Computer Simulation of the Intramolecular Reaction of Polymers

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(Received February 6, 1976)

ABSTRACT: A computer simulation is made for the intramolecular reaction of a flexible polymer chain. The reaction rate k_1 is obtained for various values of the degree of polymerization and the size of the reaction region. Previous theories for the intramolecular reaction rates are examined by a comparison with these results.

KEY WORDS Intramolecular Reaction / Diffusion-Controlled / Monte Carlo Method / Verdier—Stockmayer Model /

Recently, the diffusion-controlled intramolecular reaction of polymers has attracted the attention of many researchers because it can be used to obtain new information on dynamics of the polymer chain. Intensive experimental studies are now being carried out, though only a few results have been published so far.^{1,2}

Theoretical analyses have been also made. Wilemski and Fixman^{3,4} have discussed the ring closure reaction of polymers: a pair of active groups are attached to the chain ends of a polymer and react on each other with a certain intrinsic reaction rate k if they come into a certain reaction region, which is assumed to be a sphere of radius a . This reaction is of the first order, and the unreacted fraction $\phi(t)$ of polymers obeys the equation:

$$\frac{d\phi(t)}{dt} = -k_1\phi(t) \quad (1)$$

where k_1 is the apparent first order reaction rate. If the intrinsic reaction rate k is infinite, the active groups react immediately when they come within the distance a . In that case the reaction rate is limited by the diffusion process which brings the reactive pair into the reaction region. We shall denote the reaction rate of this case by $k_{1\infty}$. For the Rouse model, Wilemski and Fixman derived the following result using a closure approximation:

$$k_{1\infty} = 0.46\tau_m^{-1} \quad (\text{Rouse model, } a/L \ll 1) \quad (2)$$

where τ_m and L are the longest relaxation time

and the root mean square of the end-to-end vector, respectively. Equation 2 includes a qualitatively interesting feature: the reaction rate $k_{1\infty}$ becomes independent of a , for $a/L \ll 1$. This may be compared with the harmonic spring model in which the active groups are bound by a single spring with the same mean square end-to-end separation as that of the polymer. Sunagawa and Doi⁵ have shown that $k_{1\infty}$ of this model is proportional to a :

$$k_{1\infty} = 1.38\tau_m^{-1} \frac{a}{L} \quad (\text{harmonic spring model, } a/L \ll 1) \quad (3)$$

Doi^{6,7} has pointed out that such a qualitative difference comes from the difference in the behavior of the segment motion in the short time region. His discussion, however, is also based on the closure approximation, whose validity still remains open to question.

From the theoretical view point the difference between eq 2 and 3 is interesting, but it seems difficult to demonstrate the validity of eq 2 by purely mathematical manipulations.

In this paper we describe the result of a computer simulation of the intramolecular reaction of a polymer. Although the model employed in the present simulation is a highly idealized one, it takes account of the fundamental features of the Brownian motion of the polymer chain: for example, it exhibits the wedge-type relaxation spectrum. The present method of simulation can also be applied to

more complicated and realistic models.

EXPERIMENTAL METHOD

The reaction model considered here is the same as that of Wilemski and Fixman.⁴ In terms of the configurational distribution function $\phi(\mathbf{q}, t)$, the reaction process is described by the following diffusion equation:

$$\frac{\partial \phi}{\partial t} + \mathcal{L}\phi = -kS(\mathbf{q})\phi \quad (4)$$

where $\mathbf{q}=(q_1, q_2, \dots)$ is the generalized coordinate describing the polymer configuration, $\mathcal{L}$ the diffusion operator in the absence of a chemical reaction, k the intrinsic reaction rate, and $S(\mathbf{q})$ a function which takes the value unity when the reactive groups attached to the chain ends are inside the reaction sphere of radius a , and zero otherwise.

Our work is to solve eq 4 by an appropriate realization of the reaction process, using the Monte Carlo method. Note that the reaction term $-kS(\mathbf{q})\phi$ does not affect the Brownian motion of the polymer: the reaction term represents the fact that the number of active pairs in the reactive region decreases in proportion to $\exp(-kt)$. The Brownian motion of the reactive polymer is completely described by the diffusion operator $\mathcal{L}$ and is the same as that in the absence of any reaction. Thus the reaction rate is obtained by the following procedure.

Consider the Brownian motion of a sample polymer. It is described by a path $\mathbf{q}(t)$ in the phase space. Let us observe the time evolution of $S(\mathbf{q}(t))$ determined by this motion. An example of $S(\mathbf{q}(t))$ is shown in Figure 1. For this path of $\mathbf{q}(t)$, the probability that the polymer remains unreacted is given by the broken line in Figure 1, *i.e.*,

$$\left\{ \begin{array}{l} \text{unreacted probability of} \\ \text{the polymer at time } t \end{array} \right\} = \exp \left[-k \int_0^t S(\mathbf{q}(t')) dt' \right] \quad (5)$$

The mean fraction of the unreacted polymers, $\phi(t)$, is obtained as the average of eq 5 over the initial states and the various paths of $\mathbf{q}(t)$. If the system is at equilibrium at $t=0$, these averages are represented by a single average

Figure 1. An example of $S(\mathbf{q}(t))$. The broken line denotes the unreacted probability for this path.

$\langle \dots \rangle$ over the equilibrium state:

$$\phi(t) = \left\langle \exp \left[-k \int_0^t S(\mathbf{q}(t')) dt' \right] \right\rangle \quad (6)$$

The reaction rate k_1 is given by the asymptotic decay rate of $\phi(t)$:

$$\phi(t) \propto \exp(-k_1 t) \quad (7)$$

If we generate a random walk $\mathbf{q}(t)$ which is described by the diffusion operator $\mathcal{L}$, we can calculate k_1 from eq 7.

PROCEDURE OF COMPUTER SIMULATION

For the model of the Brownian motion of a polymer, Verdier and Stockmayer⁸ have presented a simple model which, for a long chain, asymptotically approximates the Rouse chain. The model adopted in our computer simulation is a modification of their model. We consider a polymer chain consisting of N bonds of the same length b , connected by universal joints. Verdier and Stockmayer have assumed that these bonds are restricted to a cubic lattice, but here we release such a condition. In our model, the bond vectors can orientate in any direction (see Figure 2).

Figure 2. Modified Verdier—Stockmayer model adopted in this simulation. The broken circle indicates the reaction sphere.

The procedure of changing the conformation of the chain is as follows:

- 1) A random number n ($0 \leq n \leq N$) is generated.
- 2) i. If $n \neq 0$ or N , the n -th bond vector, which is a relative vector from the n -th monomer to the $(n+1)$ -th, is exchanged with the $(n+1)$ -th bond vector.
- ii. If $n=0$, the first bond vector is exchanged by a new bond vector which is generated randomly.
- iii. If $n=N$, the N -th bond vector is exchanged by a new bond vector which is generated randomly.

We call this single process of such an exchange of bond vectors a "bead cycle." Further we call N bead cycles a "cycle." It is the cycle that plays the role of the time scale in the real world. According to this definition, the longest relaxation time, τ_m , of the polymer chain is given by⁹

$$\tau_m = N^2/\pi^2 \quad (\text{cycles}) \quad (8)$$

In the computation, we take the bond length b as the unit of length. Thus, for example, a actually means a/b .

For efficiency of the computation time, we replace the average of eq 6 over the initial states and the various paths by that over the time:

$$\phi(t) = \frac{1}{T_m} \int_0^{T_m} dT \exp \left[-k \int_T^{T+t} S(q(t')) dt' \right] \quad (T_m \gg \tau_m) \quad (9)$$

In our calculation, $\phi(t)$ is observed at every multiple of a certain time interval Δ . Thus $\phi(l\Delta)$ is calculated by the following equation:

$$\phi(l\Delta) = \frac{1}{j_m - l + 1} \sum_{j=l}^{j_m} e_j \cdot e_{j-1} \cdots e_{j-l+1} \quad (10)$$

where $j_m = T_m/\Delta$ and e_j is defined by

$$e_j = \exp \left[-k \int_{j\Delta}^{(j+1)\Delta} S(q(t)) dt \right] \quad (11)$$

To calculate e_j we count the number of bead cycles n_j , during which the end-to-end distance is less than a , in the time interval between $j\Delta$ and $(j+1)\Delta$. Then e_j is obtained as

$$e_j = r^{n_j} \quad (12)$$

where the factor $r = \exp(-k/N)$ is the decreasing ratio of the unreacted probability of the chain

per bead cycle when the separation of the reactive groups of the chain ends are within the radius a of the reaction region.

On a computer, the above procedure can be very much simplified. We define $\varphi(l)$ and $s(l)$, which respectively express $e_j e_{j-1} \cdots e_{j-l+1}$ and $\sum_{j=l}^{j_m} e_j \cdot e_{j-1} \cdots e_{j-l+1}$. We proceed with the computation for a time interval Δ , and obtain e_{j+1} . Thus the new $\varphi(l)$ and $s(l)$, which are $e_{j+1} \cdots e_{j-l+2}$ and $\sum_{j=l}^{j+1} e_j \cdots e_{j-l+1}$, are obtained from the substitutions:

$$\begin{aligned} \varphi(l-1) \cdot e_{j+1} &\rightarrow \varphi(l) \\ s(l) + \varphi(l) &\rightarrow s(l) \end{aligned} \quad (13)$$

After the completion of the calculation, $\phi(l\Delta)$ is given by a suitable normalization of $s(l)$.

In the present computer simulation, the stochastic motion of the chain is continued for 400 τ_m cycles, where τ_m is the longest relaxation time of the chain given by eq 8, and the values of r are chosen as 0.0 and 0.99. The experiments are carried out three times under different initial conditions, and $\phi(t)$ is determined by averaging the results.

The value of the first order reaction rate k_1 is obtained graphically from the slope of semi-log plots of the unreacted fraction $\phi(t)$ vs. time.

RESULTS AND DISCUSSION

In the case of $r=0$, which means that the intrinsic reaction rate k is infinite, the reaction becomes diffusion-controlled. For this case, $k_{1\infty}$ against the degree of polymerization N is shown in Figure 3 in the log-log scale. As N increases towards infinity, the values $k_{1\infty}$ asymptotically approach the line of slope -2 for all sizes of the reaction region. In order to see the N dependence of $k_{1\infty}$ in detail, $k_{1\infty}\tau_m$ is plotted against N in Figure 4. This figure shows clearly that the values of $k_{1\infty}\tau_m$ converge to some finite values as N increases. Especially we observe that $k_{1\infty}\tau_m$ is an increasing function of N for a 0.5 and 1.0. This clearly indicates that the harmonic spring model is quite inadequate for the description of the diffusion-controlled reaction system, because eq 3 predicts that $k_{1\infty}\tau_m$ decreases in proportion to L^{-1} or to $1/\sqrt{N}$.

Figure 4 suggests an empirical equation of

Figure 3. The diffusion-controlled reaction rate $k_{1\infty}$ is plotted against the degree of polymerization N on log-log scale.

Figure 4. The plot of $k_{1\infty}\tau_m$ against N at constant a/b 's.

$k_{1\infty}$ for very large N ,

$$k_{1\infty} = \tau_m^{-1} f(a/b) \quad (N \gg 1) \quad (14)$$

here $f(a/b)$ is a universal function independent of N . Equation 2 indicates that $f(a/b)$ takes the value 0.46 independently of a/b . This prediction does not agree with the present simulation. However, the discrepancy does not mean the failure of eq 2, nor the failure of the closure approximation, because eq 2 is proposed on the condition $b \ll a \ll L$, which is not satisfied even in the case of $N=70$. Owing to the insufficiency of the molecular weight N in this computer simulation, it is difficult to establish whether the limiting value of $k_{1\infty}\tau_m$, as $N \rightarrow \infty$, depends

Figure 5. Dependence of the reaction rate k_1 on $\gamma (=a/L)$; filled circle: the observed values; open circles: the values obtained from eq 16; and broken lines: theoretical values for $k \rightarrow 0$ (eq 15).

on the size of the reaction region. At least, however, it is concluded that $k_{1\infty}$ is about the order of τ_m^{-1} .

Various examples of the apparent reaction rates k_1 for $r=0.99$ are shown in Figure 5(a), (b), and (c). In the case where the intrinsic reaction rate k is small, the system remains almost in the equilibrium state for all the time, and the first order reaction rate k_1 is found to be given by

$$\begin{aligned} k_{1eq} &= k \int d\mathbf{q} S(\mathbf{q}) P_{eq}(\mathbf{q}) \quad (\text{for } k \rightarrow 0) \\ &= k \int_{|\mathbf{r}| < a} d^3r \left(\frac{3}{2\pi L^2} \right)^{3/2} \exp\left(-\frac{3r^2}{2L^2}\right) \\ &= k \left[\left(\frac{6}{\pi} \right)^{1/2} \gamma^3 - \frac{9}{5} \left(\frac{3}{2\pi} \right)^{1/2} \gamma^5 + \dots \right] \quad (15) \end{aligned}$$

with $\gamma = a/L$.

This relation between k_{1eq} and γ is shown by the broken lines in Figure 5(a), (b), and (c) for $k=0.20$, 0.50, and 0.70, respectively. For relatively small k , e.g., $k=0.20$ (Figure 5(a)), the experimental values k_1 agree well with k_{1eq} of eq 15. As k becomes large, the observed k_1 deviates from eq 15 due to the effect of diffusion.

For the case of intermediate k , Doi proposed the following interpolation formula:⁶

$$\frac{1}{k_1} = \frac{1}{k_{1\infty}} + \frac{1}{k_{1eq}} \quad (16)$$

From this equation, k_1 is calculated by the use of the observed $k_{1\infty}$ and k_{1eq} determined by eq

15, and is plotted in Figure 5 by open circles. Figure 5 shows that k_1 from eq 16 reproduces experimental results for all k within experimental errors. This observation supports the validity of the interpolation formula, eq 16.

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