Polymer Reaction Kinetics at Interfaces

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We study polymer reaction kinetics at interfaces. The interface of width h increments the effective dimensionality by 1: Rate constants k obey scaling laws as for 4-dimensional bulk reaction problems. For groups with small reactivity Q, $k \sim h$ and is independent of molecular weight N. For large Q, $k \sim 1/\ln N$ and $k \sim 1/N \ln N$ for unentangled and entangled polymers, respectively, with weak h dependence. Consistent with recent experiments, we find k is exponentially suppressed when copolymer product attains surface densities above a critical level, $\rho_s^{\text{crit}} \sim 1/N^{1/2}$. [S0031-9007(96)00022-1]

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Recent years have witnessed a surge in research activity in polymer interfacial science. As many bulk polymer questions have been resolved, so attention has increasingly focused on issues such as density profiles and chain configurations at polymer surfaces [1], the bulk-surface exchange kinetics [2] which generate these interfacial phases, and the modification of surfaces to endow them with special properties which are important in a range of biological [3] and industrial [4] applications. Much of this work has addressed *polymer-polymer* interfaces [5]. A topic of intense current interest and major technological importance [6] is the adhesive strength of an interface separating two immiscible polymer phases [7,8], say, A and B. The aim has been to understand how interface structure determines strength and how this strength is enhanced [8] by bridging the interface with naturally surface-active species such as A-B copolymers [9].

By far the most effective method of generating bridging copolymers is through *chemical reactions* of functionalized bulk chains at the polymer-polymer interface (see Fig. 1). A substantial experimental effort has attempted to establish how properties of the reactive polymers determine interfacial characteristics such as strength [10–13]. Compared to simple admixing of copolymers, chemical reactions generate stronger interfaces [13] and more effectively enhance mechanical blending of thermodynamically incompatible polymer species (see Fig. 2). This latter process ("reactive blending") is widely employed industrially to produce stronger and more finely mixed blends [11]. It remains a subject of debate as to whether interfacial chemically produced copolymers generate smaller droplets in nonequilibrium sheared polymer mixtures primarily through surface tension reduction (enhancing droplet breakup rates) or through reduced droplet-droplet coalescence rates (see Fig. 2).

In this Letter we develop a basic theory of irreversible polymer-polymer interfacial reaction kinetics. While a rather complete theoretical picture for *bulk* reactions has by now been assembled [14], the interfacial problem has been analyzed for small molecules [15] only. In the systems above, for example, we would like to predict how rapidly interfacial copolymers accumulate and how this reaction rate depends on polymer molecular weights, functional group reactivity, and surface density of copolymer product. More generally, reactions of this type provide a fundamental probe of polymer interfacial properties which is redundant without a rigorous theoretical basis. The principle conclusions of this work are as follows. First, we find that the presence of the interface, as for small molecules [15], increments the effective spatial dimension by 1: reaction rates obey scaling laws as for a *four-dimensional* bulk reaction system. This leads to weaker molecular weight dependencies. Second, there is a critical surface density of copolymer product above which reaction rates become exponentially suppressed. This has important implications for reactive blending which we discuss later.

Let us begin by briefly reviewing polymer-polymer reaction kinetics in bulk melts. Note that the rate constant k, which relates the reaction rate $-\dot{n}_A = -\dot{n}_B = k n_A n_B$ to the bulk number densities n_A and n_B of reactive chains

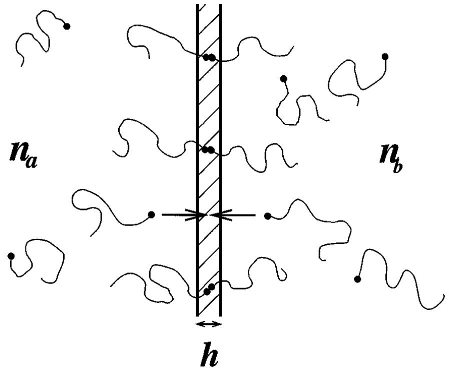

FIG. 1. Two polymer melt bulks, separated by an interface of width h, contain end-functionalized reactive polymers at densities n_a and n_b. The reactive groups can meet in the interfacial region only. Each reaction produces an AB diblock copolymer at the interface.

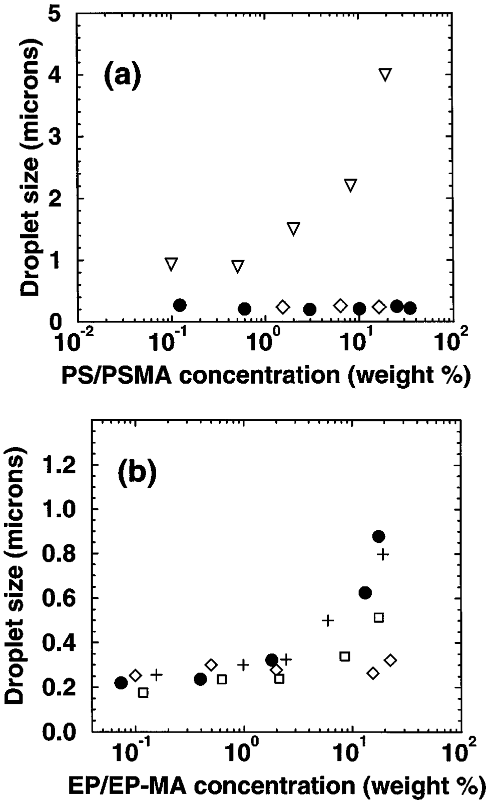

FIG. 2. Reactive blending measurements by Sundararaj and Macosko, Ref. [11]: droplet size vs dispersed phase concentration. Blending at 200 °C for 12 min. Maximum shear rate 65 $\sec^{-1}$. (a) Figure 10 of Ref. [11]. Polystyrene-maleic anhydride (PSMA), dispersed in polyamide-6,6 (diamino functional). MA and amine groups react. ●: PSMA, mol wt $225k$, 17 mole % MA; ◇; PSMA, mol wt $185k$, 1.5% MA; ▽: 0% MA (nonreactive PS, mol wt $200k$). (b) Figure 8 of Ref. [11]. Ethylene-propylene (EP) or ethylene-propylene-maleic anhydride (EP-MA), mol wt $84k$, dispersed in polystyrene (PS) or polystyrene-oxazoline J(PS-Ox), mol wt $200k$. ●: PS/EP-MA (nonreactive system); ◇: PS-Ox/EP-MA (reactive), 1% Ox react with 0.7% MA; □: PS/EP compatibilized by adding diblock copolymer; +: PS/EP with added triblocks.

of types A and B, has dimensions L^3/t (L, t denote length, time). Throughout this Letter we treat the simplest case where each reactive polymer carries one functional end group whose reactivity is Q, and A and B chains are of equal molecular weight N. It has been shown [14,16] that for small Q mean field (MF) theory is valid. Then k is proportional to the equilibrium contact probability of the functional end groups of a reactive A-B pair and involves the small local scales, $k \approx Qa^3$ where a is the group size. For large Q reaction kinetics are quite different; $k \approx R^3/\tau$ then involves the large polymer scales R, the coil size, and τ the longest relaxation time. Doi [17] and de Gennes [18] discuss how the form of k in this diffusion-controlled (DC) regime reflects the emergence of R as an effective reaction radius because small time scale motion ($t < \tau$) guarantees reaction if ever the coil volumes of a reactive pair should overlap. For a general spatial dimension d, the MF and DC results generalize to $k \approx Qa^d$ and $k \approx R^d/\tau$, respectively.

How is this bulk picture modified by the introduction of an interface? That is, suppose the A and B polymers are now immiscible and their reactive groups can meet only in a thin interfacial region of thickness h (see Fig. 1). It is conceptually helpful to consider first the general d-dimensional problem. Consider a pair of chains, one A and one B, in their respective bulks. Then $2d$ coordinates are required to label the positions of their end groups. But reaction requires that these groups are in contact within the $(d-1)$-dimensional interface: this situation corresponds to $d-1$ coordinates. The effective dimensionality of the reaction-diffusion problem is the difference $2d-(d-1) = d+1$. Thus, our three-dimensional interface problem is like a four-dimensional bulk problem. In fact, this is already hinted at by the very definition of k,

$$\frac{d\rho_s}{dt} = kn_A n_B \,, \tag{1}$$

where ρ_s is the surface density of A-B diblock copolymer product. Hence k has dimensions L^4/t which are indeed the dimensions appropriate to a four-dimensional bulk problem. This simple argument suggests that the MF (small Q) and DC (large Q) results are, respectively, $k \approx Qa^4$ and $k \approx R^4/\tau$. In fact, we will see below that this MF expression is correct only for the particular case $h = a$; more generally, we find $k \approx Qa^3h$. Turning to DC kinetics, unentangled polymers are known to obey Rouse dynamics in the melt state [19,20], $\tau \sim N^2$, whereas the reptation model [19,20], describing polymers sufficiently long to be entangled, leads to $\tau \sim N^3$. Noting that simple random walk statistics are recovered in the melt state due to screening [19], $R \sim N^{1/2}$, we conclude that $k \sim N^0$ (independent of N) and $k \sim 1/N$ for unentangled and entangled chains, respectively. These are substantially weaker than the corresponding bulk dependencies, $k \sim 1/N^{1/2}$ and $k \sim 1/N^{3/2}$. In the following we outline more formal arguments which reproduce these naive conclusions to within factors of $\ln N$.

Consider a pair of chains, one A and one B, whose reactive ends are at $\mathbf{r}_a$, $\mathbf{r}_b$. The pair correlation function P_t satisfies

$$\begin{aligned} P_t(\mathbf{r}_a,\mathbf{r}_b) = P_{\rm eq}(\mathbf{r}_a,\mathbf{r}_b) - Qa^3 \int_0^t dt' \int d\mathbf{r}' \\ \times G_{t-t'}(\mathbf{r}_a,\mathbf{r}_b;\mathbf{r}',\mathbf{r}')P_{t'}(\mathbf{r}',\mathbf{r}')\,, \end{aligned} \tag{2}$$

where $G_t(\mathbf{r}_a,\mathbf{r}_b;\mathbf{r}'_a,\mathbf{r}'_b)$ is the probability (in the absence of reactions) of $\mathbf{r}_a,\mathbf{r}_b$ at time t given initial locations $\mathbf{r}'_a,\mathbf{r}'_b$. $P_{\rm eq}$ is the equilibrium distribution. The reader is referred to Refs. [18] and [16] for detailed discussions of the analogous relationship for bulk reactions. From

Eq. (2) we can obtain the reaction rate as the total number of A-B chain pairs multiplied by the rate per pair. This latter is the time derivative of the normalization of P_t. We thus find

$$k = \frac{Qa^3 h}{1 + Qa^3 \int_0^\infty dt\, S(t)},$$
$$h \equiv \int_{-\infty}^{\infty} dx\, P_{\rm eq}(\mathbf{r},\mathbf{r})/P_\infty, \tag{3}$$

where the x direction is orthogonal to the interface and our definition of h involves the value of $P_{\rm eq}$ far from the interface, $P_\infty = 1/(V_A V_B)$ where V_A (V_B) is the volume of bulk A (B). The crucial object here is the time integral of the return probability [18] $S(t) \equiv \int d\mathbf{r}\, G_t(\mathbf{r},\mathbf{r};0,0)$. $S(t)$ is the probability that a pair of reactive groups, given to be initially in contact, have returned to the interface and are again in contact at time t. We emphasize that $S(t)$ describes chain dynamics *without* reactions; this stems from Eq. (2) which relates the reactive P_t to the nonreactive $P_{\rm eq}$ and G_t.

To deduce k we must evaluate $S(t)$. Now for d-dimensional bulk dynamics it has been shown [17,18] that $S \approx 1/x_t^d$ where x_t is the rms displacement of a reactive group. That is, the return probability is simply proportional to the inverse volume explored by either A or B group, since their exploration volumes are completely overlapping. When the interface is present, $S(t)$ is very different because these exploration volumes overlap only in the interfacial region of width h (each group heads off into its respective bulk). Thus for times greater than the diffusion time t_h corresponding to h, we have

$$S(t) \approx h/x_t^4 \qquad (t \gg t_h), \tag{4}$$

which is reduced relative to the bulk value by the fraction of the exploration volumes, h/x_t, which is overlapping. The above time dependence is evidently that of a four-dimensional bulk problem, in accord with our arguments above.

Let us now specialize to unentangled melts where the short time behavior is Rousian [20], $x_t \sim t^{1/4}$, crossing over to the standard Fickian form $x_t \sim t^{1/2}$ at long times $t > \tau$. Writing $x_t = Rf(t/\tau)$, where the scaling function f has appropriate asymptotic power law forms, we evaluate the time integral of S from Eq. (4) which is dominated by $t > t_h$. For large Q, Eq. (3) then yields

$$k \approx \frac{R^4}{\tau}\frac{1}{\ln(R/h)} \sim \frac{1}{\ln N} \qquad \text{(unentangled, } Q > Q^*\text{)}, \tag{5}$$

where $Q^* = t_a^{-1}(a/h)\ln[R/h] \sim 1/\ln N$ is the MF → DC crossover functional group reactivity.

A very similar calculation for polymers longer than the entanglement threshold N_e [21] gives

$$k \approx \frac{R^4}{\tau}\frac{1}{\ln(R/b)} \sim \frac{1}{N\,\ln N} \qquad \text{(entangled, } Q > Q^*\text{)}, \tag{6}$$

where $Q^* = t_a^{-1}(a/h)(N/N_e)\ln[R/b] \sim 1/N\ln N$ and $b = aN_e^{1/2}$ is the entanglement length scale [20].

These results should be contrasted with the weakly reactive case, $Q < Q^*$. In all cases, Eq. (3) gives the same MF result from which N dependence vanishes,

$$k \approx Qa^3 h \qquad (Q < Q^*). \tag{7}$$

All of our conclusions above concern the earlier stages of the reaction process when the surface density ρ_s of A-B diblock product is low. But when the interface becomes sufficiently crowded with diblocks, one expects k to be diminished as less and less free interface area becomes available for reactive bulk chains to access. We anticipate this effect to become strong when the diblocks form a stretched brush [22,23] whose height L is must greater than R (see Fig. 3). Let us calculate the mean number of A-B homopolymer pairs per unit area, $\rho_s^{\rm temp}$, which succeed in penetrating the brush (one from either side) such that their end groups are in contact at the interface. We imagine switching reactions off, and then we calculate this equilibrium quantity. These pairs constitute $\rho_s^{\rm temp}$ temporary diblocks in the brush in addition to the ρ_s permanent members. One can show that their chemical potential, $\mu_{AB}^{\rm temp}$, is dominated by the stretch energy (see Ref. [23]) $\approx kT(L^2/R^2)$ per diblock, where kT is the thermal energy: $\mu_{AB}^{\rm temp}/kT \approx \ln\rho_s^{\rm temp} + 9L^2/R^2 + \cdots$, where higher order terms are omitted. The equilibrium value of $\rho_s^{\rm temp}$ is determined from the relation $\mu_A + \mu_B = \mu_{AB}^{\rm temp}$ where $\mu_A = \ln n_A + \cdots$ is the chemical potential of the reactive chains in bulk A. Similar remarks apply to μ_B. We find that k in this limit is, in fact, dominated by this reduced equilibrium surface density, this being the driving force for reactions. Thus

$$k \sim \rho_s^{\rm temp} \sim \exp\{-(\rho_s/\rho_s^{\rm crit})^2\}$$
$$(\rho_s > \rho_s^{\rm crit} = 1/3N^{1/2}a^2), \tag{8}$$

where we have used the incompressibility of the brush, $L = \rho_s N a^3$. We see that the reaction rate is exponentially reduced when a critical diblock surface coverage is attained, $\rho_s^{\rm crit} \sim 1/N^{1/2}$.

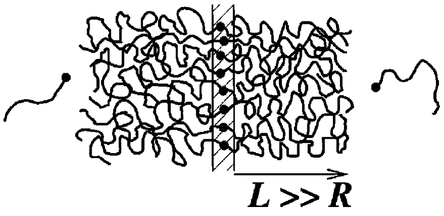

FIG. 3. At sufficiently high surface densities ρ_s, diblock copolymers form a stretched brush whose height L is greater than the unperturbed polymer dimension $R \approx N^{1/2}a$. At such densities, reactive chains from the bulk cannot penetrate the brush. Correspondingly, k becomes exponentially small.

We conclude with a brief discussion of our findings. Polymer reaction kinetics at interfaces depend critically on the reactivity Q of the functional groups. For weak reactivities mean field theory applies, and the rate constant $k \sim h$ depends linearly on interface thickness and is independent of molecular weight N. For large Q, by contrast, Q dependence drops out altogether, just as for bulk reactions [17,18]. In this case, for unentangled chains k exhibits weak logarithmic dependencies on both N and $h, k \sim 1/\ln[N/h^{1/2}]$, whereas when entanglements are important we have found $k \sim 1/N$ and k is independent of h. For crowded interfaces this picture is drastically modified: When the surface density of reaction product exceeds $\rho_s^{\mathrm{crit}} \sim 1/N^{1/2}$, $k \sim \exp\{-(\rho_s/\rho_s^{\mathrm{crit}})^2\}$ is exponentially suppressed. What this means is that the interfacial reactions essentially grind to a halt as soon as ρ_s^{crit} is reached. But the density at which the lateral diblock surface pressure first becomes large enough to substantially influence the surface tension γ is $\rho_s \approx 1/N^{1/3}a^2$, since Leibler [9] has shown that the reduction is $-\Delta\gamma/kT \approx (\rho_s a^2 N^{1/3})^3$. Rewriting this $-\Delta\gamma/kT = \{\rho_s/\rho_s^{\mathrm{crit}} N^{1/6}\}^3$, it is apparent that at $\rho_s = \rho_s^{\mathrm{crit}}$ surface tension reductions are small, $\Delta\gamma \sim 1/N^{1/2}$. We conclude that interfacial reactions are incapable of significantly reducing surface tensions and their primary influence in reactive blending is via reduced droplet-droplet coalescence rates due to the steric hindrances presented by the interfacial copolymer. This is consistent with the data of Fig. 2 and the conclusions of Sundararaj and Macosko, the authors of these data [11]. It is evident that the final steady state droplet sizes are independent of dispersed phase concentration for the reactively compatibilized samples, but not for the uncompatibilized ones. This suggests that the compatibilization process has eliminated coalescence altogether, since coalescence rates generally increase with volume fraction which is presumably the origin of the larger uncompatibilized droplets at higher concentrations. On the other hand, the convergence of the compatibilized and uncompatibilized droplet sizes in Fig. 2(b) at the lowest concentrations (where coalescence becomes unimportant) strongly suggests that the interfacial reactions are leaving droplet surface tension unaffected. This is consistent with the theoretical conclusion presented above.

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