Diffusion-Controlled Reactions at Polymer-Polymer Interfaces

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A theory is presented for the diffusion-controlled coupling of end-functionalized A and B homopolymers at an A-B interface. The effective reaction rate coefficient k_e is shown to exhibit a surprising degree of universality associated with the small center-of-mass diffusivity of high molecular weight polymers. For polymers below the entanglement threshold ($N < N_e$), k_e scales with molecular weight as $k_e \sim 1/\ln N$, and above the threshold, $k_e \sim 1/N \ln N$. [S0031-9007(96)00023-3]

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It is well known that chemical reactions occurring in complex fluid media such as polymer solutions or melts are frequently under diffusion control, a consequence of the small translational diffusivity of macromolecules. The theoretical framework to describe such phenomena in *homogeneous* reacting polymer systems is now quite mature [1–5] and is in satisfactory agreement with experiment [6–8].

In contrast, few theoretical studies exist of diffusion-controlled reactions in *inhomogeneous* polymer systems [9(a),9(b)]. This is particularly surprising given the extensive commercial application of reactive blending. In reactive blending [10], a melt of type-A homopolymer chains is mechanically mixed with a second melt of type-B chains. During the blending operation, reactive groups on A chains react with complementary functional groups on B chains in the A-B interfacial regions. These interfacial coupling reactions produce a third species, graft (or block) copolymer. The copolymer subsequently plays a dual role: First, as an emulsifying agent that lowers the A-B interfacial tension and permits a finer dispersion of the two phases, and second, as a "glue" that by virtue of entanglements strengthens the interfaces [11].

In the present Letter, I develop a formalism for treating diffusion-controlled reactions in inhomogeneous polymeric fluids and apply it to the case of a planar interface between A and B homopolymer phases, each bulk phase containing a small concentration of reactive chains. Expressions are developed for the effective reaction rate coefficient k_e, which describes the bimolecular reaction rate after transients have relaxed, but at times short enough that the interface is not perturbed by the copolymer reaction product and the bulk phases are not depleted in reactive groups. Under such conditions, if ρ_A and ρ_B denote the densities of type-A and -B reactive chains in the two bulk phases, the reaction rate is described by $\dot{\rho}_A = \dot{\rho}_B = -k_e \rho_A \rho_B$.

The specific model system under consideration is shown in Fig. [1]. The bulk A phase consists of molten chains with degree of polymerization N_A and also contains a small concentration (number density ρ_A) of otherwise identical chains that have a reactive group on one end. Similarly, the bulk B phase consists of chains of length N_B, mixed with a low concentration (ρ_B) of end-functionalized type-B chains. The A reactive groups can couple only with B groups to form diblock copolymer at the interface. I further assume that the two phases are strongly segregated, so that the interfacial thickness ξ is much smaller than a characteristic chain radius of gyration, $R = b(N/6)^{1/2}$. (Here, b is a statistical segment length [12] and $N = N_A$ or N_B is a characteristic degree of polymerization.) In particular, the Flory interaction parameter [13] between A and B monomers, χ, is assumed to be small compared with unity, but I take $\chi N \gg 1$. In this "Helfand-Tagami" regime [14], the equilibrium interfacial thickness given by $\xi = 2b/(6\chi)^{1/2}$ is much larger than the monomer size b, but much smaller than R. The two bulk phases are pure in A and B.

To describe the dynamics of reaction and diffusion in the interfacial region, I adapt a formalism introduced for homogeneous systems by de Gennes [3]. Because of the assumption that the reactive species are dilute, it is sufficient to consider the behavior of a pair distribution function $\psi(\mathbf{r}_A, \mathbf{r}_B; t)$ describing the joint probability density

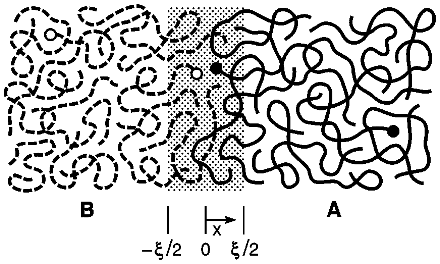

FIG. 1. Symmetric A-B polymer interface and coordinate system employed. The interfacial region (shaded) corresponds to the region $-\xi/2 \le x \le \xi/2$ in which loops of A and B polymers overlap. The bulk A phase ($x \to \infty$) consists of type-A homopolymer chains (solid curves) mixed with a low concentration ρ_A of end-functionalized (solid circle) type-A chains. The bulk B phase ($x \to -\infty$) consists of type-B homopolymer chains (dashed curves) mixed with a low concentration ρ_B of end-functionalized (open circle) type-B chains. Solid circles react with open circles irreversibly on contact in the interfacial region.

that at time t a type-A reactive end group is located at $\mathbf{r}_A$ and a type-B group is at $\mathbf{r}_B$. The initial ensemble corresponds to thermodynamic equilibrium in the absence of interfacial reaction

$$\psi(\mathbf{r}_A, \mathbf{r}_B; 0) = \rho_A \rho_B \exp[-V_A(x_A) - V_B(x_B)], \tag{1}$$

where $V_K(x_K)$ ($K = A$ or B) is the potential (units of $k_B T$) felt by a type-K chain with reactive end group located at position x_K measured normal to the midplane of the interface ($x_K = 0$). The zero of potential is taken to correspond to the bulk phases, e.g., $\lim_{x_A \to \infty} V_A(x_A) = 0$. At time $t = 0+$, the interfacial reaction is turned on and time evolution of $\psi(\mathbf{r}_A, \mathbf{r}_B; t)$ proceeds according to

$$\frac{\partial}{\partial t} \psi - \mathcal{L}\, \psi = -Q_0 \delta(\mathbf{r}_A - \mathbf{r}_B) \psi\,. \tag{2}$$

Here, $\mathcal{L}$ is an appropriate diffusive operator describing spatial evolution of reactive groups located near $\mathbf{r}_A$ and $\mathbf{r}_B$ (e.g., $\mathcal{L} = D_A \nabla_A^2 + D_B \nabla_B^2$ for simple diffusion) and Q_0 is a parameter proportional to the reaction rate of a pair of A and B reactive groups in contact.

The next step is to invert the differential operator on the left-hand side of Eq. (2), affecting a transformation to an integral equation. Invoking the diluteness assumption, the kernel of the inverse operator (a two-particle propagator) can be factored into a product of single-particle Green's functions [3]. Furthermore, only the diagonal elements of ψ are relevant to the present discussion. Introducing $\Psi(x, t) \equiv \psi(\mathbf{r}, \mathbf{r}; t)$, which represents the probability density that a pair of A and B reactive groups are coincident at position x measured from the center of the interface, the integral equation reduces to

$$\begin{aligned}\Psi(x, t) = {} & \rho_A \rho_B e^{-V_A(x) - V_B(x)} \\ & - Q_0 \int_0^t d\tau \int d\mathbf{r}'\, G_A(\mathbf{r}, \mathbf{r}'; t - \tau) \\ & \times G_B(\mathbf{r}, \mathbf{r}'; t - \tau) \Psi(x', \tau)\,,\end{aligned} \tag{3}$$

where $G_K(\mathbf{r}, \mathbf{r}'; t)$ is a single-particle Green's function representing the probability density that the reactive end of a type-K chain has undergone a diffusive displacement [in the potential field $V_K(x)$] from position $\mathbf{r}'$ at $t = 0$ to position $\mathbf{r}$ at time t.

In order to further simplify Eq. (3), I next assume that G_K can be factored into terms corresponding to propagation along the interface normal (along x) and in the transverse y-z plane. (This is exact for both simple diffusion and Rouse dynamics [12]; for entangled polymers see the discussion below.) Invoking translational invariance in the transverse coordinates $\mathbf{r}_\perp = (y, z)$, it follows that $G_K(\mathbf{r}, \mathbf{r}'; t) = G_K^\perp(\mathbf{r}_\perp - \mathbf{r}_\perp'; t) \mathcal{G}_K(x, x'; t)$. Laplace transforming both sides of the resulting integral equation over time (Laplace variable s; transformed quantities are denoted by a hat) leads to the Fredholm equation

$$\begin{aligned}\hat{\Psi}(x, s) = {} & s^{-1} \rho_A \rho_B e^{-V_A(x) - V_B(x)} \\ & - Q_0 \int dx'\, \hat{K}(x, x'; s) \hat{\Psi}(x', s)\,,\end{aligned} \tag{4}$$

with kernel

$$\hat{K}(x, x'; s) \equiv \int_0^\infty dt\, e^{-st} H_\perp(t) \mathcal{G}_A(x, x'; t) \mathcal{G}_B(x, x'; t)\,, \tag{5}$$

and where $H_\perp(t) \equiv \int d\mathbf{r}_\perp\, G_A^\perp(\mathbf{r}_\perp; t) G_B^\perp(\mathbf{r}_\perp; t)$.

In the present Letter, I restrict consideration to cases of instantaneous, irreversible reaction on contact of two reactive groups, $Q_0 \to \infty$, and ignore transients in the approach to steady state, $s \to 0$. Noting that a frequency-dependent reaction rate coefficient can be defined by $\hat{k}(s) = S_V Q_0 (\rho_A \rho_B)^{-1} \int dx\, \hat{\Psi}(x; s)$, where S_V is the ratio of the interfacial area to the volume of the system, it follows that the effective reaction rate coefficient is given by

$$k_e \equiv \lim_{t \to \infty} k(t) = S_V \int dx\, M(x)\,, \tag{6}$$

where $M(x)$ satisfies the following Fredholm equation of the first kind:

$$\exp[-V_A(x) - V_B(x)] = \int dx'\, \hat{K}(x, x'; 0) M(x')\,. \tag{7}$$

As a first application of these equations, I consider a symmetric A-B polymer interface [$N_A = N_B \equiv N$, $V_A(x) = V_B(-x) \equiv V(x)$] consisting of chains below their entanglement molecular weight [12,13] ($N < N_e$). The Rouse model [12] is appropriate for describing the reactive end dynamics under such circumstances. Helfand and Tagami [14] discussed the equilibrium properties of symmetric polymer interfaces. Of particular interest here is the potential associated with locating the end of a type-A chain at position x in the interfacial region, $V(x) = (1/2) \ln[1 + \exp(-4x/\xi)]$. To simplify the subsequent calculations, I approximate this potential by a linear expression, $V(x) = 1/2 - x/\xi$, within the interfacial region, $-\xi/2 < x < \xi/2$, and set $V(x) = 0$ for $x > \xi/2$ and $V(x) = \infty$ (reflecting boundary) for $x < -\xi/2$. (It will soon become apparent that k_e is insensitive to approximations of this sort.) An important consequence of this approximation is that both x and x' in Eqs. (6) and (7) are restricted to the *finite* interval, $(-\xi/2, \xi/2)$. Moreover, the left-hand side of Eq. (7) is x independent within that interval; i.e., $\exp[-V_A(x) - V_B(x)] = e^{-1}$.

For Rouse dynamics, the transverse reactive end motion is potential-free and it can be easily demonstrated [3] that $H_\perp(t) = 1/4\pi \overline{x}^2(t)$, where $\overline{x}(t)$ is the root-mean-square displacement of a chain end along either of the two transverse coordinates. This object has distinct asymptotic behavior for times less or greater than the longest Rouse relaxation time [12], $\tau_1 \sim N^2$. In particular [12], $\overline{x}^2(t) \approx 2Dt$ for $t \gg \tau_1$, where $D = D_0/N$ is the center-of-mass (COM) diffusion coefficient of a reactive chain and D_0 is a monomeric diffusivity. In contrast, for times much smaller than τ_1, the chain end dynamics are subdiffusive [12,15], $\overline{x}^2(t) \approx 1.303 b (D_0 t)^{1/2}$.

The other ingredient necessary for evaluation of the kernel $\hat{K}(x,x';0)$ is an expression for the propagator $\mathcal{G}(x,x';t) \equiv \mathcal{G}_A(x,x';t)$. [Note that $\mathcal{G}_B(x,x';t) = \mathcal{G}(-x,-x';t)$ for a symmetric interface of equal length chains.] An important time scale for discussing the properties of $\mathcal{G}$ is $\tau_0 \equiv b^2/D_0\chi^2$, which scales as the time required for a chain end to diffuse out of the interfacial region $[\bar{x}(\tau_0) \sim \xi]$. For $t \ll \tau_0$, the propagator $\mathcal{G}$ is insensitive to both the reflecting boundary at $x = -\xi/2$ and the finite range of the potential $(x = \xi/2)$. (From the above it should be clear that $\mathcal{G}$ is only required for $-\xi/2 < x, x' < \xi/2$.) Thus, an approximate expression for $\mathcal{G}$ at $t \ll \tau_0$ is obtained from the exact Green's function solution of the Rouse model in an *unbounded* linear potential field,

$$\mathcal{G}(x,x';t) \approx \frac{1}{\sqrt{2\pi}\bar{x}(t)} \times \exp\{-[x - x' - (D_0\chi/\xi)t]^2/2\bar{x}^2(t)\}. \tag{8}$$

This is evidently a Gaussian wave packet of width $\sim\bar{x}(t)$ and traveling to lower potential (positive x) at constant velocity $v = D_0\chi/\xi$. This velocity is easily understood: a type-A chain end at position $x = -\xi/2$ experiences a force equal to $-V'(x) = 1/\xi$ associated with the action of the chemical potential on all [14] $n \sim 1/\chi$ monomers in the chain strand spanning the interface. (Each monomer feels a force proportional to χ/ξ.) Balancing the total force on the strand, $1/\xi$, against the product of the velocity v and the friction coefficient of the strand, $n/D_0 \sim 1/\chi D_0$ recovers $v = D_0\chi/\xi$. It is also important to note that at time τ_0 the forced displacement of the packet, $v\tau_0$, is comparable in a scaling sense to both the width of the packet, $\bar{x}(\tau_0)$, and the interfacial width, ξ.

If the reactive polymers are long, $N \gg 1$, then the N-independent time scale τ_0 is much smaller than the longest Rouse relaxation time $\tau_1 \sim N^2$, which is the time required for the polymer COM to diffuse a distance of order the radius of gyration, $R = b(N/6)^{1/2}$. Thus, a chain end that is initially in the interfacial region will achieve a local equilibrium with regard to its position in the interface on a time scale comparable to τ_0 and much less than τ_1. For $t \gg \tau_0$, the chain end distribution has equilibrated over a range $\bar{x}(t) \gg \xi$; i.e., $\exp[V(x)]\mathcal{G}(x,x';t) \sim 1/\bar{x}(t)$. The numerical prefactor can be estimated by noting that Rouse dynamics cross over to classical diffusion at $t \approx \tau_1$. Use of the $t \gg \tau_1$ asymptotic prefactor leads to the following approximate representation of $\mathcal{G}$ over the interval $(-\xi/2, \xi/2)$ and for $t \gg \tau_0$:

$$\mathcal{G}(x,x';t) \approx \frac{2}{\sqrt{2\pi}\bar{x}(t)} \exp[-V(x)]. \tag{9}$$

The factor of 2 difference in the prefactor of this expression from Eq. (8) arises from the reflecting boundary at $x = -\xi/2$, which slows decay out of the interfacial region.

I now turn to consider the $s \rightarrow 0$ limit of the kernel defined by Eq. (5). Breaking the integral over t at a time τ_c of order τ_0 yields two integrals that can be approximately evaluated with Eqs. (8) and (9). (The final answer for k_e does not depend on the precise choice of τ_c.) The first contribution, $\hat{K}_1(x,x';0)$, arising from the time interval $(0,\tau_c)$, is highly localized about x' and can be approximated by a delta function, $\hat{K}_1(x,x';0) \sim \xi/(b^2D_0)\delta(x - x')$. The second contribution to $\hat{K}$ represents the time interval (τ_c,∞) and arises from substitution of Eq. (9) into Eq. (5). Asymptotic evaluation of the integral for $\tau_1/\tau_c \approx \tau_1/\tau_0 \sim N^2 \rightarrow \infty$ leads to $\hat{K}_2(x,x';0) \approx 0.001008e^{-1}(D^2\tau_1)^{-1}\ln N^2$. The reader should note that since $D \sim N^{-1}$ and $\tau_1 \sim N^2$, $\hat{K}_2 \sim \ln N$ for $N \rightarrow \infty$. Because $\hat{K}_1$ is N independent, $\hat{K}_2$ provides the dominant contribution to $\hat{K}$ for large N. Solving Eqs. (6) and (7), I find the following asymptotic result for k_e: $k_e \approx 992.1(D^2\tau_1/\ln N^2)S_V$. Using the identity [12] $D\tau_1 = (2/\pi^2)R^2$, this can be rewritten in the more illuminating form

$$k_e \approx 50.3DR(2RS_V/\ln N). \tag{10}$$

Previous studies [3,15] of diffusion-controlled reactions between end-functionalized chains in *homogeneous* polymer melts have established a reaction rate coefficient of the form $k_h \approx 50.3DR$. Evidently, the factor $2RS_V/\ln N$ in Eq. (10) can be interpreted as the volume fraction ϕ_a of an *inhomogeneous* system that is accessible to A-B coupling. The combination $2RS_V$ is natural because any reactive chain with its COM within R of the interface (on either side—hence the factor of 2) is capable of participating in a coupling reaction. Reduction of this accessible volume fraction by the factor of $1/\ln N \sim 1/\ln\tau_1$ is associated with the subdiffusive Rouse dynamics that are operative on the time scale that local equilibrium is achieved inside the interface. Overall, it is clear that Eq. (10) has the simple interpretation $k_e \approx k_h\phi_a$ and scales with molecular weight in the present Rouse regime as $k_e \sim 1/\ln N$.

Next, I turn to consider melts with reactive chains that are longer than the entanglement threshold $(N > N_e)$ and for which the reptation model is appropriate [12,13]. To discuss this situation, it is helpful to recall [12] the behavior of the mean-square end displacement of a freely reptating chain. At times less than $\tau_e \sim a^4/D_0b^2$, the time for the end to explore a distance of order the tube diameter a, the end moves but subdiffusive Rouse dynamics, $\bar{x}^2(t) \sim b(D_0t)^{1/2}$. At times intermediate between τ_e and the longest Rouse time $\tau_1 \sim N^2$, $\tau_e \ll t \ll \tau_1$, the constraints of chain entanglements produce an unusual Rouse dynamics, $\bar{x}^2(t) \sim ab^{1/2}(D_0t)^{1/4}$. A third dynamical regime is entered at times between τ_1 and the reptation time $\tau_d \sim N^3$. For $\tau_1 \ll t \ll \tau_d$, $\bar{x}^2(t) \sim R^2(t/\tau_d)^{1/2}$. Finally, at times exceeding τ_d classical diffusion is recovered, $\bar{x}^2(t) \sim R^2(t/\tau_d) \sim Dt$, where $D \sim D_0(a/b)^2N^{-2}$ is the COM diffusion coefficient of the reptation model.

In the typical situation, the tube diameter a is larger than the interfacial thickness ξ, so I will proceed on that assumption, even though the final result is insensitive to such sub-R scales. Unlike the Rouse model, longitudinal and transverse diffusion in the reptation model are in general coupled when a potential field is present. Nevertheless, an approximate factorization occurs in the present application on time scales greater than τ_0, at which local equilibrium is achieved within the interfacial region. For $t \gg \tau_0$, the product of G_A and G_B in Eq. (3) is to a good approximation independent of x and x' within the interface, and is a function only of $\mathbf{r}_\perp - \mathbf{r}'_\perp$. Note that the assumption $a > \xi$ implies that the end equilibration dynamics proceed according to the Rouse model, so τ_0 is still given by $b^2/D_0\chi^2$. As before, arguing that the dominant N-dependent contributions to the kernel $\hat{K}(x, x'; 0)$ arise from times greater than τ_0, $\hat{K}$ can be estimated as $\hat{K}(x, x'; 0) \sim e^{-1} \int_{\tau_0}^{\infty} dt\, \overline{x}^{-4}(t)$. The numerical prefactor in this expression is unspecified because the end displacement is not a Gaussian random variable at arbitrary times in the reptation model. Nevertheless, the Gaussian prefactor of $1/2\pi^2$ might be employed as an estimate in applications.

Next, I evaluate this integral for $\hat{K}$ by dividing up the domain of integration. Because a is assumed greater than ξ, $\tau_e > \tau_0$. The first contribution to $\hat{K}$ comes from the time interval (τ_0, τ_e), but is N independent. The next time interval to contend with is (τ_e, τ_1). Inserting the expression given above for $\overline{x}(t)$ over this interval leads to a contribution to the kernel that scales as $\hat{K} \sim N/a^2 D_0$. Finally, I consider the time interval (τ_1, ∞). The contribution of this interval to $\hat{K}$ is qualitatively the same as was observed previously for the Rouse model. The integral is convergent for $t \to \infty$, but exhibits a logarithmic dependence on the lower limit due to the $\overline{x}(t) \sim t^{1/4}$ behavior in the interval $\tau_1 < t < \tau_d$. The contribution to the kernel is estimated as $\hat{K} \sim (DR^2)^{-1} \ln(\tau_d/\tau_1) \sim N \ln N$, where $D \sim N^{-2}$ is now the COM diffusivity of a reptating chain. Clearly this last contribution to the kernel is the largest and can be used as in Eqs. (6) and (7) to obtain an asymptotic estimate of k_e for $N \to \infty$. I find an expression strictly analogous to Eq. (10), $k_e \approx DR(RS_V/\ln N) \sim 1/N \ln N$, except that now D is reduced by a factor proportional to $1/N$. Moreover, if the Gaussian estimate of the numerical prefactor for $\hat{K}$ is used, the overall prefactor for k_e corresponding to entangled chains is a factor of 2 larger than that shown in Eq. (10), i.e., 100.6.

Overall, the rate coefficient describing coupling reactions at polymer-polymer interfaces exhibits a surprising insensitivity to interfacial structure and dynamics. This occurs because the rate limiting step in such reactions is the slow diffusive transport of reactive chain COM's to within R of the interface. Once this has occurred, subdiffusive transport into the interfacial region and the actual coupling reaction take place on faster time scales. I am hopeful that extensions of the present analysis (e.g., to asymmetric systems, or to include convective transport) will prove fruitful in developing models of practical reactive blending operations.

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