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from that observed in dilute solutions has recently been corroborated by neutron spin-echo measurements on poly(dimethylsiloxane) solutions.[18]

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References and Notes

(1) See, for example: (a) Mathiez, P.; Mouttet, C.; Weisbuch, G. *J. Phys.* (*Paris*) **1980**, *41*, 519. (b) Chu, B.; Nose, T. *Macromolecules* **1980**, *13*, 122.
(2) Hwang, D.-H.; Cohen, C. *Macromolecules* **1984**, *17*, 1679; thereafter called paper 1.
(3) Amis, E. J.; Janmey, P. A.; Ferry, J. D.; Yu, H. *Macromolecules* **1983**, *16*, 441.
(4) (a) Chang, T.; Yu, H. *Macromolecules* **1984**, *17*, 115. (b) Brown, W. *Macromolecules* **1984**, *17*, 66.
(5) See, for example: Yamakawa, H. "Modern Theory of Polymer Solutions", Harper and Row: New York, 1971.
(6) These two modes correspond to the "across" diffusion mode and the "reptation" mode respectively in S. F. Edwards' recent terminology: Edwards, S. F. *Faraday Symp., Chem. Soc.* **1983**, *18*, paper 10, to appear.
(7) de Gennes, P.-G. *Physics* (*Long Island City, N.Y.*) **1967**, *3*, 37.
(8) Dubois-Violette, E.; de Gennes, P.-G. *Physics* (*Long Island City, N.Y.*) **1967**, *3*, 181.
(9) Akcasu, A. Z.; Benmouna, M.; Han, C. C. *Polymer* **1980**, *21*, 866.
(10) Higgins, J. S.; Nicholson, L. K.; Hayter, J. B. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1981**, *22*, 86.
(11) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980.
(12) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(13) Crank, J.; Park, G. S. "Diffusion in Polymers"; Academic Press: New York, 1968.
(14) Lin, Y. H.; Chu, B. *Macromolecules* **1981**, *14*, 385.
(15) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*, 1229.
(16) Cohen, C.; Sankur, V.; Pings, C. J. *J. Chem. Phys.* **1977**, *67*, 1436.
(17) Lindsey, C. P.; Patterson, G. D.; Stevens, J. R. *J. Polym. Sci.* **1979**, *17*, 1547.
(18) (a) Ewen, B.; Stühn, B.; Binder, K.; Richter, D.; Hayter, J. B. *Polym. Commun.* **1984**, *25*, 133. (b) Baumgartner, A.; Kremer, K.; Binder, K. *Faraday Symp., Chem. Soc.* **1983**, *18*, paper 3, to appear.

Theory of Intrachain Reaction Rates in Entangled Polymer Systems

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ABSTRACT: We give the exact solution of a model of diffusion-controlled reactions in entangled polymer melts, based on reptation theory. In particular we focus on the end-to-end intrachain cyclization rate of functionalized polymer chains, anticipating that the same fluorescence spectroscopy techniques which have proven valuable in studies of dilute solutions will also be applied to the entangled regime. We express the cyclization rate "constant", $k_{\mathrm{cyc}}(t)$, and the reaction rate, $R(t)$, in terms of a two-point Greens function or memory function and solve for this correlation function analytically, in the continuum limit, from the earthworm equations of Doi and Edwards. The full time dependence of the cyclization rate is given; the slow power law decay for $t \ll \tau_{\mathrm{rep}}$ (where τ_{rep} is the fundamental reptation or tube disengagement time) is identified with compact exploration, and the exponential decay for $t \gg \tau_{\mathrm{rep}}$ for noncompact exploration. We propose that results of the cyclization experiments for entangled polymer melts will provide a uniquely unambiguous test of reptation theory. In order to distinguish reptation from Rouse-like behavior, however, the experiment will have to be performed on a time scale near the crossover of the compact to noncompact regimes, $t \lesssim \tau_{\mathrm{rep}}$. This requirement necessitates choosing special chromophores, with particularly long-lived excited states, for attachment to the polymer chain ends. The theory also allows for corrections to the universal decay curve for the reaction rate, derived on the basis of the *discrete* earthworm equations. Our earlier solution of these equations for *finite* chains shows that the corrections due to nonuniversality are small.

1. Introduction

The study of diffusion-controlled reactions in polymer solutions has led to a great deal of new information about polymer dynamics at the molecular level.[1] In particular fluorescence spectroscopy techniques have been used to measure the end-to-end cyclization rates of functionalized polymer chains, and the molecular weight dependence of the rate constant has been accurately determined.[2,3] The results are in good agreement with the elegant Wilemski–Fixman theory for internal relaxation times of polymer chains in solution.[4]

Much less work along these lines has been done for concentrated polymer systems in the entangled regime, mainly because of the experimental difficulty of measuring the much smaller reaction rates associated with the slower diffusion processes. However, the choice of special organic chromophores, with exceptionally long-lived triplet excited states, covalently attached to the ends of the polymer chains may make cyclization reactions observable in these systems.

Theoretically, the development of models for diffusion-controlled reactions in polymer melts is attractive because one does not have to deal with the intricacies of the excluded volume effect. Thus, although the experiments will be more difficult to carry out than for the case of dilute solutions, the theoretical interpretation should be more straightforward. In this paper we propose that measurement of the cyclization rate constant, k_{cyc}, and in particular its molecular weight dependence, will allow a uniquely unambiguous test of the reptation theory of Edwards[5] and de Gennes.[6] Such a test would be welcome at this time, because recent experimental and theoretical

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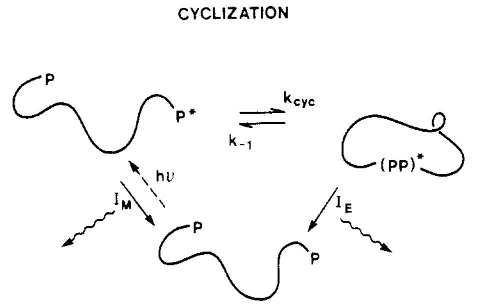

Figure 1. Schematic diagram showing intrachain cyclization reaction (rate constant k_{cyc}) in polymer solution or melt. The excited chromophore is denoted by P*, and (PP)* is the excimer. I_M and I_E are the fluorescence intensities of the chromophores and excimers, respectively.

work[7-10] indicates that the original concept of a polymer chain trapped in a tube formed by entanglements points, with tube renewal taking place only from the ends, may require revision.

In particular the results of Smith et al.[7] using fluorescence redistribution after pattern photobleaching show that the reptation model does not quantitatively describe polymer diffusion in entangled host polymer matrices, except for the case of short labeled chains. In another type of experiment, small-angle neutron scattering measurements[8] of the relaxation of uniaxially stretched deuterated chains in high molecular weight polystyrene melts are also not in good agreement with the predictions of reptation theory.[9] In addition, measurements of the zero-shear viscosity for semidilute solutions show exponents which increase with monomer concentration, a result which cannot be explained by the simple reptation model.[10]

Finally, the nonintegral power law dependence of the zero-shear melt viscosity on the molecular weight remains a problem, although some modifications[11] of the original reptation hypothesis may explain this effect. In general rheological functions calculated from the earthworm equations of Doi and Edwards are not very sensitive to the microscopic details of the reptation model. In fact similar results for polymer melt rheology can be obtained from a combination of the reptation concept with the phase-space kinetic theory of Curtiss and Bird.[13,14]

In this paper we calculate the time-dependent cyclization rate of a continuously flexible polymer chain in an entangled melt. We solve the earthworm equations in the continuum limit to obtain the exact time-dependent intrachain correlation function for very long chains. Some of the exact results for discrete, finite chains, as well as continuous chains, have been discussed earlier.[15] The correlation or memory function is used along with de Gennes' "transport equation"[16] to obtain the time dependence of the reaction rate, $R(t)$, and the cyclization rate, $k_{cyc}(t)$. In section 2 we use de Gennes' formulation[16] of the dynamics of diffusion-controlled reactions to obtain an expression for the end-to-end intrachain reaction rate. The exact result for the two-point correlation or memory function in the continuum limit is derived in section 3, and the universal curves for this quantity, as well as $k_{cyc}(t)$, are discussed in section 4. Section 5 contains the conclusions and both the short- and long-time behavior of the reaction rate are given in the appendices.

2. Intrachain-Reaction Dynamics in Polymer Systems

We consider the case of an end-to-end cyclization reaction, i.e., P + P* → (PP*), between the two ends of the *same* chain, as shown in Figure 1. Let $n(t)$ be the number of unreacted chain-end pairs in the system, with $n(0) = n_0$. Then in terms of the reaction rate $R(t)$, we have

$$\mathrm{d}n(t)/\mathrm{d}t = -n_0R(t) \qquad (2.1)$$

It is also convenient to define a time-dependent reaction rate "constant" for cyclization, $k_{cyc}(t)$, by the equation

$$\mathrm{d}n(t)/\mathrm{d}t = -k_{cyc}(t)n(t) \qquad (2.2)$$

Comparing the above two expressions, we see that the rate constant can be simply expressed in terms of the reaction rate

$$k_{cyc}(t) = R(t)/\left[1 - \int_0^t \mathrm{d}t'\,R(t')\right] \qquad (2.3)$$

In the long-time limit, if $k_{cyc}(t)$ goes to a constant value, it must have the form

$$k_{cyc}(\infty) = \alpha/\tau_{rep} \qquad (2.4)$$

where α is a numerical constant and τ_{rep} is the fundamental reptation or tube disengagement time. This result follows because the only time constant in the continuum problem is τ_{rep}, and $k_{cyc}(t)$ has the dimension $[t]^{-1}$. Thus we predict that

$$k_{cyc}(\infty) \propto M^{-3} \qquad (2.5)$$

where M is the molecular weight of the (monodisperse) polymer chains. Going back to eq 2.4 we also see that in order to satisfy eq 2.3 the reaction rate must fall off exponentially for long times

$$R(t) = (\alpha/\tau_{rep})e^{-\alpha(t/\tau_{rep})} \quad \text{for } t \gg \tau_{rep} \qquad (2.6)$$

Of course the above discussion does not give us the detailed time dependence of $k_{cyc}(t)$, which is important for a comparison with experiments performed on a time scale $t/\tau_{rep} \leq 1$, nor is the value of the numerical constant α determined.

In order to solve for the time dependence of the reaction rate, we must consider a more detailed description of the cyclization event. Let us assume that a pair of chain ends react at a rate of κ when their separation is within a distance R_C, the reaction radius, and let $\psi(\vec{R},t)$ be the probability density that a pair is unreacted at time t with a separation $\vec{R}$. Then the reaction rate probability in the system is

$$R(t) = \int_{R<R_C} \mathrm{d}^3R\ \kappa\psi(\vec{R},t) \simeq \kappa\Omega\psi(\vec{0},t) \qquad (2.7)$$

since the reaction radius R_C is usually small. Here, $\Omega = 4\pi R_C{}^3/3$.

The equation governing the evolution of $\psi(\vec{R},t)$ is then given by[15,16]

$$\psi(\vec{R},t) = \psi_0(\vec{R}) - \int_0^t \mathrm{d}t'\,\Gamma(\vec{R},t-t'|0)R(t') \qquad (2.8)$$

where $\psi_0(\vec{R})$ is the equilibrium distribution of end-to-end separations in the absence of reactions. For a Gaussian chain, it is given by

$$\psi_0(\vec{R}) = \left(\frac{3}{2\pi N_0b^2}\right)^{3/2}\exp\left(\frac{-3R^2}{2N_0b^2}\right) \qquad (2.9)$$

where N_0 is the degree of polymerization of the chain and b the Kuhn length.

The quantity $\Gamma(\vec{R},t|\vec{R}_0)$ is the probability density (in the absence of reactions) that an end pair has a separation of $\vec{R}$ at time t, given that their initial separation is $\vec{R}_0$. This, in fact, is a special case of the two-point correlation function, the points in this case being the two ends of the chain.

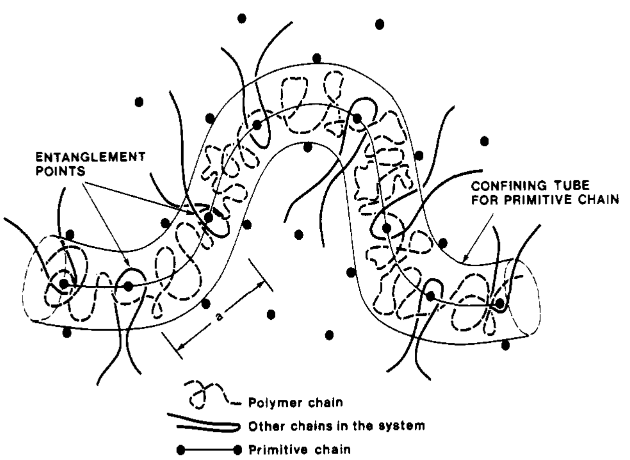

Figure 2. An entangled polymer chain is represented by a primitive chain confined in a tube. Each "blob" of the polymer chain between two entanglement points is represented by a segment on the primitive chain. a = distance between beads = distance between entanglement points = size of "blob" = width of tube. Each "blob" contains N_e monomer segments.

From eq 2.7 and 2.8, it is clear that the reaction rate $R(t)$ satisfies the equation

$$R(t) = \kappa\Omega\left[\psi_0(\vec{0}) - \int_0^t dt'\, S(t-t')R(t')\right] \quad (2.10)$$

where $S(t)$ is the memory function defined by

$$S(t) = \Gamma(\vec{0},t|\vec{0}) \quad (2.11)$$

Taking the Laplace transform of the various quantities, e.g.

$$\tilde{R}(z) = \int_0^\infty dt\, e^{-zt}R(t) \quad (2.12)$$

we obtain from eq 2.10

$$\tilde{R}(z) = \frac{\kappa\Omega\psi_0(\vec{0})}{z[1+\kappa\Omega\tilde{S}(z)]} \quad (2.13)$$

In general, the two ends react rapidly when they are within the reaction radius (i.e., $\kappa \to \infty$), so that

$$\tilde{R}(z) = \psi_0(\vec{0})/z\tilde{S}(z) \quad (2.14)$$

Thus central to the calculation of the reaction rate is the determination of the memory function $S(t)$, which is just a special case of the two-point correlation function, the solution of which is given in the next section.

3. Correlation Function

Consider a primitive chain consisting of N beads and let the distance between the beads be a, the average distance between entanglement points. The relation between the primitive chain and the real chain is indicated schematically in Figure 2.

In general, the degree of polymerization N_0 and the Kuhn length b of the real chain are related to N and a of the primitive chain by

$$N = N_0/N_e \quad (3.1)$$

$$a^2 = N_e b^2 \quad (3.2)$$

where N_e, the number of monomer segments between entanglement points, is a function of polymer concentration alone and is independent of the molecular weight. Note that $Na^2 = N_0 b^2$, as should be the case.

Let $\vec{R}_n(t)$ be the position of the nth bead in the primitive chain. Then the fundamental equation of motion in the reptation model (the so-called "earthworm" equation) is given by[12]

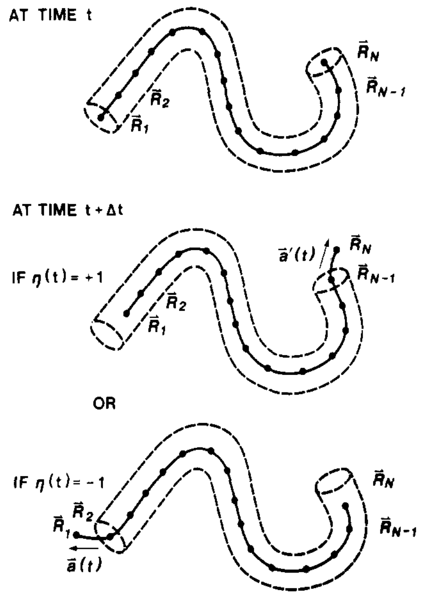

Figure 3. Schematic description of the "earthworm" model (eq 3.3–3.5). Upper panel: Primitive chain in its confining tube at time t. Lower panel: At time $t + \Delta t$, depending on whether the stochastic function $\eta(t)$ takes on a value of +1 or −1, the chain moves either forward or backward along the tube by one step. The bead that gets out of the tube ($\vec{R}_N$ or $\vec{R}_1$) moves a distance a, but in a random direction as indicated by the stochastic vectors $\vec{a}'(t)$ or $\vec{a}(t)$.

$$\vec{R}_n(t+\Delta t) = \frac{1+\eta(t)}{2}\vec{R}_{N+1}(t) + \frac{1-\eta(t)}{2}\vec{R}_{n-1}(t) \qquad (n = 1, ..., N) \quad (3.3)$$

with $\vec{R}_0$ and $\vec{R}_{N+1}$ defined by

$$\vec{R}_0(t) = \vec{R}_1(t) + \vec{a}(t) \quad (3.4)$$

$$\vec{R}_{N+1}(t) = \vec{R}_N(t) + \vec{a}'(t) \quad (3.5)$$

Here, Δt is the average time taken by the chain to move a distance a along its confining tube. $\eta(t)$ is a stochastic function which can take on values of +1 or −1 at random and determines whether the sliding motion is forward or backward. $\vec{a}(t)$ and $\vec{a}'(t)$ are stochastic vector functions of magnitude a but can point in any direction at random. Notice that $\vec{R}_0(t)$ and $\vec{R}_{N+1}(t)$ only represent possible positions of $\vec{R}_1(t+\Delta t)$ and $\vec{R}_N(t+\Delta t)$ and hence require separate definitions. The significance of these equations is shown schematically in Figure 3.

Now, for a given initial configuration of the chain, the correlation function $G_{mn}(\vec{R},t)$ between the mth and nth beads at a subsequent time t is defined as the probability density that the beads are separated by a distance $\vec{R}$ at t; i.e.

$$G_{mn}(\vec{R},t) = \langle\delta[(\vec{R}_m(t) - \vec{R}_n(t)] - \vec{R}]\rangle \quad (3.6)$$

Clearly the function $\Gamma(\vec{R},t|\vec{R}_0)$ of the previous section is the special case $G_{N1}(\vec{R},t)$ with the initial condition $G_{N1}(\vec{R},0) = \delta(\vec{R} - \vec{R}_0)$.

It is more convenient for our purpose to consider the Fourier transform of G_{mn}:

$$F_{mn}(\vec{k},t) = \int d^3R\, e^{i\vec{k}\cdot\vec{R}}G_{mn}(\vec{R},t) = \langle\exp\{i\vec{k}\cdot[\vec{R}_m(t) - \vec{R}_n(t)]\}\rangle \quad (3.7)$$

This function is in fact more directly measurable through light or neutron scattering experiments than the function G_{mn}.

From the equation of $\vec{R}_n(t)$ (eq 3.3–3.5), it is clear that the evolution of F_{mn} is governed by

$$F_{mn}(\vec{k},t+\Delta t) = \tfrac{1}{2}[F_{m+1,n+1}(\vec{k},t) + F_{m-1,n-1}(\vec{k},t)] \tag{3.8}$$

$$F_{m,0}(\vec{k},t) = \left(\frac{\sin (ka)}{ka}\right)F_{m,1}(\vec{k},t) \tag{3.9}$$

$$F_{N+1,n}(\vec{k},t) = \left(\frac{\sin (ka)}{ka}\right)F_{N,n}(\vec{k},t) \tag{3.10}$$

Note that by symmetry, we need only study the case $m \geq n$.

We define $l = ma$ and $l' = na$ as the distances of the mth and nth beads from the end as measured along the chain, and we take the coninuum limit of eq 3.8–3.10 to give

$$\frac{\partial F}{\partial t} = D\left(\frac{\partial}{\partial l} + \frac{\partial}{\partial l'}\right)^2 F \tag{3.11}$$

$$\frac{\partial F}{\partial l'} = \mu F \qquad \text{at } l' = 0 \tag{3.12}$$

$$\frac{\partial F}{\partial l} = -\mu F \qquad \text{at } l = L \tag{3.13}$$

where we have

$$F = F(l,l',t) \equiv F_{mn}(\vec{k},t) \tag{3.14}$$

and the argument $\vec{k}$ has been suppressed. Also, we have $L = Na$, the total length of the (primitive) chain and $\mu = (1/6)k^2a$. Finally

$$D = a^2/2\Delta t \tag{3.15}$$

is the tube diffusion coefficient. It is related to the diffusion coefficient D_0 of the monomers by

$$D = D_0/N_0 \tag{3.16}$$

so that it is inversely proportional to the molecular weight of the chain.

Equation 3.11 is easily solved by transforming to the variables

$$s = l + l' \tag{3.17}$$

$$p = l - l' \tag{3.18}$$

Writing $f(s,p,t) \equiv F(l,l',t)$, the equation for f is

$$\frac{\partial f}{\partial t} = 4D\frac{\partial^2 f}{\partial s^2} \tag{3.19}$$

Through the Laplace transform

$$\tilde{f}(s,p,z) = \int_0^\infty \mathrm{d}t\, e^{-zt} f(s,p,t) \tag{3.20}$$

we obtain

$$z\tilde{f} - f_0 = 4D\frac{\partial^2 \tilde{f}}{\partial s^2} \tag{3.21}$$

where $f_0 = f(s,p,0)$ is the initial condition for f.

It is possible to write down the solution of eq 3.21 for a general initial condition $f_0(s,p)$. However, for a large class of applications, the initial condition is independent of s; i.e., $f_0 = f_0(p)$. In this paper we shall only consider the latter case.

The solution of eq 3.21 is easily seen to be

$$\tilde{f}(s,p,z) = \frac{1}{z}f_0(p) + A(p,z) \cosh \left(\frac{z(L-s)^2}{4D}\right)^{1/2} \tag{3.22}$$

where $A(p,z)$ can be determined by the boundary condition (eq 3.12) to give the full solution:

$$\tilde{f}(s,p,z) = \frac{1}{z}\Bigg\{f_0(p) - \cosh\left(\frac{z(L-s)^2}{4D}\right)^{1/2} \cosh\left(\frac{z(L-p)^2}{4D}\right)^{1/2} \times e^{-\mu p}\int_0^p \frac{\mathrm{d}p'}{\cosh^2\left(\frac{z(L-p')^2}{4D}\right)^{1/2}} \frac{\mathrm{d}}{\mathrm{d}p'}[e^{\mu p'}f_0(p')]\Bigg\} \tag{3.23}$$

Another form of this solution which is more convenient for our later use can be obtained by integrating the last term by parts to give

$$\tilde{f}(s,p,z) = \frac{1}{z} \times \left[\frac{\cosh\left(\frac{z(L-s)^2}{4D}\right)^{1/2} \cosh\left(\frac{z(L-p)^2}{4D}\right)^{1/2}}{\cosh^2\left(\frac{zL^2}{4D}\right)^{1/2}} e^{-\mu p} + f_0(p)\left(1 - \frac{\cosh\left(\frac{z(L-s)^2}{4D}\right)^{1/2}}{\cosh\left(\frac{z(L-p)^2}{4D}\right)^{1/2}}\right) + \cosh\left(\frac{z(L-s)^2}{4D}\right)^{1/2} \cosh\left(\frac{z(L-p)^2}{4D}\right)^{1/2} e^{-\mu p}\int_0^p \mathrm{d}p'\, e^{\mu p'} f_0(p') \frac{\mathrm{d}}{\mathrm{d}p'} \frac{1}{\cosh^2\left(\frac{z(L-p')^2}{4D}\right)^{1/2}}\right] \tag{3.24}$$

Equation 3.23 or 3.24 gives the full expresion for the correlation function F_{mn} or G_{mn}. The exact behavior of these functions depends on the initial configuration of the chains, but in general the following observations can be made:

(a) If the initial condition of the chain is the equilibrium configuration, i.e.

$$G_{mn}(\vec{R},0) = G_{mn}{}^{\mathrm{eq}}(\vec{R}) \equiv \left(\frac{3}{2\pi|m-n|a^2}\right)^{3/2} \exp\left(\frac{-3R^2}{2|m-n|a^2}\right) \tag{3.25}$$

or correspondingly

$$F_{mn}(\vec{k},0) = F_{mn}{}^{\mathrm{eq}}(\vec{k}) = \exp\left(-\frac{1}{6}|m-n|k^2a^2\right) \tag{3.26}$$

$$f_0(p) = f_{\mathrm{eq}}(p) \equiv e^{-\mu p} \tag{3.27}$$

then eq 3.23 shows that

$$\tilde{f}(s,p,z) = \frac{1}{z}f_{\mathrm{eq}}(p) \tag{3.28}$$

or

$$f(s,p,t) = f_{\mathrm{eq}}(p) \qquad \text{for all time} \tag{3.29}$$

Thus, as one would expect, the correlation function of a system in equilibrium does not evolve with time.

(b) Starting from an arbitrary initial condition $f_0(p)$, we see from eq 3.24 that as $t \to \infty$

$$f(s,p,\infty) = \lim_{z\to 0} z\tilde{f}(s,p,z) = e^{-\mu p} \equiv f_{\text{eq}}(p) \qquad (3.30)$$

showing that the correlation function must eventually approach its equilibrium value as $t \to \infty$.

(c) For cyclization reactions, we are interested in the memory function $S(t) = \Gamma(\vec{0},t|\vec{0})$. Here, the initial condition is that the two ends are in contact while the remainder of the chain takes on all possible configurations as permitted by the constraints of a Gaussian chain. In this case, the initial condition is

$$G_{mn}(\vec{R},0) = [3/2\pi|m-n|(1-|m-n|/N)a^2]^{3/2} \exp[-3R^2/2|m-n|(1-|m-n|/N)a^2] \qquad (3.31)$$

which translates into

$$f_0(p) = e^{-\mu p(1-p/L)} \qquad (3.32)$$

Substituting this into eq 3.24, we obtain the following expression for the Laplace transform of the memory function:

$$\tilde{S}(z) = \int \frac{\mathrm{d}^3k}{(2\pi)^3}\tilde{f}(L,L,z) = \left(\frac{3}{2\pi La}\right)^{3/2}\frac{1}{z}\left\{\frac{1}{\cosh^2 (z\tau)^{1/2}} + 2(z\tau)^{1/2}\int_0^1 \frac{\mathrm{d}x}{[x(2-x)]^{3/2}}\,\frac{\sinh[(z\tau)^{1/2}x]}{\cosh^3[(z\tau)^{1/2}x]}\right\} \qquad (3.33)$$

where

$$\tau = \frac{L^2}{4D} = \frac{b^2}{4N_eD_0}N_0^3 \qquad (3.34)$$

is a time constant proportional to the third power of the molecular weight and is related to the disengagement time $\tau_{\text{rep}} = L^2/\pi^2D$ introduced by de Gennes:

$$\tau = (\pi^2/4)\tau_{\text{rep}} \qquad (3.35)$$

The Laplace transform equation (3.33) can be easily inverted to give the memory function $S(t)$:

$$S(t) = \left(\frac{3}{2\pi La}\right)^{3/2}\left\{\frac{\partial}{\partial L}\left[LH\left(\frac{t}{\tau}\right)\right] - \int_0^1 \frac{\mathrm{d}x}{[x(2-x)]^{3/2}}\,\frac{\partial^2}{\partial x^2}\left[xH\left(\frac{t}{\tau x^2}\right)\right]\right\} \qquad (3.36)$$

where

$$H(u) = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{e^{-(\pi^2/4)(2n+1)^2u}}{(2n+1)^2} = 2\left(\frac{u}{\pi}\right)^{1/2}\left\{1 + 2\sum_{n=0}^{\infty}(-1)^n\left[e^{-n^2/u} - n\left(\frac{\pi}{u}\right)^{1/2}\operatorname{erfc}\left(\frac{n}{u^{1/2}}\right)\right]\right\} \qquad (3.37)$$

We shall apply these results to the study of the reaction rates in the next section.

4. Time-Dependent Cyclization Reaction Rate

According to eq 2.9 and 2.14 the Laplace transform of $R(t)$ is given by

$$\tilde{R}(z) = \psi_0(\vec{0})/z\tilde{S}(z) = \left[\frac{1}{\cosh^2 (z\tau)^{1/2}} + 2(z\tau)^{1/2}\int_0^1 \frac{\mathrm{d}x}{[x(2-x)]^{3/2}}\,\frac{\sinh[(z\tau)^{1/2}x]}{\cosh^3[(z\tau)^{1/2}x]}\right]^{-1} \qquad (4.1)$$

which can be inverted numerically to yield $R(t)$ and $k_{\text{cyc}}(t)$ (from eq 2.3). First, however, we shall summarize the results for the long- and short-time behavior of these functions.

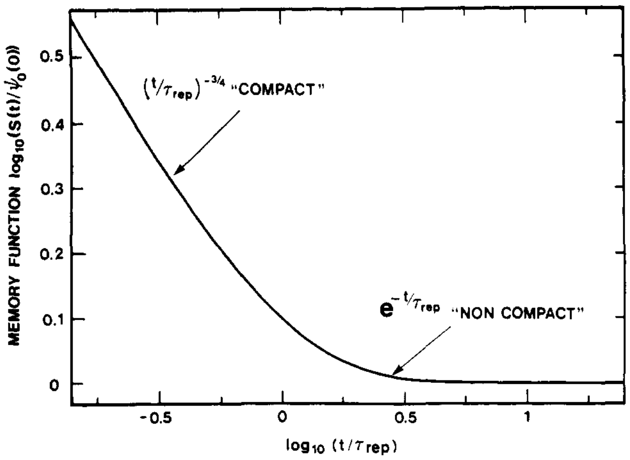

Figure 4. Universal *intrachain* memory function $S(t)$ in the continuum limit. τ_{rep} is the fundamental reptation or tube disengagement time, and $\psi_0(\vec{0})$ is the equilibrium end-to-end contact probability of a single chain. $S(t)$ is the conditional probability of end-to-end encounters at time t for a single reptating chain whose ends were in contact at $t = 0$. The regimes of compact and noncompact exploration are indicated (see text).

(a) Long-Time Limit. Here we find the reaction rate to have exponential behavior (see Appendix A):

$$R(t) \sim (0.895/\tau)e^{-0.895t/\tau} \quad \text{for } t \gg \tau \qquad (4.2)$$

Using the fact that

$$1 - \int_0^t \mathrm{d}t'\,R(t') = \int_t^\infty \mathrm{d}t'\,R(t') \qquad (4.3)$$

we see that the rate constant $k_{\text{cyc}}(t)$ does approach a constant value is argued earlier

$$k_{\text{cyc}}(\infty) = \frac{0.895}{\tau} = \frac{0.363}{\tau_{\text{rep}}} \qquad (4.4)$$

where, as noted before, $\tau = (\pi^2/4)\tau_{\text{rep}} \sim N_0^3$.

(b) Short-Time Limit. As shown in Appendix B, the short-time limit of the reaction rate can be obtained by a large-z expansion of $\tilde{S}(z)$. The following results are obtained for $t \ll \tau$:

$$\frac{S(t)}{\psi_0(\vec{0})} = 0.344\left(\frac{t}{\tau}\right)^{-3/4}\left[1 + 0.749\left(\frac{t}{\tau}\right)^{1/2} + \mathcal{O}\left(\frac{t}{\tau}\right)\right] \qquad (4.5)$$

$$R(t) = \frac{0.655}{\tau}\left(\frac{t}{\tau}\right)^{-1/4}\left[1 - 0.343\left(\frac{t}{\tau}\right)^{1/2} + \mathcal{O}\left(\frac{t}{\tau}\right)\right] \qquad (4.6)$$

and hence the reaction rate "constant" is given by

$$k_{\text{cyc}}(t) = \frac{0.655}{\tau}\left(\frac{t}{\tau}\right)^{-1/4}\left[1 - 0.343\left(\frac{t}{\tau}\right)^{1/2} + 0.874\left(\frac{t}{\tau}\right)^{3/4} + \mathcal{O}\left(\frac{t}{\tau}\right)\right] \qquad (4.7)$$

Figure 4 shows the full time dependence of the intrachain memory function $S(t)$ (eq 3.36) in the continuum limit. As is evident from the analytical result, $S(t)$ has a universal form for all chain lengths, with the time scale determined by τ_{rep}. Unlike the memory function for the *interchain* case, where the reactants are not on the same chain, the *intrachain* function relaxes to the equilibrium end-to-end contact probability $\psi_0(0)$ for long times. Considering only the transient part of $S(t)$, we find the long-

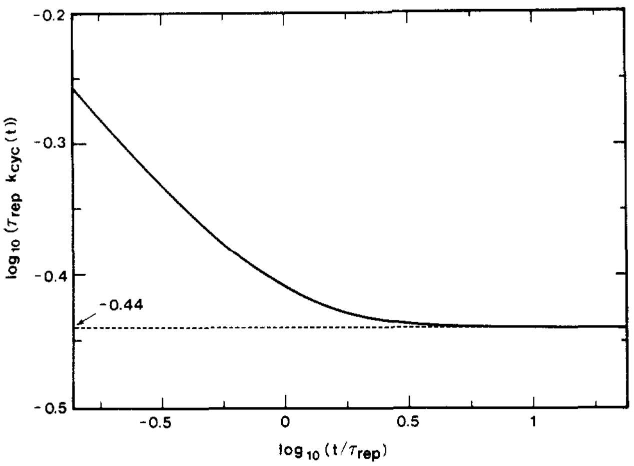

Figure 5. Universal cyclization rate function $k_{cyc}(t)$ for a collection of reptating chains in a polymer melt. The curve is derived on the basis of the continuum limit of the earthworm equations of Doi and Edwards and τ_{rep} is the fundamental reptation time. At long times the rate constant is $k_{cyc}(\infty) = 0.363/\tau_{rep}$.

time behavior $S(t)/\psi_0(0) - 1 \propto \exp(-t/\tau_{rep})$: In this case $S(t)$ decreases more rapidly than t^{-1}, and the number of sites explored by the chain ends is smaller than the number of sites available in the region of confinement during random motion for a time t. In de Gennes' terminology[16] this is a case of noncompact exploration. Conversely, for $t \ll \tau_{rep}$ we have $S(t)/\psi_0(0) \propto (t/\tau_{rep})^{-3/4}$ and the memory function decreases less rapidly than t^{-1}, so that most points inside the confinement region are visited by the chain ends (compact exploration). The short-time behavior of the memory function for our case is the same as for a Rouse model, since the motion of the chain ends is not limited by the tube constraints for $t \ll \tau_{rep}$.

Figure 5 shows the corresponding results for the cyclization rate constant, $k_{cyc}(t)$. In the compact regime, $t \ll \tau_{rep}$, $k_{cyc}(t) \propto (t/\tau_{rep})^{-1/4}$, the same as for a Rouse chain, and for $t \gg \tau_{rep}$ (noncompact regime), $k_{cyc}(\infty) = 0.363/\tau_{rep}$.

In order to analyze the results of cyclization experiments in polymer melts, it is essential to know the full time-dependent behavior of $k_{cyc}(t)$. Obviously for $t \ll \tau_{rep}$ the experiments will not be able to distinguish between the Rouse and reptation models. For $t \simeq \tau_{rep}$ we are in the crossover regime between compact and noncompact exploration, and the analysis will be delicate, particularly if there is some Rouse-like motion of the confining tubes in the entangled melt.

Finally, it is worth emphasizing that all of the above results were obtained in the continuum limit of the reptation model. The earthworm equations actually contain a spatial discreteness, $a/L = N^{-1}$, measured by the entanglement separation, and a temporal discreteness, $\Delta t/\tau_{rep} = (\pi^2/2)(a/L)^2 \propto N^{-2}$, measured by the hopping time. A universal equation for the correlation function, involving a single time constant, τ_{rep}, results only when this discreteness vanishes. Referring back to eq 3.1 and 3.2, we see that this occurs either by artificially letting $a \to 0$ for fixed molecular weight or by taking the more physical limit of infinite molecular weight for a finite entanglement separation a. For finite chains, solution of the *discrete* earthworm equations gives nonuniversal decay curves for $k_{cyc}(t)$, as has been shown in a separate paper.[17] The effects of nonuniversality show up as a nonintegral exponent in the molecular weight dependence of k_{cyc}.

5. Conclusions

As has been emphasized by Adam and Delsanti,[10] the original reptation model assumes that the diffusion coefficient of the chain in the tube is completely anisotropic, vanishing for motion perpendicular to the tube and varying inversely proportional to the molecular weight of the chain along the tube. This simplifying assumption certainly becomes invalid close to the entanglement transition[18] and is also responsible for the (incorrectly) predicted concentration-independent exponents for the zero-shear viscosity and longest relaxation time of semidilute solutions.[10] However, a broader question is: To what extent may one ignore Rouse-like motion of the tube in an entangled polymer melt? In the original reptation model it is ignored completely, and this seems reasonable for polymers in the limit of infinite molecular weight. However, for real polymer system chains there is a spectrum of lifetimes for the tube-defining constraints,[19] and the determination of this quantity, as well as the amount of tube relaxation for strained polymers,[20] is vital to understanding the nature of polymer motion in entangled melts and concentrated solutions. Hopefully the theoretical and experimental work on cyclization reactions will contribute to this understanding.

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Appendix A

To obtain the long-time behavior of the reaction rate, we note that the singularity closest to the origin in the Laplace transform

$$\tilde{R}(z) = \left[\frac{1}{\cosh^2 (z\tau)^{1/2}} + 2(z\tau)^{1/2} \int_0^1 \frac{\mathrm{d}x}{[x(2-x)]^{3/2}} \frac{\sinh [(z\tau)^{1/2}x]}{\cosh^3 [(z\tau)^{1/2}x]} \right]^{-1} \quad \text{(A.1)}$$

is a pole on the negative real z axis. Writing $z = -u^2/\tau$, we find that the pole is given by the equation

$$\frac{1}{\cos^2 u} = 2u \int_0^1 \frac{\mathrm{d}x}{[x(2-x)]^{3/2}} \frac{\sin (ux)}{\cos^3 (ux)} \quad \text{(A.2)}$$

which has the solution $u \simeq 0.946$. Thus, the pole is at $z \simeq 0.895/\tau$, leading to the result

$$R(t) = (0.895/\tau)e^{-0.895t/\tau} \quad \text{(A.3)}$$

Appendix B

The short-time behavior of the reaction rates can be obtained by an asymptotic expansion of $\tilde{S}(z)$ for large z. Thus

$$\frac{\tilde{S}(z)}{\psi_0(\vec{0})} \simeq \frac{1}{(4z\tau)^{1/4}} \int_0^{(z\tau)^{1/2}} \frac{\mathrm{d}x}{\left[x\left(1 - \frac{x}{2(z\tau)^{1/2}}\right)\right]^{3/2}} \frac{\sinh x}{\cosh^3 x} \simeq \frac{1}{(4z\tau)^{1/4}} \sum_{n=0}^{\infty} \frac{(2n+1)!!}{n!} \frac{F(n-3/2)}{(4(z\tau)^{1/2})^n} \quad \text{(B.1)}$$

where

$$F(u) = \int_0^\infty \mathrm{d}x\, x^u \frac{\sinh x}{\cosh^3 x} = \Gamma(1+u)2^{1-u}(1-2^{2-u})\zeta(u-1) = \frac{u(1-u)\pi^{u-1}}{2\sin\frac{\pi u}{2}}(2^{2-u}-1)\zeta(2-u) \quad \text{(B.2)}$$

Here, $\zeta(x)$ is the Riemann ζ-function and $\Gamma(x)$ is the Γ function. For the first two terms in the expansion, we note

$$F(-\tfrac{3}{2}) = \frac{30}{\pi^{5/2}}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^{7/2}} \simeq 1.76148 \quad \text{(B.3)}$$

$$F(-\tfrac{1}{2}) = \frac{3}{\pi^{3/2}}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^{5/2}} \simeq 0.59498 \quad \text{(B.4)}$$

Note also $La = Na^2 = N_0b^2$ so that

$$\left(\frac{3}{2\pi La}\right)^{3/2} = \psi_0(\vec{0}) \quad \text{(B.5)}$$

Writing out the first two terms explicitly, we have

$$\frac{\tilde{S}(z)}{\psi_0(\vec{0})} = F(-\tfrac{3}{2})(4z\tau)^{1-/4}\left[1 + \frac{3F(-\tfrac{1}{2})}{4F(-\tfrac{3}{2})}(z\tau)^{-1/2} + \mathcal{O}[(z\tau)^{-1}]\right] \quad \text{(B.6)}$$

$$\tilde{R}(z) = \frac{\psi_0(\vec{0})}{zS(z)} = \frac{2^{1/2}}{\tau}\frac{(z\tau)^{-3/4}}{F(-\tfrac{3}{2})}\left\{1 - \frac{3F(-\tfrac{1}{2})}{4F(-\tfrac{3}{2})}(z\tau)^{-1/2} + \mathcal{O}[(z\tau)^{-1}]\right\} \quad \text{(B.7)}$$

Taking the inverse transform, we obtain for $t \ll \tau$

$$\frac{S(t)}{\psi_0(\vec{0})} = \frac{F(-\tfrac{3}{2})}{2^{1/2}}\left\{\frac{1}{\Gamma(\tfrac{1}{4})}\left(\frac{t}{\tau}\right)^{-3/4} + \frac{3F(-\tfrac{1}{2})}{4F(-\tfrac{3}{2})}\frac{1}{\Gamma(\tfrac{3}{4})}\left(\frac{t}{\tau}\right)^{-1/4} + \mathcal{O}\left[\left(\frac{t}{\tau}\right)^{1/4}\right]\right\} \quad \text{(B.8)}$$

$$R(t) = \frac{2^{1/2}}{\tau}\frac{1}{F(-\tfrac{3}{2})}\left\{\frac{1}{\Gamma(\tfrac{3}{4})}\left(\frac{t}{\tau}\right)^{-1/4} - \frac{3F(-\tfrac{1}{2})}{4F(-\tfrac{3}{2})}\frac{1}{\Gamma(\tfrac{5}{4})}\left(\frac{t}{\tau}\right)^{1/4} + \mathcal{O}\left[\left(\frac{t}{\tau}\right)^{3/4}\right]\right\} \quad \text{(B.9)}$$

so that

$$k_{\mathrm{cyc}}(t) = \frac{R(t)}{1 - \int_0^1 \mathrm{d}t'\,R(t')} = \frac{2^{1/2}}{\tau}\frac{1}{F(-\tfrac{3}{2})\Gamma(\tfrac{3}{4})}\left(\frac{t}{\tau}\right)^{-1/4}\left\{1 - \frac{3\Gamma(\tfrac{3}{4})}{4\Gamma(\tfrac{5}{4})}\frac{F(-\tfrac{1}{2})}{F(-\tfrac{3}{2})}\left(\frac{t}{\tau}\right)^{1/2} + \frac{4}{3}\frac{2^{1/2}}{F(-\tfrac{3}{2})\Gamma(\tfrac{3}{4})}\left(\frac{t}{\tau}\right)^{3/4} + \mathcal{O}\left[\left(\frac{t}{\tau}\right)\right]\right\} \quad \text{(B.10)}$$

Substituting in numerical values, we obtain

$$\frac{S(t)}{\psi_0(\vec{0})} = 0.344\left(\frac{t}{\tau}\right)^{-3/4}\left[1 + 0.749\left(\frac{t}{\tau}\right)^{1/2} + \mathcal{O}\left(\frac{t}{\tau}\right)\right] \quad \text{(B.11)}$$

$$R(t) = \frac{0.655}{\tau}\left(\frac{t}{\tau}\right)^{-1/4}\left[1 - 0.343\left(\frac{t}{\tau}\right)^{1/2} + \mathcal{O}\left(\frac{t}{\tau}\right)\right] \quad \text{(B.12)}$$

and

$$k_{\mathrm{cyc}}(t) = \frac{0.655}{\tau}\left(\frac{t}{\tau}\right)^{-1/4}\left[1 - 0.343\left(\frac{t}{\tau}\right)^{1/2} + 0.874\left(\frac{t}{\tau}\right)^{3/4} + \mathcal{O}\left(\frac{t}{\tau}\right)\right] \quad \text{(B.13)}$$

References and Notes

(1) Cuniberti, C.; Perico, A. *Prog. Polym. Sci.*, in press.

(2) Winnik, M.; Redpath, A. E. C.; Richards, D. H. *Macromolecules* **1980**, *13*, 328.

(3) Ushiki, H.; Horie, K.; Okamoto, A.; Mita, I. *Polym. J.* **1981**, *13*, 191.

(4) Wilemski, G.; Fixman, M. *J. Chem. Phys.* **1973**, *58*, 4009; **1974**, *60*, 866, 878. Fixman, M. *J. Chem. Phys.* **1978**, *69*, 1527, 1538.

(5) Edwards, S. F. *Proc. Phys. Soc. London* **1967**, *92*, 9.

(6) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.

(7) Smith, B. A.; Samulski, E. T.; Yu, L.-P.; Winnik, M. A. *Phys. Rev. Lett.* **1984**, *52*, 45.

(8) Boué, F.; Nierlich, M.; Jannink, G.; Ball, R. *J. Phys. (Paris), Lett.* **1982**, *43*, L585, L593.

(9) Noolandi, J.; Hong, K. M. *J. Phys. (Paris), Lett.* **1984**, *45*, L149.

(10) Adam, M.; Delsanti, M. *J. Phys. (Paris)* **1983**, *44*, 1185.

(11) Wendel, H.; Noolandi, J. *Macromolecules* **1982**, *15*, 1318.

(12) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789, 1802, 1818; **1979**, *75*, 38.

(13) Curtiss, C. F.; Bird, R. B. *J. Chem. Phys.* **1981**, *74*, 2016, 2076.

(14) Bernard, D. A.; Noolandi, J. *Macromolecules* **1983**, *16*, 1358.

(15) Bernard, D. A.; Noolandi, J. *Phys. Rev. Lett.* **1983**, *50*, 253.

(16) de Gennes, P.-G. *J. Chem. Phys.* **1982**, *76*, 3316.

(17) Bernard, D. A.; Noolandi, J. *J. Math. Phys.* **1984**, *25*, 1619.

(18) Noolandi, J.; Desai, R. C. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 453.

(19) Graessley, W. *Adv. Polym. Sci.* **1982**, *47*, 67.

(20) Viovy, J. L.; Monnerie, L.; Tassin, J. F. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 2427.