

## Flow effects in the polymer cyclization reaction

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### SUMMARY:

We investigate the effect of shear and uniaxial extensional flows on the rate of the cyclization reaction in polymers. We find that for such an *intramolecular* diffusion-controlled reaction the flow always reduces the reaction rate, in contrast to the previously studied case of *intermolecular* reactions, where linear flows enhance the reaction rate.

### Introduction

Diffusion-controlled reactions in polymeric systems have attracted considerable interest in recent years due to their importance in a variety of technologically relevant processes including: free radical termination reactions, reactive blending, and irreversible adsorption of macromolecules during liquid-phase separations. Subsequent to the pioneering work of Wilemski and Fixman<sup>1)</sup>, a number of theoretical studies have appeared that address both intramolecular<sup>2)</sup> and intermolecular<sup>3)</sup> diffusion-controlled reactions. The current status of theory and experiment in this field has been surveyed by Friedman and O'Shaughnessy<sup>4)</sup>.

The influence of *convection* on the rates of polymeric diffusion-controlled reactions has only very recently been investigated<sup>5)</sup>. Since many polymerization and process steps are carried out with stirring or continuous flow, an understanding of how reaction rates can be affected is of considerable interest. Moreover, if the aggregation equilibria of functional groups in associating polymers is viewed as a type of *reversible* chemical reaction, the rheology of associating polymers might be addressed by a theory of reversible diffusion-controlled reactions under flow. It is currently believed that the unusual nonlinear rheology of associating polymers is due to changes in the populations of intermolecular and intramolecular aggregates with flow rate<sup>6)</sup>. In particular, shear (or extensional) flows are thought to decrease the number of intramolecular associations and to increase the population of intermolecular contacts. Unfortunately, no comprehensive theoretical framework currently exists to assess these effects. Recently, however, Fredrickson and Leibler<sup>5)</sup> examined the effect of linear flows on the rate coefficient for *irreversible intermolecular* coupling reactions in polymer melts. Convective transport of reactive groups was found to dramatically enhance the reaction rate, regardless of flow type, and interesting nonanalytic dependences on flow rate were obtained.

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In the present paper, we extend the Fredrickson-Leibler analysis to a model *irreversible intramolecular* reaction under flow; namely, the polymer cyclization reaction. Previous theoretical work on this problem under quiescent conditions was carried out by Doi<sup>2)</sup> and Friedman and O’Shaughnessy<sup>4)</sup>. A comprehensive review of the experimental situation was presented by Winnik<sup>7)</sup>. Because our principal objective is to examine the role of convection on the rate of a model intramolecular reaction, we ignore complicating effects associated with excluded volume and hydrodynamic interactions, which are important for experiments carried out in solution<sup>8)</sup>. Instead, we focus on the Rouse model of chain dynamics, so our results are most applicable to relatively low molecular weight end-functionalized chains dispersed in a melt of unfunctionalized, but otherwise identical, chains. For simplicity, we also assume that the cyclization reaction occurs instantaneously and irreversibly when the two functionalized ends of a reactive polymer approach to within a “capture radius”  $a$  of each other. Generalizations to relax these assumptions are straightforward, but will not be considered here. The capture radius  $a$  is further assumed to be a microscopic length of order of a monomer size and is taken to be negligible compared with the chain radius-of-gyration.

Our primary focus in the present paper is on the long time decay rate of the concentration of unreacted chains  $\rho(t)$  in a melt of polymers undergoing cyclization reactions and subjected to a steady, linear flow. At times exceeding the longest Rouse time  $\tau_R$ , we shall see that this concentration satisfies the first order kinetic equation

$$\frac{d\rho}{dt} = -k\rho \quad (1)$$

where  $k$  is the cyclization rate constant. Subsequent sections will examine how  $k$  depends on the strength and type (shear versus extension) of linear flow applied.

### Cyclization dynamics

In this section we review a formalism for studying irreversible diffusion-controlled reactions in polymer systems. This formalism was originally introduced by de Gennes<sup>3)</sup> to treat intermolecular reactions and was extended by Fredrickson and Leibler<sup>5)</sup> to account for flow effects. Here we extend it to an intramolecular reaction carried out under flow. In addition to the assumptions made above, we take the molten polymer system to be monodisperse and dilute in chains capable of cyclization. Since the two reactive sites on such a chain are located at the extremities, all the relevant information regarding the reaction rate can be deduced from a pair distribution function  $\psi(\mathbf{u}; t)$ , namely, the probability density that the end-to-end vector of an unreacted chain is given by  $\mathbf{u}$  at time  $t$ .

The underlying dynamics of the population of reactive chains is described by the following generalized reaction-diffusion equation:

$$L\psi = -Q\psi \quad (2)$$

where  $L$  is a non-local differential operator governing the spatial and temporal evolution of  $\psi$  under both diffusion and convection. The sink operator  $Q$  describes the loss of probability density caused by reaction of the sites attached at the ends of the chain.

Although explicit forms are available for the operator  $L$ , it proves more convenient to invert Eq. (2) into its corresponding integral form<sup>3,5)</sup>:

$$\psi(\mathbf{u}, t) = \psi_{ss}(\mathbf{u}) - \int_0^t d\tau \int d\mathbf{u}_0 G(\mathbf{u}, \mathbf{u}_0, t - \tau) Q(\mathbf{u}_0) \psi(\mathbf{u}_0, \tau) \quad (3)$$

where  $\psi_{ss}(\mathbf{u})$  is the steady state distribution of the end-to-end vector in the absence of reaction. (We assume that the system is at steady state under flow prior to  $t = 0$ , at which point the reaction is turned on.) The time-dependent Green function  $G(\mathbf{u}, \mathbf{u}_0, t - \tau)$  (or propagator) describes the conditional probability (in the absence of reaction) that a chain has an end-to-end vector  $\mathbf{u}$  at time  $t$ , given that the value of the end-to-end vector was  $\mathbf{u}_0$  at time  $t = 0$ . Eq. (3) thus simply states that the density of chain configurations with end-to-end vector  $\mathbf{u}$  and at a time  $t$  after initiating the flow and reaction, is the equilibrium density, deprived of those configurations that connected or diffused at any time between  $t = 0$  and  $t$  from within the range of the reaction sink, i. e. separation  $\mathbf{u}_0$ , to the current separation  $\mathbf{u}$ .

A convenient form that can be ascribed to the reaction operator is the delta function  $Q(\mathbf{u}) = q\delta(\mathbf{u})$ , where the sink strength  $q$  is the product of the capture volume with a microscopic capture rate. In the limit of very fast capture rates (instantaneous reaction on contact, i. e.,  $q \rightarrow \infty$ ) the reaction rate constant  $k$  proves independent of  $q$ . Thus, we find that the cyclization rate is, as in other diffusion-controlled reactions of polymers<sup>3)</sup>, rather insensitive to the local chemical details of the reaction.

Applying this sink model to Eq. (3) leads to the following equation for the fraction of unreacted chains:

$$\begin{aligned} -d\rho(t)/dt &= \int d\mathbf{u} Q(\mathbf{u})\psi(\mathbf{u}; t) = q\psi(\mathbf{0}, t) \\ &= q\psi_{ss}(\mathbf{0}) - q^2 \int_0^t d\tau G(\mathbf{0}, \mathbf{0}, t - \tau)\psi(\mathbf{0}, \tau) \end{aligned} \quad (4)$$

The quantity  $G(\mathbf{0}, \mathbf{0}; t) \equiv G(t)$  in the above equation is the “memory function” for this problem, describing the conditional probability of observing a closed, ring-like configuration at time  $t$ , given that the chain was in such a closed configuration at time  $t = 0$ . Note that  $G(t)$  is computed in the *presence* of flow, but in the absence of reaction. Eq. (4) can be solved by Laplace transformation (taking  $\rho(0) = 1$  for simplicity):

$$1 - s\tilde{\rho}(s) = \frac{q\psi_{ss}(\mathbf{0})}{s(1 + q\tilde{G}(s))} \quad (5)$$

where we denote Laplace transformed quantities by a tilde. It is also now convenient to take the limit of instantaneous reaction,  $q \rightarrow \infty$ , yielding:

$$1 - s\tilde{p}(s) = \frac{\psi_{ss}(0)}{s\tilde{G}(s)} \quad (6)$$

For times much longer than the longest Rouse relaxation time<sup>9)</sup>  $\tau_R \equiv \tau_1$ , the memory function  $G(t)$  approaches the steady state distribution  $\psi_{ss}(0)$ . Thus, information about the relevant relaxation processes under flow is contained in the function  $h(t) = G(t)/\psi_{ss}(0) - 1$ . Reexpressing Eq. (6) in terms of the Laplace transform of  $h(t)$  gives

$$\tilde{p}(s) = \frac{\tilde{h}(s)}{1 + s\tilde{h}(s)} \quad (7)$$

The analytic structure of the function  $\tilde{h}(s)$  can be quite complex, indicating that the time evolution of the unreacted chain fraction does not satisfy the simple first-order Eq. (1) at short times. However, as discussed by Doi<sup>2)</sup>, the long-time rate constant  $k$  is obtained by finding the pole of Eq. (7) closest to the origin along the negative real  $s$  axis. This leads to the following equation for  $k$ :

$$1 - k\tilde{h}(-k) = 0 \quad (8)$$

where the smallest positive real root corresponds to the long-time rate constant.

### Memory function for the cyclization reaction

The Green function for the end-to-end-vector distribution under a steady, linear, and incompressible flow is the conditional probability that an end-to-end vector  $\mathbf{u}_0$  at  $t = 0$  transforms to the vector  $\mathbf{u}$  after a time  $t$ . It is convenient to calculate this function as the ratio of the joint probability density  $P(\mathbf{u}, \mathbf{u}_0; t) = \langle \delta[\mathbf{u} - \mathbf{U}(t)]\delta[\mathbf{u}_0 - \mathbf{U}(0)] \rangle$  ( $\mathbf{U}$  is the microscopic end-to-end vector) and the stationary distribution of the end-to-end-vector  $\psi_{ss}(\mathbf{u}_0)$ . The joint distribution can be written quite generally as a 2-dimensional Gaussian distribution:

$$P(\mathbf{u}, \mathbf{u}_0; t) = \frac{1}{(2\pi)^3 [\det(\mathbf{M})]^{1/2}} \cdot \exp\left[-\frac{1}{2} (\mathbf{u} \ \mathbf{u}_0) \mathbf{M}^{-1} \begin{pmatrix} \mathbf{u} \\ \mathbf{u}_0 \end{pmatrix}\right] \quad (9)$$

where the matrix  $\mathbf{M}$  can be expressed in block form in terms of equal-time correlations,  $B_{ij} = \langle U_i(0)U_j(0) \rangle$ , and time-dependent correlations,  $C_{ij}(t) = \langle U_i(t)U_j(0) \rangle$ :

$$\mathbf{M} = \begin{pmatrix} \mathbf{B} & \mathbf{C} \\ \mathbf{C}^T & \mathbf{B} \end{pmatrix} \quad (10)$$

The stationary distribution is simply given as

$$\psi_{ss}(\mathbf{u}_0) = \frac{1}{(2\pi)^{3/2} \sqrt{\det(\mathbf{B})}} \exp\left[-\frac{1}{2} \mathbf{u}_0^T \mathbf{B}^{-1} \mathbf{u}_0\right] \quad (11)$$

Next, we turn to evaluate the matrices  $\mathbf{B}$  and  $\mathbf{C}$ . The end-to-end vector in the Rouse model can be expressed in terms of Rouse modes,  $\{\mathbf{X}_p\}$ , by the formula<sup>\*)</sup>  $\mathbf{u}(t) = -4 \sum_{p, \text{odd}} \mathbf{X}_p(t)$ . The Rouse normal modes satisfy decoupled equations<sup>9)</sup>, facilitating the calculation of the correlation matrices. In particular,

$$\mathbf{B} = 16 \sum_{p, \text{odd}} \mathbf{C}_p \quad (12)$$

where  $\mathbf{C}_p \equiv \langle \mathbf{X}_p(0) \mathbf{X}_p(0) \rangle$  is the equilibrium equal-time correlation matrix of the  $p$ th Rouse mode<sup>9)</sup>:

$$\mathbf{C}_p = \frac{k_B T}{k_p} \mathbf{I} + \frac{1}{2} \tau_p \mathbf{F} \mathbf{C}_p + \frac{1}{2} \tau_p \mathbf{C}_p \mathbf{F}^T \quad (13)$$

In this expression,  $k_p$  denotes the  $p$ th spring constant and  $\tau_p = \zeta_p/k_p$  is the  $p$ th internal relaxation time of a Rouse polymer. The unit tensor is denoted by  $\mathbf{I}$  and  $\zeta_p$  is the friction coefficient of the  $p$ th mode. Finally,  $\mathbf{F}$  is the transpose of the uniform velocity gradient tensor, which enters the linear expression of the velocity field,  $\mathbf{v}(\mathbf{r}) = \mathbf{F}\mathbf{r}$ .

Using the Rouse Langevin equation, it is straightforward to show that the time-dependent correlation matrix is given by

$$\mathbf{C}(t) = 16 e^{\mathbf{F}t} \sum_{p, \text{odd}} e^{-t/\tau_p} \mathbf{C}_p \quad (14)$$

Next, we form the Green function as the ratio of joint probability  $P$  to the stationary distribution  $\psi_{ss}$ :

$$G(\mathbf{u}, \mathbf{u}_0; t) = P(\mathbf{u}, \mathbf{u}_0; t) / \psi_{ss}(\mathbf{u}_0) \quad (15)$$

Finally, the memory function  $G(t)$  is obtained by setting  $\mathbf{u} = \mathbf{u}_0 = \mathbf{0}$ :

$$G(t) = G(\mathbf{0}, \mathbf{0}; t) = \frac{\sqrt{\det(\mathbf{B})}}{(2\pi)^{3/2} \sqrt{\det(\mathbf{M})}} \quad (16)$$

and

$$h(t) = \frac{\det(\mathbf{B})}{\sqrt{\det(\mathbf{M})}} - 1 \quad (17)$$

<sup>\*)</sup> We employ the Rouse model notations of Doi and Edwards<sup>9)</sup>, throughout.

## Applications

### Quiescent conditions

As a first application of our formalisms, we reproduce the well-known theoretical results for the cyclization rate in the absence of flow<sup>1,2)</sup>. Without flow, the correlation matrices  $\mathbf{B}$  and  $\mathbf{C}$  are diagonal and the Green function is easily constructed:

$$G(\mathbf{u}; \mathbf{u}_0; t) = \left[ \frac{3}{2\pi Nb^2} \right]^{3/2} \left[ \frac{1}{1 - \kappa^2(t)} \right]^{3/2} \cdot \exp \left[ \frac{-3[\mathbf{u} - \kappa(t)\mathbf{u}_0]^2}{2Nb^2(1 - \kappa^2(t))} \right] \quad (18)$$

where  $\kappa(t) = \frac{8}{\pi^2} \sum_{p, \text{odd}} e^{-p^2 t} / p^2$  and  $Nb^2/6$  is the mean-squared radius-of-gyration of the Rouse chain. The function  $h(t)$  is then given as

$$h(t) = \left[ \frac{1}{1 - \kappa^2(t)} \right]^{3/2} - 1 \quad (19)$$

Solving Eq. (8) with this expression for  $h(t)$  immediately recovers the quiescent result,  $k = 0.46/\tau_R$ , of the papers of Wilemski and Fixman<sup>1)</sup> and Doi<sup>2)</sup>. Here, we use  $\tau_R$  to denote the longest Rouse time  $\tau_1 \sim N^2$ .

### Shear flow

Next, we consider the application of a simple shear flow characterized by the (transposed) uniform velocity gradient tensor

$$\mathbf{\Gamma} = \dot{\gamma} \mathbf{E} = \dot{\gamma} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (20)$$

where  $\dot{\gamma}$  is the shear rate and  $\mathbf{E}$  is a dimensionless tensor expressing the type of flow. At this point, it is convenient to introduce a dimensionless time  $\tilde{t} = t/\tau_R$  and a *Deborah number* based on the longest Rouse relaxation time:

$$\text{De} = \dot{\gamma} \tau_R \quad (21)$$

For notational simplicity in the following, we will drop the tilde's and not distinguish between  $t$  and  $\tilde{t}$ . At the end of the calculation, however, dimensional units will be restored for the rate coefficient  $k$ .

Our first step is to solve Eq. (13) for  $\mathbf{C}_p$  under steady shear conditions and insert the resulting matrix into the formula for  $\mathbf{B}$ . Explicitly performing the resulting sums over  $p$  yields:

$$\mathbf{B} = \frac{Nb^2}{3} \begin{pmatrix} 1 + \frac{\pi^4}{240} \text{De}^2 & \frac{\pi^4}{24} \text{De} & 0 \\ \frac{\pi^4}{24} \text{De} & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (22)$$

The  $C$  matrix is similarly evaluated by substituting the expression for  $C_p$  into Eq. (14):

$$C(t) = \frac{Nb^2}{3} e^{\text{De}Et} \begin{pmatrix} \kappa(t) + \kappa_3(t)\text{De}^2 & \kappa_2(t)\text{De} & 0 \\ \kappa_2(t)\text{De} & \kappa(t) & 0 \\ 0 & 0 & \kappa(t) \end{pmatrix} \quad (23)$$

where  $\kappa_2(t)$  and  $\kappa_3(t)$  are time-dependent functions defined by the following expressions:

$$\kappa_2(t) = \frac{4}{\pi^2} \sum_{p, \text{odd}} e^{-p^2 t} / p^4 \quad (24)$$

$$\kappa_3(t) = \frac{4}{\pi^2} \sum_{p, \text{odd}} e^{-p^2 t} / p^6 \quad (25)$$

### Weak shear flow

Here we examine the first flow correction for weak shear flows ( $\text{De} \ll 1$ ). First, we develop the functions appearing in Eq. (23) in asymptotic series for  $t \ll 1$ :

$$\kappa(t) = 1 - \frac{4}{\pi^{3/2}} \sqrt{t} + \dots$$

$$\kappa_2(t) = \frac{\pi^2}{24} - \frac{t}{2} + \frac{4t^{3/2}}{3\pi^{3/2}} \dots$$

$$\kappa_3(t) = \frac{\pi^2}{240} - \frac{\pi^2 t}{24} + \frac{t^2}{4} \dots$$

Substitution of these expressions into Eq. (17) leads to the following asymptotic form of  $h(t)$  for  $t \ll 1$ :

$$h_{\text{short}}(t) \approx \frac{\pi^{9/4}}{\sqrt{512}} t^{-3/4} \left( 1 + \frac{7\pi^4}{5760} \text{De}^2 \right) \quad (26)$$

In contrast, at long times, i. e.,  $t \gg 1$ , only the terms corresponding to the longest relaxation times survive in the  $p$ -sums. Thus, to leading order, we can invoke the approximations:  $\kappa_2(t) \approx \kappa_3(t) \approx \kappa(t)/2 \approx 4/(\pi^2 e^{-t})$ . This produces the following expression for the  $t \gg 1$  behavior of  $h(t)$ :

$$h_{\text{long}}(t) \approx \frac{96}{\pi^4} e^{-2t} \left[ 1 + \left[ \frac{720 - 80\pi^2 + \pi^4}{1440} + \frac{12 - \pi^2}{18} t + \frac{1}{3} t^2 \right] \text{De}^2 \right] \quad (27)$$

Next, we construct a uniform approximation for  $h(t)$  by superimposing the two asymptotic forms (Eqs. (26) and (27)):

$$h(t) \approx h_{\text{long}}(t) + h_{\text{short}}(t)e^{-4t} \quad (28)$$

where the factor  $e^{-4t}$  serves to damp the second term at long times and also to bound the error made by the approximation to less than 5% over the entire time interval. Finally, using the above approximation for  $h(t)$  in Eq. (8) yields the following numerical results for the first flow correction to the reaction rate ( $De \ll 1$ ):

$$k \approx \frac{0.46}{\tau_R} (1 - 0.18De^2) \quad (29)$$

### Strong shear flow

Next, we turn to consider strong shear flows characterized by  $De \gg 1$ . We follow an approach similar to that in the previous section, developing separate asymptotic expressions for short,  $t \ll 1$ , and long,  $t \gg 1$ , times. For  $De \gg 1$  and  $t \ll 1$  we find:

$$\det(\mathbf{M}) \approx De^2 \frac{56}{45\pi^{1/2}} t^{3/2} + De^4 \frac{\pi}{90} t^3 \quad (30)$$

and from Eq. (22),  $\det(\mathbf{B}) \approx 7\pi^4/(2880 De^2)$ . Comparison of the two terms in Eq. (30) leads to the identification of a characteristic timescale,  $\tau_e \sim De^{-4/3} \ll 1$ . This timescale sets a threshold, below which the highest frequency Rouse modes are unperturbed by the flow.

At times greatly exceeding the longest Rouse time, i.e.,  $t \gg 1$ ,  $h(t)$  is asymptotically independent of the Deborah number and scales like

$$h_{\text{long}}(t) \approx t^2 e^{-2t} \quad (31)$$

However, as will be argued shortly, this time regime proves irrelevant to the strong shear behavior of the rate coefficient.

A considerable simplification arises in solving Eq. (8) for  $De \rightarrow \infty$ . Because it will be shown that  $k$  vanishes like  $De^{-2/3}$  in this limit, the equation can be expanded about  $s = -k = 0$ , yielding the relation  $k \approx 1/\tilde{h}(0) = 1/\int_0^\infty h(t)dt$ . This ‘‘Kubo-like’’ integral, however, is dominated by times of order  $\tau_e \ll 1$ , which is easily verified by substitution of Eq. (30) into Eq. (17) and then performing the Kubo integral. Finally, we rescale the time in the integral by  $\tau_e$ , which immediately gives the strong shear result

$$\begin{aligned} k &\approx \frac{1920\sqrt{2}}{\sqrt{5}\pi^4 14^{2/3} c_1} \frac{1}{\tau_R} De^{2/3} \\ &\approx \frac{0.38}{\tau_R} De^{-2/3} \end{aligned} \quad (32)$$

where  $c_1 = \int_0^\infty dx/\sqrt{x^{3/2} + x^3} = 5.609$ . The shear rate and molecular weight dependence implied by this formula is  $k \sim \dot{\gamma}^{2/3} N^{-10/3}$ .



In Fig. 1, we show numerical results for the full shear rate dependence of the cyclization rate constant  $k$ . Expressed as a dimensionless log-log plot of  $k\tau_R$  versus  $De$ , it is evident that the crossover behavior between the weak and strong flow expressions developed above is smooth and monotonic. The asymptotic strong flow formula is seen to be accurate for  $De \geq 5$ .

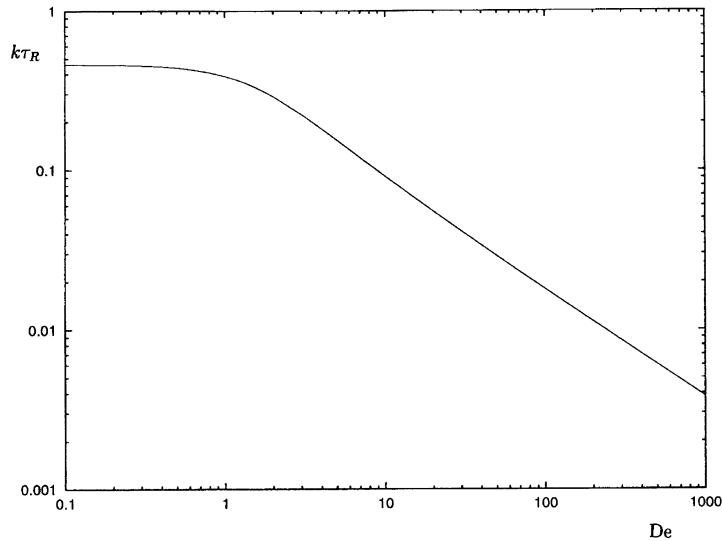


Fig. 1. The reaction rate  $k\tau_R$  plotted against the Deborah number for the case of simple shear. For strong flows, the  $De^{-2/3}$  scaling is evident

#### Extensional flow

In the present section we turn to consider a uniaxial extensional flow characterized by a uniform (transposed) velocity gradient tensor

$$\mathbf{\Gamma} = \dot{\gamma} \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (33)$$

where  $\dot{\gamma}$  is now the extension rate (along the  $z$ -axis) and the matrix on the right hand side is the corresponding form of  $\mathbf{E}$ .

Again, the first step is to solve the matrix equation (13) for this form of  $\mathbf{\Gamma}$  and then use the result to deduce expressions for  $\mathbf{B}$  and  $\mathbf{C}(t)$ . We find

$$\mathbf{B} = \frac{Nb^2}{3} \begin{pmatrix} f(De/2) & 0 & 0 \\ 0 & f(De/2) & 0 \\ 0 & 0 & f(-De) \end{pmatrix} \quad (34)$$

where the function  $f(a)$  is defined by  $f(a) = \frac{8}{\pi^2} \sum_{p, \text{ odd}} 1/(p^2 + a)$  and

$$\mathbf{C}(t) = \frac{Nb^2}{3} e^{\text{De}Et} \begin{pmatrix} g(t, \text{De}/2) & 0 & 0 \\ 0 & g(t, \text{De}/2) & 0 \\ 0 & 0 & g(t, -\text{De}) \end{pmatrix} \quad (35)$$

with  $g(t, a) \equiv \frac{8}{\pi^2} \sum_{p, \text{odd}} e^{-p^2 t} / (p^2 + a)$ . These diagonal forms yield the following expression for the function  $h(t)$

$$h(t) = \frac{1}{(1 - \kappa^2(t, \text{De}/2))(1 - \kappa^2(t, -\text{De}))^{1/2}} - 1 \quad (36)$$

where  $\kappa(t, a) \equiv e^{-at} g(t, a) / f(a)$ .

In the following, we will investigate the extension rate dependence of  $k$  only in the weak flow limit,  $\text{De} \ll 1$ , because of the well-known unbounded stretching instability of the Rouse model under strong extensional flows<sup>10</sup>. We begin by calculating the short-time behavior of  $g(t, a)$ :

$$g(t, a) / f(a) = 1 - \frac{4}{\pi^{3/2} f(a)} t^{1/2} + at + \dots \quad (37)$$

where  $a$  will be replaced by either  $\text{De}/2$  or  $-\text{De}$ . Moreover, the series defining the function  $f(a)$  can be exactly summed<sup>11</sup>:

$$f(a) = \begin{cases} \pi [\cosh(\sqrt{a}\pi) - 1] / [2\sqrt{a} \sinh(\sqrt{a}\pi)] & \text{for } a > 0 \\ \pi [1 - \cos(\sqrt{-a}\pi)] / [2\sqrt{-a} \sinh(\sqrt{-a}\pi)] & \text{for } a < 0 \end{cases} \quad (38)$$

This leads directly to the behavior of  $h(t)$  for  $t \ll 1$  and  $\text{De} \ll 1$ :

$$h_{\text{short}}(t) \approx \frac{\pi^{9/4}}{\sqrt{512}} t^{-3/4} \left[ 1 + \frac{7\pi^4}{1920} \text{De}^2 \right] \quad (39)$$

In the limit of  $t \gg 1$ , again only the slowest relaxation modes survive and we find an exponential decay of  $h(t)$ :

$$h_{\text{long}}(t) \approx \frac{64}{\pi^4} \left[ \frac{e^{-2(1-\text{De})t}}{2(1-\text{De})^2 f^2(-\text{De})} + \frac{e^{-(2+\text{De})t}}{(1+\text{De}/2)^2 f^2(\text{De}/2)} \right] \quad (40)$$

We again superimpose both asymptotic results to obtain an approximate expression homogeneous in time and for  $\text{De} \ll 1$ :

$$h(t) \approx h_{\text{long}}(t) + h_{\text{small}}(t) e^{-4t} \quad (41)$$

As before, this approximation proves accurate to within 5% over the entire range of  $t$ . Employing this formula to numerically extract the first weak extensional flow correction to  $k$ , we obtain

$$k \approx \frac{0.46}{\tau_R} (1 - 0.76 \text{De}^2) \quad (42)$$

It is interesting to note that this first correction is of the same sign as that derived for shear [cf. Eq. (29)], i.e. flow *slows* the rate of cyclization, but the numerical coefficient is larger, indicating that extensional flow is more effective than shear flow at suppressing the cyclization rate. This is evidently due to the larger steady state deformation of the coil (and hence, end-to-end vector) in an extensional flow.

In Fig. 2, we show the dependence of the cyclization rate constant on the extensional flow strength over the Deborah number range  $De \in [0, 1]$ . These numerical results, obtained by using the exact form of  $h(t)$  given in Eq. (36), can be accurately described by a cubic polynomial in  $De$  given in the Figure caption.

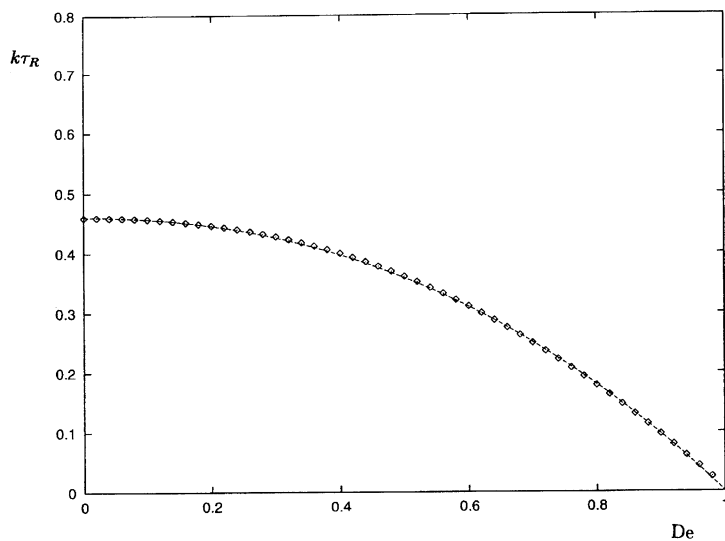


Fig. 2. The numerically calculated reaction rate coefficient  $k\tau_R$  plotted against the Deborah number for the uniaxial extensional flow represented by the points. The solid curve is a fit of the numerical results with a third order polynomial. The best fit gives  $0.46 - 0.31 De^2 - 0.11 De^3$

## Discussion

In the present paper we have considered a simple model of an irreversible, intramolecular diffusion-controlled reaction, subjected to an external linear flow. Unlike intermolecular reactions, where convective transport was shown to enhance the reaction rate<sup>5)</sup>, we find that the coil stretching produced by both shear and extensional flows slows the rate of the cyclization reaction. Although this reduction can be rationalized as the consequence of chain stretching under flow, it also shows that for this particular geometry the classical convection enhancement at work in intermolecular reactions is superseded here by the stretching of the chains. Besides this feature, there are other significant qualitative differences between intermolecular and intramolecular reactions under flow. For example, in the present paper we found that the first correction to the cyclization rate coefficient for weak flows was found to be

$O(De^2)$ . In contrast, the first flow correction in the case of irreversible intermolecular reactions is much stronger and nonanalytic<sup>5)</sup> and  $O(De^{1/2})$ . Moreover, for strong shear flows,  $De \gg 1$ , the asymptotic cyclization rate is  $O(De^{-2/3})$ , while the intermolecular reaction rate is  $O(De^{1/3})$ .

An important direction for future research would be to generalize these results and the theoretical approach to situations in which the reactions are reversible, as in associating polymers and other self-assembling systems under flow. Such a formalism would provide a microscopic basis for unraveling the complex nonlinear rheology of these poorly understood fluids.

Another important extension of the present formalism would be to introduce excluded volume and hydrodynamic interactions into the cyclization model. As demonstrated by Friedman and O'Shaughnessy<sup>8)</sup>, such factors are critical in developing a quantitative description of the cyclization reaction in dilute solution and in the absence of flow. With convection present, excluded volume and hydrodynamic interactions may contribute in a qualitatively different fashion than in the quiescent state.

Finally, we note that extensions to other model systems, such as telechelics, where both intermolecular and intramolecular reactions are possible, would provide insights into the effect of flow on the competition between the two types of reactions. Overall, much remains to be explored in this fascinating area of nonequilibrium science.

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