

Diffusion-Influenced Kinetics of Reactions Involving Polymers

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Received February 28, 2003

We present a brief account of the theory of diffusion-influenced kinetics of reactions involving polymers. The review will be based on the recent contributions from the authors. Both intrapolymer and interpolymer reactions are considered, and the effects of various physical factors, such as the chain length, chain stiffness, and hydrodynamic interactions, are described within a unified theoretical framework.

Key Words : Diffusion-influenced kinetics, Intrachain and interchain reactions

Introduction

Chemical reactions between functional groups on polymeric molecules are ubiquitous in many applications. Termination in radical polymerization, crosslinking of polymer gels, and reactions involving biopolymers such as proteins and receptors are a few examples.^{1,2} In spite of their practical importance, understanding of the principles behind their reaction kinetics is still in a primitive stage. This is due to the difficulty arising from the strong constraint of chain connectivity as well as of chain entanglements, leading to a deviation of the dynamics of reactive groups from the free Brownian motion. It is in contrast to the reaction kinetics of small molecules, which have been studied extensively for many years.^{3,4}

Much attention has been paid to the intrachain reactions of polymers because such reactions occur in a variety of reacting polymer systems and measurements of the intrachain reaction rates provide valuable information on the conformational structure and dynamical behavior of polymer chains.^{5,6} A general theory for describing the diffusion-influenced kinetics of intrachain reactions was first advanced by Wilemski and Fixman.⁷ By utilizing a factorization approximation (also called the closure approximation), they could derive analytic expressions for the reaction rate and the time-dependent survival probability of unreacted polymer for several types of intrachain reactions. More specific aspects of the intrachain reactions have been investigated also. Friedman and O'Shaughnessy developed a renormalization group method for calculating the cyclization rates of chain polymers as a function of reactive group locations along the backbone.⁸ Stampe and Sokolov investigated the effects of electrostatic interaction between the charged end groups on the cyclization rate.⁹ Dua and Cherayil considered the effect of backbone rigidity on the dynamics of chain closure.¹⁰ Bandyopadhyay and Ghosh utilized a non-Markovian reaction-diffusion equation to investigate the memory effect in the fluorescence resonance energy transfer.¹¹ Rey and Freire,¹² and more recently Podtelezchnikov and Vologodskii¹³ investigated the effect of excluded volume interactions by using Brownian

dynamics simulations.

Investigations on reactions between polymers have also been made for a number of situations. de Gennes discovered a regime of time-dependent reaction rates with and without the effects of entanglements.¹⁴ Oshanin and his coworkers have made investigations on trapping reactions involving polymers in two and three dimensions,¹⁵ and summarized the many-particle effects occurring in various polymeric reactions.¹⁶ Reactions at polymeric interfaces were studied extensively by O'Shaughnessy *et al.*¹⁷ and by Fredrickson.¹⁸

In this review, we present a brief account of the theory of diffusion-influenced kinetics of reactions involving polymers, based on the recent contributions from the authors. In particular, we show that for both intrachain and interchain reactions, the reaction event and the inherent polymer dynamics can be decoupled approximately in many cases. The effects of various physical factors, such as the chain length, chain stiffness, and hydrodynamic interactions, on the reaction kinetics can thus be described within a unified theoretical framework.

Intrachain Reactions

Figure 1 illustrates schematically a typical intrachain reaction. For simplicity, the polymer is modeled as a chain of spherical beads connected by harmonic springs. As shown in the figure, we consider the general case in which the reacting groups are located at any position on the chain. Most previous theories dealt with the case where the reaction occurs between the reacting groups at the chain ends. Although we will use the terms tailored for a simple cyclization reaction, the theory can also be applicable to intrachain energy transfer¹⁹ and the excimer-formation reaction²⁰ with a little modification.

Derivation of the Rate Expressions. Let $\psi_o(\mathbf{r}^{N+1}, t)$ be the probability density for the polymer being in the open form, with the $N + 1$ beads constituting the chain located at $\mathbf{r}^{N+1} \equiv (\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N)$. Similarly, $\psi_R(\mathbf{x}^{N+1}, t)$ is the probability density for the polymer making a ring due to the bond formation between the i th and j th beads, with the $N + 1$

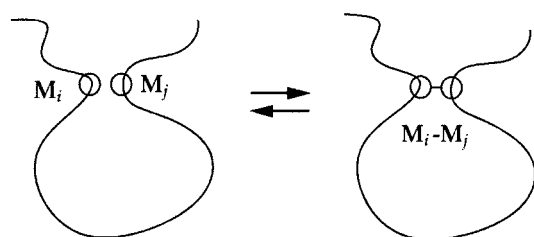


Figure 1. Pictorial representation of the reversible cyclization reaction. The bond forms between the i th and the j th monomers.

beads located at $\mathbf{x}^{N+1} \equiv (\mathbf{x}_0, \mathbf{x}_1, \dots, \mathbf{x}_N)$. The probability density function $\psi_o(\mathbf{r}^{N+1}, t)$ evolves in time according to⁷

$$\begin{aligned} \frac{\partial}{\partial t} \psi_o(\mathbf{r}^{N+1}, t) &= L(\mathbf{r}^{N+1}) \psi_o(\mathbf{r}^{N+1}, t) \\ &- \int d\mathbf{x}^{N+1} R_f(\mathbf{x}^{N+1} | \mathbf{x}^{N+1}) \psi_o(\mathbf{r}^{N+1}, t) \\ &+ \int d\mathbf{x}^{N+1} R_r(\mathbf{x}^{N+1} | \mathbf{r}^{N+1}) \psi_R(\mathbf{x}^{N+1}, t). \end{aligned} \quad (1)$$

Here $L(\mathbf{r}^{N+1})$ is the Smoluchowski operator governing the thermal evolution of the open-chain distribution in the absence of reaction. The sink functions R_f and R_r represent the inherent rates of bond formation and dissociation at the bead configurations given by \mathbf{r}^{N+1} and \mathbf{x}^{N+1} , respectively. We assume that they have the simple forms given by

$$\begin{aligned} R_f(\mathbf{r}^{N+1} | \mathbf{x}^{N+1}) &= S_f^0(\mathbf{r}^{N+1}) \delta(\mathbf{r}^{N+1} - \mathbf{x}^{N+1}), \\ R_r(\mathbf{x}^{N+1} | \mathbf{r}^{N+1}) &= S_r^0(\mathbf{x}^{N+1}) \delta(\mathbf{r}^{N+1} - \mathbf{x}^{N+1}), \end{aligned} \quad (2)$$

where $\delta(\mathbf{r}^{N+1} - \mathbf{x}^{N+1}) = \delta(\mathbf{r}_0 - \mathbf{x}_0) \dots \delta(\mathbf{r}_N - \mathbf{x}_N)$. Equation (2) tells us that the inherent bond formation and dissociation occur so rapidly that the polymer conformation does not change much during the course of the reactive transitions. With Eq. (2), Eq. (1) reduces to

$$\begin{aligned} \frac{\partial}{\partial t} \psi_o(\mathbf{r}^{N+1}, t) &= L(\mathbf{r}^{N+1}) \psi_o(\mathbf{r}^{N+1}, t) \\ &- S_f^0(\mathbf{r}^{N+1}) \psi_o(\mathbf{r}^{N+1}, t) + S_r^0(\mathbf{r}^{N+1}) \psi_R(\mathbf{r}^{N+1}, t). \end{aligned} \quad (3)$$

We now assume the following sink functions:

$$S_f^0(\mathbf{r}^{N+1}) = \kappa_f S_f(|\mathbf{r}_i - \mathbf{r}_j|), \quad (4)$$

$$S_r^0(\mathbf{r}^{N+1}) = \kappa_r S_r(|\mathbf{r}_i - \mathbf{r}_j|). \quad (5)$$

With these sink functions, integration of Eq. (1) over $(\mathbf{r}_0, \dots, \mathbf{r}_{i-1}, \mathbf{r}_{i+1}, \dots, \mathbf{r}_{j-1}, \mathbf{r}_{j+1}, \dots, \mathbf{r}_N)$ gives

$$\begin{aligned} \frac{\partial}{\partial t} P'_o(\mathbf{r}_i, \mathbf{r}_j, t) &= L'(\mathbf{r}_i, \mathbf{r}_j) P'_o(\mathbf{r}_i, \mathbf{r}_j, t) \\ &- \kappa_f S_f(|\mathbf{r}_i - \mathbf{r}_j|) P'_o(\mathbf{r}_i, \mathbf{r}_j, t) + \kappa_r S_r(|\mathbf{r}_i - \mathbf{r}_j|) P'_R(\mathbf{r}_i, \mathbf{r}_j, t). \end{aligned} \quad (6)$$

$P'_o(\mathbf{r}_i, \mathbf{r}_j, t) [P'_R(\mathbf{r}_i, \mathbf{r}_j, t)]$ is the probability density for the polymer being in the open [ring] form at time t with the i th and j th beads at \mathbf{r}_i and \mathbf{r}_j . $L'(\mathbf{r}_i, \mathbf{r}_j)$ is the reduced Smoluchowski operator governing the thermal evolution of $P'_o(\mathbf{r}_i, \mathbf{r}_j, t)$ in the absence of a reaction. When the external

flows and forces are absent, it is clear that $P'_o(\mathbf{r}_i, \mathbf{r}_j, t)$ and $P'_R(\mathbf{r}_i, \mathbf{r}_j, t)$ depend only on $R (\equiv |\mathbf{r}_i - \mathbf{r}_j|)$:

$$\begin{aligned} P'_o(\mathbf{r}_i, \mathbf{r}_j, t) &= V^{-1} P_o(R, t), \\ P'_R(\mathbf{r}_i, \mathbf{r}_j, t) &= V^{-1} P_R(R, t). \end{aligned} \quad (7)$$

$P_o(R, t) [P_R(R, t)]$ is the probability density for the polymer being in the open [ring] form at time t with the distance between the i th and j th beads being given by R . Hence, Eq. (6) reduces to

$$\begin{aligned} \frac{\partial}{\partial t} P_o(R, t) &= L(R) P_o(R, t) \\ &- \kappa_f S_f(R) P_o(R, t) + \kappa_r S_r(R) P_R(R, t). \end{aligned} \quad (8)$$

Here, $L(R)$ is an effective thermal operator governing the reaction-free evolution of $P_o(R, t)$, whose explicit expression need not be known at the moment.

If the vibration of the ring-forming bond is very fast, the deviation of $P_R(R, t)$ from the internal equilibrium distribution $P_R^{eq}(R)$ should be negligible, so that we can write

$$P_R(R, t) \equiv P_R^{eq}(R) S_R(t). \quad (9)$$

$S_R(t)$ is the probability that the polymer is in the ring form at time t . With this approximation, Eq. (8) can be rewritten as

$$\begin{aligned} \frac{\partial}{\partial t} P_o(R, t) &= L(R) P_o(R, t) \\ &- \kappa_f S_f(R) P_o(R, t) + \kappa_r S_r(R) P_R^{eq}(R) S_R(t). \end{aligned} \quad (10)$$

Integrating Eq. (10) over \mathbf{R} (i.e., over the relative separation and orientation of the i th and j th beads), we obtain the rate equation as

$$\frac{d}{dt} S_o(t) = -\kappa_f \int d\mathbf{R} S_f(R) P_o(R, t) + k_r^{eq} [1 - S_o(t)]. \quad (11)$$

Here $S_o(t) [1 - S_R(t)]$ is the probability that the polymer is in the open form at time t , and k_r^{eq} denotes the equilibrium rate constant for the bond-dissociation:

$$S_o(t) = \int d\mathbf{R} P_o(R, t), \quad (12)$$

$$k_r^{eq} = \kappa_r \int d\mathbf{R} S_r(R) P_R^{eq}(R). \quad (13)$$

We assume that initially the polymer is in the equilibrium configuration of the open chain:

$$S_o(t=0) = 1, \quad P_o(R, t=0) = P_o^{eq}(R). \quad (14)$$

For this initial condition, Laplace transformation of Eq. (10) yields the following perturbative solution:

$$\begin{aligned} \int d\mathbf{R} S_f(R) \hat{P}_o(R, s) &= s^{-1} \int d\mathbf{R} S_f(R) P_o^{eq}(R) \\ &- \kappa_f s^{-1} \left\{ \int d\mathbf{R} S_f(R) \int d\mathbf{R}_0 \hat{G}(R, s | R_0) S_f(R_0) P_o^{eq}(R_0) \right. \end{aligned}$$

$$\begin{aligned}
& -\kappa_f \int d\mathbf{R} S_f(R) \int d\mathbf{R}_1 \hat{G}(R, s | R_1) S_f(R_1) \\
& \times \int d\mathbf{R}_0 \hat{G}(R_1, s | R_0) S_f(R_0) P_O^{eq}(R_0) + \dots \Big\} \\
& + \kappa_r \hat{S}_R(s) \Big\{ \int d\mathbf{R} S_f(R) \int d\mathbf{R}_0 \hat{G}(R, s | R_0) S_r(R_0) P_O^{eq}(R_0) \\
& - \kappa_f \int d\mathbf{R} S_f(R) \int d\mathbf{R}_1 \hat{G}(R, s | R_1) S_f(R_1) \\
& \times \int d\mathbf{R}_0 \hat{G}(R_1, s | R_0) S_r(R_0) P_R^{eq}(R_0) + \dots \Big\}. \quad (15)
\end{aligned}$$

We denote the Laplace transform of any function $f(t)$ as $\hat{f}(s)$. In Eq. (15), the Green's function $\hat{G}(R, s | R_0)$ is defined by

$$\hat{G}(R, s | R_0) = \frac{1}{s - L(R)} \frac{\delta(R - R_0)}{4\pi R_0^2}. \quad (16)$$

By using the decoupling approximation suggested by Weiss,²¹ we can resum the series solution in Eq. (15) as

$$\begin{aligned}
\int d\mathbf{R} S_f(R) \hat{P}_O(R, s) & \equiv \frac{V_f}{s} - \frac{\kappa_f}{s} \cdot \frac{\hat{D}_f(s)}{1 + \kappa_f \hat{D}_f(s) / V_f} \\
& + \kappa_r \hat{S}_R(s) \frac{\hat{D}_r(s)}{1 + \kappa_f \hat{D}_f(s) / V_f}, \quad (17)
\end{aligned}$$

where

$$V_f = \int d\mathbf{R} S_f(R) P_O^{eq}(R), \quad (18)$$

$$D_f(t) = \int d\mathbf{R} S_f(R) \int d\mathbf{R}_0 G(R, t | R_0) S_f(R_0) P_O^{eq}(R_0), \quad (19)$$

$$D_r(t) = \int d\mathbf{R} S_f(R) \int d\mathbf{R}_0 G(R, t | R_0) S_r(R_0) P_R^{eq}(R_0). \quad (20)$$

On the other hand, Laplace transformation of Eq. (11) gives

$$\kappa_f \int d\mathbf{R} S_f(R) \hat{P}_O(R, s) - \kappa_r^{eq} [s^{-1} - \hat{S}_O(s)] = 1 - s \hat{S}_O(s). \quad (21)$$

Substitution of Eq. (17) into Eq. (21) finally gives

$$\begin{aligned}
\hat{S}_R(s) & = s^{-1} - \hat{S}_O(s) \\
& = \frac{\kappa_f^{eq}}{s} \left\{ s + \kappa_f^{eq} \frac{s \hat{D}_f(s)}{D_f(\infty)} + \kappa_r^{eq} + \kappa_f^{eq} \kappa_r^{eq} \left[\frac{\hat{D}_f(s)}{D_f(\infty)} - \frac{\hat{D}_r(s)}{D_r(\infty)} \right] \right\}^{-1}. \quad (22)
\end{aligned}$$

where

$$\kappa_f^{eq} = \kappa_f \int d\mathbf{R} S_f(R) P_O^{eq}(R) = \kappa_f V_f. \quad (23)$$

Note that $D_f(\infty) = V_f^2$ and $D_r(\infty) = V_f \int d\mathbf{R} S_r(R) P_R^{eq}(R)$.

Equation (22) is the key result of the formalism developed in this section. This can be compared with the WF result:⁷

$$\begin{aligned}
\hat{S}_R^{WF}(s) & = \frac{\kappa_f^{eq}}{s} \left\{ s + \kappa_f^{eq} \frac{s \hat{D}_f(s)}{D_f(\infty)} + \kappa_r^{eq} \right. \\
& \left. + \kappa_f^{eq} \kappa_r^{eq} \left[\frac{\hat{D}_f(s)}{D_f(\infty)} - V_f^{-1} \hat{R}(s) \right] \right\}^{-1} \quad (24)
\end{aligned}$$

with

$$R(t) = \int d\mathbf{R} S_f(R) \int d\mathbf{R}_0 G(R, t | R_0) P_R^{eq}(R_0).$$

At long times, when the equilibrium state is restored, we should have

$$\lim_{t \rightarrow \infty} S_R(t) = \lim_{s \rightarrow 0} s \hat{S}_R(s) = \frac{\kappa_f^{eq}}{\kappa_f^{eq} + \kappa_r^{eq}} \equiv S_R^{eq}. \quad (25)$$

However, neither of the solutions given by Eqs. (22) and (24) satisfies this requirement in general. We can remedy this problem immediately. When the system is restored to the equilibrium state, we should have $P_O(R, t) = P_O^{eq}(R) S_O^{eq}$ and Eq. (10) reduces to

$$\kappa_f S_f(R) P_O^{eq}(R) S_O^{eq} = \kappa_r S_r(R) P_R^{eq}(R) S_R^{eq}. \quad (26)$$

With this detailed balance condition, Eq. (22) becomes

$$\hat{S}_R(s) = \frac{\kappa_f^{eq}}{s} \left\{ s + \kappa_f^{eq} \frac{s \hat{D}_f(s)}{D_f(\infty)} + \kappa_r^{eq} \right\}^{-1}. \quad (27)$$

One can immediately see that Eq. (27) satisfies the equilibrium condition given by Eq. (25).

In contrast, the WF solution cannot be saved by the above detailed balance condition. The reason is that in the WF theory a couple of approximations were made at the stage of Eq. (3). First, $S_r^0(\mathbf{r}^{N+1})$ was set equal to a constant κ_r . Second, $\psi_R(\mathbf{r}^{N+1}, t)$ was approximated by $\psi_R^{eq}(\mathbf{r}^{N+1}) S_R(t)$ where $\psi_R^{eq}(\mathbf{r}^{N+1})$ is the equilibrium chain distribution function for the ring polymer. Thus, one can easily see that the WF solution is regained from our solution if $S_r(R)$ is set equal to unity.

When the sink functions can be modeled as δ -functions [*i.e.*, when $S_f(R) = S_r(R) = \delta(R - \sigma) / (4\pi\sigma^2)$], Eq. (27) reduces to

$$\hat{S}_R(s) = \frac{1}{s} \cdot \frac{\kappa_f^{eq}}{s + \kappa_f s \hat{G}(\sigma, s | \sigma) + \kappa_r^{eq}}. \quad (28)$$

It should be remarked that the decoupling approximation of Weiss becomes exact in this δ -function sink case.

The Green's Function. To calculate the intrachain reaction rate between two reactive groups on a polymer, we need an explicit Green's function expression for the relative motion of the beads carrying the groups *in the absence of reaction*.

To the best of our knowledge, only the Green's function for the end-to-end motion of a polymeric chain has been given in the literature. For the free draining Rouse chain, the following expression has been derived by Wilemski and Fixman⁷ using the boson representation method and also by Doi²² using the more straightforward integration procedure:

$$G(\mathbf{R}, t | \mathbf{R}_0) = \left(\frac{3}{2\pi L^2 [1 - \phi^2(t)]} \right)^{3/2} \exp \left\{ -\frac{3}{2L^2} \frac{[\mathbf{R} - \phi(t)\mathbf{R}_0]^2}{[1 - \phi^2(t)]} \right\}. \quad (29)$$

Here, \mathbf{R} is the end-to-end vector $\mathbf{r}_0 - \mathbf{r}_N$, and $L^2 (= Nb^2)$ is the

equilibrium mean squared end-to-end distance with b^2 denoting the equilibrium mean squared length of a single bond of the Rouse chain. $\phi(t)$ is given by

$$\phi(t) = \frac{8}{\pi^2} \sum_{\text{odd } k} \frac{1}{k^2} \exp(-3\lambda_k^o t/t_1), \quad \lambda_k^o = \left(\frac{k\pi}{N}\right)^2$$

$$(k = 0, 1, \dots, N), \quad (30)$$

where t_1 is the characteristic diffusion time scale defined by $t_1 \equiv b^2/D_1$, and D_1 is the diffusion constant of a single bead. The expression for $\phi(t)$ given in Eq. (30) is valid only for large N . A more accurate expression for $\phi(t)$ is^{20,23}

$$\phi(t) = \frac{8}{N(N+1)} \sum_{\text{odd } k} \left(\frac{1}{\lambda_k^R} - \frac{1}{4}\right) \exp(-3\lambda_k^R t/t_1), \quad (31)$$

where λ_k^R ($k = 0, 1, \dots, N$) is the Rouse eigenvalue given by

$$\lambda_k^R = 4\sin^2\left(\frac{k\pi}{2(N+1)}\right). \quad (32)$$

Note that in Eqs. (30) and (31) summation includes only the odd values of k .

In Ref. 20, we derived a more general expression for $G(\mathbf{R}, t|\mathbf{R}_0)$ with $\mathbf{R} = \mathbf{r}_i - \mathbf{r}_j$ ($0 \leq i \leq j \leq N$). We also took into account the dynamic effects of hydrodynamic interactions among the beads. The analysis was based on the Rouse-Zimm model of a linear chain.²⁴ In this model, the potential energy of the chain is given by

$$U/k_B T = \frac{3}{2b^2} \sum_{i=1}^N (\mathbf{r}_i - \mathbf{r}_{i-1})^2 = \frac{3}{2b^2} \sum_{\gamma=x,y,z} \mathbf{X}_\gamma^T \cdot \mathbf{A} \cdot \mathbf{X}_\gamma, \quad (33)$$

where \mathbf{A} is the $(N+1) \times (N+1)$ matrix given by

$$\mathbf{A} = \begin{bmatrix} 1 & -1 & 0 & 0 & \dots & 0 & 0 & 0 \\ -1 & 2 & -1 & 0 & \dots & 0 & 0 & 0 \\ 0 & -1 & 2 & -1 & \dots & 0 & 0 & 0 \\ 0 & 0 & -1 & 2 & \dots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \dots & 2 & -1 & 0 \\ 0 & 0 & 0 & 0 & \dots & -1 & 2 & -1 \\ 0 & 0 & 0 & 0 & \dots & 0 & -1 & 1 \end{bmatrix} \quad (34)$$

and \mathbf{X}_γ is the $(N+1)$ -dimensional vector defined by

$$\mathbf{X}_x = \begin{pmatrix} x_0 \\ x_1 \\ \vdots \\ x_N \end{pmatrix} \quad \mathbf{X}_y = \begin{pmatrix} y_0 \\ y_1 \\ \vdots \\ y_N \end{pmatrix} \quad \mathbf{X}_z = \begin{pmatrix} z_0 \\ z_1 \\ \vdots \\ z_N \end{pmatrix} \quad (35)$$

with the superscript T denoting the transpose.

In the absence of reaction, the probability density function $\psi(\mathbf{r}^{N+1}, t)$ for the $N+1$ beads being located $\mathbf{r}^{N+1} \equiv (\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N)$ at time t evolves as

$$\frac{\partial \psi}{\partial t} = D_1 \sum_{\gamma=x,y,z} \left[\left(\frac{\partial}{\partial \mathbf{X}_\gamma} \right)^T \cdot \mathbf{H} \cdot \left(\frac{\partial \psi}{\partial \mathbf{X}_\gamma} \right) + \frac{3}{b^2} \left(\frac{\partial}{\partial \mathbf{X}_\gamma} \right)^T \cdot \mathbf{H} \cdot \mathbf{A} \cdot \mathbf{X}_\gamma \psi \right]. \quad (36)$$

\mathbf{H} is the matrix describing the pre-averaged hydrodynamic interaction between the beads that is given by

$$H_{ij} = \begin{cases} 1 & (i=j) \\ \frac{\zeta_1}{\eta b(6\pi^3|i-j|^{1/2})} & (i \neq j) \end{cases} \quad (37)$$

where $\zeta_1 = k_B T/D_1$ denotes the friction coefficient for a single bead, and η is the solvent viscosity.

Let \mathbf{Q} denote a matrix whose $N+1$ columns are the eigenvectors of the matrix $\mathbf{H} \cdot \mathbf{A}$, so that $\mathbf{H} \cdot \mathbf{A}$ is diagonalized by the similarity transformation:

$$\mathbf{Q}^{-1} \cdot \mathbf{H} \cdot \mathbf{A} \cdot \mathbf{Q} = \mathbf{\Lambda} \quad \text{with} \quad \Lambda_{ij} = \lambda_i \delta_{ij}. \quad (38)$$

Zimm showed that the same matrix \mathbf{Q} can also be used to diagonalize \mathbf{H} and \mathbf{A} separately, though not by similarity transformations:²⁴

$$\mathbf{Q}^T \cdot \mathbf{A} \cdot \mathbf{Q} = \mathbf{M} \quad \text{with} \quad M_{ij} = \mu_i \delta_{ij},$$

$$\mathbf{Q}^{-1} \cdot \mathbf{H} \cdot \mathbf{Q}^{-1T} = \mathbf{\Lambda} \cdot \mathbf{M}^{-1} = \mathbf{N} \quad \text{with} \quad N_{ij} = \nu_i \delta_{ij} = (\lambda_i/\mu_i) \delta_{ij}. \quad (39)$$

Hence by introducing the normal coordinates $\{\mathbf{q}_k = (q_{kx}, q_{ky}, q_{kz})\}$ defined by

$$\mathbf{r}_i = \sum_{k=0}^N \mathbf{Q}_{ij} \mathbf{q}_k, \quad (40)$$

Eq. (36) can be rewritten as

$$\frac{\partial}{\partial t} \psi(\mathbf{q}^{N+1}, t) = D_1 \sum_{i=0}^N \nu_i \left[\frac{\partial^2 \psi}{\partial \mathbf{q}_i^2} + 2\alpha_i \left(\frac{\partial}{\partial \mathbf{q}_i} \right)^T \cdot \mathbf{q}_i \psi \right], \quad (41)$$

where $\alpha_i = (3\mu_i)/(2b^2)$ and $\mathbf{q}^{N+1} = (\mathbf{q}_0, \mathbf{q}_1, \dots, \mathbf{q}_N)$. Except for \mathbf{q}_0 which corresponds to the center-of-mass motion, the normal modes are over-damped harmonic oscillators with force constants $2\alpha_i k_B T$ and diffusion constants $D_1 \nu_i$.

From Eq. (40), we have

$$\mathbf{R} = \mathbf{r}_i - \mathbf{r}_j = \sum_{k=0}^N c_k \mathbf{q}_k \quad (42)$$

with $c_k = \mathbf{Q}_{ik} - \mathbf{Q}_{jk}$. Note that $c_0 = 0$ since \mathbf{R} should be independent of the center-of-mass coordinates. Hence the Green's function $G(\mathbf{R}, t|\mathbf{R}_0)$ can be expressed as

$$G(\mathbf{R}, t|\mathbf{R}_0) = N \int d\mathbf{q}^{N+1} \int d\mathbf{q}_0^{N+1} \delta \left(\sum_{i=1}^N c_i \mathbf{q}_i - \mathbf{R} \right) \\ \times G_F(\mathbf{q}^{N+1}, t|\mathbf{q}_0^{N+1}) \delta \left(\sum_{j=1}^N c_j \mathbf{q}_{j0} - \mathbf{R}_0 \right) \psi_{eq}(\mathbf{q}_0^{N+1}). \quad (43)$$

Here, $G_F(\mathbf{q}^{N+1}, t|\mathbf{q}_0^{N+1})$ is the full Green's function for Eq. (41) satisfying the initial condition, $G_F(\mathbf{q}^{N+1}, t=0|\mathbf{q}_0^{N+1})$

$= \prod_{i=0}^N \delta(\mathbf{q}_i - \mathbf{q}_{i0}) \cdot \psi_{eq}(\mathbf{q}^{N+1})$ is the equilibrium distribution function, and N is the normalization constant.

First, $\psi_{eq}(\mathbf{q}^{N+1})$ can be obtained easily by solving

$$\sum_{i=0}^N v_i \left[\frac{\partial^2 \psi_{eq}}{\partial \mathbf{q}_i^2} + 2\alpha_i \left(\frac{\partial}{\partial \mathbf{q}_i} \right)^T \cdot \mathbf{q}_i \psi_{eq} \right] = 0. \quad (44)$$

We have

$$\psi_{eq}(\mathbf{q}^{N+1}) = V^{-1} \prod_{i=1}^N (\alpha_i/\pi)^{3/2} \exp(-\alpha_i \mathbf{q}_i^2), \quad (45)$$

where V is the volume of the system. The normalization constant N appearing in Eq. (43) is obtained by requiring that $\int d\mathbf{R} G(\mathbf{R}, t|\mathbf{R}_0) = 1$. For $t = 0$, this requirement on Eq. (43) gives

$$N \int d\mathbf{q}^{N+1} \delta \left(\sum_{i=1}^N c_i \mathbf{q}_i - \mathbf{R}_0 \right) \psi_{eq}(\mathbf{q}^{N+1}) = 1. \quad (46)$$

With the expression for $\psi_{eq}(\mathbf{q}^{N+1})$ in Eq. (45), we have

$$N^{-1} = \left(\pi \sum_{i=1}^N c_i^2 / \alpha_i \right)^{-3/2} \exp \left(-R_0^2 / \sum_{i=1}^N c_i^2 / \alpha_i \right) = R_0^{eq}(\mathbf{R}_0). \quad (47)$$

Next, Eq. (42) shows that \mathbf{R} is a Gaussian random variable. Hence the reduced Green's function (RGF) $G(\mathbf{R}, t|\mathbf{R}_0)$ should be a Gaussian function with respect to both \mathbf{R} and \mathbf{R}_0 :

$$G(\mathbf{R}, t|\mathbf{R}_0) = N \exp \left\{ -\frac{1}{2} [\mathbf{R} \cdot \mathbf{H}_1 \cdot \mathbf{R} + 2\mathbf{R} \cdot \mathbf{H}_2 \cdot \mathbf{R}_0 + \mathbf{R}_0 \cdot \mathbf{H}_3 \cdot \mathbf{R}_0] \right\}. \quad (48)$$

where N is a normalization constant, and \mathbf{H}_i ($i = 1, 2, 3$) is a time-dependent matrix. For an isotropic system, $G(\mathbf{R}, t|\mathbf{R}_0)$ depends on the magnitudes of \mathbf{R} and \mathbf{R}_0 and on the relative angle between \mathbf{R} and \mathbf{R}_0 , but is independent of the respective orientations of \mathbf{R}_0 and \mathbf{R} in the laboratory fixed frame. Hence, \mathbf{H}_i must be proportional to unit matrix, i.e. $\mathbf{H}_i = h_i(t)\mathbf{I}$.

In addition, the RGF satisfies the following properties:

$$\int d\mathbf{R} G(\mathbf{R}, t|\mathbf{R}_0) = 1, \quad (49)$$

$$\int d\mathbf{R}_0 G(\mathbf{R}, t|\mathbf{R}_0) P_O^{eq}(\mathbf{R}_0) = P_O^{eq}(\mathbf{R}), \quad (50)$$

where $P_O^{eq}(\mathbf{R})$ is the equilibrium distribution. From Eq. (49), we can show that $N = (h_1/2\pi)^{3/2}$ and $h_2^2 = h_1 h_3$, so that Eq. (48) becomes

$$G(\mathbf{R}, t|\mathbf{R}_0) = \left(\frac{h_1}{2\pi} \right)^{3/2} \exp \left\{ -\frac{h_1}{2} [\mathbf{R} + h_2 \mathbf{R}_0 / h_1]^2 \right\}, \quad (51)$$

At long times, we must have $h_1(\infty) = 3/\langle \mathbf{R}^2 \rangle \equiv h_1^\infty$ and $h_2(\infty) = 0$, since $\lim_{t \rightarrow \infty} G(\mathbf{R}, t|\mathbf{R}_0) = P_O^{eq}(\mathbf{R})$ and $\langle \mathbf{R}^2 \rangle = \int d\mathbf{R} \mathbf{R} \mathbf{R}^T P_O^{eq}(\mathbf{R})$.

From Eq. (50), we can obtain $h_1 = h_1^\infty / (1 - \phi)^2$ with

$\phi = -h_2/h_1$, and Eq. (51) becomes

$$G(\mathbf{R}, t|\mathbf{R}_0) = \left\{ \frac{3}{2\pi \langle \mathbf{R}^2 \rangle [1 - \phi^2]} \right\}^{3/2} \exp \left\{ \frac{3[\mathbf{R} - \phi \mathbf{R}_0]^2}{2 \langle \mathbf{R}^2 \rangle [1 - \phi^2]} \right\}, \quad (52)$$

We can relate ϕ to $\langle \mathbf{R}(t) \cdot \mathbf{R}(0) \rangle$ by

$$\langle \mathbf{R}(t) \cdot \mathbf{R}(0) \rangle = \int d\mathbf{R} \int d\mathbf{R}_0 \mathbf{R} \cdot \mathbf{R}_0 G(\mathbf{R}, t|\mathbf{R}_0) P_O^{eq}(\mathbf{R}_0) = \phi \langle \mathbf{R}^2 \rangle \quad (53)$$

Finally, after some algebra, we can show that the equilibrium mean squared distance between the i th and j th beads, $\langle \mathbf{R}^2 \rangle$, and the normalized time correlation function of the vector \mathbf{R} , $\phi(t)$, are given by

$$\langle \mathbf{R}^2 \rangle = b^2 \sum_{k=1}^N \frac{c_k^2}{\mu_k} = |i - j| b^2, \quad (54)$$

$$\phi(t) = \frac{\langle \mathbf{R}(t) \cdot \mathbf{R}(0) \rangle}{\langle \mathbf{R}^2 \rangle} = \frac{1}{|i - j|} \sum_{k=1}^N \frac{c_k^2}{\mu_k} \exp(-3\lambda_k t / t_1), \quad (55)$$

where $t_1 = b^2/D_1$. The equilibrium distribution function for the distance R is given by

$$P_O^{eq}(R) = P_O^{eq}(\mathbf{R}) = \left(\frac{3}{2\pi \langle \mathbf{R}^2 \rangle} \right)^{3/2} \exp \left(-\frac{3R^2}{2 \langle \mathbf{R}^2 \rangle} \right). \quad (56)$$

An expression for the orientation-averaged Green's function $G(R, t|R_0)$ can be readily obtained from Eq. (52):

$$G(R, t|R_0) = \left\{ \frac{3}{2\pi \langle \mathbf{R}^2 \rangle [1 - \phi^2(t)]} \right\}^{1/2} \frac{1}{4\pi R R_0 \phi(t)} \times \left\{ \exp \left(-\frac{3}{2 \langle \mathbf{R}^2 \rangle} \frac{[R - \phi(t) R_0]^2}{[1 - \phi^2(t)]} \right) - \exp \left(-\frac{3}{2 \langle \mathbf{R}^2 \rangle} \frac{[R + \phi(t) R_0]^2}{[1 - \phi^2(t)]} \right) \right\}. \quad (57)$$

For the free-draining Rouse chain, more explicit expressions can be obtained. In this case, we have for $k = 0, 1, \dots, N$

$$\lambda_k^R = \mu_k^R = 4 \sin^2 \left(\frac{k\pi}{2(N+1)} \right),$$

$$c_k^R = -2 \left(\frac{2 - \delta_{k0}}{N+1} \right)^{1/2} \sin \left[\frac{(i+j+1)k\pi}{2(N+1)} \right] \sin \left[\frac{(i-j)k\pi}{2(N+1)} \right], \quad (58)$$

with the superscript R denoting a quantity for the free-draining Rouse chain. In particular, when the reaction occurs between the beads at the chain ends (i.e. $i = 0$, and $j = N$), we have $\langle \mathbf{R}^2 \rangle = N b^2$, and the expression for $G(\mathbf{R}, t|\mathbf{R}_0)$ reduces to that given by Eqs. (29) and (31).

Effect of Chain Stiffness. The effect of chain stiffness can be incorporated into the present theoretical framework by adopting the optimized Rouse-Zimm (ORZ) model.²⁵ The ORZ model differs from the Rouse-Zimm model in that the bond angles are fixed; see Figure 2. The chain stiffness does not affect the inherent reaction step, so that its influence is

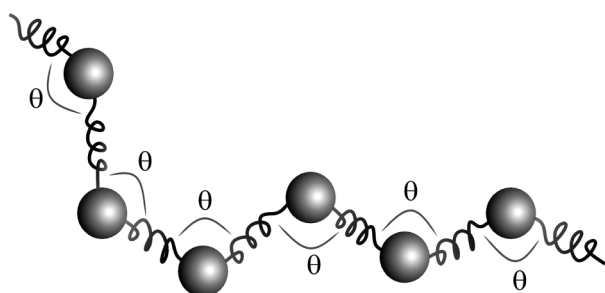


Figure 2. The optimized Rouse-Zimm model of a linear chain. The bond angles are fixed at a constant value θ .

reflected only in the nonreactive chain dynamics.

The evolution equation governing the random thermal motion of the chain is again given by the Smoluhowski equation as given by Eq. (36), but with the **A** and **H** matrices replaced by

$$\mathbf{A}_s = \frac{1}{1-q^2} \begin{pmatrix} 1 & -(1+q) & q & 0 \\ -(1+q) & 2+2q+q^2 & -(1+q)^2 & q \\ q & -(1+q)^2 & 2+2q+2q^2 & -(1+q)^2 \\ 0 & q & -(1+q)^2 & (2+2q+2q^2) \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \dots & 0 & 0 & 0 \\ \dots & 0 & 0 & 0 \\ \dots & 0 & 0 & 0 \\ \dots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots \\ \dots & 2+2q+2q^2 & -(1+q)^2 & q \\ \dots & -(1+q)^2 & 2+2q+q^2 & -(1+q) \\ \dots & q & -(1+q) & 1 \end{pmatrix}$$

$$(\mathbf{H}_s)_{ij} = \delta_{ij} + (1 - \delta_{ij}) \frac{\zeta_1}{\eta(6\pi^3 \langle R_{ij}^2 \rangle^{1/2})}, \quad (59)$$

where $q = -\cos\theta$ with θ denoting the bond angle (see Fig. 2), and we have put the subscript “S” to the matrices to designate the quantities for the “stiff” chain.

The procedure to get the Green’s function expression follows the same line as in the previous subsection. Let us introduce the following notations:

$$\mathbf{Q}_s^{-1} \cdot \mathbf{H}_s \cdot \mathbf{A}_s \cdot \mathbf{Q}_s = \mathbf{\Lambda}_s \quad \text{with} \quad (\mathbf{\Lambda}_s)_{ij} = \lambda_i^s \delta_{ij};$$

$$\mathbf{Q}_s^T \cdot \mathbf{A}_s \cdot \mathbf{Q}_s = \mathbf{M}_s \quad \text{with} \quad (\mathbf{M}_s)_{ij} = \mu_i^s \delta_{ij};$$

$$\mathbf{Q}_s^{-1} \cdot \mathbf{H}_s \cdot \mathbf{Q}_s^{-1T} = \mathbf{\Lambda}_s \cdot \mathbf{M}_s^{-1} = \mathbf{N}_s$$

$$\text{with } (\mathbf{N}_s)_{ij} = \nu_i^s \delta_{ij} = (\lambda_i^s / \mu_i^s) \delta_{ij};$$

$$\mathbf{r}_i = \sum_{k=0}^N (\mathbf{Q}_s)_{ik} \mathbf{q}_k^s;$$

$$\mathbf{R} = \mathbf{r}_i - \mathbf{r}_j = \sum_{k=0}^N c_k^s \mathbf{q}_k^s \quad \text{with} \quad c_k^s = (\mathbf{Q}_s)_{ik} - (\mathbf{Q}_s)_{jk}. \quad (60)$$

Then the expressions for the Green’s functions given by Eqs. (52) and (57) remain the same, but with the expressions for $\langle \mathbf{R}^2 \rangle$ and $\phi(t)$ given by

$$\langle \mathbf{R}^2 \rangle = b^2 |i-j| \left[\frac{1+q}{1-q} - \frac{2q}{|i-j|} \frac{1-q^{|i-j|}}{(1-q)^2} \right], \quad (61)$$

$$\phi(t) = \frac{b^2}{\langle \mathbf{R}^2 \rangle_{k=0}} \sum_{k=0}^N \frac{(c_k^s)^2}{\mu_k^s} \exp(-3\lambda_k^s t / t_1). \quad (62)$$

Intrachain Reaction Kinetics. We have set up the theoretical apparatus that can be used to analyze the time-dependent kinetics of intrachain reactions. One can now investigate the effects of various physical factors, such as the chain length, chain stiffness, and hydrodynamic interactions, within a unified theoretical framework. Some of the results have been presented in Refs. 19 and 20.

A useful experimental technique for probing the dynamical properties of a flexible chain polymer is to measure the time-dependent intensity of fluorescence emitted from a fluorophore attached at one end of the chain, which is sensitized by an external illumination and quenched by an energy acceptor located at the other end.²⁶ Time-resolved fluorescence data are most commonly obtained by exciting the reaction system with a short pulse of light and thereafter measuring the time-dependent fluorescence emission.²⁷ However, the excitation light pulse has a finite time span so that an extensive deconvolution of the data needs to be carried out. Even if one uses a picosecond laser, the observed instrument response function often spans over 0.1 ns. Hence it can be rather difficult to obtain adequate resolution. An alternative method is to measure the frequency response of the emission to intensity-modulated light. This method, called the frequency-domain fluorometry, is known to have high sensitivity to resolve the complex decay of fluorescence intensity. It was first implemented by Gratton and Limkeman,²⁸ and has been widely applied by Lakowicz and Gryczynski.²⁹ In particular, Lakowicz *et al.* used the method to investigate the intramolecular energy transfer reactions occurring in flexible molecules.³⁰

In Ref. 19, we presented a theory for analyzing the frequency-domain fluorometric experiments on intrachain fluorescence-quenching reactions occurring in flexible chain polymers. The results were applied to investigate the qualitative dependence of the modulation and the phase angle on the chain length of the polymer.

In Ref. 20, we formulated a general theory for analyzing the kinetics of intrachain excimer-formation reactions. While most previous theories for intrachain reactions dealt with the end-to-end reaction case, we considered the general situation in which the reacting groups are located at any position on the chain backbone. Various aspects of the reaction kinetics, such as the effect of hydrodynamic interaction and the dependence of reaction rate on the positions of reacting groups as well as on the chain length, were investigated.

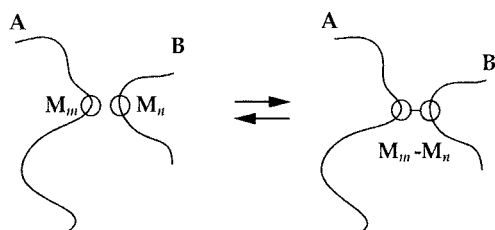


Figure 3. Pictorial representation of an interpolymer reaction. The bond forms between the m th monomer of polymer A and the n th monomer of polymer B.

Interchain Reactions

In this section we will consider a typical interpolymer reaction, as illustrated schematically in Figure 3. Theories for other types of interpolymer reactions can be formulated in a similar way.^{31,32} Again, we model the polymer as a chain of beads connected by harmonic springs. We consider two different kinds of linear polymers, A and B, with $(N_A + 1)$ and $(N_B + 1)$ beads, respectively. We assume that the chain A has a single reactive group at the m th bead, while the chain B at the n th bead.

Derivation of the Rate Expressions. We consider a reaction system containing N_A chains of the type A and N_B chains of the type B. To describe the reaction kinetics systematically, we introduce a set of hierarchical kinetic equations describing the reaction-diffusion process of the chains. The lowest-order equation in the hierarchy is given by

$$\begin{aligned} \frac{\partial}{\partial t} \psi_{A_i}(\mathbf{r}_A^{N_A+1}, t) &= L(\mathbf{r}_A^{N_A+1}) \psi_{A_i}(\mathbf{r}_A^{N_A+1}, t) \\ &- \sum_{j=1}^{N_B} \int d\mathbf{r}_B^{N_B+1} S_f^0(\mathbf{r}_A^{N_A+1}, \mathbf{r}_B^{N_B+1}) \psi_{A_i B_j}(\mathbf{r}_A^{N_A+1}, \mathbf{r}_B^{N_B+1}, t) \\ &+ \sum_{j=1}^{N_B} \int d\mathbf{r}_B^{N_B+1} S_r^0(\mathbf{r}_A^{N_A+1}, \mathbf{r}_B^{N_B+1}) \psi_{C_{ij}}(\mathbf{r}_A^{N_A+1}, \mathbf{r}_B^{N_B+1}, t) . \quad (63) \end{aligned}$$

$\psi_{A_i}(\mathbf{r}_A^{N_A+1}, t)$ is the probability density for the i th chain of A being in the unreacted form at time t , with the $N_A + 1$ beads constituting the chain located at $\mathbf{r}_A^{N_A+1} \equiv (\mathbf{r}_{A0}, \mathbf{r}_{A1}, \dots, \mathbf{r}_{AN_A})$. $\psi_{A_i B_j}(\mathbf{r}_A^{N_A+1}, \mathbf{r}_B^{N_B+1}, t)$ is the joint probability density that both the i th chain of A and the j th chain of B are in the unreacted form at time t , with the beads constituting the chains located at $\mathbf{r}_A^{N_A+1} \equiv (\mathbf{r}_{A0}, \mathbf{r}_{A1}, \dots, \mathbf{r}_{AN_A})$ and $\mathbf{r}_B^{N_B+1} \equiv (\mathbf{r}_{B0}, \mathbf{r}_{B1}, \dots, \mathbf{r}_{BN_B})$. Similarly, $\psi_{C_{ij}}(\mathbf{r}_A^{N_A+1}, \mathbf{r}_B^{N_B+1}, t)$ is the probability density for these chains, A_i and B_j , making a bond between the m th bead of A_i and n th bead of B_j , with beads located at $(\mathbf{r}_A^{N_A+1}, \mathbf{r}_B^{N_B+1})$. The first term on the right side of Eq. (63) represents the change due to random thermal motion of the chain A_i . The second term represents the change due to the bond formation between the chains A_i and B_j , while the third term represents the change due to the reverse dissociation. The sink functions $S_f^0(\mathbf{r}_A^{N_A+1}, \mathbf{r}_B^{N_B+1})$ and $S_r^0(\mathbf{r}_A^{N_A+1}, \mathbf{r}_B^{N_B+1})$ denote the respective reactive transition rates at the configuration $(\mathbf{r}_A^{N_A+1}, \mathbf{r}_B^{N_B+1})$.

We then neglect the excluded volume interactions between

the beads, so that the sink functions are assumed to have the following forms:

$$S_f^0(\mathbf{r}_A^{N_A+1}, \mathbf{r}_B^{N_B+1}) = \kappa_f \delta(\mathbf{r}_{Am} - \mathbf{r}_{Bn}) , \quad (64)$$

$$S_r^0(\mathbf{r}_A^{N_A+1}, \mathbf{r}_B^{N_B+1}) = \kappa_r \delta(\mathbf{r}_{Am} - \mathbf{r}_{Bn}) . \quad (65)$$

Since we cannot keep track of the fate of individual chains, we introduce the reduced distribution functions (RDF):

$$C_A(\mathbf{r}_{Am}, t) = \sum_{i=1}^{N_A} \int d\mathbf{r}_A^{N_A} \psi_{A_i}(\mathbf{r}_A^{N_A+1}, t) , \quad (66)$$

$$C_{AB}(\mathbf{r}_{Am}, \mathbf{r}_{Bn}, t) = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \int d\mathbf{r}_A^{N_A} \int d\mathbf{r}_B^{N_B} \psi_{A_i B_j}(\mathbf{r}_A^{N_A+1}, \mathbf{r}_B^{N_B+1}, t) , \quad (67)$$

$$C_C(\mathbf{r}_{Am}, \mathbf{r}_{Bn}, t) = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \int d\mathbf{r}_A^{N_A} \int d\mathbf{r}_B^{N_B} \psi_{C_{ij}}(\mathbf{r}_A^{N_A+1}, \mathbf{r}_B^{N_B+1}, t) , \quad (68)$$

where $\int d\mathbf{r}_A^{N_A}$ denotes the integration over the bead coordinates of A except \mathbf{r}_{Am} , and $\int d\mathbf{r}_B^{N_B}$ is defined similarly. In a homogeneous and isotropic reaction system, the number density field of A, $C_A(\mathbf{r}_{Am}, t)$, is independent of \mathbf{r}_{Am} and can be equated with the bulk number density $a(t)$, and the two-particle RDF depends only the separation of the reactive beads, namely, $C_{AB}(\mathbf{r}_{Am}, \mathbf{r}_{Bn}, t) = C_{AB}(r = |\mathbf{r}_{Am} - \mathbf{r}_{Bn}|, t)$.

With Eqs. (64)–(67), integrating Eq. (63) over the irrelevant coordinates and then summing the resultant equation over i from 1 to N_A gives

$$\frac{d}{dt} a(t) = -\frac{d}{dt} c(t) = -\kappa_f C_{AB}(0, t) + \kappa_r c(t) . \quad (69)$$

In writing Eq. (69) we identified $C_C(\mathbf{r}_{Am}, \mathbf{r}_{Bn} = \mathbf{r}_{Am}, t)$ with the bulk number density of the product polymers, $c(t)$, since $\mathbf{r}_{Bn} = \mathbf{r}_{Am}$ in all C molecules (as assumed in writing the sink functions) and $C_C(\mathbf{r}_{Am}, \mathbf{r}_{Bn} = \mathbf{r}_{Am}, t)$ is independent of \mathbf{r}_{Am} in a homogeneous system.

The kinetic equation for $C_{AB}(r, t)$ can be obtained by integrating the evolution equation for $\psi_{A_i B_j}(\mathbf{r}_A^{N_A+1}, \mathbf{r}_B^{N_B+1}, t)$ over the irrelevant bead coordinates and then summing the resultant equation over the reactant molecule indices i and j . In the pseudo-first order case, where one species of chains (say B) are present in excess over the other, we obtain³³

$$\begin{aligned} \frac{\partial}{\partial t} C_{AB}(r, t) &= L_{AB}(r) C_{AB}(r, t) + \delta(r) [-\kappa_f C_{AB}(r, t) + \kappa_r c(t)] \\ &- \kappa_f C_{ABB}(r, 0, t) + \kappa_r C_{AB}^-(r, t) , \quad (70) \end{aligned}$$

where $L_{AB}(r)$ denotes an effective thermal evolution operator for the RDF $C_{AB}(r, t)$ in the absence of reaction, whose explicit expression need not be known at the moment. The second term on the right side takes account of the changes in $C_{AB}(r, t)$ due to binary reaction events. When the reactant number densities are small, only the binary reaction events are important and it is less probable that two or more reactant molecules of one species compete for a target reactant molecule of the other species. The third and the fourth terms

arise from the competitive participation of a third chain of B in the binary reaction event. The three-particle RDF $C_{ABB}(r, r', t)$ is the product of $a(t)$ and the number densities of chains of B, whose reactive groups are separated by r and r' from that of an A chain, and $C_{\bar{A}B}(r, t)$ is the two-particle RDF for \bar{A} -B chain pairs with \bar{A} denoting an A captured by a third chain of B.

Eq. (70) for $C_{AB}(r, t)$ is coupled with those for $C_{ABB}(r, r', t)$ and $C_{\bar{A}B}(r, t)$. The evolution equations for these RDFs are in turn given by

$$\frac{\partial}{\partial t} C_{\bar{A}B}(r, t) = L_{\bar{A}B}(r) C_{\bar{A}B}(r, t) + \kappa_f C_{ABB}(r, 0, t) - \kappa_r C_{\bar{A}B}(r, t), \quad (71)$$

$$\begin{aligned} \frac{\partial}{\partial t} C_{ABB}(r, r', t) &= [L_{AB}(r) + L_{AB}(r')] C_{ABB}(r, r', t) \\ &+ \delta(\mathbf{r}) [-\kappa_f C_{ABB}(r, r', t) + \kappa_r C_{\bar{A}B}(r', t)] \\ &+ \delta(\mathbf{r}') [-\kappa_f C_{ABB}(r, r', t) + \kappa_r C_{\bar{A}B}(r, t)] \\ &- \kappa_f C_{ABBB}(r, r', 0, t) + \kappa_r C_{\bar{A}BB}(r, r', t). \end{aligned} \quad (72)$$

Equation (72) for $C_{ABB}(r, r', t)$ is further coupled with higher-order RDFs $C_{ABBB}(r, r', 0, t)$ and $C_{\bar{A}BB}(r, r', t)$. In fact, we have an infinite hierarchy of evolution equations.

In Ref. 33, we developed a very accurate and systematic procedure to deal with the hierarchical set of reaction-diffusion equations. The many-particle kernel (MPK) theory of Ref. 33 gives the following Laplace-transform expression for the time-dependence of the reactant number densities:

$$\frac{\Delta \hat{a}(s)}{\Delta a(0)} = \frac{\Delta \hat{c}(s)}{\Delta c(0)} = \left(s + \frac{\lambda}{\hat{F}(s)} \right)^{-1}, \quad (73)$$

where $\Delta a(t) \equiv a(t) - a(\infty)$ and $\Delta c(t) \equiv c(t) - c(\infty)$. If the reaction is not retarded by slow diffusion, $\hat{F}(s)$ becomes unity and the system relaxes exponentially with the relaxation rate constant λ given by

$$\lambda = \kappa_f^{eq} C_B + \kappa_r^{eq}. \quad (74)$$

C_B is the constant number density of B; note that we have been considering the pseudo-first-order case in which B molecules are present in excess. κ_f^{eq} and κ_r^{eq} are the equilibrium rate constants given by

$$\kappa_f^{eq} = \kappa_f g_{AB} \quad \text{and} \quad \kappa_r^{eq} = \kappa_r, \quad (75)$$

where $g_{AB}(r)$ is the equilibrium pair correlation function for the reactive groups of the chains A and B. The reactant number densities at equilibrium, $a(\infty)$ and $c(\infty)$ are given by $\kappa_r^{eq} [a(0) + c(0)] / \lambda$ and $\kappa_f^{eq} C_B [a(0) + c(0)] / \lambda$, respectively. The effect of slow diffusion of reactant molecules on the relaxation kinetics is counted by the key dynamic function $\hat{F}(s)$:

$$\begin{aligned} \hat{F}(s) &= 1 + \frac{\kappa_r^{eq}}{\lambda} \kappa_f \hat{G}(\mathbf{0}, s | \mathbf{0}) + \frac{\kappa_f^{eq} C_B}{\lambda} \left[\frac{\lambda \hat{Y}^{ir}(s | C_B')}{1 - s \hat{Y}^{ir}(s | C_B')} - 1 \right], \\ Y^{ir}(t | C_B) &= \exp[-C_B \int_0^t d\tau \kappa_f^{SM}(\tau)], \end{aligned} \quad (76)$$

where $C_B' = C_B + (\kappa_r^{eq} / \kappa_f^{eq})$ and $\kappa_f^{SM}(t)$ is the rate coefficient for the irreversible reaction. In the Laplace domain it can be expressed as

$$\hat{\kappa}_f^{SM}(s) = \frac{\kappa_f^{eq}}{s[1 + \kappa_f \hat{G}(\mathbf{0}, s | \mathbf{0})]}. \quad (77)$$

We can now calculate the time-dependence of reactant number densities once the Green's function expression is given.

The Greens Function. In this subsection we will derive an expression for the Green's function $G(\mathbf{0}, t | \mathbf{0})$. The physical meaning of this Green's function is the probability that the reactive groups of the chains A and B reencounter at a time t , given that they were in contact with each other at $t = 0$. Hence we can write

$$G(\mathbf{0}, t | \mathbf{0}) = \int d\mathbf{r} G_{Am}(\mathbf{r}, t | \mathbf{0}) G_{Bn}(\mathbf{r}, t | \mathbf{0}), \quad (78)$$

where $G_{Am}(\mathbf{r}, t | \mathbf{0})$ is the probability density that the m th bead of the chain A will be at \mathbf{r} , given that it was at the origin at $t = 0$. $G_{Bn}(\mathbf{r}, t | \mathbf{0})$ has the similar meaning.

We can calculate the propagator for the bead, $G_{Am}(\mathbf{r}, t | \mathbf{0})$, based on the ORZ model depicted in Figure 2. The propagator has the Gaussian form

$$G_{Am}(\mathbf{r}, t | \mathbf{0}) = \frac{1}{[2\pi\phi_{Am}(t)]^{3/2}} \exp\left[-\frac{\mathbf{r}^2}{2\phi_{Am}(t)}\right]. \quad (79)$$

$\phi_{Am}(t)$ is the mean square displacement given by

$$\begin{aligned} \phi_{Am}(t) &= \langle [\mathbf{r}_{Am}(t) - \mathbf{r}_{Am}(0)]^2 \rangle \\ &= 6D_{Af}t + 2b_A^2 \sum_{k=1}^{N_A} \frac{(\mathbf{Q}_{AS})_{mk}^2}{\mu_{Ak}^S} [1 - \exp(-t/\tau_{Ak}^S)] \end{aligned} \quad (80)$$

Here, D_{Af} is the center-of-friction diffusion coefficient of A and τ_{Ak}^S is the relaxation time for the k th normal mode of the ORZ chain A. These are given by

$$D_{Af} = [v_{A0}^S D_{A1} / (N_A + 1)], \quad (81)$$

$$\tau_{Ak}^S = \frac{b_A^2}{3\lambda_{Ak}^S D_{A1}}, \quad (82)$$

where D_{A1} is the diffusion constant of a single bead of A. Other parameters in Eqs. (80)-(82) were defined by Eq. (60) except that they include a subscript "A" designating a quantity for the chain A.

Inserting Eq. (79) into Eq. (78), we obtain

$$G(\mathbf{0}, t | \mathbf{0}) = (3/2\pi)^{3/2} [\phi_{Am}(t) + \phi_{Bn}(t)]^{-3/2} \quad (83)$$

where the mean square displacement $\phi_{Bn}(t)$ of the n th bead of the ORZ chain B is given by a similar formula as $\phi_{Am}(t)$ given in Eq. (80).

When we neglect the hydrodynamic interactions among the beads as well as the chain stiffness (that is, for a Rouse

chain), the expression for $\phi_{Am}(t)$ given in Eq. (80) reduces to

$$\phi_{Am}(t) = 6 \left(\frac{D_{A1}}{N_A + 1} \right) t + \frac{b_A^2}{N_A + 1} \sum_{k=1}^{N_A} \frac{\cos^2 \left[\left(m + \frac{1}{2} \right) k \pi / (N_A + 1) \right]}{\sin^2 [k \pi / 2 (N_A + 1)]} \times \left[1 - \exp \left(- \frac{12 \sin^2 [k \pi / 2 (N_A + 1)] D_{A1} t}{b_A^2} \right) \right]. \quad (84)$$

For a very long chain ($N_A \rightarrow \infty$), Eq. (84) further reduces to the expression given in the textbook of Doi and Edwards.³⁴

Interchain Reaction Kinetics. We have set up the theoretical apparatus that can be used to analyze the time-dependent kinetics of interchain reactions. One can now investigate the effects of various physical factors, such as the chain length, chain stiffness, and hydrodynamic interactions, within a unified theoretical framework. Some of the results have been presented in Refs. 31 and 32.

In Ref. 31 we demonstrated how polymeric reactants affect reversible energy transfer reactions in a number of situations. Depending upon the reactivity as well as upon the Rouse relaxation time of the shorter chain, the relaxation of the excited polymeric reactants was found to be described by a scaling function or by an exponential form. The Stern-Volmer coefficient, which is important in fluorescence quenching experiments, was found to exhibit dramatic changes as the spontaneous decay rate varies; power-law dependencies on the molecular weight of the polymeric quenchers and on the spontaneous decay rate were predicted in separate regions, which are completely different from the behavior observed in the small molecular reactions.

In Ref. 32, we presented a theory for studying the reactions of the irreversible quenching of an excitation migrating on a fluctuating polymer. An expression for the survival probability of an excitation was derived as a function of time for various values of chain length and excitation mobility. As the mobility increases, the quenching reaction rate is enhanced and this is more pronounced for a longer chain. In the limit of infinitely fast-moving excitation, the excitation is completely delocalized immediately after the initial excitation, and the randomness in the initial location produces no effect on the quenching. In this case the "effective reaction radius" becomes a useful concept, which turns out to be comparable to the radius of gyration of the polymer. With this effective reaction radius and the well-known Smoluchowski's rate expression, the quenching reaction process can be viewed in a simple way. From such observation, one can conclude that the fast migration of the excitation significantly enhances the quenching rate by the factor of the linear dimension of the chain molecule. For more general situations with intermediate values of the excitation mobility, the quenching reaction process is governed by the interplay between excitation migration and dynamics of the polymer. On time scales smaller than the inverse of the

excitation mobility, dynamics of the polymer, which depends on the chain molecular weight, as well as of the quenchers influences the quenching rate, while otherwise the quenching rate converges to the results in the fast-moving excitation limit.

Conclusion

In this short review, we have shown that how the complicated dynamics of reactions involving polymers can be disentangled. In a situation where the excluded-volume effects can be neglected and the reaction is not too long-ranged, the reaction events and the polymer dynamics can be approximately decoupled. Hence the sophisticated theories developed for diffusion-influenced reactions involving simple molecules can be easily adopted to treat the polymer reaction dynamics. Then, the key dynamic quantity that should be supplemented is the Green's function which describes the dynamics of the relative motion of the reacting groups. We have presented more general expressions for the Green's functions of nonreactive polymer dynamics, which take into account the effects of chain lengths, chain-stiffness, and hydrodynamic interactions. Generalizations of the theory to include the excluded volume interactions as well as the more realistic model of the polymers are under progress.

Acknowledgments. This work was supported by Korea Research Foundation Grant (KRF-2001-015-DP0230).

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