Polymerization Kinetics of Rodlike Molecules under Quiescent Conditions

J. Srinivasalu Gupta, Ameya Agge, and D. V. Khakhar
Dept. of Chemical Engineering, Indian Institute of Technology—Bombay, Powai, Mumbai 400076, India

The kinetics of solution polymerization to synthesize poly(p-phenylene terephthalamide), a rodlike polymer, was studied theoretically and experimentally. The reaction was conducted under quiescent conditions to eliminate effects of flow-induced orientation that are known to affect the kinetics of the process. Experiments included determining the degree of polymerization and polydispersity index for different times of reaction. Theoretical study comprised calculating the effective rate constant for the diffusion-controlled reaction using Smoluchowski's approach and computing the evolution of the molecular-weight distribution using the length-dependent effective rate constant obtained in the first part. Experiments showed significant slowing of the reaction and narrow molecular-weight distributions due to diffusion control. The degree of polymerization and the polydispersity index variation with time is nearly the same for the two initial monomer concentrations. The Smoluchowski theory predicts the effective rate constant to be $k_{eff} \propto \rho^{-0.8}L^{-3.5}$ *for large L, with ρ the local number concentration of rods and L the length of the reacting rodlike molecule. The model has two parameters obtained by a least-squares fit to one set of data of degree of polymerization vs. time. Results of the population balance calculations using the computed effective rate constant matched with experimental data for degree of polymerization and polydispersity vs. time for both initial monomer concentrations. The model, augmented to account for slow, end-capping side reactions, predicted an optimal initial monomer concentration for obtaining the highest degree of polymerization for a fixed reaction time, as reported in previous experimental studies.*

Introduction

Rodlike polymers formed into fibers and films are finding increasing commercial use because of their superior mechanical properties and excellent thermal resistance (Kwolek et al., 1988; Preston, 1988). The polymerization reaction for most such molecules follows the step-reaction mechanism [any two oligomers with the appropriate functional groups can react to form a larger molecule, (Flory, 1953)], and becomes strongly diffusion controlled at moderate degrees of polymerization (Cotts and Berry, 1981). The slowing of the primary reaction due to diffusion control usually precludes the formation of high molecular-weight polymer due to the capping of functional groups by side reactions that become significant. The kinetics of polymerization of rodlike molecules has consequently been the subject of a number of previous studies, and a recent review is given in Khakhar (1999). We summarize some of the important results below.

In an early study Cotts and Berry (1981) proposed that slowing of the polymerization process was due to rotational diffusion control, basing their argument on the sharp decrease in rotational diffusivity with molecular length ($D_r \propto L^{-7}$; Doi and Edwards, 1986), and the requirement that any two reacting oligomers must be nearly parallel to each other for a bond to form. The orientation constraint for reaction requires rotation of the entire molecule, which is very slow for long molecules. This is in contrast to flexible molecules in which orientational constraints for reaction between end groups are not rate limiting due to rapid segmental diffusion (Flory, 1953). Experimental measurements by Cotts and Berry

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Correspondence concerning this article should be addressed to D. V. Khakhar.

(1981) showed the slowing of the reaction to be accompanied by a relatively narrow molecular-weight distribution (polydispersity index less than 2). This is consistent with the mechanism just given, since longer molecules react much more slowly than shorter ones, leading to a distribution that is narrower than the Flory (1953) distribution for equal reactivity (polydispersity index equal to 2). Most previous studies of polymerization kinetics of rodlike molecules report slowing of the polymerization reaction due to diffusion control (Bair et al., 1977; Cotts and Berry, 1981; Jingsheng et al., 1981; Dvornic et al., 1993). An exception is the study of Roitman et al. (1993) carried out under high shearing in the neumatic phase in which the rate of polymerization was nearly constant throughout the reaction. Another common feature of the polymerization of rodlike molecules is the existence of an optimal monomer concentration at which the highest molecular-weight polymer is obtained (Bair et al., 1977; Jingsheng et al., 1981; Dvornic et al., 1993). An explanation for this effect is not available.

Flow during polymerization has an important effect on the process. Intensive mixing is found to be necessary for obtaining high molecular-weight polymer (Bair et al., 1977), and the type of mixer used has a significant effect on the molecular weight (Volbracht, 1989). Agarwal and Khakhar (1992a, 1993a) carried out studies of the polymerization of rodlike molecules [poly (*p*-phenylene terephthalamide)] under well-defined flow conditions using a Couette flow geometry. Shearing during polymerization resulted in a significant increase in the rate of polymerization, with up to a twofold increase in the degree of polymerization for a fixed time of reaction. Simultaneous birefringence measurements showed that the cause for increase in the polymerization rate is due to shear induced orientation, which results in a greater number of pairs of molecules that are suitably oriented for reaction. The wide molecular-weight distributions obtained in the sheared systems (polydispersity index greater than 4) are in accordance with the proposed mechanism, since the longer molecules are oriented to the greatest extent and thus are more likely to react. The Brownian dynamics study of Agarwal and Khakhar (1993b) for diffusion-controlled reaction between bead-chain molecules carried out in two dimensions gave predictions in qualitative agreement with the preceding results. Jo et al. (1997) carried out an experimental study of solution polymerization to form rodlike polyesters similar to that of Agarwal and Khakhar (1992a) and also observed an increase in the polymerization rate with shearing. These results indicate that most earlier studies of kinetics have an uncontrolled factor—flow-induced orientation due to stirring—that affects the rate of polymerization. Since the flow field in most cases is complex, different results are obtained in the different studies, even with the same reaction system.

The objective of the present work is to obtain a fundamental understanding of the kinetics of diffusion-controlled polymerization of rodlike polymers under quiescent conditions (no flow) by means of experiments and theory. Previous theoretical studies report the calculation of the effective rate constant for diffusion-controlled polymerization of rodlike molecules by means of computations based on the Smoluchowski (1917) approach using the finite-element method (Agarwal and Khakhar, 1992b, 1993c) and Brownian dynamics (Gupta and Khakhar, 1997, 1998), and these are briefly reviewed in the section titled "Theory." An experimental study of the kinetics of solution polymerization of *p*-phenylene diamine and terephthaloyl chloride to poly(*p*-phenylene terephthalamide) (PPTA) under no-flow conditions is carried out. Theoretical estimates of the effective rate constant for the diffusion-controlled polymerization in terms of the system parameters are obtained by means of finite-element method computations. The functional form for the rate constant with a simple dependence on the lengths of the reacting molecules and the concentration is extracted from these results. Finally, we present a population balance model for the evolution of the molecular-weight distribution using the obtained expression for the rate constant. Predictions of the model are compared with experimental results.

Experimental Procedure

Kinetics

Experimental studies of the kinetics of solution polymerization to synthesize PPTA were carried out under no flow conditions. The reaction between *p*-phenylene diamine (PPD) and terephthaloyl dichloride (TPC) was carried out in mixed solvents *N*-methyl pyrrolidone (NMP) and hexamethyl phospharamide (HMPA) (HMPA is known to be carcinogenic in rats, and appropriate precautions must be taken when handling it) in a 3:1 volume ratio. The monomers PPD (Aldrich) and TPC (Aldrich) were purified by vacuum sublimation, and the solvents NMP (SD Fine) and HMPA (Aldrich) were purified by vacuum distillation under nitrogen streams of 10-mm Hg and 5-mm Hg absolute pressure, respectively. The solvents after purification were stored over 4-Å molecular sieves (SD Fine). All the purified monomers and solvents were placed in a glove box where the powdering of the monomers, weighing, and the reaction were carried out. The moisture content in the glove box was reduced to less than 100 ppm by drying with air circulation over sodium hydroxide and potassium hydroxide pellets. The polymerization was carried out in a jacketed glass reactor. Initially, the solvent mixture (33 mL NMP and 11 mL HMPA), along with powdered PPD, was stirred well. When all the PPD was dissolved, the mixture was cooled to 3°C for 10 min. The polymerization was initiated at this stage by adding powdered TPC under rapid stirring at 3,000 rpm. The stirring was stopped after 1 min of adding TPC. For 0.2 mol/L concentration, the amounts of PPD and TPC used were 0.951 g and 1.786 g, respectively, while for 0.1 mol/L concentration, 0.475 g and 0.894 g were used. The kinetics of the reaction were studied by quenching with water at a desired time. The precipitated polymer was washed thoroughly with water and dried under vacuum at 80°C for 10 h. The viscosity (μ) of a solution of the polymer in 98% sulfuric acid of concentration $C_s = 0.5$ wt % at 30°C was measured using an Ubbelodhe viscometer. The inherent viscosity was obtained as $\eta_{inh} = \ln(\mu/\mu_0)/C_s$, where μ_0 is the viscosity of the solvent (98% sulphuric acid). The weight-average molecular weight $\overline{M}_w$ was then calculated using the Mark-Houwink relationship obtained by Arpin and Strazielle (1977)

$$\overline{M}_w = 3{,}902.39\eta_{inh}^{1.556}, \tag{1}$$

where the units of η_{inh} are dL/g. The weight average degree of polymerization $\overline{DP}_w$ was computed as $\overline{DP}_w = \overline{M}_w/238$, where 238 is the molecular weight of the repeat unit of PPTA.

Molecular-weight distribution determination

The molecular-weight distribution (MWD) was determined by gel permeation chromatography (GPC). Although PPTA is not soluble in conventional solvents (such as tetrahydrofuran), the solubility is greatly increased by modifying the amide linkages through an *N*-alkylation reaction. We followed the *N*-alkylation procedure of Ogata et al. (1984) and Takayanagi and Katayose (1981), in which the metallation reaction of PPTA with sodium hydride in dimethyl sulfoxide (DMSO) was carried out, followed by reactions with *N*-octadecyl bromide.

DMSO (SD Fine) was purified by vacuum distillation under nitrogen stream (5 mmHg absolute pressure) over sodium hydroxide, and stored over 4-Å molecular sieves (SD Fine). PPTA of 0.0021 mol amide unit (0.25 g) is sliced into fine flakes. Slight excess of sodium hydride (60% suspension in *N*-paraffin, Emerck) (0.105 g) was dissolved in 30 mL DMSO under a nitrogen stream in a jacketed reactor in the dry glove box. The temperature was raised slowly to 70°C and maintained for 1 h, until a clear solution was obtained, and the mixture was allowed to cool to 30°C. The PPTA was added, and reaction continued for 10 h, until all the PPTA had dissolved, giving a transparent deep red coloration to the now viscous solution. A slight excess of *N*-octadecyl bromide was added, which caused the solution viscosity to drop very quickly. The mixture was stirred for 18 h. At this time, the polymer was precipitated in water, collected by filtration, and washed repeatedly with water and acetone. The resulting polymer was dried under vacuum at 80°C. The molecular weight of each repeat unit of *N*-octadecyl PPTA is 742.

The GPC of *N*-alkylated polymer was carried out using a LC-10AS solvent delivery system, Chromatopac Monitor C-R 7A, RID-6A differential refractometer detector, and a Shimpack GPC-805 column. Calibration of the column was carried out using polystyrene standards (Polymer Lab). The reduction in melting points and degree of crystallinity of the polymer due to alkylation, observed by Takayanagi and Kayatose (1981), lead to the conclusion that the alkylated polymer must be flexible. Thus alkylated molecules should form globular rather than rodlike structures in dilute solutions, and the calibration of the column using polystyrene standards is reasonable. The solvent used was tetrahydrofuran at a temperature of 25°C and at a flow rate of 1 mL/min.

Theory

Diffusion-controlled polymerization of rodlike molecules

We obtain the effective rate constant for the diffusion-controlled reaction between rodlike molecules, following the Smoluchowski (1917) approach. The mathematical formulation of the theory for this case is given by Agarwal and Khakhar (1993c), incorporating the orientational constraint for reaction as well as rotational and translational diffusion resistances. Computational results obtained using the finite-element method show that both rotational diffusion and translational diffusion perpendicular to the rod axis (which also decreases sharply with molecular length) limit the rate of polymerization. For a fixed value of the translational diffusivity perpendicular to the rod axis, reducing the rotational diffusivity results initially in a sharp decrease in the effective rate constant, followed by an asymptote to a constant value corresponding to the case of nearly zero rotational diffusivity. In this limit the reaction flux is entirely due to the translational diffusion of molecules that have an orientation that satisfies the orientational constraint for the reaction. Lower values of the translational diffusion perpendicular to the rod axis give lower effective rate constants for a fixed rotational diffusivity. Gupta and Khakhar (1997, 1998) used an alternate numerical method—pairwise Brownian dynamics (Northrup et al., 1984)—to calculate the effective rate constant. The method is attractive because of its simplicity and robustness. It is, however, computationally intensive. Results obtained using Brownian dynamics were in agreement with those obtained by the finite-element method. Here we give a brief formulation of the problem, following closely Agarwal and Khakhar (1993c), and details of estimation of the parameters required for the computations. The finite-element method is used in the computations and details of the solution procedure can be found in Agarwal and Khakhar (1993c).

Consider the reaction between equal-sized molecules of length L. The diffusion of rodlike molecules at steady state is given by (Doi and Edwards, 1986)

$$\frac{\partial}{\partial \boldsymbol{R}} \cdot \left[D_{\parallel} \boldsymbol{uu} + D_{\perp} (\boldsymbol{I} - \boldsymbol{uu}) \right] \cdot \frac{\partial \psi}{\partial \boldsymbol{R}} + \frac{\partial}{\partial \boldsymbol{u}} \cdot \left(D_r \frac{\partial \psi}{\partial \boldsymbol{u}} \right) = 0, \quad (2)$$

where $\psi(\boldsymbol{r}, \boldsymbol{u})$ is the rod number density, $\boldsymbol{r}$ is the position vector to the rod center of mass, and $\boldsymbol{u}$ is a unit vector along the rod axis. The operators $\partial/\partial \boldsymbol{R}$ and $\partial/\partial \boldsymbol{u}$ denote spatial and rotational gradients, $D_{\parallel}$ and $D_{\perp}$ are the translational diffusivities parallel and perpendicular to the rod axis, D_r is the rotational diffusivity, and $\boldsymbol{I}$ is the unit tensor. The calculation of the rate constant requires the estimation of the diffusive flux of molecules to a reactive site at the tip of a test molecule, as shown in Figure 1. Agarwal and Khakhar (1992b) showed that the corresponding boundary condition is

$$\left[D_{\parallel} \boldsymbol{uu} + D_{\perp} (\boldsymbol{I} - \boldsymbol{uu}) \right] \cdot \left(\frac{\partial \psi}{\partial \boldsymbol{R}} \right) \cdot \boldsymbol{n} = \begin{cases} k_s \psi & \theta \le \theta_c, \quad |\boldsymbol{r}| = a \\ 0 & \theta > \theta_c, \quad |\boldsymbol{r}| = a \end{cases}, \quad (3)$$

where $\boldsymbol{n}$ is the unit vector perpendicular to the spherical reaction surface of radius a, θ_c is the critical orientation angle for reaction, and k_s is the surface intrinsic reaction rate constant. The far-field condition is

$$\psi = \rho \quad |\boldsymbol{r}| \to \infty, \quad (4)$$

where ρ is the bulk number concentration. For $\theta_c \ll 1$, the number density field is axisymmetric so that $\psi = \psi(r, \theta_r, \theta)$, where (r, θ_r) specify the position of center of mass in spherical coordinates and θ is the orientation angle (Figure 1). The

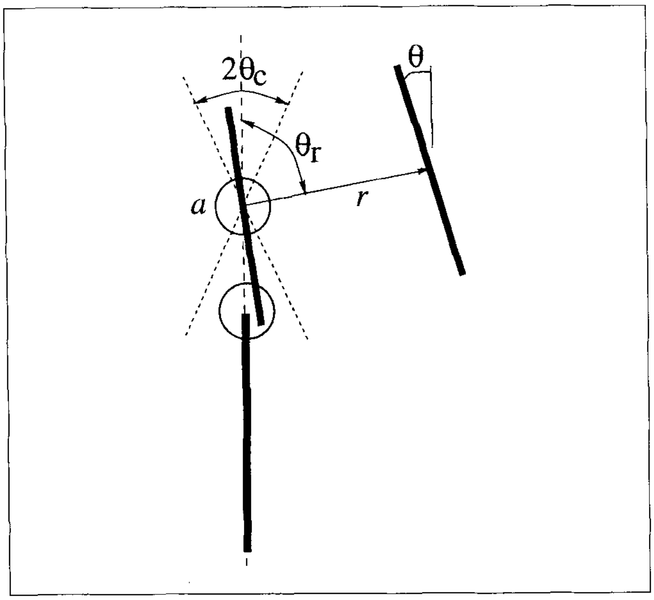

Figure 1. Condition for reaction between two rodlike molecules.

The coordinate system used in the computations is also shown.

effective rate constant in molar units is then

$$k_{\text{eff}} = \frac{4\pi a^2 k_s}{N_A} \int_0^{\pi/2} \int_0^{\theta_c} [\psi(a, \theta_r, \theta)/\rho] \sin\theta \, d\theta \sin\theta_r \, d\theta_r, \tag{5}$$

where N_A is Avogadro's number. The preceding equation gives $k_s = k_h N_A / [4\pi a^2(1-\cos\theta_c)]$ in the limit of no diffusional limitations $[\psi(r, \theta_r, \theta) = \rho]$, where k_h is the intrinsic second-order rate constant, that is, the rate constant in the absence of diffusional limitations.

Rescaling the number density with respect to ρ, lengths with respect to a, and casting the governing equations in dimensionless form, we obtain the rate constant in terms of the following dimensionless parameters: the dimensionless rotational diffusion resistance $[s = D_{\parallel}/(a^2 D_r)]$, the dimensionless translational diffusivity perpendicular to the rod axis ($\gamma = D_{\perp}/D_{\parallel}$), the dimensionless intrinsic reactivity ($\alpha = k_s a/D_{\parallel}$), and the critical orientation angle (θ_c). In order to find the dependence of the relative rate constant, $k_{\text{rel}} = k_{\text{eff}}/k_h$ on molecular length (L) and number concentration (ρ), the values of dimensionless parameters are required for different values of the degree of polymerization ($DP = L/L_0$, where L_0 is the length of one repeat unit) and for different initial monomer concentrations. The parameters depend on the diffusivities that may be estimated from correlations; details of the correlations used are given below.

The rotational diffusivity and perpendicular diffusivity of the rod are calculated from Teraoka and Hayakawa (1988, 1989)

$$D_r = D_{r0}(1 + A\rho L^3)^{-2} \tag{6}$$

$$D_{\perp} = D_{\perp 0}(1 + B\rho L^3)^{-2}, \tag{7}$$

where $A = 0.0275$ and $B = 0.044122$ are constants, and D_{r0} and $D_{\perp 0}$ are the corresponding dilute solution diffusivities. The translational diffusivity parallel to the rod axis is taken to be equal to its dilute solution value ($D_{\parallel} = D_{\parallel 0}$).

The dilute solution diffusivities are evaluated using the equations given by Broersma (1981)

$$D_{r0} = \frac{3k_B T(\ln p + \gamma_r)}{\pi \eta L^3} \tag{8}$$

$$D_{\perp 0} = \frac{k_B T[\ln(2p) + \gamma_{\perp}]}{4\pi \eta L} \tag{9}$$

$$D_{\parallel 0} = \frac{k_B T[\ln(2p) + \gamma_{\parallel}]}{2\pi \eta L}, \tag{10}$$

where k_B is Boltzmann constant, T is temperature, η is viscosity, and $p = L/d$ is the aspect ratio. The constants γ_r, $\gamma_{\perp}$, and $\gamma_{\parallel}$ are evaluated by using expressions given by Broersma (1981) of the form

$$\gamma = \Sigma_k a_k (\ln 2p)^{-k} \tag{11}$$

for $0 \leq 1/(\ln 2p) \leq 0.45$, where d is the diameter of the molecule. The values of the coefficients a_k are given in Broersma (1981).

The values of L_0 and d used here are 12 Å and 6 Å, respectively (Onogi et al., 1980). The temperature is 276 K and the viscosity is 2.57 mPa s for the experiments reported here. The reaction site parameters are difficult to estimate, and here we assume reasonable values. Following estimates given in Agarwal and Khakhar (1993c), the reaction site radius is taken to be $a = d/2$, and the critical orientation angle to be $\theta_c = 0.001$ rad. During polymerization, the concentration (ρ) falls with increasing conversion, and to simulate this we take $\rho L = \rho_0 L_0$, where ρ_0 is the initial number concentration of monomers. This relation represents a mol balance if the reaction mixture is at all times monodisperse. Different values of the homogeneous rate constant are taken so as to obtain specific values of the dimensionless intrinsic reactivity (α) at $DP = 100$. Since precise values of some of the parameters are not available, the computations primarily yield a simple functional form (containing fitting parameters) for the effective rate constant in terms of the concentration and lengths that can be utilized in the molecular-weight distribution calculations.

Calculation of the molecular-weight distribution

The evolution of the molecular-weight distribution during polymerization depends primarily on the dependence of the rate constant on the lengths of the reacting molecules and the local concentration of molecules. A few studies have considered the rate constant to vary with molecular length during polymerization. Nanda and Jain (1968) obtained analytical results for the linear dependence of the rate constant on molecular length. More recently Oshanin and Moreau (1995) have presented results for power law and the exponential decrease of the rate constant with length. In contrast, Park

(1988) studied the effect of the acceleration of the rate with increasing length by means of computations. Since expressions for the rate constant for specific systems were not available, these studies give only a qualitative understanding of the polymerization process. We present here a model for the polymerization reaction based on an empirical expression for the rate constant, which takes into account the decrease in the rate constant with polymer length and concentration.

We assume that the polymerization of PPTA follows the irreversible step-growth mechanism represented by the following set of elementary reactions:

$$A_i + A_j \overset{k_{ij}}{\rightarrow} A_{i+j} \quad i,j = 1,2,3,\ldots,N, \tag{12}$$

where A_i denotes molecules with i repeat units, k_{ij} is the rate constant for the reaction the two oligometers, and N is the size of the largest molecule. A population balance analysis of the process gives the following set of balance equations for the molecules for different lengths (Peebles, 1971):

$$\frac{dP_1}{dt} = -P_1 \sum_{j=1}^{N} k_{1j} P_j \tag{13}$$

$$\frac{dP_i}{dt} = -P_i \sum_{j=1}^{N} k_{ij} P_j + \sum_{j=1}^{i^*} k_{j,i-j} P_j P_{i-j}, \tag{14}$$

where P_i is the concentration of species i, and i^* is the integer part of $i/2$.

The rate constant for reaction of the rod molecules is dependent on rod length and number concentration, and we assume the rate constant to be of the following form:

$$k_{ij} = \frac{k_h}{2\left(1 + Z\left(\rho L_i^3\right)^{\beta}\left(L_i/d\right)^{\delta}\right)} + \frac{k_h}{2\left(1 + Z\left(\rho L_j^3\right)^{\beta}\left(L_j/d\right)^{\delta}\right)}, \tag{15}$$

where k_h is the homogeneous rate constant, and Z, β, and δ are parameters of the model. This form is chosen to give $k_{ij} \approx k_h$ when $L_i = L_j = L_0$, and with a power-law dependence on length $k_{\mathrm{eff}} \propto L^{-(3\beta+\delta)}$ for $L \gg L_0$. The concentration dependence is obtained on dimensional grounds: the product ρL^3 is dimensionless. Both dimensionless factors (ρL^3 and L/d) appear in the expressions for the diffusivities. The validity of Eq. 15 is checked by comparing it with the predictions of the model for the diffusion-controlled reaction-rate constant given in the previous section. The exponents in the model (β, δ) are obtained by fitting to the theoretical results, and the parameters k_h and Z are obtained by fitting to experimental data.

Defining the dimensionless quantities $\bar{k}_{ij} = k_{ij}/k_h$, $\tau = (k_h C_0 t)/2$, and $\bar{P}_i = P_i/C_0$, where $C_0 = \rho_0/N_A$ is the initial monomer concentration, Eqs. 13 and 14 become

$$\frac{d\bar{P}_1}{d\tau} = -2\bar{P}_1 \sum_{j=1}^{N} \bar{k}_{1j} \bar{P}_j \tag{16}$$

$$\frac{d\bar{P}_i}{d\tau} = -2\bar{P}_i \sum_{j=1}^{N} \bar{k}_{ij} \bar{P}_j + 2\sum_{j=1}^{i^*} \bar{k}_{j,i-j} \bar{P}_j \bar{P}_{i-j}, \tag{17}$$

with the initial condition

$$\bar{P}_1 = 1, \quad \bar{P}_i = 0 \quad i = 2,3,\ldots,N \quad \tau = 0. \tag{18}$$

The rate constants are given by

$$\bar{k}_{ij} = \frac{0.5}{1 + \chi i^{\epsilon} \mathcal{Q}_0^{\delta}} + \frac{0.5}{1 + \chi j^{\epsilon} \mathcal{Q}_0^{\delta}}, \tag{19}$$

where $\epsilon = (3\beta + \delta)$, $\chi = Z(C_0 N_A L_0^3)^{\beta}(L_0/d)^{\delta}$, and $\mathcal{Q}_0 = C/C_0$ is the zeroth moment of the distribution. The moments of the molecular-weight distribution are defined as

$$\mathcal{Q}_k = \sum_{j=1}^{N} j^k \bar{P}_j. \tag{20}$$

The number averaged degree of polymerization in terms of the moments is

$$\overline{DP}_n = \mathcal{Q}_1/\mathcal{Q}_0, \tag{21}$$

the weight averaged degree of polymerization is

$$\overline{DP}_w = \mathcal{Q}_2/\mathcal{Q}_1, \tag{22}$$

and the polydispersity index σ is

$$\sigma = \frac{\overline{DP}_w}{\overline{DP}_n}. \tag{23}$$

Equations 16 and 17 are integrated using the fourth-order Runge-Kutta method with step-size correction (Press et al., 1986). In the computations, the number of equations is increased with conversion using the following criterion: if the number fraction of the $(N-5)$th species exceeds a specified value ($\bar{P}_{N-5} > 10^{-10}$), the number of equations is increased by 5. A mol balance gives $\mathcal{Q}_1 = 1$, and the tolerance for the computations is specified so that $|\mathcal{Q}_1 - 1| < 10^{-4}$.

Results and Discussions

Experimental results

The variation of the weight-average degree of polymerization $\overline{DP}_w$ with reaction time t is presented in Figure 2 for two different initial monomer concentrations ($C_0 = 0.1$ mol/L and $C_0 = 0.2$ mol/L). Each data point in the plot represents a different experiment, and $\overline{DP}_w$ is obtained from measurement of inherent viscosity. The graph shows the typical behavior of a diffusion-controlled step-growth polymerization: the degree of polymerization increases slowly after an initial period of rapid increase. The reaction appears to be diffusion controlled from the first data point onwards. In contrast, for a polymerization in which the rate constant is independent of chain length, the degree of polymerization increases linearly with time (t) with the slope proportional to the rate constant and the initial monomer concentration ($\overline{DP}_w = 1 + k_h C_0 t$).

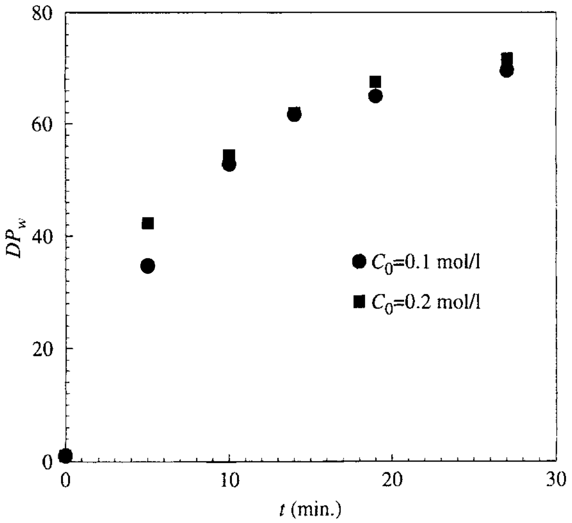

Figure 2. Variation of the weight-average degree of polymerization ($\overline{DP}_w$).

Calculated from inherent viscosity measurements, with time for two different initial monomer concentrations (C_0).

The polymerization kinetics shown in Figure 2 are also nearly identical for the two initial monomer concentrations. This is a consequence of two effects that compensate each other. The rotational diffusivity and translational diffusivity perpendicular to the rod axis decrease with increasing concentration (Eqs. 6, 7), resulting in a lower effective rate constant. However, the rate remains nearly unchanged in the cases considered, because it is proportional to the product of the rate constant and the square of concentration, which is higher. This is considered in quantitative terms below. The experimental results for $C_0 = 0.2$ mol/L presented here are in good agreement with those of Agarwal and Khakhar (1992a) for the same system under quiescent conditions.

The experimental results for the weight-average molecular weight and polydispersity index obtained by gel permeation chromatography of the *N*-octadecyl PPTA, for different reaction times and the two initial monomer concentrations are presented in Table 1. The values of the polydispersity index for the two concentrations are close to each other in magnitude and nearly constant over time. Arpin and Strazielle (1977), using sulphuric acid as the eluent, reported values of polydispersity index between 1.51 and 3.20, for the samples with inherent viscosity varying from 1.84 dL/g to 6 dL/g (corresponding to $\overline{DP}_w$ ranging from 42 to 266). These polydispersity-index values are significantly higher than the values obtained in the current study, and this is most likely an effect of stirring. As discussed earlier, stirring should result in higher values of the polydispersity index due to polymer orientation (Agarwal and Khakhar, 1992a). Table 1 also gives a comparison of the values of the $\overline{DP}_w$ obtained by inherent viscosity measurements and gel permeation chromatography. The degree of polymerization obtained by the two procedures differs by as much as 50%. The variation is because the GPC column is calibrated with polystyrene, and due to any errors introduced by the *N*-alkylation process. We thus assume an inherent viscosity-based degree of polymerization data to be more accurate.

Table 1. Experimental Results of the Kinetics of Polymerization of PPTA

Time (min)	$\overline{DP}_w$ (η_{inh})	$\overline{DP}_w$ (GPC)	σ (GPC)
	$C_0 = 0.1$ mol/L		
5	34.7	48.7	1.29
10	52.8	48.9	1.23
14	61.6	50.6	1.23
19	64.9	58.4	1.31
27	69.5	60.2	1.32
	$C_0 = 0.2$ mol/L		
5	42.3	54.1	1.32
10	54.3	56.1	1.33
14	61.9	67.3	1.66
19	67.5	59.4	1.34
27	71.6	58.0	1.33

Note: The evolution of degree of polymerization ($\overline{DP}_w$) and polydispersity index (σ) for two different initial monomer concentrations is shown. The results from inherent viscosity measurements (η_{inh}) and gel permeation chromotagraphy of *N*-alkylated samples (GPC) are both given.

Effective rate constant

The calculated values of the dimensionless parameters required in the finite-element computations are given in Table 2 for two concentrations ($C_0 = 0.1$ and 0.2 mol/L) and one value of the homogeneous rate constant (k_h) so as to obtain $\alpha = 1$ at $DP = L/L_0 = 100$. Parameters are similarly calculated for higher values of k_h so as to obtain $\alpha_{100} = 10$ and $\alpha_{100} = 100$, where the subscript denotes that the intrinsic reactivity is calculated at $DP = 100$.

For monodisperse molecules, the rate constant given in Eq. 15 reduces to

$$k_{\text{rel}} = \frac{1}{1 + Z' C_0^{\beta} DP^{2\beta+\delta}}, \tag{24}$$

where $Z' = Z N_A^{\beta} L_0^{3\beta} (L_0/d)^{\delta}$. Figure 3 shows a plot of $(1/k_{\text{rel}} - 1)$ vs. the degree of polymerization on log-log axes using the data from finite-element computations. Straight lines are obtained in accordance with this equation. Figure 4 shows a similar plot for the variation with initial concentration for a fixed degree of polymerization ($DP = 50$), and again straight lines are obtained. The best fit values for the parameters obtained are given in Table 3. Different values of the exponents and the parameter Z are obtained for different values of α_{100}; however, the best-fit parameters are independent of the initial monomer concentration and the degree of polymerization as required. The rate constant decreases monotonically with the degree of polymerization, and the decrease is greater for higher values of α (Figure 3). Based on the reduction in the magnitude of the rate constant (about a factor of 10), the $\alpha_{100} = 1$ results appear to be closest to the experimental data.

Molecular-weight distribution computations

Figure 5 shows the comparison of the predicted and experimental values of the weight average degree of polymerization and polydispersity index for the initial monomer concentration $C_0 = 0.1$ mol/L. The values of the exponents (β and δ) used in the computations correspond to the values ob-

Table 2. Dimensionless Parameters Used in the Calculation of the Effective Rate Constant Using the Smoluchowski (1917) Approach for $C_0 = 0.1$ mol/L and $C_0 = 0.2$ mol/L

$C_0 = 0.1$ mol/L				$C_0 = 0.2$ mol/L			
DP	$s \times 10^{-5}$	$\gamma \times 10^3$	α	DP	$s \times 10^{-5}$	$\gamma \times 10^3$	α
10	0.003	338.41	0.20	10	0.004	195.80	0.20
20	0.031	83.19	0.31	20	0.072	30.65	0.31
30	0.203	24.62	0.41	30	0.602	7.56	0.41
40	0.909	9.14	0.50	40	3.013	2.59	0.50
50	3.102	4.04	0.59	50	10.932	1.10	0.59
60	8.724	2.03	0.67	60	31.877	0.54	0.67
70	21.251	1.12	0.76	70	79.441	0.29	0.76
80	46.372	0.67	0.84	80	176.010	0.17	0.84
90	92.791	0.42	0.92	90	355.973	0.11	0.92
100	173.165	0.28	1.00	100	669.474	0.07	1.00

Note: The homogeneous rate constant is taken to be $k_h = 1.17 \times 10^3$ L/mol s so as to get $\alpha = 1$ at a degree of polymerization $DP = 100$.

tained in the previous section from the Smoluchowski (1917) -theory-based finite-element computations for $\alpha_{100} = 1$, and $k_h = 3.4$ L/mol s and $\chi = 6.5 \times 10^{-4}$ ($Z = 1.8 \times 10^{-3}$) are obtained from a least-square error fit to the data of $\overline{DP}_w$ vs. time. There is reasonable agreement between theory and experiment for both degree of polymerization and polydispersity index variation with time. The magnitude of the homogeneous rate constant (k_h) obtained also appears to be reasonable in comparison with similar systems (Agarwal and Khakhar, 1993c). The homogeneous rate constant used in the finite-element computations of the effective rate constant is three orders of magnitude higher than the value obtained by fitting the model to the experimental results. The finite-element calculations were repeated using the homogeneous rate constant from experiments and a lower value of the critical orientation angle (θ_c), so as to keep $\alpha_{100} = 1$. The exponents obtained are very close to those reported in the previous section for $\alpha_{100} = 1$. Figure 6 shows the comparison of the predicted and experimental values of the weight-average degree of polymerization and polydispersity index for the concentration $C_0 = 0.2$ mol/L using the parameters (k_h, Z) obtained from fitting to the data at the lower concentration ($C_0 = 0.1$ mol/L). There is again good agreement between experiment and theory.

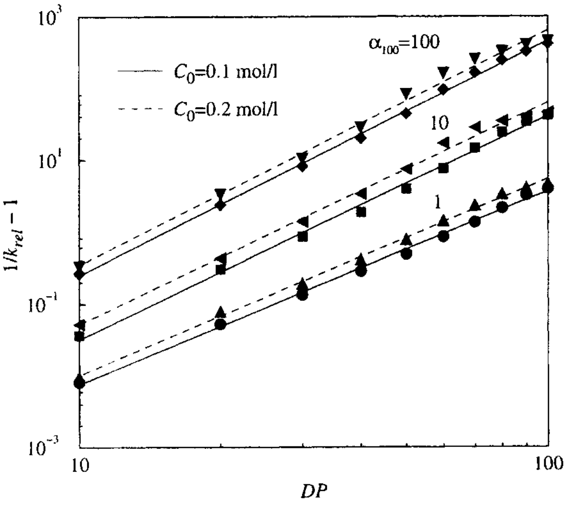

Figure 3. Variation of $(1/k_{rel}-1)$ with degree of polymerization (DP) for initial monomer concentrations (C_0) and intrinsic reactivity at a degree of polymerization $DP = 100$ (α_{100}).

Symbols are the computational results of the Smoluchowski theory and solid lines are fits of Eq. 24.

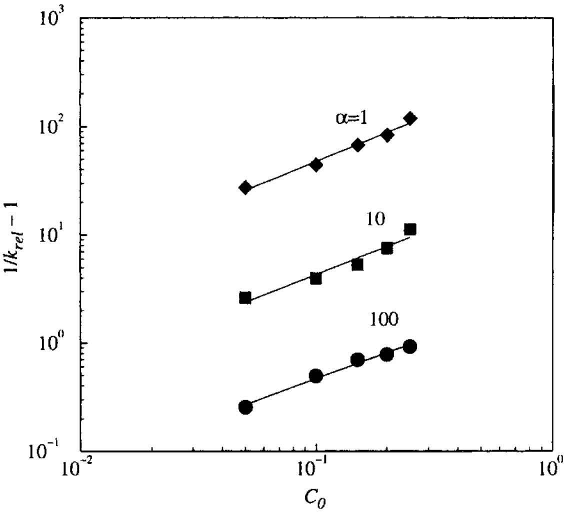

Figure 4. Variation of $(1/k_{rel}-1)$ with initial monomer concentrations (C_0) for a fixed degree of polymerization ($DP = 50$) and intrinsic reactivity at a degree of polymerization $DP = 100$ (α_{100}).

Symbols are the computational results of the Smoluchowski theory and solid lines are fits of Eq. 24.

Side reactions may have an important effect on the process, and we obtain a qualitative insight by considering a simple case. We assume that an excess of impurity is present, and this results in a slow consumption of the functional groups by means of a first-order reaction that is independent of the impurity concentration. The reaction rate is then

$$r_i = -k_1 P_i, \tag{25}$$

and rescaling both sides with respect to $k_h C_0^2/2$, we get

$$\bar{r}_i = -\bar{k}_1 \bar{P}_i, \tag{26}$$

where $\bar{k}_1 = 2k_1/(k_h C_0)$. The effect of the side reaction is incorporated in the model by adding $\bar{r}_i$ to the righthand sides of Eqs. 13 and 14. The dashed lines in Figures 5 and 6 computed for $\bar{k}_1 = 10^{-2}$ show that the effect of the side reaction

Table 3. Parameters of the Estimated by Means of Least Square Fit for $C_0 = 0.1$ mol/L and $C_0 = 0.2$ mol/L

α	β	δ	ln (Z)
1	0.80	1.1	−10.2
10	0.85	1.4	−9.7
100	0.90	1.5	−8.1

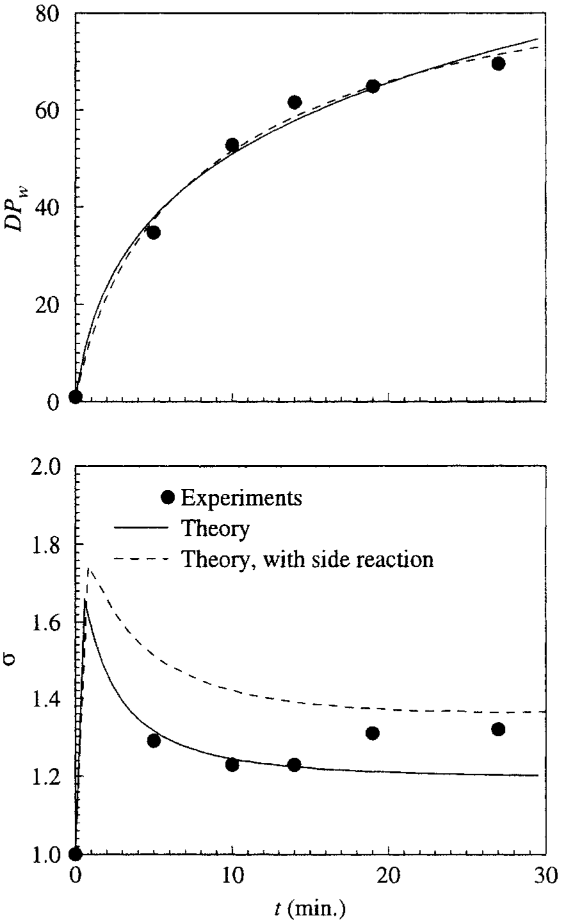

Figure 5. Variation of the degree of polymerization ($\overline{DP}_w$) obtained from inherent viscosity measurements and polydispersity index obtained from GPC measurements, with time (t) for C_0 = 0.1 L/m·s.

Symbols show $\overline{DP}_w$ and solid lines the predictions of the population analysis in which the parameters β and δ are obtained from the Smoluchoski theory, and k_h and Z are obtained by fitting theoretical results to the experimental data of $\overline{DP}_w$ vs. time. Dashed lines show the effect of a slow-side reaction.

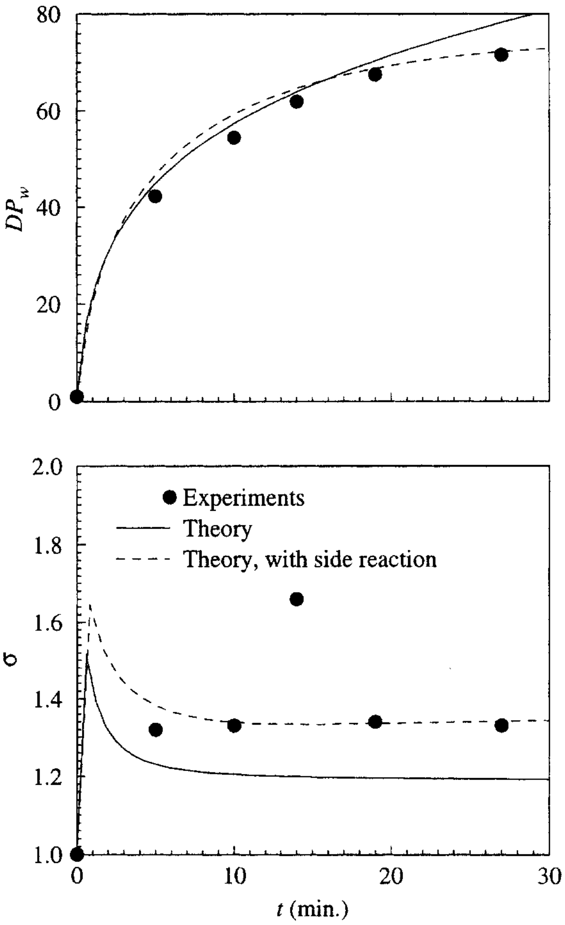

Figure 6. Variation of the degree of polymerization ($\overline{DP}_w$) obtained from inherent viscosity measurements and polydispersity index obtained from GPC measurements, with time (t) for C_0 = 0.2 L/mol·s.

Symbols show $\overline{DP}_w$ and solid lines the predictions of the population analysis in which the parameters used are the same as in Figure 5. Dashed lines show the effect of a slow side reaction.

on the variation of degree of polymerization with time is slight and manifests as a flattening out at higher times. The polydispersity index increases a small amount due to the side reaction. The reduction in rate at the later stages due to the side reaction occurs because the side reaction rate becomes comparable to the primary reaction rate, and consumption of the end groups by the side reactions does not result in an increase in the degree of polymerization. The end groups on small and large molecules are consumed with equal probability by the side reaction reducing the biased consumption of the smaller oligomers by the diffusion-controlled primary reaction. Consequently, the molecular-weight distribution is broader, resulting in a higher polydispersity index.

The model just discussed allows us to investigate the effect of changing the initial monomer concentration. Figure 7 shows the degree of polymerization after 30 min of reaction for different initial monomer concentrations. In the case of no side reaction there is a monotonic increase in the final degree of polymerization, though at higher concentrations there is an approach to an asymptotic value. In the case with side reactions there is, however, a maximum at $C_0 \approx 0.2$. The maximum at a particular concentration occurs because an increase in monomer concentrations results in a higher rate of side reactions, and consequently a lower molecular weight. The calculations presented here indicate that effects of diffusion control as well as side reactions may be responsible for the experimentally observed optimal monomer concentration.

Experimental results from previous studies as well as the current work are also shown in Figure 7. In all cases there is a maximum in the degree of polymerization vs. initial monomer composition curve, though the optimal concentration ranges from 0.2 mol/L to 0.4 mol/L, and the peak degree of polymerization ranges from 70 to 350. These differences arise primarily from differences in the type of stirring

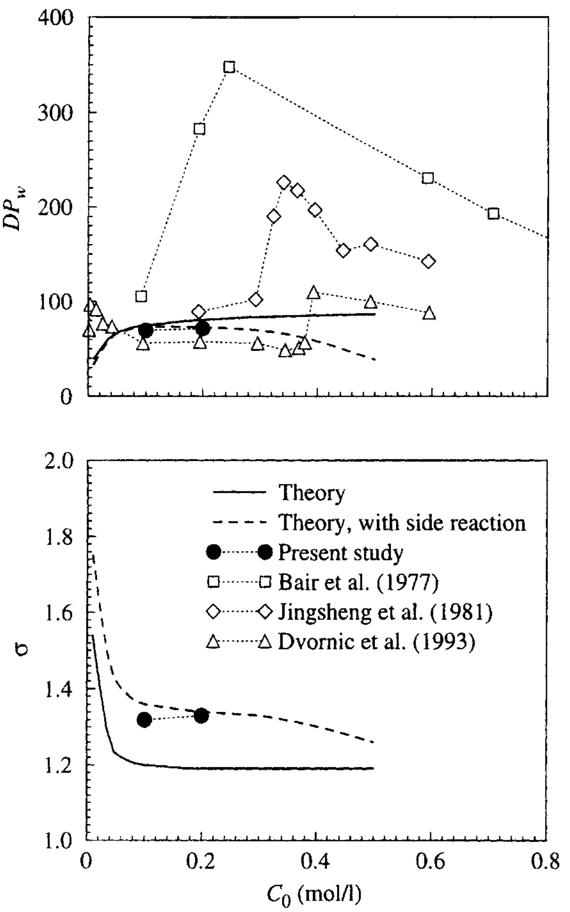

Figure 7. Model predictions of the effect of initial monomer concentration on the degree of polymerization ($\overline{DP}_w$) after 30 min of reaction.

Solid lines show model predictions and dashed lines the case when there is a slow side reaction. Symbols are experimental results from both this work and previous studies.

used in the different cases, since the systems used are otherwise the same. The degree of polymerization is the lowest for the present work (quiescent system), since there is no flow-induced molecular orientation. In contrast, flow-induced molecular orientation increases the rate of polymerization and final degree of polymerization to different extents in the other studies. This underscores the need for studying the kinetics of such systems under quiescent conditions or in well-defined flows.

Conclusions

A theoretical and experimental study of the kinetics of diffusion-controlled polymerization to form PPTA was carried out. Experimental data for the variation of the weight-average degree of polymerization with time showed the typical behavior of a diffusion-controlled step-growth polymerization with severe slowing of the reaction at the later stages, resulting in a low degree of polymerization ($\overline{DP}_w = 70$) at the end of the process. There was little effect on degree of polymerization or polydispersity index of increasing the initial monomer concentration from 0.1 mol/L to 0.2 mol/L. The measured polydispersity index in both cases was small ($\sigma \approx 1.3$), which is a consequence of diffusion control.

Computation of the effective rate constant by the Smoluchowski (1917) approach requires parameters characterizing the reaction site: the radius of the reaction zone (a) and the critical orientation angle for reaction (θ_c). Since these parameters were not available, physically reasonable estimates were used in the computations. All other parameters were estimated from published correlations. The computations showed the effective rate constant to be of the form

$$k_{\text{eff}} = \frac{k_h}{1 + Z\rho^{\beta} L^{3\beta+\delta}/d^{\delta}},$$

where the exponents $\beta = 0.8$ and $\delta = 1.1$ were obtained from a least-square fit to the data for the intrinsic reactivity parameter $\alpha = 1$ at a degree of polymerization $DP = 100$. This value of the intrinsic reactivity gives the decrease in the relative rate constant that is of the order of that observed experimentally. The parameters k_h and Z were obtained by fitting to experimental data.

The population balance model based on the expression for the rate constant given earlier gave good predictions of the variation of the degree of polymerization with time and polydispersity index, with time for both initial monomer concentrations. The parameters $k_h = 3.4$ L/mol s and $Z = 1.8 \times 10^{-3}$ were obtained by a least-square fit to one set of experimental data for degree of polymerization vs. time. The homogeneous rate constant obtained (k_h) appears to be of reasonable magnitude. The effect of an end group consuming the side reaction was studied using the model. Computations for this case showed the existence of an optimal initial monomer concentration at which the degree of polymerization at a fixed time of reaction was maximum. Such an optimal initial monomer concentration has been reported in previous experimental studies (Bair et al., 1977; Jingsheng et al., 1981; Dvornic et al., 1993).

The analysis presented here gives a good quantitative description of diffusion-controlled polymerization of rodlike molecules under quiescent conditions. A practically useful extension of the work would be to include the effect of flow-induced orientation, which significantly accelerates the polymerization and also results in broader molecular-weight distributions (Agarwal and Khakhar, 1992a). A computational study of this problem is currently in progress.

Acknowledgments

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