate of bimolecular reactions between macromolecules containing a reactive end with the concentration of an unreactive polymer. Our earlier results showed that the dominant effect of the presence of the background polymer is a reduction of the effective repulsion between probe coils, as manifested in the decrease of A_2(app) and D_P^T. In the dilute regime, this effect is much larger than changes in the size or mobility of the probe and has not yet been considered in the context of the termination reaction in free-radical polymerization. It appears that the decrease in the effective repulsion between reactive coils leads to an increase in the rate of termination by increasing the probability of reaction during an encounter. This interpretation has been shown[30] to be consistent with a large body of experimental data concerning the kinetics of bimolecular reactions, most notably the dependences of the initial rate increase on the molecular weight of the two polymers and the quality of the solvent, obtained from both studies of initial polymerization rates and studies of model polymer–polymer reactions.

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Registry No. PS (homopolymer), 9003-53-6; PMMA (homopolymer), 9011-14-7.