Acceleration of the Polymerization of Rodlike Molecules by Flow

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Abstract: Polymerization of rigid rodlike molecules with reactive end groups (e.g., poly(*p*-phenylene terephthalamide)) requires near parallel orientation of the molecules. The reaction becomes diffusion-limited as the rotational diffusivity of the reacting molecules decreases to low values in the later stages of the reaction, and this ultimately limits the molecular weight of the polymers formed. Here a theoretical study of the step-growth reaction between rodlike molecules in a solution under extensional flow is carried out. A model for the process is developed using the Smoluchowski approach which yields the effective reaction rate constant for the process in terms of the system parameters. The rate of reaction increases with extensional rate because of flow-induced orientation of molecules, and for sufficiently high extensional rates, the rate constant becomes higher than the intrinsic value. This is an instance where flow has a catalyst-like effect on the reaction. The results indicate that flow can be a useful tool for accelerating reactions and thus improving yield and selectivity for orientation-dependent reactions between large anisotropic molecules.

Introduction

Commercially important rodlike polymers (e.g., poly(*p*-phenylene terephthalamide)) (PPDT) typically have phenylene rings in their backbone which restrict their internal rotation, thus preventing local bending and making the polymers take an elongated form.[1] The reaction between such rodlike molecules with reactive sites at the rod ends requires the translation of reacting pair of molecules such that their ends are within a critical reaction radius, and rotation of the molecules to a near parallel orientation. Both of these steps can occur only by diffusion in an unstirred, isotropic solution. With increasing degree of polymerization, diffusivities decrease, and the reaction may become diffusion-limited.[2] The reorientation of molecules is particularly important[2] since their rotational diffusivities decrease sharply with length,[3] thus significantly limiting the rate of reaction. Low rates of reaction limit the final molecular weight obtained due to end-capping side reactions which become important.

Agarwal and Khakhar[4,5] carried out experiments to synthesize PPDT in a two-reactor system to investigate the effect of shear flow. The reactants were mixed in the first reactor for 1 min, and then they were transferred to the second reactor which had a concentric cylinder Coutte flow geometry. A uniform shear flow was generated in the gap between the cylinders by rotating the inner cylinder. At low shear rates in the second reactor, the rate of polymerization decreased sharply with increasing molecular lengths. However, the rate of polymerization increased with shear rate if the shear rates were high ($\sim$400 s^{-1}) in the final stage of reaction, when shear flow produced significant orientation of molecules along streamlines. Similar results were obtained by Jo et al.[6] for solution polymerization of rodlike polyesters.

A related phenomenon is the increase in the rate of reaction due to transition to the liquid crystalline nematic state, observed by Chow et al.[7] in the synthesis of rodlike polymer poly(*p*-phenylene benzobisthiazole). Thus, formation of liquid crystalline domains of highly oriented rodlike molecules may increase the rate of reaction. However, when the transition to the nematic phase occurs early in the reaction, Spencer and Berry[8] found that there is no significant increase in the rate of polymerization after the transition, because of the slow translational diffusivity of the rods in the direction perpendicular to the rod axis.

The studies reviewed above indicate the importance of molecular orientation in the reaction between rodlike molecules. Here we present a theoretical model to study the effect of an orienting flow on the diffusion-limited reaction between rodlike molecules in solution. Diffusion-limited reactions of anisotropic molecules have been studied for several systems, including rodlike molecules, and reviews of previous work are available.[9−13] However, the effect of flow-induced orientation on the process has not been previously analyzed with the exception of a 2D computational study by Agarwal and Khakhar[14] of noninteracting bead rod chains in shear flow. A model to calculate the

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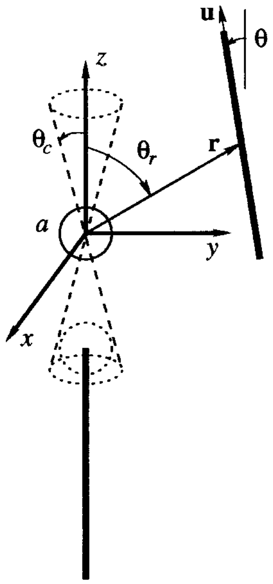

Figure 1. Schematic diagram showing the criteria for reaction of rodlike molecules. Molecules can react only if proximity ($r < a$) and orientation ($\theta < \theta_c$) requirements are satisfied. The coordinate system used in the model is also defined.

effective rate constant for the diffusion-limited polymerization reaction of rodlike molecules in a semidilute solution under extensional flow is formulated below using the Smoluchowski[15] approach. Computational results, obtained by the finite difference method, are given next, followed by the conclusions of the study.

Model and Computations

We consider the diffusion-limited reaction between rodlike molecules of length L in a solution as a model for the step growth reaction to synthesize PPDT. The solution is subjected to an axisymmetric extensional flow given by the velocity field

$$v_x = -\frac{1}{2}\epsilon x \quad v_y = -\frac{1}{2}\epsilon y \quad v_z = \epsilon z \tag{1}$$

where ϵ is the extensional rate and the coordinate directions are shown in Figure 1. The flow has a tendency to orient molecules along the z-axis. The reaction requires molecules to satisfy a relative orientation criterion (described below), and the concentration of the solution is sufficiently high as to be in the semidilute regime.[3] In this regime, molecules are easily oriented by flow due to their low rotational diffusivities. Thus, flow and reaction are coupled. In the model given below, the molecules are treated as rods in a continuum, and the presence of solvent molecules, hydrogen bonding between molecules, and so forth are neglected. These simplifications, however, may be justified considering that diffusion, which occurs over length scales which are much larger than the length scales for molecular interactions, dominates the process. Solvent effects are lumped into the diffusivities and into the intrinsic second-order rate constant for the reaction, which are parameters of the model.

The steady-state convective-diffusion equation for the molecules in the absence of any interaction potential between the molecules is given by[3]

$$\frac{\partial}{\partial \mathbf{r}}\cdot[D_{\parallel}\mathbf{uu} + D_{\perp}(\mathbf{I} - \mathbf{uu})]\cdot\left(\frac{\partial C}{\partial \mathbf{r}}\right) - \frac{\partial}{\partial \mathbf{r}}\cdot(\mathbf{K}\cdot\mathbf{r}C) + \mathbf{R}\cdot(\hat{\mathbf{D}}_{\mathrm{r}}\mathbf{R}C) - \mathbf{R}\cdot[\mathbf{u}\times(\mathbf{K}\cdot\mathbf{u}C)] = 0 \tag{2}$$

where $D_{\parallel}$ is diffusivity parallel to the rod axis, $D_{\perp}$ is diffusivity perpendicular to the rod axis, $\mathbf{u}$ is the unit vector along the rod axis, $C(\mathbf{r}, \mathbf{u})$ is the number density of rods, $\mathbf{K}$ is the velocity gradient tensor, and the operators $\partial/\partial\mathbf{r}$ and $\mathbf{R} \equiv \mathbf{u} \times \partial/\partial\mathbf{u}$ denote the spatial and rotational gradients, respectively. The anisotropic rotational diffusivity $\hat{D}_{\mathrm{r}}$ is given by[3]

$$\hat{D}_{\mathrm{r}} = D_{\mathrm{r}}\left[\frac{4}{\pi}\int C(\mathbf{r}, \mathbf{u}')\,|\mathbf{u} \times \mathbf{u}'|\,d\mathbf{u}'\right]^{-2} \tag{3}$$

where D_{r} is the rotational diffusivity in an isotropic solution.

The approximate reaction criterion for the approach of two reactive neighboring tips in terms of the position of the center of mass of the diffusing molecules is given by the condition $|\mathbf{r}| \le a$ (Figure 1).[16,17] The near parallel alignment required for reaction between two rodlike molecules is quantitatively given by $\theta \le \theta_{\mathrm{c}}$, where θ is the relative angle of orientation between the molecules and θ_{c} is the specified critical angle. The reaction zone is considered impenetrable, and the partially absorbing reaction boundary condition for translational diffusion flux to the reaction surface ($|\mathbf{r}| = a$) is then

$$\mathbf{n}\cdot[D_{\parallel}\mathbf{uu} + \mathrm{D}_{\perp}(\boldsymbol{I} - \mathbf{uu})]\cdot\left(\frac{\partial C}{\partial \mathbf{r}}\right) = \begin{cases} k_{\mathrm{hom}}C/[2\pi a^2(1 - \cos\theta_c)], & \theta \le \theta_c \\ 0, & \theta > \theta_c \end{cases} \tag{4}$$

where $\mathbf{n}$ is a unit vector perpendicular to the spherical reaction surface and k_{hom} is the intrinsic second-order reaction rate constant (i.e., the rate constant in the absence of diffusional limitations and flow).

Due to axisymmetry of the problem and for $\theta_{\mathrm{c}} \ll 1$, we find $C = C(r, \theta, \theta_r)$ (Figure 1), which results in simplification of the governing equation (eq 2). The rate constant in this case is obtained from the computed number density field as

$$k_{\mathrm{eff}} = \frac{k_{\mathrm{hom}}\int_0^{\pi/2}\int_0^{\theta_c}(C/\langle C_\infty\rangle)_{r=a}\sin\theta\,d\theta\,\sin\theta_r d\theta_r}{1 - \cos\theta_c} \tag{5}$$

where $C_\infty(\theta)$ is the far field number density and $\langle\rangle$ denotes an average over all orientations. The far field boundary conditions and the symmetry boundary conditions for the problem are

$$C = C_\infty(\theta), \quad r \to \infty \tag{6}$$

$$\frac{\partial C}{\partial \theta} = 0, \quad \theta = 0, \quad \frac{\pi}{2} \tag{7}$$

$$\frac{\partial C}{\partial \theta_r} = 0, \quad \theta_r = 0, \quad \frac{\pi}{2} \tag{8}$$

The finite difference method (FDM) in three dimensions is used here to obtain the solution of the governing equation (eq 2) with the boundary conditions (eqs 4, 6−8). The governing equations are discretized into intervals using specific difference schemes for each variable, and the coefficients of the nodal points are stored in the indexed sparse matrix form.[18] The assembled equations are solved by using biconjugate gradient method.[18] Grid sizes are taken to be small enough so that further reduction in size does not give any improvement in the solution. The homogeneous (no spatial variation) but anisotropic far field number density ($C_\infty(\theta)$) is similarly obtained using the finite difference method. The governing equation in this case is eq 2 with spatial gradient terms (terms containing $\partial/\partial\mathbf{r}$) omitted, with boundary conditions given by eqs 7 and 8. Predictions of the model for the no-

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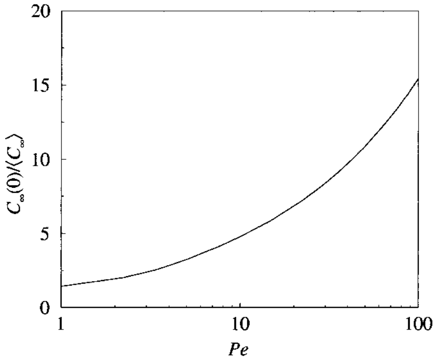

Figure 2. Variation of the normalized far field number density of molecules oriented along the axis of stretching ($C_\infty(0)/\langle C_\infty\rangle$) with Peclet number ($Pe$).

Table 1. Parameters for Calculation of the Effective Rate Constant (k_{eff}) for Different Polymer Lengths (L)

L_0	12 Å
d	6 Å
a	3 Å
θ_c	0.01 rad
C_0	0.2 mol/L
k_{hom}	6.28×10^{-4} l/mol s
η	2.57 mPa s
T	293 K

flow case ($\epsilon = 0$) are in good agreement with the numerical results of Agarwal and Khakhar[16,17] for the same system. The solution is isotropic in this case, with $C_\infty = \langle C_\infty\rangle$ constant.

Results and Discussion

The far field number density, $C_\infty(\theta)$, depends only on the Peclet number defined as

$$Pe = \frac{\epsilon}{D_r} \tag{9}$$

As the polymerization proceeds, the rotational diffusivity decreases due to increasing polymer lengths. Thus, for a constant extensional rate (ϵ), the Peclet number increases with polymerization. Computed results for the number density of molecules (C_∞) oriented in the direction of extension ($\theta = 0$) show that the solution is nearly isotropic at $Pe = 1$ since $C_\infty(0)/\langle C_\infty\rangle \approx 1$ (Figure 2). However, for $Pe > 10$, $C_\infty(0)/\langle C_\infty\rangle \gg 1$ indicating that a significant fraction of the molecules are oriented in the flow direction (Figure 2).

The effective rate constant is computed for different polymer lengths using the parameters given in Table 1. The parameters correspond to PPDT polymerization.[19] The translational and rotational diffusivities are computed from correlations given by Broersma[20] and Teraoka and Hayakawa.[21,22] Figure 3 shows the change in relative rate constant, $k_{\mathrm{rel}} = k_{\mathrm{eff}}/k_{\mathrm{hom}}$, with degree of polymerization, $\mathrm{DP} = L/L_0$, where L_0 is the monomer length, under different flow conditions. At low degrees of polymerization (DP < 10) the reaction is kinetically controlled and thus k_{rel} for all cases. In the absence of flow ($\epsilon = 0$) the rate constant falls monotonically with increasing degree of polymerization (DP). At higher extensional rates (ϵ), however, the rate constant first falls and then increases. This is in agreement with the experimental data of Agarwal and Khakhar[4] for simple shear flow. Computations carried out for a wide range of Peclet numbers indicate that $k_{\mathrm{rel}}(Pe)/k_{\mathrm{rel}}(0) \propto Pe^{0.6}$, where $k_{\mathrm{rel}}(0)$ is the relative rate constant in the absence of flow.[17] For a fixed extensional rate, this implies that the rate relative to the no-flow case goes as $D_{\mathrm{r}}^{-0.6}$.

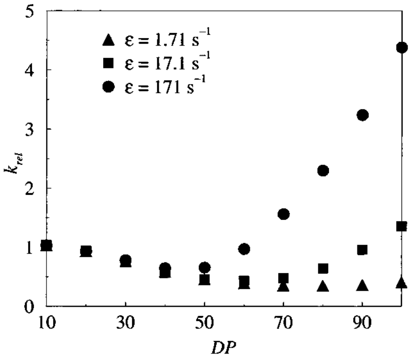

Figure 3. Variation of relative rate constant k_{rel} with the degree of polymerization (DP) for different extensional rates (ϵ). The parameters used in the computations are given in Table 1.

An unanticipated result obtained here is that the relative rate constant increases to values greater than unity (Figure 3), which implies that the rate constant is higher than the intrinsic value. In hindsight, the explanation for this effect is straightforward. Flow-induced orientation results in an increased number density of molecules which satisfy the reaction criterion ($\theta < \theta_{\mathrm{c}}$). Thus, the rate constant, which is based on the bulk number density ($\langle C_\infty\rangle$), becomes larger than unity.

The mechanism of flow-induced enhancement of reaction rate is analogous to that in template-based catalysts[23] where molecular adsorption increases the number density of molecules with mutual orientations favorable for reaction and to that in molecular sieve catalysts in which the pore structure may provide a framework for orientation of molecules relative to reactive sites, improving selectivity of reactions.[24] Here flow arranges molecules into orientations favorable for reaction. The effect is of practical significance since it occurs at quite modest extensional rates. Higher shear rates would be required to obtain the same orientation in simple shear flow.

Conclusions

Predictions of a model for diffusion-controlled reaction between rodlike molecules in a solution subjected to an extensional flow show that flow-induced orientation can significantly increase the rate of reaction. The acceleration of the reaction is found to occur beyond a critical degree of polymerization when the molecules are long enough to be significantly oriented by the flow. The rate constant relative to the value in the absence of flow is found to vary as $(\epsilon/D_{\mathrm{r}})^{0.6}$; thus, with increasing length, the rotational diffusivity decreases, and the effective rate constant increases. The effective rate constant is found to become larger than the intrinsic rate constant for the reaction at relatively low extensional rates (ϵ). The mechanism for flow-induced acceleration of the reaction is analogous to that in template and molecular sieve catalysts.

The results obtained here have a direct relevance for polymerization of rodlike molecules in solution. The results would also be applicable for polymerization of rodlike molecules in

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the melt phase, provided the melt is not in the nematic phase. In this case, slow diffusion of the condensation product could, however, limit the conversion because of the reverse reaction. Polymerization in the nematic phase may be benefitted by shearing; however, diffusional limitations due to slow translation perpendicular to the rod axis may be controlling.[8] In the case of main-chain liquid crystalline polymers with flexible spacers, the orientation constraint would be greatly relaxed; thus, benefits of shearing would not be as significant as for the case of rodlike polymers. Finally, we note that this mechanism is not relevant for chain-growth polymerizations, in which monomers add on one at a time to a growing chain, because of the high rotational diffusivity of the monomers. However, carrying out a free radical reaction to synthesize flexible polymers in a liquid crystalline medium may be beneficial.[25]

Traditionally, flow has been primarily used as a means of mixing in liquid-state reactions. Here on the basis of computations for a simple prototype system (rodlike molecules in solution) we show it can be useful tool for accelerating reactions and thus improving yield and selectivity for orientation-dependent reactions between large anisotropic molecules. The results also suggest that experimental studies of the kinetics of such reactions could be affected in a complex way by reactor geometry and stirring, and careful experimentation is required to eliminate these effects.

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