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Time-Dependent Reactive Coupling at Polymer−Polymer Interfaces

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ABSTRACT: Using recently calculated rate coefficients for reactive coupling of chains at polymer−polymer interfaces, we describe the diffusion-controlled growth of diblock copolymer at the interface between dissimilar molten homopolymer films. The growth exhibits several regimes, successively controlled by (1) the quasilocal reaction rate near the interface, (2) center-of-mass diffusion of reactive homopolymer to the interface, and (3) the diffusion barrier presented by the growing copolymer layer. Our results can be tested by time-dependent measurements of the copolymer coverage or concentration of reacted coupling groups.

I. Introduction

In spite of the importance of reactive blending technologies in commercial applications of polymers, surprisingly little is understood about reaction-diffusion problems at polymer melt interfaces. Very recently, two groups have independently presented theories for the diffusion-controlled reactive coupling of polymer chains at a polymer−polymer interface.[1,2] In the simplest situation, these authors considered a flat, symmetric interface between A and B melts with all chains having degree of polymerization N. Dispersed in the bulk A(B) phases are a low concentration ρ_0 of A(B) chains with a terminal reactive group that are otherwise identical to the unreactive chains. "Low" concentration implies that the reactive ends are spaced on average by a distance that exceeds the radius of gyration $R \sim N^{1/2}$, i.e. $\rho_0 R^3 \ll 1$. The type-A reactive groups are assumed to couple instantaneously and irreversibly with type-B reactive groups on contact in the interfacial region. Since the reactive groups are located only at chain ends, the reaction product is symmetric A−B diblock copolymer and is produced directly at the interface. Figure 1 summarizes the situation just described.

A relevant experimental protocol would be to cast a film of A homopolymer that contains a uniform number density ρ_0 of reactive A-chains and a separate film of B homopolymer containing reactive B-chains at the same concentration. The films are put together at low temperature to produce a diffusion couple and then are rapidly heated to a temperature above the melting (or glass transition) temperatures to initiate diffusion and interfacial reaction. We denote by $\sigma(t)$ the number of copolymer chains per area of interface that have been formed in the time interval t after initiating the reaction. The authors of refs 1 and 2 showed that, after a short induction period of order the terminal relaxation time τ, the initial growth rate of the copolymer population is described by

$$\mathrm{d}\sigma/\mathrm{d}t|_{t=0} = K_0 \rho_0{}^2 \tag{1}$$

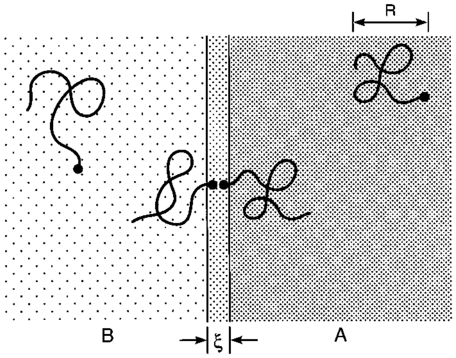

Figure 1. Model reacting system considered in the present paper. Two macroscopic molten films of type A and B homopolymers are sandwiched together. The chains are assumed to be symmetric in size ($N_A = N_B \equiv N$), frictional, and relaxation properties. The equilibrium interfacial width, ξ, is further assumed to be very narrow compared with the chain radii of gyration, R. Into each bulk phase is dispersed a number density ρ_0 of chains with a single reactive end that are otherwise identical to the matrix chains. The type A reactive ends couple with the type B ends in the interfacial region instantaneously and irreversibly on contact. The reaction product is an A−B diblock copolymer.

where K_0 is an interfacial rate coefficient given by

$$K_0 = c\frac{R^4}{\tau \ln(\tau/\tau_0)} \tag{2}$$

In this expression, $c \approx 40.7$ is a numerical coefficient that has been estimated in ref 1 and τ_0 is a reference time whose definition depends on the state of entanglement. For chains below the entanglement threshold ($N < N_e$), τ_0 is an N-independent time comparable to the time for a chain end to diffuse out of the narrow interfacial region and τ corresponds to the longest Rouse time, $\tau \sim N^2$. For entangled chains ($N > N_e$), τ_0 is the longest Rouse time and τ represents the reptation time, $\tau \sim N^3$. These expressions imply that the rate coefficient scales as $K_0 \sim 1/\ln N$ for unentangled melts and as $K_0 \sim 1/(N \ln N)$ for entangled melts.

Although eq 1 for the initial rate of copolymer formation is useful, in many circumstances it is also important to study the evolution of $\sigma(t)$ at longer times when

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diffusive transport to the interface can become rate limiting.[3] Moreover, the copolymer layer that builds up at the interface presents a chemical potential barrier that can impede coupling at late stages. Although these effects have been previously recognized,[2,4] their implications for the qualitative and quantitative description of $\sigma(t)$ have not been adequately addressed. In the present paper, we provide a theoretical framework for interpreting experiments that probe the time-dependent coverage. It should be noted that similar analyses have been carried out in the literature on related problems.[5−9]

II. Analysis

A. Case of Dilute Reactants, $\rho_0 R^3 \ll 1$. To extend eq 1 to arbitrary times, we propose replacing the initial rate equation by

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma(t) = K(\sigma(t))[\rho_i(t)]^2 \qquad (3)$$

where $\rho_i(t)$ represents the concentration of type A (or B) reactive end groups in the interfacial region and $K(\sigma)$ is a coverage-dependent rate coefficient. The latter quantity can be expressed as

$$K(\sigma) = K_0\mathcal{K}(\sigma/\sigma^*) \qquad (4)$$

where $\mathcal{K}(x)$ is a dimensionless scaling function and σ^* is the copolymer coverage at which the chemical potential barrier is of order $k_\mathrm{B}T$. Scaling arguments based on brush physics suggest that $\sigma^* = b^2/(vR) \sim N^{-1/2}$, where b is the statistical segment length and v the segment volume. At low coverage, we demand that $\mathcal{K}(x) = 1$ for $x \ll 1$. O'Shaughnessy and Sawhney[2] argue that at high coverage

$$\mathcal{K}(x) \sim x^2 \exp(-c'x^2) \quad x \gg 1 \qquad (5)$$

consistent with activated "tunneling" through a potential barrier of strength $\mu^{\ddagger}/k_\mathrm{B}T \sim (\sigma/\sigma^*)^2$. The quantity $c' \approx 9$ is a second numerical coefficient estimated in ref 2.

In order to integrate eq 3 to obtain the time-dependent coverage, an expression is required for the time-dependent concentration of reactive species at the interface, $\rho_i(t)$. An equation for this quantity is obtained by equating the rate of disappearance of type-A reactive groups in the interfacial region (due to the coupling reaction) with the diffusive flux of type-A reactive ends to the interface:

$$K(\sigma(t))[\rho_i(t)]^2 = D_0\partial_x\rho(x,t)|_{x=0+} \qquad (6)$$

An identical relation follows by symmetry for the balance of B-species fluxes on the B side ($x = 0-$) of the interface. D_0 is the center-of-mass diffusion coefficient of a reactive chain and $\rho(x,t)$ is the (number) density profile of type-A reactive chains at distance x from the interface. We assume that $\lim_{x\to\infty}\rho(x,t) = \rho_0$ and identify the interfacial concentration of A-species by $\rho_i(t) = \rho(0,t)$.

By Laplace transform methods, it is straightforward to construct the solution of the one-dimensional diffusion equation $\partial_t\rho = D_0\partial_x{}^2\rho$ that satisfies the above boundary conditions. Combination with eq 6 leads to the following nonlinear integral equation for the interfacial concentration of reactive species, $\rho_i(t)$:

$$\rho_i(t) = \rho_0 - \int_0^t \mathrm{d}t' \frac{1}{[D_0\pi(t-t')]^{1/2}}K(\sigma(t'))\rho_i{}^2(t') \qquad (7)$$

At this point, it proves convenient to introduce dimensionless variables

$$\tilde{\sigma}(t) \equiv \sigma(t)/\sigma^* \qquad \tilde{\rho}(t) \equiv \rho_i(t)/\rho_0 \qquad \tilde{t} \equiv t/\tau_\rho \qquad (8)$$

where

$$\tau_\rho \equiv \frac{D_0}{K_0{}^2\rho_0{}^2} \sim \tau\frac{\ln^2 N}{(\rho_0R^3)^2} \qquad (9)$$

is a characteristic time for the density in the interfacial region, initially at ρ_0, to decay. The final expression in eq 9 is obtained by combining the scaling relation[10] $D_0 \sim R^2/\tau$ with eq 2. Evidently, τ_ρ can greatly exceed the terminal relaxation time τ for systems that are initially very dilute in reactants, $\rho_0R^3 \ll 1$. With the above rescalings, eqs 3 and 7 become

$$\frac{\mathrm{d}}{\mathrm{d}\tilde{t}}\tilde{\sigma}(\tilde{t}) = \epsilon\mathcal{K}(\tilde{\sigma}(\tilde{t}))[\tilde{\rho}(\tilde{t})]^2 \qquad (10)$$

$$\tilde{\rho}(\tilde{t}) = 1 - \int_0^{\tilde{t}}\mathrm{d}\lambda\frac{1}{[\pi(\tilde{t}-\lambda)]^{1/2}}\mathcal{K}(\tilde{\sigma}(\lambda))[\tilde{\rho}(\lambda)]^2 \qquad (11)$$

where ϵ is a dimensionless group defined by

$$\epsilon \equiv \frac{D_0}{K_0\sigma^*} \sim N^{-1/2}\ln N \qquad (12)$$

Physically, ϵ^2 can be interpreted as the ratio of the time scale for the reactant density in the interface to decay, τ_ρ, to the time scale

$$\tau_\sigma \equiv \frac{(\sigma^*)^2}{D_0\rho_0{}^2} \qquad (13)$$

that will subsequently be shown to be relevant for the buildup of the copolymer coverage. The regime of small ϵ, which according to eq 12 can evidently be achieved at large N, thus corresponds to a situation in which the copolymer coverage at the interface grows more slowly than the rate at which the reactant concentration at the interface depletes. The initial condition associated with eq 10 is evidently $\tilde{\sigma}(0) = 0$, i.e. no copolymer initially present.

Because $\epsilon \sim N^{-1/2}\ln N \ll 1$ for high molecular weight reactive polymers, we can use ϵ as a perturbation parameter for the analysis of eqs 10 and 11. The *early* and *intermediate* time behavior can be extracted by inserting the $\epsilon \to 0$ solution to eq 10, i.e. $\tilde{\sigma}(\tilde{t}) = 0$, into eq 11 and noting that $\mathcal{K}(0) = 1$. This gives rise to the simpler equation

$$\tilde{\rho}(\tilde{t}) = 1 - \int_0^{\tilde{t}}\mathrm{d}\lambda\frac{1}{[\pi(\tilde{t}-\lambda)]^{1/2}}\tilde{\rho}^2(\lambda) \qquad (14)$$

The short-time behavior of this nonlinear Volterra equation is easily obtained by a Neumann series expansion:

$$\tilde{\rho}(\tilde{t}) \approx 1 - \frac{2}{\pi^{1/2}}\tilde{t}^{1/2} \qquad \tilde{t} \ll 1 \qquad (15)$$

The $\tilde{t} \gg 1$ asymptotic behavior of eq 14 can be extracted with the ansatz $\tilde{\rho}(\tilde{t}) \sim A\tilde{t}^{-1/4} + B\tilde{t}^{-1/2} + ...$ Substitution into both sides of the integral equation leads to $A = 1/\pi^{1/4}$, $B = -\Gamma(3/4)/[2\Gamma(1/4)] \approx -0.16899$. Thus,

$$\tilde{\rho}(\tilde{t}) \approx 1/(\pi\tilde{t})^{1/4} - 0.16899\,\tilde{t}^{-1/2} \qquad \tilde{t} \gg 1 \tag{16}$$

The physics of this leading behavior is easily established. Because the saturation of copolymer coverage is negligible in the present regime, we can return to eq 6 and replace $K(\sigma)$ by K_0 on the left-hand side. On the right-hand side, the derivative $\partial_x\rho(x,t)|_{x=0+}$ can be crudely estimated as the ratio of the density difference $\rho_0 - \rho_i(t) \approx \rho_0$ to the diffusive scale $(D_0t)^{1/2}$, which is a measure of the thickness of the "depletion hole" of reactants in the interfacial region. Balancing these two terms leads to the indicated scaling, $\rho_i(t) \sim t^{-1/4}$.

We now return to eq 10 and deduce $\tilde{\sigma}(\tilde{t})$ at early and intermediate times by means of $\tilde{\sigma}(\tilde{t}) \approx \epsilon \int_0^{\tilde{t}} d\lambda\, \tilde{\rho}^2(\lambda)$. For $\tilde{t} \ll 1$, we find

$$\tilde{\sigma}(\tilde{t}) \approx \epsilon\tilde{t} - \frac{8}{3\pi^{1/2}}\epsilon\tilde{t}^{3/2} \qquad \tilde{t} \ll 1 \tag{17}$$

the leading term of which reproduces eq 1. In contrast, for $\tilde{t} \gg 1$,

$$\tilde{\sigma}(\tilde{t}) \approx \frac{2}{\pi^{1/2}}\epsilon\tilde{t}^{1/2} - 1.0155\epsilon\tilde{t}^{1/4} \qquad \tilde{t} \gg 1 \tag{18}$$

The above formulae are valid up to a dimensionless time t_c for which $\tilde{\sigma}(t_c) \sim 1$ and the approximation $K(\tilde{\sigma}(t_c)) \approx 1$ is no longer valid. It follows from eq 18 that $t_c \sim \epsilon^{-2} \gg 1$. Restoring dimensional time units, this characteristic time for buildup of the coverage, $\tau_\sigma = t_c\tau_\rho$, can be estimated as

$$\tau_\sigma \sim \tau_\rho\epsilon^{-2} \sim \tau_\rho N/\ln^2 N \gg \tau_\rho \tag{19}$$

and is evidently consistent with eq 13.

Next, we examine the asymptotic behavior of the interfacial reactant concentration and copolymer coverage at times exceeding τ_σ. Working in scaled variables, we return to eqs 10 and 11 and introduce the ansatz

$$\tilde{\rho}(\tilde{t}) \approx 1 - f(\epsilon^2\tilde{t}) \qquad \epsilon^2\tilde{t} \gg 1 \tag{20}$$

where $f(x)$ is a function that vanishes for $\epsilon^{-2} \ll \tilde{t} \to \infty$. Substitution of this expression into eq 10 and asymptotic expansion for $\epsilon^2\tilde{t} \to \infty$ yields at leading order

$$\tilde{\sigma}(\tilde{t}) \approx [(1/c')\ln(\epsilon\tilde{t})]^{1/2} \tag{21}$$

where c' is the coefficient appearing in the exponent of eq 5. Further substitution into eq 11 and asymptotic evaluation of the integral for $\epsilon^2\tilde{t} \to \infty$ confirm the internal consistency of eq 20 and provide the explicit form $f(x) \approx c''/(2c'\,\pi^{1/2})\ln^2(x)/x^{1/2}$. The constant c'' represents the numerical prefactor omitted in eq 5. Thus, the reduced density of reactive A (or B) ends in the interface scales for $\epsilon^2\tilde{t} \gg 1$ as

$$\tilde{\rho}(\tilde{t}) \approx 1 - \frac{c''}{2c'\,\pi^{1/2}}\frac{\ln^2(\epsilon^2\tilde{t})}{(\epsilon^2\tilde{t})^{1/2}} \tag{22}$$

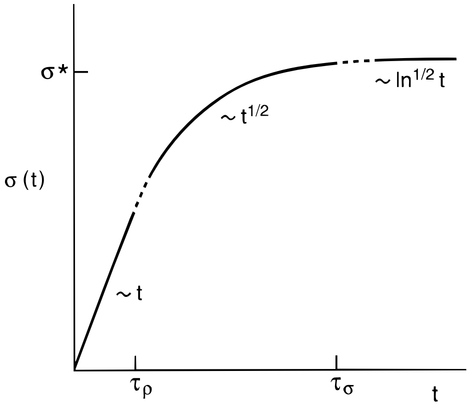

Figure 2. Qualitative summary of the time-dependent growth of copolymer coverage (number of diblocks/area of interface) $\sigma(t)$ for the case of an initially dilute concentration of reactive chains in the two bulk phases, $\rho_0R^3 \ll 1$. At times longer than the terminal relaxation time τ but less than $\tau_\rho \sim \tau \ln^2 N(\rho_0R^3)^{-2}$, there is a linear growth regime, $\sigma(t) \approx K_0\rho_0{}^2t$. At intermediate times in the interval $\tau_\rho \ll t \ll \tau_\sigma$, depletion of reactants in the interfacial region leads to a center-of-mass diffusion-dominated regime: $\sigma(t) \approx (2/\pi^{1/2})\rho_0(D_0t)^{1/2}$. Finally, for times exceeding the characteristic time for the buildup of the copolymer layer, $\tau_\sigma \sim \tau_\rho N/\ln^2 N$, the potential barrier presented by the copolymer layer dramatically suppresses progress of the reaction: $\sigma(t) \sim N^{-1/2}\ln^{1/2}[N^{1/2}t/(\tau_\sigma \ln N)]$.

At this point, it is appropriate to return to dimensional variables and summarize the qualitative evolution of $\sigma(t)$ and $\rho_i(t)$ for experiments that start with a *low* concentration of reactive chains, $\rho_0R^3 \ll 1$. In such cases, there are three well-distinguished regimes that will subsequently be denoted *early, intermediate, and late*. Figure 2 qualitatively depicts the behavior of $\sigma(t)$ in each regime.

In the *early* stages of the reaction, corresponding to times satisfying $\tau \ll t \ll \tau_\rho$, both depletion of reactants at the interface and copolymer saturation effects are negligible. The interfacial concentration of reactive chains is approximately fixed at the initial concentration, $\rho_i(t) \approx \rho_0$, and the coverage grows linearly in time with a slope proportional to K_0, $\sigma(t) \approx K_0\rho_0{}^2t$.

At times satisfying $\tau_\rho \ll t \ll \tau_\sigma$, the *intermediate* regime, saturation of the interface by copolymer remains negligible, but a depletion hole builds up around the interface in which the reactant concentration $\rho_i(t) \approx \rho_0(\pi t/\tau_\rho)^{-1/4}$ is reduced below the bulk concentration ρ_0. The copolymer coverage grows as $\sigma(t) \approx (2/\pi^{1/2})\sigma^*(t/\tau_\sigma)^{1/2} = (2/\pi^{1/2})\rho_0(D_0t)^{1/2}$ in this regime, the latter expression indicating that this growth is dominated by center-of-mass polymer diffusion and is independent of the reaction kinetics, i.e. K_0. Because $\tau_\sigma/\tau_\rho \sim N/\ln^2 N$, this diffusion-controlled intermediate regime can easily extend over 3 or 4 decades of time.

Finally, the *late* stage regime corresponds to $t \gg \tau_\sigma$. Here, the coverage has built up to the point that a significant chemical potential barrier ($\gg k_BT$) is presented to reactive chains near the interface. The reaction rate is dramatically reduced and $\rho_i(t)$ (the concentration of reactants just outside the copolymer brush) builds back up to closely approach ρ_0. Thus, reactant depletion effects are negligible in this regime, but copolymer saturation effects are critical. The coverage grows exquisitely slowly in the asymptotic late stages as $\sigma(t) \sim \sigma^* \ln^{1/2}[N^{1/2}t/(\tau_\sigma \ln N)]$.

In principle, the late stage regime may be disrupted by an accordion-like deformation of the interface, producing a local morphology that resembles a microemulsion.[11] This interfacial instability occurs when the increase in copolymer coverage has affected a dramatic lowering of the A−B interfacial tension; beyond this point the interfacial free energy is largely controlled by curvature elasticity (bending of the polymer brushes that compose the saturated interfaces), rather than by the number of A−B monomer contacts. Recent experiments in the laboratory of E. J. Kramer have provided direct visualization of this instability, which seems to be more prevalent in low molecular weight systems.[12] The analysis of Leibler[13] suggests that the interfacial tension reduction leading to the instability should be most pronounced for symmetric diblock copolymers (such as those considered here), since micelles can then less effectively compete for the copolymer. Leibler's calculations (assuming a "dry brush") indicate that the net interfacial tension should vanish (and thus an instability should be expected) for a symmetric copolymer film at a coverage given by

$$\sigma/\sigma^* \approx 0.17(\chi N)^{1/6} \tag{23}$$

This formula is probably only accurate for $\chi N \gtrsim 50$, but this is the typical situation for strongly incompatible polymers. Asymptotically for $\chi N \gg 1$, we see that the instability will occur at a coverage σ that greatly exceeds the reference coverage $\sigma^* \sim N^{-1/2}$ and hence at a time well beyond τ_σ, i.e. $\sim \tau_\sigma N^{-1/2} \ln N \exp[\text{const} \times (\chi N)^{1/3}]$, in the late stage regime. It is also interesting to note that the reduction in the interface instability threshold with decreasing N predicted by eq 23 is qualitatively consistent with the molecular weight trends observed in the experiments by Kramer.[12]

B. Case of Semidilute Reactants, $\rho_0 R^3 \gg 1$. While the situation just described for systems *dilute* in reactants is ideal for experimental investigations because the relevant time scales are widely separated from the terminal time τ, there appear to be few experiments carried out under such conditions.[6] Moreover, several model studies have been performed in which *every* chain in the melt contains a reactive end.[14,15] In such cases, $\rho_0 = 1/(vN)$, so that $\rho_0 R^3 \sim N^{1/2} \gg 1$ and τ_ρ no longer exceeds the terminal relaxation time τ. Evidently, to analyze the "semidilute" case of $\rho_0 R^3 \sim N^{1/2}$, we must go back and include time-dependent corrections to the expression for K_0 given in eq 2. In particular, for times less than τ, which are now relevant to the decay of $\rho_i(t)$, K_0 must be generalized to a time-dependent function $K_0(t)$. Following the approach outlined in ref 1, it is not difficult to show that the Laplace transform of $K_0(t)$, defined by $\hat{K}_0(s) = \int_0^\infty \mathrm{d}t \exp(-st)K_0(t)$, can be written for $s\tau_0 \ll 1$ in the form

$$\hat{K}_0(s) = c\frac{R^4}{s\tau \ln[(\tau/\tau_0)/(1 + s\tau)]} \tag{24}$$

In the limit $t/\tau \gg 1$ or $s\tau \ll 1$, the inverse Laplace transform of eq 24 evidently reduces to eq 2. At shorter times, i.e. the regime $\tau_0 \ll t \ll \tau$, we are faced with inverting the transfom of the object $\hat{g}(s) \equiv -1/[s \ln(s\tau_0)]$. While this inverse Laplace transform does not appear in standard tables, it can be given a contour integral representation and manipulated (via the substitution $x = \ln s$) into the following form:

$$g(t) = \int_{-\infty}^{\infty} \mathrm{d}x \, \frac{\exp(-te^x/\tau_0)}{x^2 + \pi^2} \tag{25}$$

For $t/\tau_0 \gg 1$ (recall that eq 24 was valid only for $s\tau_0 \ll 1$), Laplace's method[16] (with a "moveable maximum" at $x = -\infty$) can be used to extract the desired asymptotic behavior

$$g(t) \approx \frac{\pi^{1/2}}{[\ln(t/\tau_0)]^{3/2}} \tag{26}$$

In summary, we find that for $t \gg \tau$, $K_0(t)$ is well approximated by the constant K_0 given in eq 2, while for $\tau_0 \ll t \ll \tau$, $K_0(t)$ is given by

$$K_0(t) \approx \pi^{1/2} c \frac{R^4}{\tau[\ln(t/\tau_0)]^{3/2}} \tag{27}$$

We can now return to eqs 3 and 7, replace K_0 with $K_0(t)$, and assess the qualitative growth of $\sigma(t)$. A natural time scale that characterizes the decay of $\rho_i(t)$ turns out to be

$$\theta_\rho \equiv \tau(\rho_0 R^3)^{-2} \sim \tau/N \tag{28}$$

which differs from τ_ρ in eq 9 only by the absence of the factor $\ln^2 N$. In the present case of $\rho_0 \sim 1/N$, however, θ_ρ is a time *much shorter* than the terminal relaxation time τ. The *early stage* behavior now corresponds to times satisfying $t \ll \theta_\rho$, for which both depletion of reactants and saturation of copolymer are negligible. Thus, $\rho_i(t) \approx \rho_0$ in this regime and $\sigma(t)$ is given by

$$\sigma(t) \approx {\rho_0}^2 \int_0^t \mathrm{d}t' \, K_0(t') \tag{29}$$

with $K_0(t)$ evaluated using eq 27. This corresponds to a nearly linear growth regime.

The *intermediate* stage of growth, defined by $\theta_\rho \ll t \ll \theta_\sigma$, is again associated with a situation in which copolymer saturation is negligible, but the interface is depleted of reactants. Here, θ_σ is the characteristic time associated with the buildup of coverage:

$$\theta_\sigma \equiv \theta_\rho(\sigma^* R^2)^2 \sim \theta_\rho N \sim \tau \tag{30}$$

The last relation in the above expression shows that the time scale for achieving saturation in the present situation where all chains have a reactive end is comparable (in a scaling sense) to the terminal relaxation time. Using techniques similar to those already described above, it is straightforward to show that the interfacial concentration decays in the intermediate stage as

$$\rho_i(t) \sim \rho_0 \frac{[\ln(t/\tau_0)]^{3/4}}{(t/\theta_\rho)^{1/4}} \tag{31}$$

Integration of eq 3 then leads to

$$\sigma(t) \sim R^{-2}(t/\theta_\rho)^{1/2} \tag{32}$$

which is again a $\sim t^{1/2}$ growth law. Note that $\sigma(\theta_\sigma) \sim N^{-1/2} \sim \sigma^*$ and that the depletion hole of reactants about the interface never extends beyond a distance of order R.

Finally, the *late stage* regime corresponds to times satisfying $t \gg \theta_\sigma$. Since $\theta_\sigma \sim \tau$, we can now use the constant rate coefficient K_0 given by eq 2, but copolymer saturation must again be accounted for through the use of eqs 4 and 5. The interfacial concentration returns to close to the bulk value, $\rho_i(t) \approx \rho_0$, and the coverage grows as in eq 21:

$$\sigma(t) \sim \sigma^* \ln^{1/2}[N^{1/2} t/(\tau \ln N)] \tag{33}$$

An interfacial instability at the very late stages is a strong possibility for melts containing large concentrations of reactive chains; indeed, recent experiments show that the tendency for interfacial folding increases as the concentration of functionalized chains is raised.[12]

III. Summary and Discussion

In summary, we have seen that in situations with a dilute initial concentration of reactive chains, $\rho_0 R^3 \ll 1$, there are three regimes that characterize the growth of the copolymer layer. The early stage regime is controlled by the quasilocal reaction rate coefficient, K_0 (itself diffusion-controlled[1,2]), the intermediate stage regime is controlled by center-of-mass diffusion of reactive chains to fill a depletion hole of reactants about the interface, and the late stages are controlled by the potential barrier arising from previously formed copolymers at the interface. These three regimes are delineated by characteristic time scales τ_ρ and τ_σ that greatly exceed the terminal relaxation time τ; the dependence of these time scales on N and ρ_0 has been explicitly established.

The case of all ends labeled, $\rho_0 R^3 \sim N^{1/2}$, is qualitatively similar to the dilute reactant case, except that the time scales are all compressed to much shorter times. Indeed, saturation effects begin to set in at the terminal relaxation time τ, after which the growth of copolymer coverage is dramatically slowed. Unless the molecular weight of an experimental system characterized by $\rho_0 R^3 \gg 1$ is very high, it seems unlikely that the early stage growth can be resolved. In most circumstances, only the crossover from center-of-mass diffusion-limited behavior ($\sim t^{1/2}$) to saturation behavior ($\ln^{1/2} t$) would be expected to be observed.[17]

In closing, we note that the analysis described in the present paper has been restricted to the simplest one-dimensional, symmetric system. Extensions to asymmetric systems (i.e. $N_A \neq N_B$), systems in which the matrix (unreactive) chains and functionalized chains have different molecular weights,[9] and higher dimensional interfacial structures (e.g. droplets), while straightforward, are clearly important if realistic blending situations are to be described. Moreover, convection[18] may act to dramatically suppress depletion zones of reactants, such as those considered in the present study. Additional model experiments (such as those of refs 4, 14, 15, and 19) would go a long way toward advancing our understanding of the complex diffusion and reaction processes that control the temporal evolution of the copolymer reaction product.

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