Polymerization kinetics of rigid-rod-like molecules: 2. Polymerization of poly(1,4-phenylene-2,6-benzobisthiazole) in the nematic state

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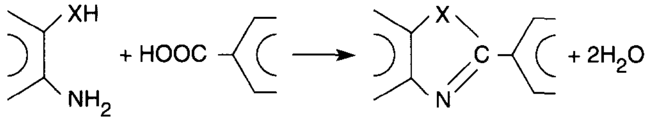
The kinetics of the polymerization to form the rod-like poly(1,4-phenylene-2,6-benzobisthiazole) in the nematic phase are discussed. The kinetics are not affected by a phase transformation from isotropic to nematic, provided that transformation occurs early in the polymerization. Suppressed diffusion rate parallel to the molecular axes appears to control the kinetics over much of the conversion, resulting in a constant rate of increase of the intrinsic viscosity with polymerization time. At high conversions, additional constraints due to restricted rotational diffusion may occur. The molecular-weight distribution is close to most-probable.

(Keywords: rod-like; polymerization kinetics; nematic; poly(1,4-phenylene-2,6-benzobisthiazole))

INTRODUCTION

In a study of the polymerization kinetics of the rod-like poly(1,4-phenylene-2,6-benzobisoxazole) (PBO) in isotropic solutions in part 1, it was concluded that the reaction became diffusion-controlled with increasing conversion[1]. That behaviour was attributed to a substantial decrease in the average rotational diffusion constant D_R as the polymerization proceeded. The effect of decreased D_R is enhanced in the case of PBO or similar chains since these must be in (essentially) collinear alignment to achieve cyclization in the polymerization reaction:



where X = O for PBO. Possible uncyclized intermediates are not stable at the reaction conditions, and depolymerize. Here, we describe a study of the polymerization kinetics of the rod-like poly(1,4-phenylene-2,6-benzobisthiazole) (PBT) (i.e. X = S) in solutions that become anisotropic as the conversion proceeds. The use of a monomer concentration sufficiently high to permit formation of an anisotropic solution on conversion to polymer is made possible by an increase in the P_2O_5 content of the polyphosphoric acid (PPA) used as the solvent in the polymerization[2]. The P_2O_5 content must be high enough that the water of polymerization does not decrease the P_2O_5 content of the PPA below about 0.83 weight fraction at any time. As discussed in the next section, this is accomplished by a staged P_2O_5 content in the early phases of the polymerization.

The results of studies on the polymerization of PBT are discussed in the following to elucidate the conditions under which an isotropic–nematic phase change might affect the polymerization, and the effects of suppressed molecular diffusion on the reaction rate as the conversion advances.

EXPERIMENTAL

Polymerization methods

The 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) and terephthalic acid (TPA) monomers were provided by SRI International through the courtesy of Dr J. F. Wolfe. They were dried under vacuum (10^{-4} Torr) for 24 h before use. Granular P_2O_5 (J. T. Baker) was added to phosphoric acid (85.7% H_3PO_4, J. T. Baker) to form PPA with 0.75 weight fraction P_2O_5 by stirring overnight at room temperature. The P_2O_5 content was verified by potentiometric titration against 0.05 N sodium hydroxide. The required amount of DABDT was then added to the PPA in a stirred round-bottomed flask under a nitrogen blanket to release the two moles of hydrogen chloride per mole of DABDT. The HCl was removed as a gas at 50–60°C. Subsequently, a stoichiometric amount of TPA was added, and heated to 120°C with agitation for 1 h. Finally, sufficient granular P_2O_5 to ensure 0.85 weight fraction P_2O_5 in the PPA composition at 100% conversion of the monomer was added. All additions were made through a side-arm designed to prevent atmospheric intrusion.

The solution was further heated with agitation at 120°C for 2–3 h to give conversion to an isotropic solution of

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a low-molecular-weight polymer. The reaction was then quenched in an ice bath and the contents, called a precursor solution, were used to fill a number of small (ca. 2 cm^3 volume) ampoules. These were sealed under vacuum, and held at -5°C until needed. Precursor solutions were prepared with 0.117 $\mathrm{mol\,kg^{-1}}$ (precursor A) and 0.307 $\mathrm{mol\,kg^{-1}}$ (precursor B) of each monomer. These monomer concentrations would give 0.03 and 0.074 weight fraction polymer, respectively, at full conversion (assuming no loss of the water of polymerization).

The polymerization kinetics were studied by the transfer of a number of ampoules (all with the same precursor) to an oil bath at the polymerization temperature. Ampoules were then removed sequentially and quenched in liquid nitrogen at the desired time of polymerization. These were subsequently opened and used for analysis as discussed below.

Polymer characterization

The polymer in each ampoule was characterized by one or both of two techniques: viscometry and size exclusion chromatography (s.e.c.). The methods used are described elsewhere[3,4]. In all cases, dilute solutions were prepared in methanesulphonic acid (MSA) by dilution of an appropriate volume of the polymerization solution in PPA in a large excess of MSA. The latter was freshly distilled at ca. 10^{-3} Torr, and all solutions were maintained under strict anhydrous conditions.

Viscosities measured in a capillary viscometer were used with the usual expressions to deduce the intrinsic viscosity $[\eta]$:

$$\eta_{\mathrm{sp}}/c = [\eta] + k'[\eta]^2 c + \cdots \qquad (1)$$

$$(\ln \eta_{\mathrm{rel}})/c = [\eta] - (\tfrac{1}{2} - k')[\eta]^2 c + \cdots \qquad (2)$$

$$[\eta]_c = [\eta] - (\tfrac{1}{3} - k')[\eta]^2 c + \cdots \qquad (3)$$

where $[\eta]_c = \, = [2(\eta_{\mathrm{sp}} - \ln \eta_{\mathrm{rel}})]^{1/2}/c$. Since $k' \sim 1/3$, equation (3) provides a useful approximation to $[\eta]$ if the amount of polymer is too small to permit measurements over a range of c. Estimates of $[\eta]$ were made on the basis of extrapolations with four concentrations in almost all cases in this study.

The s.e.c. apparatus used in this study is described elsewhere[4]. The optical absorbance A was determined as a function of the elution volume V_{e}, using a column set (Porasil packing) for which V_{e} is calibrated against $[\eta]M$ using samples of polystyrene with a narrow molecular-weight distribution. The weight fraction w_{v} of polymer with absorbance A_{v} and elution volume $V_{\mathrm{e,v}}$ was calculated as:

$$w_{\mathrm{v}} = \frac{A_{\mathrm{v}}/\varepsilon_{\mathrm{v}}}{\sum_{\mathrm{v}} A_{\mathrm{v}}/\varepsilon_{\mathrm{v}}} \qquad (4)$$

where ε_{v} is the extinction coefficient of the component eluted at $V_{\mathrm{e,v}}$ at the wavelength (442 nm) used to measure A_{v}. Sample chromatograms are not included herein as they were entirely unexceptional, monomodal peaks, that progressed smoothly to smaller elution volumes with increasing polymerization time. Experiments with low-molecular-weight PBT showed that the wavelength $\lambda_{\max}$ for maximum extinction and the extinction coefficient $\varepsilon_{\max}$ at that wavelength both decreased with decreasing V_{e}. Thus, for a fixed wavelength corresponding to $\lambda_{\max}$ and $\varepsilon_{\max}$ for high-molecular-weight PBT:

$$\varepsilon_{\mathrm{v}} = \varepsilon_{\max} - \left(\frac{\partial \varepsilon_{\mathrm{v}}}{\partial V_{\mathrm{e,v}}}\right)(V_{\mathrm{e,v}} - V_{\mathrm{e,}c}) \qquad (5)$$

for elution volumes greater than a certain value $V_{\mathrm{e,}c}$, and $\varepsilon_{\mathrm{v}} = \varepsilon_{\max}$ for smaller $V_{\mathrm{e,v}}$, where $(\varepsilon_{\max}/V_{\mathrm{e,}c})(\partial\varepsilon_{\mathrm{v}}/\partial V_{\mathrm{e,v}}) = 3.3$ for $V_{\mathrm{e,v}}/V_{\mathrm{e,}c}$ from 1 to 1.17, with $V_{\mathrm{e,}c} = 98$ ml; in this range, the column calibration gives

$$M[\eta] = \exp[V_{\mathrm{e,}c}(1.22 - V_{\mathrm{e}}/V_{\mathrm{e,}c})/4.28]$$

Values of $([\eta]M)_{\mathrm{v}}$ obtained from $V_{\mathrm{e,v}}$ were used to compute quantities $R_\delta^{(s)}$ defined as:

$$R_\delta^{(s)} = \sum w_{\mathrm{v}}([\eta]M)_{\mathrm{v}}^{s/(1+\alpha_{\mathrm{A}})} \qquad (6)$$

where $\delta = (\alpha - \alpha_{\mathrm{A}})/(1 + \alpha_{\mathrm{A}})$, with $\alpha = \partial \ln[\eta]/\partial \ln M$, and α_{A} is an approximate estimate of α. As shown elsewhere[5]:

$$R_\delta^{(1)} R_\delta^{(-1)} = (M_{\mathrm{w}}/M_{\mathrm{n}})F_1(\delta, M_{\mathrm{w}}/M_{\mathrm{n}}) \qquad (7)$$

$$R_\delta^{(2)}/(R_\delta^{(1)})^2 = (M_z/M_{\mathrm{w}})F_2(\delta, \mathrm{M}_z/M_{\mathrm{w}}) \qquad (8)$$

where the F_i are both unity if δ is zero, and do not deviate much from unity given a reasonable estimate α_{A}. For example, for a most-probable distribution of M, $F_i = \Gamma(3 + \delta)\Gamma(1 - \delta)/2$, where $\Gamma(\ )$ is the gamma function[5]. For rod-like chains with length L and diameter d[3,6]:

$$[\eta] = \frac{\pi N_{\mathrm{A}} d^2}{48 M_L}\left(\frac{L}{d}\right)^{1.8} f(L/d) \qquad (9)$$

where $M_L = M/L$ and $f(L/d) = 2(L/d)^{0.2}/\ln(3L/2d)$ is about equal to unity for L/d of interest here[3]. Thus, $\alpha = 1.8$ in this case. Further, in this case $[\eta]$ and M_{n} may be estimated from the s.e.c. data as $R_0^{(1.8)}K^{5/14}$ and $1/R_0^{(-1)}K^{5/14}$, respectively, where $K = \pi N_{\mathrm{A}} d^{0.2}/48 M_L$. In subsequent calculations, we take $M_L = 213\ \mathrm{nm}^{-1}$ and $d = 0.5$ nm.

RESULTS

Values of $M_{\mathrm{w}}/M_{\mathrm{n}}$ were determined for the precursor solutions and for samples of these polymerized at various times at 180°C. The results gave $M_{\mathrm{w}}/M_{\mathrm{n}}$ increasing from 1.8 for precursor A to 2.0 within 1 h, with no appreciable change thereafter. Similarly, $M_{\mathrm{w}}/M_{\mathrm{n}}$ increased from 1.7 for precursor B to 2.0 within 2 h, then levelled off at about 2.1 for longer polymerization. Data on the number-average degree of polymerization X_{n} deduced from the s.e.c. data and calculated from $[\eta]$ measured viscometrically are given in *Figure 1* for a polymerization at 180°C with precursor A. In this case, $[\eta]$ measured viscometrically and deduced from the s.e.c. data generally agreed within about 10%. Similarly, X_{n} computed from $[\eta]$ measured viscometrically for polymerization at four temperatures for precursor B is given in *Figure 1*. The viscometrically determined $[\eta]$ are given directly in *Figure 2*. A two-parameter exponential molecular-weight distribution was assumed in computing X_{n} from $[\eta]$. That is, for a heterodisperse rod-like polymer, equation (9) is modified to read $[\eta] = KM_{\mathrm{v}}^{1.8}$, with:

$$M_{\mathrm{v}} = M_{\mathrm{n}}\left(\frac{\Gamma(2.8 + h)}{h\Gamma(1 + h)}\right)^{5/9} \qquad (10)$$

where $h^{-1} = (M_{\mathrm{w}}/M_{\mathrm{n}}) - 1$ and Γ is the gamma function. Thus, if $h \approx 1$, $M_{\mathrm{v}} \approx 2.35 M_{\mathrm{n}}$; the observed $M_{\mathrm{w}}/M_{\mathrm{n}}$ were used to compute M_{v}.

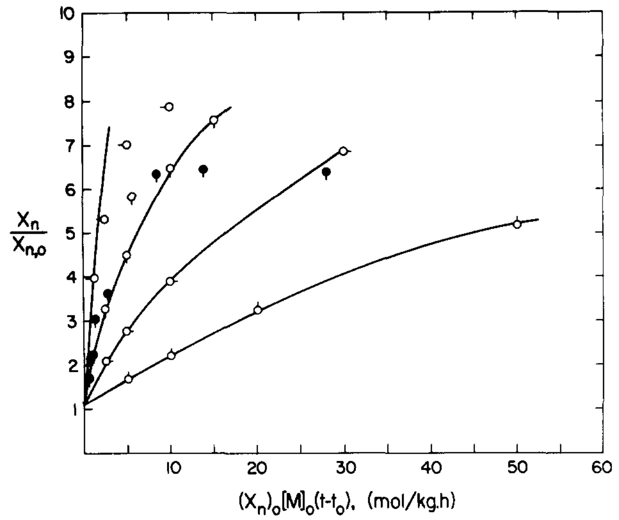

Figure 1 The number-average degree of polymerization X_n at time t divided by its value $(X_n)_0$ at time t_0 vs. $(X_n)_0[M]_0(t-t_0)$ for polymerizations with precursors A and B (full and open circles, respectively). The pips denote temperatures 200, 180, 160 and 140°C, respectively, with clockwise pip rotation from pip up for 140°C; $(X_n)_0$ is equal to 11.8 and 8.2 for precursors A and B, respectively

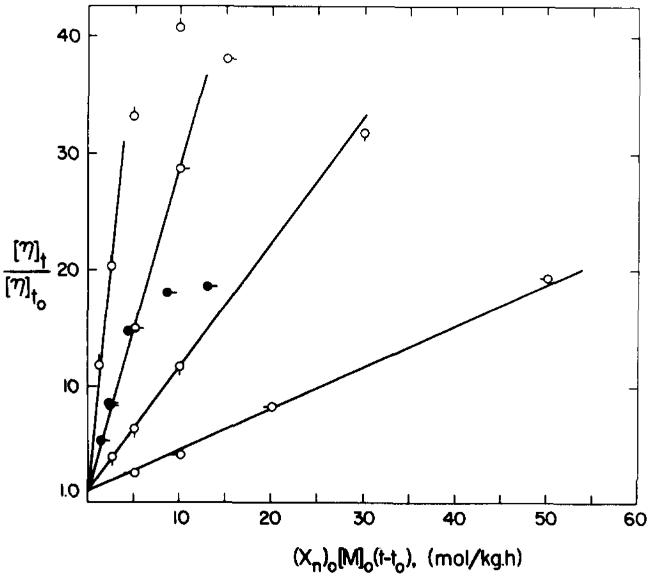

Figure 2 The intrinsic viscosity at time t divided by its value $[\eta]_0$ at time t_0 vs. $(X_n)_0[M]_0(t-t_0)$ for polymerizations with precursors A and B. Full and open circles are as in *Figure 1*. The pips denote temperatures 200, 180, 160 and 140°C, respectively, with clockwise pip rotation from pip up for 200°C; $[\eta]_0$ is equal to 140 and 60 cm^3 g^{-1} for precursors A and B, respectively

As shown in *Figure 1*, plots of X_n *versus* the polymerization time t are not linear for X_n greater than 25–30. Remarkably, as shown in *Figure 2*, plots of $[\eta]$ *versus* t are linear to larger t. In any case, conversion appears to cease, or become very slow, with increasing t.

Observations with a polarizing microscope showed that all of the polymerization samples were anisotropic for precursor B, and that the polymerization samples changed from isotropic at low conversion to anisotropic between 1 and 2 h of polymerization with precursor A.

DISCUSSION

For polymerization by a bimolecular reaction, with reactivity independent of conversion, $[M]_0^{-1}\,dX_n/dt$ is equal to the bimolecular rate constant k (ref. 7), and:

$$X_n = (X_n)_0 + [M]_0 k(t-t_0) \tag{11}$$

where $(X_n)_0$ is the value of X_n at time t_0, $[M]_0$ is the total initial monomer concentration, and t is the polymerization time. Thus, k may be deduced from $\partial X_n/\partial t$. The results for the initial polymerization rate, given in *Figure 3*, appear to be independent of whether the solution is isotropic or anisotropic. Similarly, no change in the rate of polymerization is noted in *Figure 1* for the time the solution undergoes a phase change to the ordered state. This suggests that the polymerization is not controlled by diffusion at early polymerization times. Because of the requirement for collinear alignment of the rod-like reactants in the polymerization of either PBT or PBO, it seems reasonable that k may depend on the rotational diffusion constant D_R if the conversion is large enough, especially if the polymerization solution is isotropic. For low $[M]_0$, the system may remain isotropic for any reasonable polymerization time, in which case D_R decreases markedly with increasing conversion. By contrast, a transition to a nematic polymerization solution may occur quickly with large $[M]_0$, changing both the influence of D_R on the polymerization in the ordered state (see below) and the rate of decrease of D_R with increasing conversion.

A simplified computation making use of theoretical expressions[8,9] for D_R can illustrate the variation of D_R with conversion (i.e. with chain length). For rod-like chains D_R may be approximated by the relation:

$$D_R = D_{R,0}\left\{1+\left[\left(\frac{L}{d}\right)^4\left(\frac{\phi}{B}\right)^2 F^{-1}\right]^{\gamma}\right\}^{-1/\gamma} \tag{12}$$

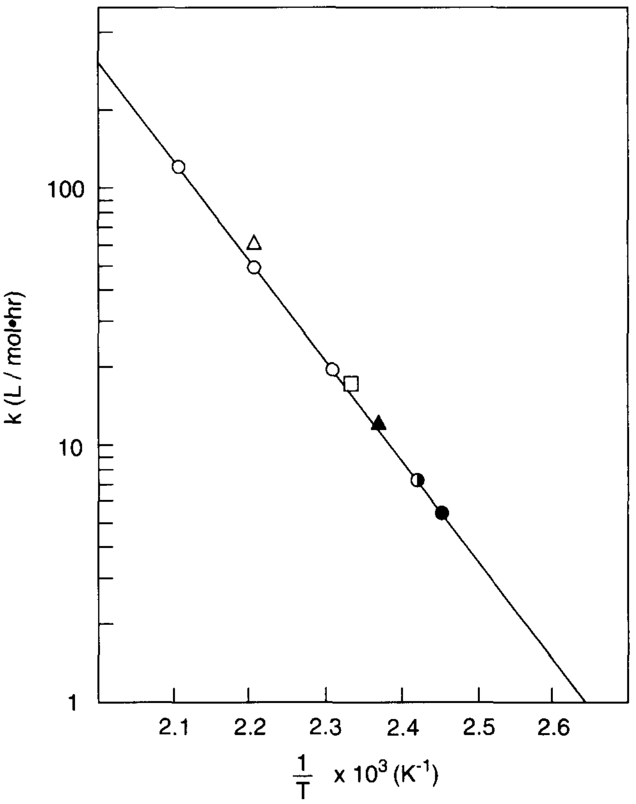

Figure 3 Rate constants k computed from data at low conversion *versus* T^{-1} for polymerization with precursor A and B (triangles and circles, respectively). The square gives k during preparation of precursor A. The open and full symbols are for subsequent polymerization in the isotropic or nematic phases, respectively; the half-filled symbol (for precursor A at 140°C) underwent an isotropic–nematic phase transition over the time used to determine k

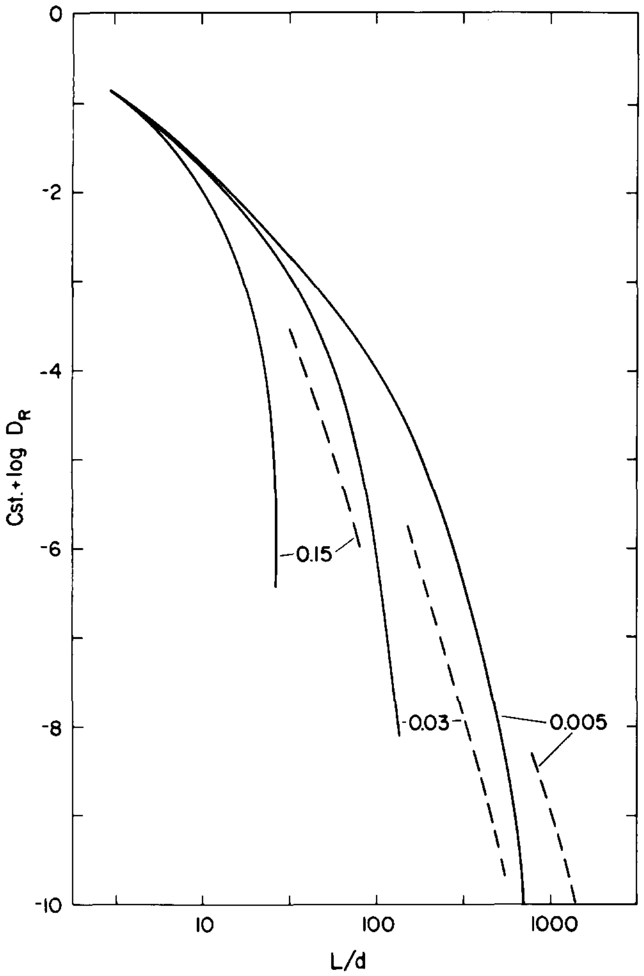

Figure 4 Double logarithmic plot of D_R/const. vs. L/D for the indicated ϕ calculated with equations (12)–(15) as discussed in the text. The full and broken curves were obtained with the use of equation (13) for isotropic and equation (14) for nematic solutions, respectively

where $D_{R,0} \propto (M[\eta])^{-1}$ is the limiting value of D_R at infinite dilution, the volume fraction ϕ is given by $(\pi/4)\nu d^2L$, with ν the number concentration of polymer, γ is an empirical parameter (see below), and $B = \nu_{NI}dL^2$, with ν_{NI} the value of ν required for stability of the ordered phase; $B \approx 5.1$ (ref. 8). The function F depends on whether the solution is isotropic or nematic. Various theories have been advanced to predict F for the isotropic case. The simplest of these may be expressed in the form[9]:

$$F = \beta A^{-2}\left(1 - \alpha\frac{\phi}{B}\frac{L}{d}\right)^2 \tag{13}$$

where β and α are constants, α being about equal to unity. In the polymerization, ϕ is about constant (with neglect of the water of polymerization, etc.). Use of equations (12) and (13) with $\alpha = 4/\pi$, $\beta \approx 6200$ and $\gamma = 0.5$ fits data[10] on $D_R/D_{R,0}$ for isotropic solutions of poly(benzyl glutamate). As shown in *Figure 4*, D_R calculated with equations (12) and (13) decreases sharply as L/d approaches the value $\pi B/4c_p$ required for stability of the ordered phase. The behaviour in *Figure 4* cannot be expected to predict the results observed here, since the effects of molecular-weight polydispersity are not included. The sharp decrease in D_R with increasing conversion (i.e. increasing L/d) is interrupted by the transition to the nematic phase, for which[9]:

$$F = \beta A^{-2}(1 - S^2)^2 \tag{14}$$

where S is the ordered parameter:

$$S = \frac{1}{4}\left[1 + 3\left(1 - \frac{8}{9}\frac{B}{\phi}\frac{d}{L}\right)^{1/2}\right] \tag{15}$$

On conversion to the nematic phase, the order relieves the potential constraints to polymerization resulting from low D_R in the isotropic phase. As illustrated in *Figure 4*, the value of D_R at the isotropic–nematic phase transition decreases markedly with decreasing ϕ. Consequently, with polymerizations at low ϕ, as in part 1, D_R is so low prior to the conversion required to form a nematic phase that the polymerization effectively stops. For the larger ϕ used in this study, it appears that the reaction did not become diffusion-controlled prior to the formation of the nematic phase, and that there was no substantial change in the reaction rate constant on formation of the ordered phase.

The preceding appears to contradict results given in ref. 2 for the kinetics of polymerization of PBT in PPA (180°C) with $[M]_0$ adjusted to give 0.15 weight fraction PBT at full conversion. According to the preceding, in such a polymerization the mass should become ordered early in the reaction, under conditions for which D_R is still relatively large (e.g. see *Figure 4*). Nevertheless, the $\partial[\eta]/\partial t$ was reported to decrease with increasing t during an initial period, even as the polymerization temperature was increasing from 150 to 180°C. On reaching 180°C, a substantial increase in $\partial[\eta]/\partial t$ was reported, and the solution was reported to become anisotropic. Partial solubility of TPA in PPA, especially at low T, may compromise the interpretation of these results.

The observation that X_w/X_n is close to 2 for the conditions studied here is consistent with the lack of diffusion-controlled reactivity over most of the reaction. Since the monomers are not observed in the detection method used in the s.e.c. (i.e. $\varepsilon \approx 0$ for the monomers), the observed X_w/X_n is not representative of all species. For a step-growth polymerization with equal reactivity of all species:

$$\frac{X_w}{X_n} = \frac{4 - 3p + p^2}{(2 - p)^2} \tag{16}$$

if monomers are not observed (as compared with $1 + p$ if all species are observed). Equation (16) provides a good fit to the X_w/X_n observed here, with p calculated from $X_n = (1 - p)^{-1}$.

As illustrated in *Figure 2*, the polymerization in the nematic state gave results with $[\eta]$ nearly linear in t, for p less than about 0.98. This deviation from equation (11) may reflect eventual diffusion control of the reaction in the nematic phase. The reaction rate constant for chains in the ordered phase might be proportional to the translation diffusion constant $D_T^{(\parallel)}$ for diffusion along the molecular axis. One can expect that[8]:

$$D_T^{(\parallel)} = D_{T,0}^{(\parallel)} f(\phi, L/d) \tag{17}$$

where $D_{T,0}^{(\parallel)}$ is the value of $D_T^{(\parallel)}$ at infinite dilution:

$$D_{T,0}^{(\parallel)} = \frac{kT}{2\pi\eta_s}\frac{\ln(3L/2d)}{L} \approx \frac{kT}{4\pi\eta_s d}\left(\frac{d}{L}\right)^{0.8} \tag{18}$$

It is usual[8] to put $f(\phi, L/d)$ equal to unity for a relatively dilute nematic phase (however, see below). If, further, it is assumed that $[M]_0\,\partial X_n/\partial t$ at each t is proportional to $D_T^{(\parallel)} \propto X_n^{-0.8}$, instead of being equal to a constant, then $[M]_0X_n^{0.8}\,\partial X_n/\partial t$ becomes a constant. The latter corresponds to constant $\partial[\eta]/\partial t$, as observed over a fairly wide range in t.

It appears that the rate of polymerization slows still further for higher conversions ($p > 0.98$). This could reflect any or all of several effects, including: (1) deviation of $f(\phi, L/d)$ from unity; (2) intervention of some additional constraint on the polymerization (see below); (3) degradation of chain ends, spoiling the expected stoichiometry; or (4) initial non-stoichiometric monomer concentrations. For example, $f(\phi, L/d)$ might contain a factor $6\pi\eta_s d/\zeta(\phi)$ to account for enhanced segmental friction with increasing ϕ; $\zeta(\phi)$ might be given by free-volume considerations. We note, however, that ϕ is (essentially) constant during the polymerization, making it seem unlikely that $f(\phi, L/d)$ would vary much owing to such an effect. Alternatively, the bimolecular rate constant could become dependent on the order parameter S through effects on D_R if S becomes close to unity. Thus, with equations (12) and (14), for nematic solutions, $D_R \propto (1 - S^2)^2$. With very low D_R, and a low population of chain ends, the number of aligned chain ends in juxtaposition will decline markedly, thereby reducing the conversion rate. This may be the effect observed in this study and in the similar results reported in ref. 2.

CONCLUSIONS

In the polymerization of the rod-like polymer PBT (or, presumably, PBO), it appears that the polymerization kinetics are not affected by a phase transformation from isotropic to nematic that occurs with increasing conversion early in the reaction. Thus, the kinetics are not affected unless the reaction rate is controlled by a diffusion-limited step, and that does not occur with PBT unless the starting monomer concentration is low. If, however, the monomer concentration is low enough, then a precipitous decrease in D_R may occur before the system becomes nematic at high conversion, with consequent decrease in the rate of polymerization. With increasing conversion in the nematic state, it appears that the reaction may be controlled by translational diffusion of the rod-like chains along their axes, leading to behaviour with $\partial[\eta]/\partial t$ independent of t. Thus, $\partial X_n/\partial t$ decreases with increasing t, instead of remaining constant. At still higher conversion ($p > 0.98$ for PBT), a further reduction in the rate of polymerization observed may be associated with a decreasing rate of rotational diffusion with increasing conversion, and the consequent low population of the aligned rod-like chains that are juxtaposed for reaction.

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