Effect of Entanglements on Polymer Reaction Rates

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Intramolecular diffusion-controlled reactions between internal groups on an entangled polymer are considered in the "reptation" or "tube" model. The results motivate new direct microscopic experimental tests of reptation. For short times compact exploration is found in which the fraction $R(t)$ that has reacted grows like the exploration volume of a monomer followed by a noncompact regime when $R(t)$ scales like the distance moved along the tube. At long times compact behavior is recovered and a rate constant is found which is much smaller than the relaxation rate of the polymer.

Entanglements play an essential role in many systems involving reacting polymers in the melt or concentrated solution. For example, in many condensation and additional polymerization reactions intermolecular and intramolecular reactions compete in a highly entangled environment.[1] Other examples include curing reactions[1] such as vulcanization of natural rubber or irradiation treatments, in which preexisting entangled linear chains react to form a network of interchain links and intrachain loops, and other reactions commonly used industrially.[2]

In this Letter, the simplest intramolecular case, that of diffusion-controlled reactions between two groups along a polymer whose dynamics (in the absence of reactions) are those of the "reptation" model[3,4] of entangled polymers, is studied. My aim is both to help elucidate the role of entanglements in intramolecular reactions in the above systems and to provide new and direct microscopic tests of the reptation model by comparison with experimentally measured reaction rates. (Such comparisons have been made extensively in nonentangled dilute and semidilute solutions by use of photophysical measurement techniques.[5]) While many bulk properties have been explained in terms of reptation,[6] important anomalies remain[7,8] and many predictions of reptation have yet to be conclusively tested: Computer simulations have provided some support,[9-11] but direct microscopic probes are very limited.[12]

Previous theoretical studies of entangled systems have addressed intermolecular reactions[13] and the intramolecular case of cyclization[14] where the reactive groups are at the chain ends. The conclusion is that entanglements reduce reaction rates $k(t)$ by slowing down the dynamics: $k(t) \propto \tau_0^{-1}$ where τ_0, the longest relaxation time of a polymer, is greatly increased by entanglements.[7] We will see below that intramolecular reactions between internal groups are affected in a more fundamental way since such groups are far more limited by the topological constraints of other chains in their ability to explore space: While an end group fills out a dense structure in space, an internal group traces an open stringy structure (see Fig. 1). Note that the structure depicted in Fig. 1(b) is essentially a scaled-up version of that in Fig.
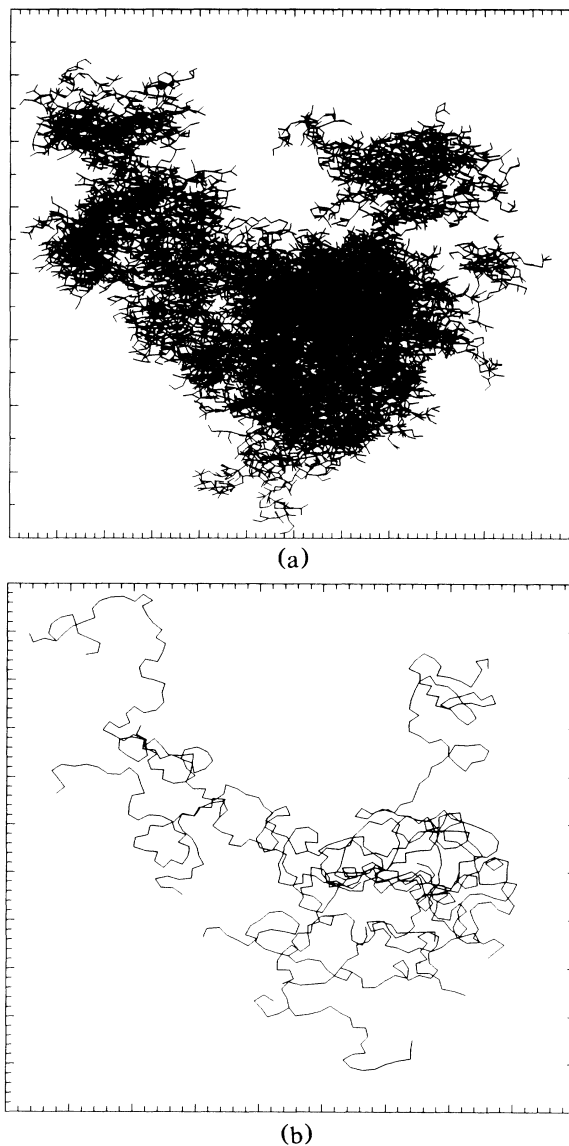

(a)

(b)

FIG. 1. Typical paths of groups attached to a polymer of $L/a = 200$ steps reptating in two dimension (for clarity) with "Doi-Edwards" dynamics. (a) End group. (b) Internal group at $a/a = 30$ (same run). Run time was one reptation time.

1(a). However, the shortest–length-scale fluctuations, which are omitted from the dynamics used to generate Fig. 1, are space filling and it follows that an end group fills out all of space, unlike an internal group which explores a small fraction. In consequence $k(t)$ is *much* lower for internal groups.

In the reptation picture[3] the topological constraints of neighboring chains are modeled as the walls of an open-ended tube of length L and diameter a which contains the polymer of N segments. The tube comprises $N/N_e = L/a$ "blobs" of size a, each containing $\sim N_e$ polymer segments. On time scales $t < t_a$, the dynamics are those of a free Rouse chain[15] of N_e segments: $x^3(t) = (t/t_a)^{3/4}a^3$, where $x(t)$ is rms displacement and $t_a \propto N_e^2$ is the time for a segment to explore a blob. For $t > t_a$ a segment feels entanglements and is constrained to move along the tube with rms displacement $h(t)$ where

$$h(t) \simeq (t/t_a)^{1/4}a, \quad t_a < t < t_L, \tag{1a}$$

$$h(t) \simeq (D^T t)^{1/2}, \quad t_L < t < \tau_{\text{rep}}. \tag{1b}$$

Here $t_L \simeq (L/a)^2 t_a$ is the relaxation time of the "breathing modes" along the tube, Eq. (1a), after which the chain diffuses coherently with curvilinear diffusivity $D^T \equiv a^3/Lt_a$. In the "reptation time" $\tau_{\text{rep}} = L^2/D^T$, the polymer reptates away into a new tube. Since the tube is itself a random walk in space the spatial displacement is $x^2(t) = ah(t)$ for $t > t_a$.

I now outline the calculation of $k(t)$, details of which will be presented elsewhere.[16] I take the probability $\phi_t(\{r(h)\})$ of a polymer configuration $\{r(h)\}$ as obeying a Fokker-Planck equation of the type first proposed by Wilemski and Fixman[17]:

$$\dot{\phi}_t + H\phi_t = -Q\Omega\delta(r(\alpha) - r(L-\beta))\phi_t. \tag{2}$$

H is the reptation operator in the absence of reactions and $0 < h < L$ labels a segment's position along the tube. The groups at $h = \alpha$, $L - \beta$ (with the convention $\alpha < L - \beta$) react with intrinsic probability Q per unit time whenever they lie within the "trap" volume Ω ($\Omega \ll a^3$) of one another. Taking $\phi_{t=0}$ to be the equilibrium distribution, and assuming equilibrium statistics for those

chains whose reactive groups are in contact (the "closure approximation" of Wilemski and Fixman[17]), we find $\dot{N} = -k(t)N(0)$, where $N(t)$ is the number of unreacted chains and, for small times, $k(t) \simeq \rho_{\text{eq}}d[1/S(t)]/dt$, where we write

$$S(t) \equiv \Omega/V_R(t), \quad \rho_{\text{eq}} \equiv \Omega V_s. \tag{3}$$

Here $S(t)$ is the "return probability," the probability that the reactive groups are in contact at time t given that they were initially, in terms of which I define the "reaction volume" $V_R(t)$. $\rho_{\text{eq}} = \lim_{t \to \infty} S(t)$ is the equilibrium contact probability; $s \equiv L - \alpha - \beta$ and $V_s = (sa)^{3/2}$ is the volume occupied (statistically) by one reactive group relative to the other. Introducing the reacted fraction $R(t) \equiv [N(0) - N(t)]/N(0)$, we obtain

$$R(t) \simeq V_R(t)/V_s, \quad t < \tau_{\text{rep}}. \tag{4}$$

Now for short times we will see that the reaction volume is simply the exploration volume, $V_R(t) = x^3(t)$. Thus $R(t) = x^3(t)/V_s$ and hence $R(t)$ is simply the fraction of polymers whose reactive groups were initially within $x(t)$ of each other. This is a form typical of compact exploration[13]: The groups react if ever their exploration volumes $[x^2(t)]$ overlap. To see why $V_R(t) = x^3(t)$, note that for times $t < t_s$, where $t_s = (s/a)^2 t_a$ is the relaxation time for the length of chain separating the groups, their motions are *uncorrelated*. Thus for $t < t_a$, $S(t)$ corresponds to two Rouse chains of length N_e in the overlap region of volume a^3 in a looped tube [Fig. 2(a)]. This is in effect the *intermolecular* case of de Gennes,[13] who finds $S(t) \simeq \Omega/x^3(t)$: Thus from Eq. (3) $V_R(t) = x^3(t)$. For $t_a < t < t_s$ each group drifts *independently* along the tube a distance characterized by a probability distribution of width $\sim h(t)$. Thus the probability of return to the originally occupied intersection is $S_1(t) \simeq [a/h(t)]^2(\Omega/a^3)$. However, as noted by de Gennes,[13] given one tube intersection at $h = 0$ there are $\sim [h(t)/a]^{1/2}$ others nearby where the groups may reencounter [Fig. 2(b)]. Each contributes of order $S_1(t)$, so

$$S(t) \simeq \Omega/[ah(t)]^{3/2} = \Omega/x^3(t)$$

and thus $V_R(t) = x^3(t)$ as for $t < t_a$. Thus from Eqs. (1a) and (4) we have

$$R(t) \simeq \frac{x^3(t)}{V_s} = \begin{cases} (t/t_a)^{3/4}a^3/(sa)^{3/2}, & t < t_a, \\ (t/t_a)^{3/8}a^3/(sa)^{3/2}, & t_a < t < t_s. \end{cases} \tag{5}$$

By the time t_s a fraction Ω_b/V_s has reacted, where $\Omega_b \equiv x^3(t_s) = (h_b a)^{3/2}$, and the static quantity $h_b \equiv h(t_s) = (sa)^{1/2}$ [see Eq. 1(a)] is the fluctuation in length of the polymer connecting the groups: This is its breathing mode which relaxes in a time t_s. For $t > t_s$ it moves coherently along the tube with constant length s. Thus the probability of return to the multiple intersection region of volume Ω_b in Fig. 2(b) is of *one-dimensional* form $\sim h_b/h(t)$. Given their return, we find the conditional probability of contact $\simeq \Omega/\Omega_b$. Now for $t > t_s$ the only intersections (of volume Ω_b) contributing to $S(t)$ are those involving *equal* tube lengths on the $h = \alpha$ and $h = \beta$ branches; one can show that there are only $(\sim 1) + O([a/h(t)]^{1/2})$ of these, i.e., the originally occupied intersection dominates.
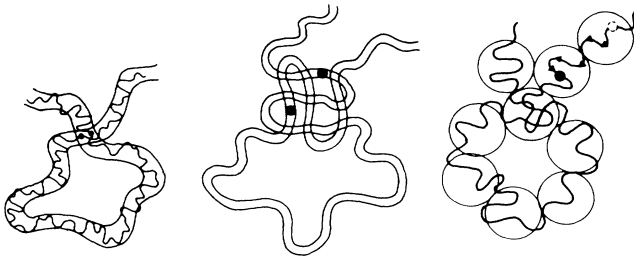
FIG. 2. Configurations which react at times (a) $t < t_a$, (b) $t_a < t < t_s$, and (c) $t_s < t < \tau_{\text{rep}}$.

FIG. 3. Diagrams contributing to $S(t)$. Add all mirror images about the "horizontal" and "vertical" axes to generate complete set.

$S(t) \simeq [h_b/h(t)] \Omega/\Omega_b$ and Eqs. (1) and (3) in Eq. (4) yield

$$R(t) \simeq \frac{h(t)}{h_b} \frac{\Omega_b}{V_s} = \begin{cases} (t/t_a)^{1/4}(a/s)^{5/4}, & t_s < t < t_L, \\ (t/t_a)^{1/2}(a/s)^{5/4}(a/L)^{1/2}, & t_L < t < \tau_{\text{rep}}. \end{cases} \tag{6}$$

We can now interpret $V_R(t)$ as the volume *compactly* explored by the relative position vector of the reactive groups. From Eq. (6) $V_R(t) = [h(t)/h_b]\Omega_b$ is the volume of a *blobbed tube*, each blob of volume Ω_b containing a length of tube [Fig. 2(c)]. Up to t_s a single blob is explored [Eq. (5)]. While this tube is compactly explored, the tube itself fills space noncompactly (recall $x \sim h^{1/2}$); consequently, the reacted fraction $R(t)$ is much less than in the case of cyclization where end groups are not constrained by the tube and the end-to-end vector explores space compactly, i.e., $V_R(t) = x^3(t)$ for all $t < \tau_{\text{rep}}$. Thus for cyclization $R(t) \simeq x^3(t)/V_L$ and so for $t < t_a$ Eq. (5) gives $R(t) \simeq (t/t_a)^{3/4}(a/L)^{3/2}$ and for $t_a < t < t_L$, $R(t) \simeq (t/t_a)^{3/8}(a/L)^{3/2}$. For $t > t_L$, we obtain $R(t) \simeq (t/\tau_{\text{rep}})^{3/4}$ from Eq. (1b); this is the result of Bernard and Noolandi[14] whose calculations were in the model of Doi and Edwards,[4] which is a version of reptation in which the $t < t_L$ dynamics are ignored.

Let us now consider long-time behavior, $t \gg \tau_{\text{rep}}$. $S(t)$ is now a sum over all the different ways the groups can be in contact in the final tube (time t) given their contact initially; each way we represent with a different diagram (Fig. 3). The top and bottom of the H are respectively the initial and final tubes whose configurations are integrated over with Gaussian weighting, and dotted lines are δ functions connecting reactive groups. The diagrams are summed with weighting appropriate to the lengths u and v of initial tube lost at either end and the distance h diffused forwards in the time t. By the nature of reptation dynamics, this weighting is the probability that in the time t the maximum distance the polymer ever moved forwards (backwards) along its tube was $u(v)$, and the net distance moved forwards was h.

For long times we find $N(t) \sim e^{-kt}$, where the rate constant k for $\alpha = \beta$ can be derived by the following simple argument: For large N [specifically, $(a/s)^{1/4} \ll 1$] the system relaxes in a time $\simeq \tau_a$; in this time the fraction which reacts is $-\Delta N/N \simeq V_R(\tau_a)/V_s = (a/h_b)$
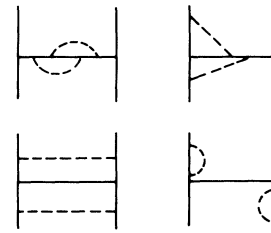
$\times \Omega_b/V_s$. Then $k = -\Delta N/(N\Delta t)$ with $\Delta t = \tau_a$ yields

$$k \simeq \frac{(a/s)(a/s)^{1/4}}{\tau_a}[1 + O((a/s)^{1/4})], \tag{7}$$

where $\tau_a \equiv a^2/D^T$.

In the formal derivation of Eq. (7) $S(t)$ can be safely evaluated in the Doi-Edwards model [Eq. (1b)] provided we use an *effective* trap volume $\Omega = \Omega_b$ since groups within Ω_b of each other will react because of the small-time fluctuations, Eq. (5). In the large-N limit we find that the originally occupied blob (of volume Ω_b) dominates: This is the $h = 0$ part of the top left diagram of Fig. 3. Solving Eq. (2) for $N(t)$ in the "closure approximation" one finds[17,18] $N(t) \sim e^{-kt}$ where $k \simeq \rho_{\text{eq}}/\int_0^\infty dt[S(t) - \rho_{\text{eq}}]$ and for $\alpha = \beta$ we obtain Eq. (7). For general α, β we find $k = \tau_{a+\beta}^{-1}(\alpha+\beta)^3(a/s)^{1/4}/\alpha\beta s$, where $\tau_{a+\beta} \equiv (\alpha+\beta)^2/D^T$.

To compare with cyclization note that at fixed $a/L, \beta/L$ we have $k \sim N^{-13/4}$, which is slower than the cyclization result,[14] $k \propto \tau_{\text{rep}}^{-1} \propto N^{-3}$.

It is interesting to compare the present case to *inter-molecular*[13] reactions in melts: In this case the reactive groups move *independently* for all times along two structures of the type shown in Fig. 1 and so can encounter at any of the numerous intersections. In the same way as for the intramolecular case for $t < t_s$, it follows[13] that the groups in effect explore space compactly as if there were no tube: There is no dramatic difference between reaction rates for end and internal groups.

Let us return now to the structure depicted in Fig. 1(b). Imagine further "blobbing" of our blobbed tube into blobs containing length α of tube, each of volume $(\alpha a)^{3/2}$: The reactive blobs are now at the chain ends, i.e., one has cyclization on a lattice of cell size $\simeq (\alpha a)^{1/2}$ for which V_s is explored *compactly*. Roughly, what one sees in Fig. 1(b) is a portion of this lattice. Equation (7) is a non-diffusion-controlled "law of mass action" on this

lattice since the effective reaction rate Q_{eff} during the period τ_a for which the reactive groups occupy the same site, namely $\tau_a^{-1} V_R(\tau_a)/(aa)^{3/2}$, is small: k is the product of Q_{eff} with the equilibrium contact probability $(aa)^{3/2}/V_s$. We remark that for finite N, and correspondingly finite Q_{eff}, the cyclization result (diffusion controlled, $Q_{eff} \gg 1$) and Eq. (7) ("law of mass action," $Q_{eff} \ll 1$) constitute bounds on k. Thus $AM^{-3} \le k \le BM^{-13/4}$ in general, where A and B are constants.

In conclusion, we find that space is explored compactly on length scales $x \lesssim x^T$, noncompactly on scales $x^T \lesssim x \lesssim x_m$, and once again compactly on scales $x \gtrsim x_m$ where $x^T = (h_b a)^{1/2}$ is the diameter of the blobbed tube and $x_m \simeq (aa)^{1/2}$ is the mesh size of Fig. 1(b). To each spatial regime corresponds a reaction regime in time. Particularly experimentally interesting is the possibility of exploring the regimes $t < \tau_a$, $x < x_m$ using photophysical methods which probe times $\simeq 10^{-5}$ s (cf. $t_L \gtrsim 10^{-6}$ s typically). Such techniques have been used to measure reaction rates involving internal groups[19] but hitherto only up to concentrations just short of the entanglement threshold.

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