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Diffusion-limited polymerization of rigid rodlike molecules: Semidilute solutions

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The rotational diffusivity and the translational diffusivity perpendicular to the rod axis of rigid rodlike (RRL) molecules decreases rapidly with increasing molecular length, during polymerization in semidilute solutions. This can result in slowing of step-growth polymerizations of RRL molecules with reactive groups at the rod ends and a near-collinearity requirement for reaction. Here a theoretical analysis of the rate of RRL polymerization in semidilute solutions, based on Smoluchowski's approach, and incorporating the rotational and anisotropic translational diffusion of the molecules is presented. The work is an extension of our analysis of polymerization in dilute solutions in which the translational diffusion was assumed to be isotropic [J. Chem. Phys. **96**, 7125 (1992)]. The effective second order rate constant for the system is obtained for different parameter values using a numerical finite element method. With reduction in rotational diffusivity, for a fixed translational diffusivity, the effective reaction rate constant is found to decrease to a limiting value determined by only the translational flux of the correctly oriented molecules. Similarly, for a given rotational diffusivity, with reduction in translational diffusivity perpendicular to the rod axis, the reaction rate constant is found to decrease to a limiting value determined by the flux only due to translational diffusion parallel to the rod axis, aided by rotational diffusion. An asymptotic analysis for this case is presented. For low rotational diffusivities, reduction in the translational diffusion perpendicular to the rod axis results in a significant decrease in the effective rate constant, even for reactions with relatively slow intrinsic kinetics. A qualitative comparison of the theoretical predictions with experimental results is presented.

I. INTRODUCTION

Chemical reaction between two reacting species in solution is preceded by their translation to within a critical separation, and their rotation to a suitable relative orientation. In case of fast chemical reactions between molecules of anisotropic reactivity, such as polymerization of rigid rodlike (RRL) molecules, the overall reaction rate may be limited by translational and rotational diffusion. In a recent publication¹ we have analyzed the effect of rototranslational diffusion limitations for reactions between rodlike molecules with reactive sites at the rod ends and with a near-collinearity criterion for reaction. We found that if the intrinsic chemical reaction is sufficiently rapid, then very slow rotational diffusion at late stages of polymerization results in reduction of the effective reaction rate constant. In the analysis we assumed the translational diffusion of the molecules to be isotropic. However, this assumption becomes invalid as the molecular length (L) increases during polymerization and the dimensionless number concentration defined as $\nu = CL^3$ (C being the number concentration of rods) becomes large enough for the solution to enter the semidilute regime ($\nu \gg \nu^*$, $\nu^* \sim 40$). In semidilute solutions the diffusion of the RRL molecules becomes prominently anisotropic, with diffusivity perpen-

dicular to rod axis approaching zero because of the restriction on rod movement imposed by the neighboring rods.^{2,3} Thus the overall reaction may become diffusion controlled even for reactions which are intrinsically not very rapid.

The primary effect of the diffusional limitations on the polymerization process is that the effective reaction rate constant becomes dependent on the lengths of the reacting oligomers.¹ Consequently, the molecular weight distribution obtained differs considerably from the Flory distribution for step-growth polymerization obtained for an irreversible reaction,⁴ i.e., when the condensation product is not available for reaction. The precise dependence of the effective rate constant on the lengths of the reacting rods would be useful for the prediction of the molecular weight distribution for such polymerizations. In this work we obtain the rate constant for the step-growth polymerization of equal sized rigid rodlike molecules in a homogeneous semidilute solution. We follow Smoluchowski's approach as in Ref. 1, however, the translational diffusivity of the rods is taken to be anisotropic in this case.

In Sec. II, we briefly give the mathematical formulation of the problem. In Sec. III, we present the simplifications of the governing equations. The formulation for numerical solution using the finite element method (FEM) is presented in Sec. IV. An asymptotic analysis in the limit of severe orientational constraints for reaction, and vanishing perpendicular translation diffusivity is presented in Sec. V. The results are presented in Sec. VI and conclusions are summarized in Sec. VII.

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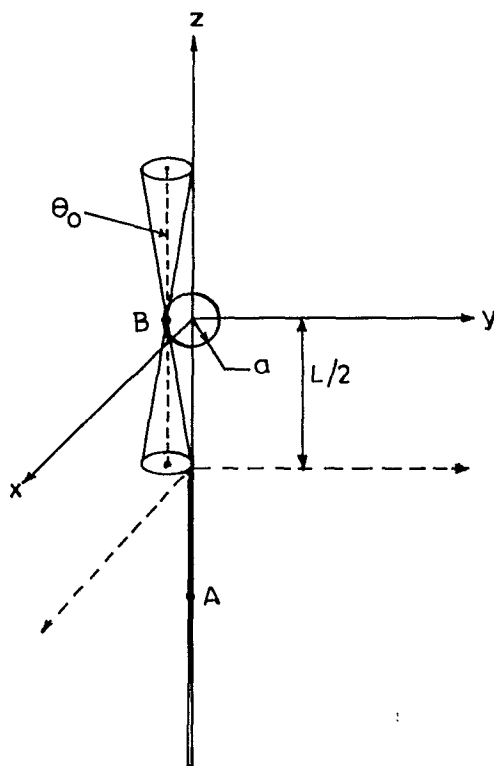


FIG. 1. Schematic of simplified reaction criteria (Ref. 1). The center of diffusing molecule B must approach the spherical (radius a) reaction zone at the origin of coordinate system, and Θ must be less than or equal to Θ_0 .

II. MODEL FOR DIFFUSION-LIMITED REACTIONS OF RODLIKE MOLECULES

We follow Smoluchowski's⁵ approach to calculate the flux of reactive ends of appropriately oriented rodlike molecules (B) to the reactive "sink" at the tip of an isolated stationary molecule (A) (Fig. 1). The coordinate system has its origin fixed at a distance $L/2$ along the z axis from the reactive tip of the molecule A , and \mathbf{r} is the position of the center of mass of any diffusing molecule B . The relative orientation of the RRL molecule B is defined by a unit vector (\mathbf{u}) along its molecular axis.

The diffusion equation for the molecules in the absence of an interaction potential between the molecules is^{2,3}

$$\frac{\partial C}{\partial t} = \mathcal{L}_r C + \mathcal{L}_u C, \quad (2.1)$$

where C is the number density of the molecules and

$$\mathcal{L}_r = [D_{r\parallel} \mathcal{F}_{r\parallel}^2 + D_{r\perp} (\mathcal{F}_r^2 - \mathcal{F}_{r\parallel}^2)], \quad (2.2a)$$

$$\mathcal{L}_u = D_r \frac{\partial^2}{\partial u^2}, \quad (2.2b)$$

$$\mathcal{F}_r = \frac{\partial}{\partial \mathbf{r}}, \quad (2.2c)$$

$$\mathcal{F}_{r\parallel} = \mathbf{u}(\mathbf{u} \cdot \mathcal{F}_r), \quad (2.2d)$$

The first term on the right-hand side of Eq. (2.1) represents the components of the translational diffusive flux along the rod or perpendicular to it, and the second term represents the rotational diffusive flux.

For dilute solutions ($\nu \ll \nu^*$), the diffusivities are given by^{2,3}

$$D_{r0\parallel} = k_B T \ln(L/d) / 2\pi\eta_s L, \quad (2.3a)$$

$$D_{r0\perp} = D_{r0\parallel} / 2, \quad (2.3b)$$

$$D_{r0} = 6D_{r0\parallel} / L^2, \quad (2.3c)$$

where η_s is the solvent viscosity, k_B is the Boltzmann constant, and T is the temperature. In semidilute solutions ($\nu > \nu^*$) the translational diffusion parallel to the rod axis remains unhindered, and

$$D_{r\parallel} = D_{r0\parallel}. \quad (2.4a)$$

However, the rotational diffusion, and the translational diffusion of the rod perpendicular to the rod axis, are severely restricted by the surrounding molecules to a tube ("cage"). Neglecting small scale motion of the order of cage size,

$$D_{r\perp} \sim 0, \quad (2.4b)$$

$$D_r = \beta D_{r0} (CL^3)^{-2}, \quad (2.4c)$$

where $\beta \approx 1350$ corresponds to incomplete caging at $\nu < \nu^*$.⁶ We take $D_{r\parallel}$, $D_{r\perp}$, and D_r to be relative diffusivities, i.e., sum of the diffusivities of individual molecules, to account for the diffusion of the sink.^{7,8} For a monodisperse system, the relative diffusivities are twice the diffusivities of individual molecules.

As in Ref. 1, we define the approximate reaction criteria for approach of reactive tips of A and B in terms of position of the center of mass of the diffusing molecule B (Fig. 1) by the condition $|\mathbf{r}| \leq a$. The collinearity criterion for reaction between RRL molecules is given by $\Theta \leq \Theta_0$, where Θ is the relative orientation angle between the molecules and Θ_0 is a specified angle.¹ The reaction zone is considered impenetrable, and the partially absorbing reaction boundary condition for translational flux on the reaction surface $|\mathbf{r}| = a$ is given as

$$\begin{aligned} (D_{r\parallel} \mathcal{F}_{r\parallel} C + D_{r\perp} (\mathcal{F}_r C - \mathcal{F}_{r\parallel} C)) \cdot \mathbf{n}_s \\ = k_s C \quad \text{for } \Theta \leq \Theta'_0, \\ = 0 \quad \text{for } \Theta > \Theta'_0, \end{aligned} \quad (2.5)$$

where \mathbf{n}_s is the unit vector perpendicular to the spherical reaction surface, and k_s is the intrinsic reaction rate constant.

Besides the symmetry boundary conditions due to the axisymmetric nature of the field, the far field boundary condition is

$$C = C_B \quad |\mathbf{r}| \rightarrow \infty, \quad (2.6)$$

where C_B is the bulk concentration of the RRL molecules.

III. SIMPLIFIED GOVERNING EQUATIONS

The dominant anisotropy of translation diffusion of the RRL molecules in semidilute solutions necessitates the consideration of the spatial dependence of number density not only with the radial position (r), but also the polar position (θ_r). However, for reducing the dimensionality of the problem, we retain the axisymmetry assumption here as in Ref. 1.

In terms of the spherical coordinates $\mathbf{r} = \mathbf{r}(r, \theta_r, \phi_r)$ and $\mathbf{u} = \mathbf{u}(\Theta, \phi)$, we get the following expressions for the terms in Eq. (2.2) (Appendix A):

$$\mathbf{u} \cdot \nabla_{\mathbf{r}} = A \frac{\partial}{\partial r} + \frac{B}{r} \frac{\partial}{\partial \theta_r}, \quad (3.1a)$$

$$\frac{\partial}{\partial \mathbf{u}} = \mathbf{e}_{\Theta} \frac{\partial}{\partial \Theta}, \quad (3.1b)$$

where

$$A = \cos \Theta \cos \theta_r + \sin \Theta \sin \theta_r \cos(\phi - \phi_r) = -\frac{\partial B}{\partial \theta_r}, \quad (3.2a)$$

$$B = -\cos \Theta \sin \theta_r + \sin \Theta \cos \theta_r \cos(\phi - \phi_r) = \frac{\partial A}{\partial \theta_r}. \quad (3.2b)$$

An examination of the above equations shows that for small values of Θ that are of interest here, the terms containing $(\phi - \phi_r)$ are small compared to the other terms over most of the domain (θ_r), and are neglected in this analysis. This reduces the problem to 3 dimensions i.e., r , Θ , and θ_r . The terms in the governing equation (2.1) are now obtained as

$$\begin{aligned} \nabla_{\mathbf{r}}^2 C = & A^2 \frac{\partial^2 C}{\partial r^2} + \frac{B^2}{r^2} \frac{\partial^2 C}{\partial \theta_r^2} + \frac{AB}{r} \left(\frac{\partial^2 C}{\partial r \partial \theta_r} + \frac{\partial^2 C}{\partial \theta_r \partial r} \right) \\ & - \frac{2AB}{r^2} \frac{\partial C}{\partial \theta_r} + \frac{B^2}{r} \frac{\partial C}{\partial r}, \end{aligned} \quad (3.3a)$$

$$\nabla_{\mathbf{r}}^2 C = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) + \frac{1}{r^2 \sin \theta_r} \frac{\partial}{\partial \theta_r} \left(\sin \theta_r \frac{\partial C}{\partial \theta_r} \right), \quad (3.3b)$$

$$\frac{\partial^2 C}{\partial \mathbf{u}^2} = \frac{1}{\sin \Theta} \frac{\partial}{\partial \Theta} \left(\sin \Theta \frac{\partial C}{\partial \Theta} \right). \quad (3.3c)$$

The far field boundary conditions, and the symmetry boundary conditions for the simplified problem are

$$C = C_B \quad r \rightarrow \infty, \quad (3.4a)$$

$$\frac{\partial C}{\partial \Theta} = 0 \quad \Theta = 0, \quad (3.4b)$$

$$\frac{\partial C}{\partial \Theta} = 0 \quad \Theta = \pi/2, \quad (3.4c)$$

$$\frac{\partial C}{\partial \theta_r} = 0 \quad \theta_r = 0, \quad (3.4d)$$

$$\frac{\partial C}{\partial \theta_r} = 0 \quad \theta_r = \pi/2. \quad (3.4e)$$

A. Evaluation of the effective rate constant

The reaction flux on the spherical surface at $r = a$ is

$$\begin{aligned} j_t = & \int_0^\pi \int_0^{2\pi} \int_0^{\Theta_0} \int_0^{2\pi} k_s C_{r=a} d\phi \sin \Theta d\Theta \\ & \times a d\phi_r a \sin \theta_r d\theta_r / \int_0^{\pi/2} \int_0^{2\pi} d\phi \sin \Theta d\Theta. \end{aligned} \quad (3.5)$$

Following the procedure as in Ref. 1, and using the axisymmetry assumption we get the effective second order reaction rate constant as

$$\begin{aligned} k'_{\text{eff}} = & j_t / C_B \\ = & 4\pi a^2 k_s \int_0^{\pi/2} \int_0^{\Theta_0} (C/C_B)_{r=a} \sin \Theta d\Theta \sin \theta_r d\theta_r. \end{aligned} \quad (3.6)$$

The rate constant thus obtained is based on the concentration of reactive end groups. (To convert to a rate constant based on the concentration of molecules we require to divide the above by a factor 2.) k_s is evaluated in terms of the homogeneous rate constant (k'_{hom}) in the absence of diffusional resistance ($C_{r=a} = C_B$) as

$$k_s = \frac{k'_{\text{hom}}}{4\pi a^2 (1 - \cos \Theta_0)}. \quad (3.7)$$

B. Dimensionless equations

From Eqs. (2.1)–(2.2) the dimensionless steady state governing equation is

$$[s(1 - \gamma) \nabla_{\xi}^2 N + s\gamma \nabla_{\xi}^2 N] + \frac{\partial^2 N}{\partial \mathbf{u}^2} = 0, \quad (3.8)$$

where $N = (1 - C/C_B)$ and $\xi = r/a$ are the dimensionless concentration and distance, respectively. In addition, we have defined the parameters $s = D_{t\parallel} / (a^2 D_r)$ representative of rotational diffusional resistance, and $\gamma = D_{t\perp} / D_{t\parallel}$ representative of translational diffusivity perpendicular to rod axis. The corresponding boundary conditions are

$$\begin{aligned} [s(1 - \gamma) \nabla_{\xi}^2 N + s\gamma \nabla_{\xi}^2 N] \cdot \mathbf{n}_s \\ = -\alpha s(1 - N) \quad \text{for } \xi = 1, \quad \Theta \leq \Theta_0, \\ = 0 \quad \text{for } \xi = 1, \quad \Theta > \Theta_0, \end{aligned} \quad (3.9)$$

$$N = 0, \quad \xi \rightarrow \infty, \quad (3.10a)$$

$$\frac{\partial N}{\partial \Theta} = 0, \quad \Theta = 0, \quad (3.10b)$$

$$\frac{\partial N}{\partial \Theta} = 0, \quad \Theta = \pi/2, \quad (3.10c)$$

$$\frac{\partial N}{\partial \theta_r} = 0, \quad \theta_r = 0, \quad (3.10d)$$

$$\frac{\partial N}{\partial \theta_r} = 0, \quad \theta_r = \pi/2, \quad (3.10e)$$

where we have defined $\alpha = k_s a / D_{t\parallel}$, a dimensionless parameter representing surface reaction rate constant. Finally, the rate constants, which have been made dimensionless by dividing by $a D_{t\parallel}$, are obtained as

$$k_{\text{eff}} = 4\pi\alpha \int_0^{\pi/2} \int_0^{\Theta_0} (1-N)_{\xi=1} \sin \Theta d\Theta \sin \theta_r d\theta_r, \quad (3.11)$$

$$k_{\text{hom}} = 4\pi\alpha (1 - \cos \Theta_0). \quad (3.12)$$

The effective reduced reaction rate constant is

$$k_{\text{rel}} = k_{\text{eff}} / k_{\text{hom}} \\ = \int_0^{\pi/2} \int_0^{\Theta_0} (1-N)_{\xi=1} \sin \Theta d\Theta \sin \theta_r d\theta_r / \\ (1 - \cos \Theta_0). \quad (3.13)$$

The additional parameter here, as compared to the case of dilute solutions,¹ is γ . $\gamma=1$ represents isotropic diffusion corresponding to the dilute solution case, and smaller values of γ represent reduced translational diffusivity perpendicular to the rod axis.

IV. FINITE ELEMENT METHOD (FEM) FORMULATION

We use the FEM technique to obtain a solution to the steady state equation (3.8) with the boundary conditions

(3.9) and (3.10). Multiplying Eq. (3.8) by weight function v , and integrating over $dV = d\xi du = \xi^2 d\xi \sin \theta_r \times d\theta_r d\phi_r \sin \Theta d\Theta d\phi$, we get

$$s(1-\gamma) \int v \mathcal{F}_{\xi\parallel}^2 N dV + s\gamma \int v \mathcal{F}_{\xi\perp}^2 N dV \\ + \int v \frac{\partial^2 N}{\partial u^2} dV = 0. \quad (4.1)$$

Using chain rule for differentiation and the Gauss divergence theorem, we get (Appendix B)

$$v \mathcal{F}_{\xi\parallel}^2 N = -\mathcal{F}_{\xi\parallel} v \cdot \mathcal{F}_{\xi\parallel} N + \mathcal{F}_{\xi\parallel} \cdot (v \mathcal{F}_{\xi\parallel} N) \quad (4.2)$$

and

$$\int \mathcal{F}_{\xi\parallel} \cdot (v \mathcal{F}_{\xi\parallel} N) d\xi = \int v \mathcal{F}_{\xi\parallel} N \cdot \mathbf{n} dS, \quad (4.3)$$

where \mathbf{n} is the unit vector perpendicular to the surface element at $\xi=1$, $dS = d\theta_r \sin \theta_r d\phi_r$. Substituting in Eq. (4.1), and using boundary condition (3.9), we get the weak formulation as

$$s(1-\gamma) \int \mathcal{F}_{\xi\parallel} v \cdot \mathcal{F}_{\xi\parallel} N dV + s\gamma \int \mathcal{F}_{\xi\perp} v \cdot \mathcal{F}_{\xi\perp} N dV \\ + \int \frac{\partial v}{\partial u} \cdot \frac{\partial N}{\partial u} dV = -\alpha s \int_{\Gamma'} v(1-N) dS', \quad (4.4)$$

where $dS' = du dS$, and Γ' represents the boundary at $\xi=1$, $\Theta \leq \Theta_0$. Expanding in spherical coordinates, we get

$$s(1-\gamma) \int \left(A \frac{\partial v}{\partial \xi} + \frac{B}{\xi} \frac{\partial v}{\partial \theta_r} \right) \left(A \frac{\partial N}{\partial \xi} + \frac{B}{\xi} \frac{\partial N}{\partial \theta_r} \right) \xi^2 d\xi \sin \Theta d\Theta \sin \theta_r d\theta_r + s\gamma \int \left(\frac{\partial v}{\partial \xi} \frac{\partial N}{\partial \xi} + \frac{1}{\xi^2} \frac{\partial v}{\partial \theta_r} \frac{\partial N}{\partial \theta_r} \right) \xi^2 d\xi \sin \Theta d\Theta \sin \theta_r d\theta_r \\ + \int \frac{\partial v}{\partial \theta_r} \frac{\partial N}{\partial \theta_r} \xi^2 d\xi \sin \Theta d\Theta \sin \theta_r d\theta_r = -\alpha s \int_{\Gamma'} v(1-N) \sin \Theta d\Theta \sin \theta_r d\theta_r. \quad (4.5)$$

A three dimensional domain with eight node rectangular sided elements is used. The piecewise approximation of N is given by

$$N = \sum_{j=1}^8 N_j \psi_j(\xi, \Theta, \theta_r), \quad (4.6)$$

where ψ_j are tri-linear shape functions, and N_j are nodal values to be determined. Using weight functions $v = \psi_i / (\xi^2 \sin \Theta \sin \theta_r)$, we get

$$\sum_j N_j \left[s(1-\gamma) \left\{ \int A^2 \left(\frac{\partial \psi_i}{\partial \xi} - \frac{2}{r} \psi_i \right) \frac{\partial \psi_j}{\partial \xi} d\xi d\Theta d\theta_r + \int \frac{B^2}{\xi^2} \left(\frac{\partial \psi_i}{\partial \theta_r} - \cot \theta_r \psi_i \right) \frac{\partial \psi_j}{\partial \theta_r} d\xi d\Theta d\theta_r + \int \frac{AB}{\xi} \left(\frac{\partial \psi_i}{\partial \xi} - \frac{2}{r} \psi_i \right) \frac{\partial \psi_j}{\partial \theta_r} d\xi d\Theta d\theta_r + \int \frac{AB}{\xi} \left(\frac{\partial \psi_i}{\partial \theta_r} - \cot \theta_r \psi_i \right) \frac{\partial \psi_j}{\partial \xi} d\xi d\Theta d\theta_r \right\} + s\gamma \left\{ \int \left(\frac{\partial \psi_i}{\partial \xi} - \frac{2}{r} \psi_i \right) \frac{\partial \psi_j}{\partial \xi} d\xi d\Theta d\theta_r + \int \frac{1}{\xi^2} \left(\frac{\partial \psi_i}{\partial \theta_r} - \cot \theta_r \psi_i \right) \frac{\partial \psi_j}{\partial \theta_r} d\xi d\Theta d\theta_r \right\} + \int \left(\frac{\partial \psi_i}{\partial \Theta} - \cot \Theta \psi_i \right) \frac{\partial \psi_j}{\partial \Theta} d\xi d\Theta d\theta_r - \alpha s \int_{\Gamma'} \psi_i \psi_j d\Theta d\theta_r \right] = -\alpha s \int_{\Gamma'} \psi_i d\Theta d\theta_r \quad (4.7)$$

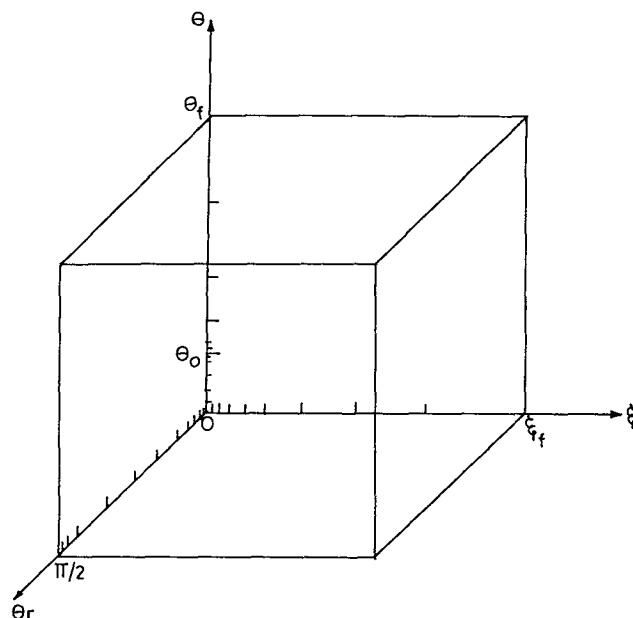


FIG. 2. Mesh for FEM solution in 3D. Only a schematic of the mesh is drawn here, and is not to scale. Smaller elements are taken in the regions of steep gradients, i.e., near $\xi = \xi_f$, $\Theta = \Theta_0$, $\theta_r = 0$, $\pi/2$.

with

$$\begin{aligned} A^2 &= \cos^2 \Theta \cos^2 \theta_r, \\ B^2 &= \cos^2 \Theta \sin^2 \theta_r, \\ AB &= -\cos^2 \Theta \sin \theta_r \cos \theta_r. \end{aligned} \quad (4.8)$$

To solve the set of equations Eq. (4.7), the domain is divided into approximately 1000 elements. Typical mesh discretization is illustrated in Fig. 2. Instead of the infinite system, a system of finite size ξ_f is used and the boundary condition (3.10a) is modified as

$$N=0, \quad \xi=\xi_f. \quad (4.9a)$$

Also, for large s and small Θ_0 , the concentration profile levels out to $C=C_B$ at $\Theta \approx \Theta_0 + 1/\sqrt{s}$,¹ and we modify the boundary condition (3.10c) to

$$N=0, \quad \Theta=\Theta_f, \quad (4.9b)$$

where ξ_f and Θ_f are taken large enough that further increase in the system size does not change the solution. The element integrations are carried out using trapezoidal rule with 20 divisions per element along each dimension. Some terms become unbounded at $\Theta=0$ and $\theta_r=0$, and we circumvent this by considering the domain $\Theta=(0.0005 \text{ rad}, \Theta_f)$, $\theta_r=(0.0001 \text{ rad}, \pi/2)$ and modifying boundary condition (3.10b) and (3.10d) as

$$\frac{\partial N}{\partial \Theta}=0, \quad \Theta=0.0005 \text{ rad} \quad (4.9c)$$

and

$$\frac{\partial N}{\partial \theta_r}=0, \quad \theta_r=0.0001 \text{ rad}. \quad (4.9d)$$

The element matrices are assembled,⁹ and solved for $\{N_i\}$ using a sparse matrix solver.¹ We ensure convergence by taking smaller elements until a finer mesh does not affect the solution. The nodal values of N at $\xi=1$, $\Theta \leq \Theta_0$ are used to calculate the reduced reaction rate constant using Eqs. (3.11)–(3.13). Computation for a given s and α takes about 1000 CPUs on HCL Magnum. For large values of α and s , and small γ , the gradients in concentration are long range along the z axis, and sharp perpendicular to it. Hence, for these cases, convergence could not be reached with as many as 1000 elements in the domain.

V. ASYMPTOTIC SOLUTION ($\gamma=0$, $\Theta_0 \ll 1$)

We consider the limit $\gamma=0$, when the diffusion perpendicular to the rod axis vanishes, and translational diffusion is limited to that along the rod axis (\mathbf{u}). The diffusion equation [Eq. (3.8)] in this case reduces to

$$s(\mathbf{u} \cdot \mathcal{F}_r)^2 N + \frac{\partial^2 N}{\partial \mathbf{u}^2} = 0. \quad (5.1)$$

As mentioned earlier, for small values of Θ_0 and large s the concentration profile levels out to the far-field value ($N=0$) at small Θ . Thus the molecules contributing to the reaction flux are all oriented at small Θ , i.e., nearly parallel to the z axis. The translational diffusion in this case is most conveniently specified in dimensionless cylindrical coordinates (ρ, ϕ, z) , for which we obtain (Appendix C),

$$\mathbf{u} \cdot \mathcal{F}_r = A_c \frac{\partial}{\partial \rho} + B_c \frac{\partial}{\partial z}, \quad (5.2)$$

where

$$A_c = \sin \Theta \cos(\phi - \phi_r), \quad (5.3a)$$

$$B_c = \cos \Theta \quad (5.3b)$$

and the $\partial/\partial \phi_r$ terms have been neglected based on the axisymmetry assumption. For small Θ , we have $A_c \rightarrow 0$, $B_c \rightarrow 1$, and Eq. (5.1) reduces to

$$s \frac{\partial^2 N}{\partial z^2} + \frac{1}{\Theta} \frac{\partial}{\partial \Theta} \left(\Theta \frac{\partial N}{\partial \Theta} \right) = 0. \quad (5.4)$$

With the above approximations, the problem reduces to 1-dimensional translational diffusion augmented by rotational diffusion in the Θ direction. Due to the former, molecules contributing to the reaction flux are all from a cylindrical domain of unit radius, as shown in Fig. 3. In arriving at Eq. (5.4), the translational diffusion of the molecules in the radial (ρ) direction which is $o(s\Theta)$ was neglected in comparison to the other terms simplicity. When this contribution to the translational diffusive flux is taken into account, the domain of the molecules contributing to the reaction flux expands into a cone (Fig. 3), with an angle which increases with s . The problem thus formulated neglecting the radial contribution of the translational dif-

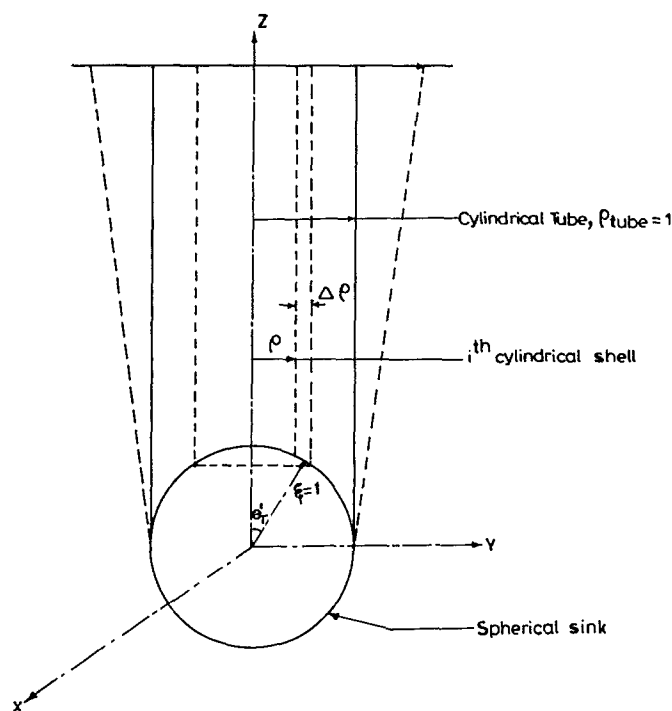


FIG. 3. Schematic view of the cylindrical domain for the asymptotic analysis. The schematic view of the conical domain which would result due to translational diffusion in the ρ direction is also shown.

fusion would give a lower bound for the effective rate constant for $\gamma=0$. The solution would be most accurate for moderate values of s and small Θ_0 ; large values of s will give small range of Θ in which N is nonzero, however very large values of s would give a significant radial diffusive flux compared to the rotational diffusive flux.

To take into account the geometry of the sink, we consider the cylindrical tube to be made up of h cylindrical shells of inner radius ρ_i and outer radius ρ_{i+1} , $i=1, 2, \dots, h$ (Fig. 3). We further use $\theta'_{r,i}$ to denote polar angular position (Fig. 3) on the spherical sink at $\xi=1$ so that

$$\rho_i = \sin \theta'_{r,i} \quad i=1, 2, \dots, h, \quad (5.5)$$

$$\theta'_{r,i} = \pi(i-1)/2h. \quad (5.6)$$

As the diffusion along ρ is neglected, each shell can be considered independently, and we denote the average (over small shell thickness $\Delta\rho$) concentration of the i th shell by N_i . Substituting $p=\Theta\sqrt{s}$ in Eq. (5.4), the governing equation for the i th shell is obtained as

$$\frac{\partial^2 N_i}{\partial z^2} + \frac{1}{p} \frac{\partial}{\partial p} \left(p \frac{\partial N_i}{\partial p} \right) = 0. \quad (5.7)$$

The modified boundary conditions for the i th shell are

$$N_i = 0, \quad z \rightarrow \infty, \quad (5.8a)$$

$$\frac{\partial N_i}{\partial p} = 0, \quad p = 0, \quad (5.8b)$$

$$N_i = 0, \quad p = p_f, \quad (5.8c)$$

$$\frac{\partial N_i}{\partial z} = -(\alpha/\cos \bar{\theta}'_{r,i})(1-N_i) \quad z=1, \quad p < p_0, \quad (5.8d)$$

$$= 0 \quad z=1, \quad p > p_0, \quad (5.8e)$$

where $\bar{\theta}'_{r,i}$ is the average θ'_r for the i th shell. The factor $1/\cos \bar{\theta}'_{r,i}$ in Eq. (5.8d) corresponds to the ratio of sink surface area ($2\pi\rho_i\Delta\rho/\cos \bar{\theta}'_r$) for reaction to the cross-sectional area ($2\pi\rho_i\Delta\rho$) for diffusion in the z direction. The z axis has been considered to be translated so that $z=1$ corresponds to position on the sink surface. Further, $p_f = \Theta_f\sqrt{s}$ is chosen large enough so that further increase does not influence the results.

The general solution is obtained as a series¹

$$N_i = \sum_{m=1}^M A_m \exp(-\lambda_m z) J_0(\lambda_m p), \quad (5.9)$$

where λ_m are obtained from the boundary condition (5.8c)

$$J_0(\lambda_m p_f) = 0 \quad \text{for } m=1 \cdots M'. \quad (5.10)$$

Here M' corresponds to truncation of the series of finite number of terms, and is taken large enough that further increase in M' does not affect the results. The coefficients $A_m = B_m \exp(\lambda_m)$ are obtained from the boundary condition (5.8d) by solution of the system of linear equations

$$XB = Y, \quad (5.11)$$

where the matrices are defined as

$$X_{nm} = \alpha p_0 \frac{\lambda_n J_0(\lambda_m p_0) J_1(\lambda_n p_0) - \lambda_m J_0(\lambda_n p_0) J_1(\lambda_m p_0)}{\lambda_n^2 - \lambda_m^2} \quad (5.12)$$

for $n \neq m$,

$$X_{mm} = \frac{\alpha p_0^2}{2} [J_1^2(\lambda_m p_0) + J_0^2(\lambda_m p_0)] + \frac{\lambda_m p_f^2}{2} J_1^2(\lambda_m p_f), \quad (5.13)$$

$$Y_n = (\alpha p_0/\lambda_n) J_1(\lambda_n p_0). \quad (5.14)$$

Thus $N_i(\Theta)$ can be determined and used to calculate the dimensionless rate constant as

$$k_{\text{eff}} = \alpha \sum_{i=1}^h 2\pi \sin(\bar{\theta}'_{r,i}) (\theta'_{r,i+1} - \theta'_{r,i}) \times \int_0^{\Theta_0} (1-N_i)_{z=1} \sin \Theta d\Theta. \quad (5.15)$$

VI. RESULTS AND DISCUSSION

In Figs. 4(a) and 4(b) we have plotted the FEM results for the effect of rotational diffusional resistance (s) on the rate constant (k_{rel}) for $\alpha=0.08$ and 0.8 , $\Theta_0=0.01$ rad, and different values of γ . $\gamma=1$ corresponds to isotropic diffusion, and the results from present simulation agree within 1% with the analytical results of Ref. 1. With increase in the rotational diffusion resistance (i.e., s), the rate constant decreases and reaches a plateau beyond $s=s^*$. In this limit ($s \gg s^*(\gamma)$) the reaction flux is entirely due to translation diffusion of the appropriately oriented molecules from the far field, and rotational diffusion is

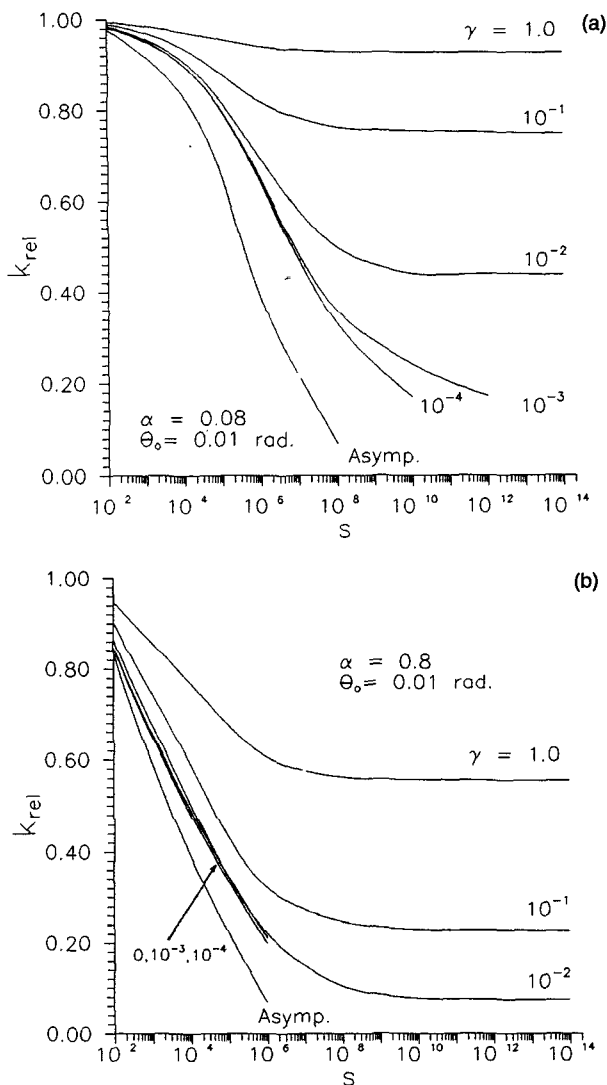


FIG. 4. Effect of rotational diffusional resistance (s) on the relative rate constant (k_{rel}), for $\Theta_0=0.01$ rad and different values of dimensionless perpendicular diffusivity γ (a) $\alpha=0.08$ (b) $\alpha=0.8$. FEM results, as well as the asymptotic analysis result for $\gamma=0$ are plotted.

negligible. Hence, further increase in s does not reduce the rate constant. At smaller γ , the effect of rotational diffusional resistance (s) is more severe, resulting in larger decrease in rate constant with s . Hence, the overall reaction rate being small, even a small contribution of rotational diffusional flux at large s influences the overall reaction rate. This results in larger s^* at smaller γ . At $\gamma=0$, the perpendicular translational diffusion vanishes, and with vanishing contribution from rotational diffusion at increasing s , the diffusion of the rods gradually becomes limited to 1-dimensional translation along rod axis. No steady state solution for the diffusion problem is possible in this case for $s \rightarrow \infty$ as is apparent from Eq. (5.4). The present FEM simulations, however, could not be extended to this range of parameters as the sink influence becomes very long range along the z axis and very steep along the ρ direction. Hence, convergence of numerical approximation could not

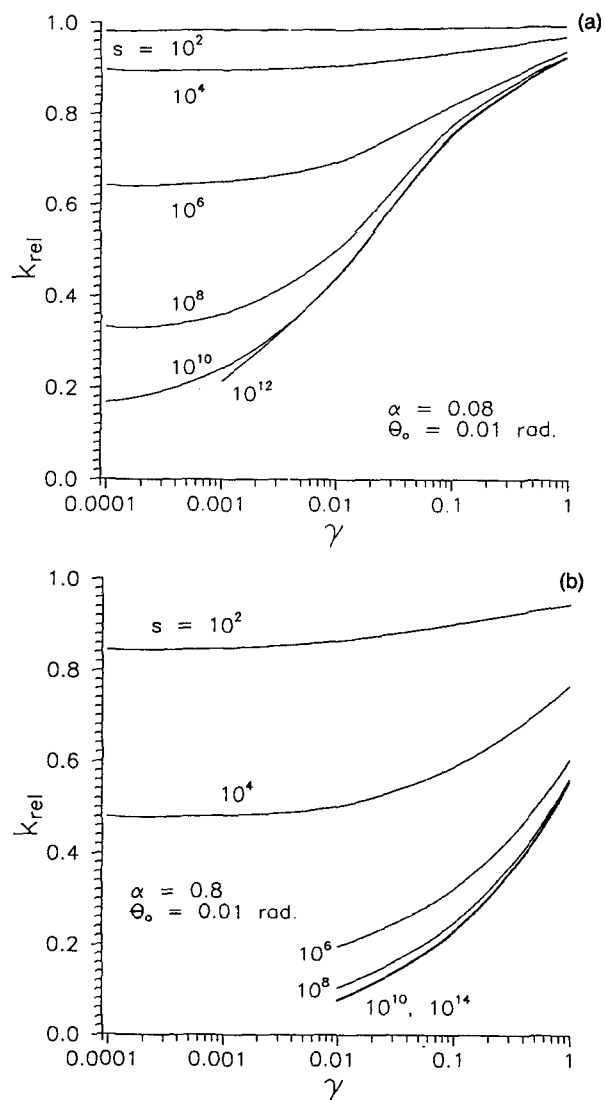


FIG. 5. Effect of perpendicular diffusivity (γ) on the relative rate constant (k_{rel}), for $\Theta_0=0.01$ rad and different rotational diffusional resistances (s) (a) $\alpha=0.08$, (b) $\alpha=0.8$.

be obtained for small γ and large s , with number of grid points limited by the available computational time and memory. As in Ref. 1, we find that for larger values α (i.e., faster intrinsic kinetics) reduction in rate constant with s is more severe and is obtained at smaller values of s (Fig. 4).

In Figs. 5(a) and 5(b) we replot the computed values to show the variation in rate constant with perpendicular translational diffusivity (γ), for different values of s . We find that the rate constant decreases with decrease in γ , before leveling out at small $\gamma = \gamma^*(s)$. In this limit ($\gamma < \gamma^*$), the contribution of the perpendicular translation diffusion to the reaction flux is negligible, and the entire reaction flux is made up of the parallel translational diffusion and the rotational diffusion. At larger s , rotational flux and hence overall reaction rate are smaller. Therefore, even a small contribution of perpendicular diffusion at small γ influences the overall reaction rate. Thus $\gamma^*(s)$, below

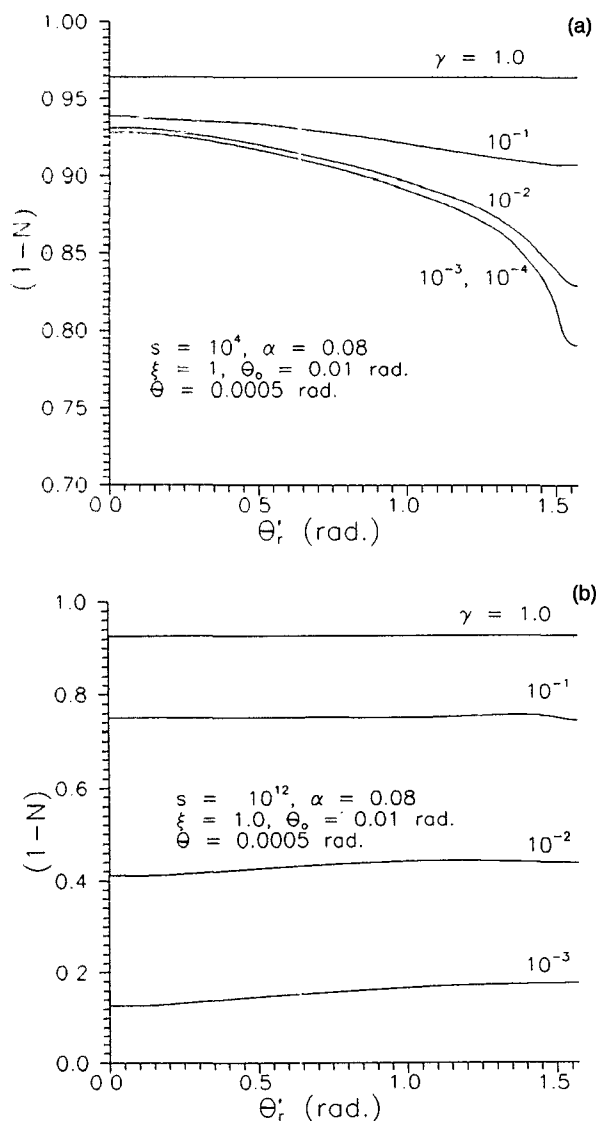


FIG. 6. Dimensionless number density $(1-N)$ of rodlike molecules versus angular position (θ_r') on sink surface $(\xi=1)$, for $\alpha=0.08$, $\Theta_0=0.01$ rad, $\Theta=0.0005$ rad, different γ (a) $s=10^4$, (b) $s=10^{12}$.

which further decrease in γ does not affect the reaction rate, is smaller for larger s .

The FEM results for the variation of the concentration on the sink surface $(\xi=1)$, for $\alpha=0.08$, $\Theta=0.0005$ rad, is presented in Figs. 6(a) and 6(b). We first consider the results for $s=10^4$, corresponding to significant rotational diffusion. For $\gamma=1$, the concentration is independent of θ_r' , corresponding to spherical symmetry for the isotropic translational diffusion case. At smaller γ , the translational diffusion is increasingly limited to only the parallel diffusion along the tube axis, and the rotational diffusion becomes the major source of reaction flux. Considering the tube model of Fig. 3, the effective intrinsic rate constant $(\alpha/\cos \bar{\theta}_{r,i})$ increases with θ_r' [Eq. (5.8d)], resulting in lower surface concentration at higher θ_r' . This decrease is more pronounced at smaller γ because of the more pronounced anisotropy and one dimensional nature of translational diffusion.

Similar profiles for the case of strongly hindered rotational diffusion ($s=10^{12}$) are plotted in Fig. 6(b). At $\gamma=1.0$, the result is qualitatively similar to the small s case. However, at smaller γ , we find an increase in the number density $(1-N)$ with θ_r' , followed by a small decrease near $\theta_r' = \pi/2$. In this case the rotational diffusion is negligible (large s), and diffusion of the RRL molecules perpendicular to the rod axis (i.e., in the ρ direction, Fig. 3) makes significant contribution to the overall flux. Contribution of this flux is more near the tube wall, and results in higher concentrations away from the tube axis. However, based on parallel diffusion alone, the concentration on sink surface is expected to decrease with θ_r' , particularly near $\theta_r' = \pi/2$, as per the arguments put forward for the small s case. The profiles observed in Fig. 6(b) are a result of a combination of these two phenomena.

In Figs. 4(a) and 4(b) we have also plotted the rate constants obtained from the asymptotic solution, and they are found to be smaller than the corresponding FEM results for $\gamma=0$. This is because the translational diffusion in the radial (ρ) direction is neglected. The agreement is better at small s because the relative contribution of the radial diffusion is smaller in this case. This is further seen in Fig. 7, where we compare the concentration profiles at $\xi=1$ for small Θ ($=0.0005$ rad), as obtained from the FEM and the asymptotic analysis. The asymptotic solution gives lower concentrations, particularly near $\theta_r' = \pi/2$, because the radial diffusive flux is largest in this region. The disagreement of the concentration profile from the asymptotic solution with the FEM solution is more pronounced at larger values of s as expected (Fig. 7).

We next compare the results of this analysis with the experiments of Cotts and Berry¹⁰ for polymerization of 4,6-diamino-1,3-benzenediol and terephthalic acid in a 2.0 wt. % solution in poly(phosphoric acid) at 185 °C. The reaction was found to become diffusion controlled at weight average degree of polymerization $\overline{DP}_w \approx 100$. The actual system is polydisperse, and evaluation of the rate constant between each pair of molecules should be carried out using the approach given in Ref. 1. However, for simplicity we assume here that the rate constant obtained for monodisperse molecules with $L=\bar{L}_w$ gives a reasonable estimate of the overall rate constant, where \bar{L}_w is the weight average molecular length. For the above degree of polymerization, we get $\bar{L}_w \approx 1200$ Å, so that $v \approx 832$, $D_{r\parallel} = 7.2 \times 10^{-7}$ cm² s⁻¹ [Eqs. (2.3a) and (2.4a)], $D_r = 6.5$ s⁻¹ [Eqs. (2.3c) and (2.4c)], and $s = 7 \times 10^7$. In the above calculations we have taken $a = 4$ Å, $d = 6$ Å, $\eta_s = 1$ cP, and $T = 373$ K. Using $k'_{\text{hom}} = 7.5$ l/mol s,¹⁰ we get $k_{\text{hom}} = 4.3 \times 10^{-7}$, and $\alpha = 3.4 \times 10^{-8} / (1 - \cos \Theta_0) \approx 6.8 \times 10^{-8} \Theta_0^{-2}$.¹ If we assume $\Theta_0 = 0.001$ rad, we get $\alpha = 0.068$, and the FEM solution (corresponding to $\gamma=0$) gives $k_{\text{rel}} \approx 0.7$, which has an order of magnitude agreement with the experimental observation. Considering the rigidity of this rodlike molecule, perhaps the orientational requirement for reaction defined by this value of Θ_0 is reasonable, and less severe than that based on dilute solution analysis in Ref. 1.

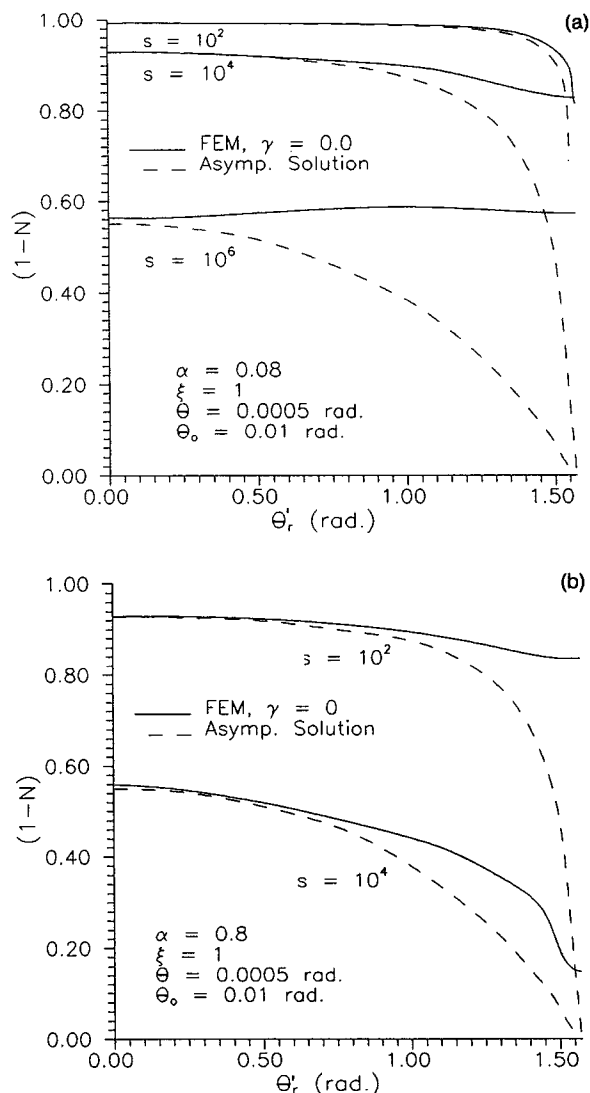


FIG. 7. Dimensionless number density $(1-N)$ of rodlike molecules versus angular position (θ_r) on sink surface $(\xi=1)$, for $\gamma=0$, $\Theta_0=0.01$ rad, $\Theta=0.0005$ rad, different s , and (a) $\alpha=0.08$, (b) $\alpha=0.8$.

VII. CONCLUSIONS

Following Smoluchowski's approach and simplified reaction criteria and diffusion process, rate constants have been calculated for diffusion limited reactions between rigid rodlike molecules in semidilute solutions. Good match of the present numerical FEM results with analytical results of dilute solution case and with an asymptotic analysis, in the appropriate limits, verifies the accuracy of the numerical FEM results.

Rototranslational diffusional limitations during homogeneous solution step-growth polymerization of RRL molecules result in reduction of the reaction rate constant. Increasing anisotropy of the translational diffusion of the RRL molecules results in even larger reduction in the reaction rate constant. While the effects of diffusional limitations are more pronounced for intrinsically faster chemical reactions and stringent reaction criteria, significant

reduction in rate constants is obtained even for reactions that are intrinsically not very rapid, e.g., when compared with conventional diffusion controlled reactions.

With reduction in the rotational diffusivity and the translational diffusivity perpendicular to the rod axis as the molecular length increases during the RRL solution step-growth polymerization, the diffusional limitations may result in reduction of the reaction rate constant. This is in agreement with the experimental observations.¹⁰⁻¹² Also, the limiting molecular weight may be reduced because of the competing side reactions that consume the chain ends, terminating further growth. Further, a preferential depletion of the smaller molecules, due to their higher diffusivities and hence higher reactivities, may result in a narrower molecular weight distribution. This has been found to be the case experimentally.¹⁰ Experimental results also show that the alignment of RRL molecules under an externally imposed shear flow during polymerization facilitates the collinearity requirement for reaction, thereby enhancing the rate of rotational diffusion controlled reaction.¹² Theoretical analyses of the above effects have not as yet been carried out. The results of such studies would be of considerable practical interest.

APPENDIX A: SIMPLIFIED TERMS FOR ROTOTRANSLATIONAL DIFFUSION EQUATION IN SPHERICAL COORDINATES

Using spherical coordinates, with (r, θ, ϕ_r) denoting the radial positional and polar and azimuthal angular coordinates of the center of mass of the rod, and θ and ϕ denoting the polar and azimuthal orientation of the rod with respect to z axis, the orientation vector in Cartesian coordinates is given by

$$\mathbf{u} = \cos \Theta \mathbf{e}_z + \sin \Theta \cos \phi_r \mathbf{e}_x + \sin \Theta \sin \phi_r \mathbf{e}_y \quad (\text{A1})$$

and the gradient operator by

$$\mathcal{F}_r = \frac{\partial}{\partial r} = \mathbf{e}_x \frac{\partial}{\partial x} + \mathbf{e}_y \frac{\partial}{\partial y} + \mathbf{e}_z \frac{\partial}{\partial z} \quad (\text{A2})$$

The above partial derivatives can be written in terms of spherical coordinates as¹³

$$\frac{\partial}{\partial x} = \sin \theta_r \cos \phi_r \frac{\partial}{\partial r} + \frac{\cos \theta_r \cos \phi_r}{r} \frac{\partial}{\partial \theta_r} - \frac{\sin \phi_r}{r \sin \theta_r} \frac{\partial}{\partial \phi_r}, \quad (\text{A3})$$

$$\frac{\partial}{\partial y} = \sin \theta_r \sin \phi_r \frac{\partial}{\partial r} + \frac{\cos \theta_r \sin \phi_r}{r} \frac{\partial}{\partial \theta_r} + \frac{\cos \phi_r}{r \sin \theta_r} \frac{\partial}{\partial \phi_r}, \quad (\text{A4})$$

$$\frac{\partial}{\partial z} = \cos \theta_r \frac{\partial}{\partial r} - \frac{\sin \theta_r}{r} \frac{\partial}{\partial \theta_r}. \quad (\text{A5})$$

The gradient operator for rotational diffusion corresponds to variation on the surface of a sphere of unit radius. The operator is thus identical to the translational diffusion operator with $r=1$, and

$$\frac{\partial}{\partial \mathbf{u}} = \frac{\partial}{\partial \mathbf{r}} \Big|_{r=1}. \quad (\text{A6})$$

Using the above equations, we get

$$\mathcal{F}_{r\parallel} = \mathbf{u}(\mathbf{u} \cdot \mathcal{F}_r) = \mathbf{u} \left(A \frac{\partial}{\partial r} + \frac{B}{r} \frac{\partial}{\partial \theta_r} \right), \quad (\text{A7})$$

$$\frac{\partial}{\partial \mathbf{u}} = e_\Theta \frac{\partial}{\partial \Theta}, \quad (\text{A8})$$

where

$$A = \sin \Theta \sin \theta_r \cos(\phi - \phi_r) + \cos \Theta \cos \theta_r = -\frac{\partial B}{\partial \theta_r}, \quad (\text{A9})$$

$$B = \sin \Theta \cos \theta_r \cos(\phi - \phi_r) - \cos \Theta \sin \theta_r = \frac{\partial A}{\partial \theta_r}. \quad (\text{A10})$$

In the above equations, $(\partial/\partial\phi)$ and $(\partial/\partial\phi_r)$ terms have been neglected based on the assumption of axisymmetry of the rodlike molecule and the reactive site.

APPENDIX B: PROOF OF VECTOR IDENTITIES FOR THE TRANSLATIONAL DIFFUSION OPERATOR ALONG ROD AXIS

Chain rule

Using Cartesian coordinates and $\mathbf{u} \cdot \mathbf{u} = 1$, we obtain

$$\mathcal{F}_{r\parallel} \cdot (v \mathcal{F}_{r\parallel} f) \stackrel{\text{def}}{=} \mathbf{u} \left(\mathbf{u} \cdot \frac{\partial}{\partial \mathbf{r}} \right) \cdot \left[v \mathbf{u} \left(\mathbf{u} \cdot \frac{\partial f}{\partial \mathbf{r}} \right) \right] \quad (\text{B1})$$

$$= v \left(\mathbf{u} \cdot \frac{\partial}{\partial \mathbf{r}} \right) \left(\mathbf{u} \cdot \frac{\partial f}{\partial \mathbf{r}} \right) + \left(\mathbf{u} \cdot \frac{\partial v}{\partial \mathbf{r}} \right) \times \left(\mathbf{u} \cdot \frac{\partial f}{\partial \mathbf{r}} \right). \quad (\text{B2})$$

Again using $\mathbf{u} \cdot \mathbf{u} = 1$, we get from the above equation

$$\mathcal{F}_{r\parallel} \cdot (v \mathcal{F}_{r\parallel} f) = v \mathbf{u} \left(\mathbf{u} \cdot \frac{\partial}{\partial \mathbf{r}} \right) \cdot \mathbf{u} \left(\mathbf{u} \cdot \frac{\partial f}{\partial \mathbf{r}} \right) + \mathbf{u} \left(\mathbf{u} \cdot \frac{\partial v}{\partial \mathbf{r}} \right) \cdot \mathbf{u} \left(\mathbf{u} \cdot \frac{\partial f}{\partial \mathbf{r}} \right). \quad (\text{B3})$$

On simplifying we finally obtain

$$\mathcal{F}_{r\parallel} \cdot (v \mathcal{F}_{r\parallel} f) = v \mathcal{F}_{r\parallel}^2 f + \mathcal{F}_{r\parallel} v \cdot \mathcal{F}_{r\parallel} f. \quad (\text{B4})$$

Divergence theorem

Integrating Eq. (B1) over an arbitrary volume V , we get

$$\int_V \mathcal{F}_{r\parallel} \cdot (v \mathcal{F}_{r\parallel} f) d\mathbf{r} = \int_V \mathbf{u} \left(\mathbf{u} \cdot \frac{\partial}{\partial \mathbf{r}} \right) \left[v \mathbf{u} \left(\mathbf{u} \cdot \frac{\partial f}{\partial \mathbf{r}} \right) \right] d\mathbf{r}. \quad (\text{B5})$$

Defining

$$\mathbf{G} = \mathbf{u} G = \mathbf{u} \left[v \left(\mathbf{u} \cdot \frac{\partial f}{\partial \mathbf{r}} \right) \right] \quad (\text{B6})$$

Eq. (B5) becomes

$$\int_V \mathcal{F}_{r\parallel} \cdot (v \mathcal{F}_{r\parallel} f) d\mathbf{r} = \int_V \mathbf{u} \left(\mathbf{u} \cdot \frac{\partial}{\partial \mathbf{r}} \right) \cdot \mathbf{G} d\mathbf{r} \quad (\text{B7})$$

$$= \int_V \left(\mathbf{u} \cdot \frac{\partial \mathbf{G}}{\partial \mathbf{r}} \right) d\mathbf{r}. \quad (\text{B8})$$

On simplification we get

$$\int_V \left(\mathbf{u} \cdot \frac{\partial \mathbf{G}}{\partial \mathbf{r}} \right) d\mathbf{r} = \int_V \left(u_i \frac{\partial G}{\partial x_i} \right) d\mathbf{r} = \int_V \frac{\partial (G u_i)}{\partial x_i} d\mathbf{r} \quad (\text{B9})$$

since u_i and x_i are independent variables. Thus

$$\int_V \left(\mathbf{u} \cdot \frac{\partial \mathbf{G}}{\partial \mathbf{r}} \right) d\mathbf{r} = \int_V \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{G} d\mathbf{r} = \int_S \mathbf{G} \cdot \mathbf{n} dS \quad (\text{B10})$$

using the Gauss divergence theorem.⁹ \mathbf{n} is an outward pointing unit normal vector to the surface S which bounds the volume V . On simplification we finally obtain

$$\int_V \mathcal{F}_{r\parallel} \cdot (v \mathcal{F}_{r\parallel} f) d\mathbf{r} = \int_S v \mathcal{F}_{r\parallel} f \cdot \mathbf{n} dS. \quad (\text{B11})$$

APPENDIX C: SIMPLIFIED TERMS FOR THE ROTOTRANSLATIONAL DIFFUSION EQUATION USING CYLINDRICAL COORDINATES FOR TRANSLATIONAL DIFFUSION

Here we retain spherical coordinates for \mathbf{u} (Appendix A), while the spatial gradient operator is expanded in cylindrical coordinates (ρ, ϕ_r, z) , where ρ , z , and ϕ_r denote the radial, axial, and azimuthal positional coordinates of the center of mass of the rod, respectively. We follow the procedure of Appendix A. The gradient operator is given by Eq. (A2), and the partial derivatives in cylindrical coordinates are given by¹³

$$\frac{\partial}{\partial x} = \cos \phi_r \frac{\partial}{\partial \rho} - (\sin \phi_r / \rho) \frac{\partial}{\partial \phi_r}, \quad (\text{C1})$$

$$\frac{\partial}{\partial y} = \sin \phi_r \frac{\partial}{\partial \rho} + (\cos \phi_r / \rho) \frac{\partial}{\partial \phi_r}, \quad (\text{C2})$$

$$\frac{\partial}{\partial z} = \frac{\partial}{\partial z}. \quad (\text{C3})$$

Using these we get

$$\mathcal{F}_{r\parallel} = \mathbf{u}(\mathbf{u} \cdot \mathcal{F}_r) = \mathbf{u} \left(A_c \frac{\partial}{\partial \rho} + B_c \frac{\partial}{\partial z} \right), \quad (\text{C4})$$

where

$$A_c = \sin \Theta \cos(\phi - \phi_r), \quad (\text{C5})$$

$$B_c = \cos \Theta. \quad (\text{C6})$$

In the above equations, $\partial/\partial\phi_r$ terms have been neglected based on the assumption of azimuthal symmetry.

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