on an Instron Tensile Tester, Model 1102, at 0.02 in/min.

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Polymerization Kinetics of Rigid Rodlike Molecules: Polycondensation of Poly([benzo(1,2-*d*:5,4-*d'*)bisoxazole-2,6-diyl]-1,4-phenylene)

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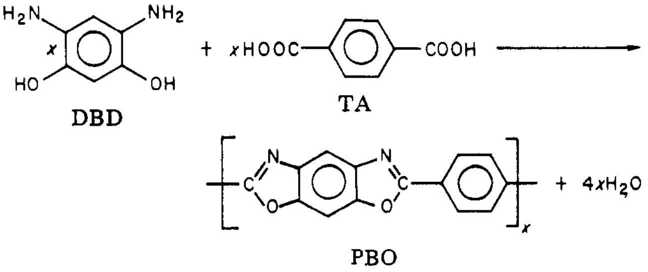
ABSTRACT: The molecular weight and molecular weight distribution of the rigid rodlike polymer poly([benzo(1,2-*d*:5,4-*d'*)bisoxazole-2,6-diyl]-1,4-phenylene) (PBO) have been measured as a function of the extent of reaction to conversions up to 98%. The analysis of the molecular weight data indicates that the polymerization rate decreases sharply with increasing molecular weight. This conclusion—based on measurements of the intrinsic viscosity, size-exclusion chromatography, and an end-group analysis of the number-average molecular weight—is in accord with a diffusion-limited polymerization rate for the condensation of rigid rods.

The statistical analysis of polycondensation reactions is based on the understanding that reaction rates are independent of molecular weight.[1] The reactive end groups of flexible coils indeed diffuse, reorient, and react in solution at a rate independent of the polymer molecular weight. For rigid rods, however, diffusion of reactive end groups must be coordinated with that of the entire molecule. The transport properties[2] of rodlike molecules in general show a greatly enhanced dependence on molecular weight, in comparison with flexible macromolecules. In view of the extraordinary thermomechanical properties[3] that rodlike heteroaromatic polymers display, we have characterized the polymerization kinetics of poly([benzo-(1,2-*d*:5,4-*d'*)bisoxazole-2,6-diyl]-1,4-phenylene) (PBO) to determine if shape anisotropy affects the polymerization process and its products. PBO is prepared by the step-growth polymerization of 4,6-diamino-1,3-benzenediol (DBD) and terephthalic acid (TA):



The reaction is carried out in poly(phosphoric acid) (PPA), which serves to remove the water formed in the polymerization step.

Experimental Section

The monomer 4,6-diamino-1,3-benzenediol dihydrochloride was synthesized under conditions reported in ref 9. Polymerizations were carried out in freshly prepared poly(phosphoric acid) (85% P_2O_5) following the general procedure outlined in ref 9, but several important features were changed to facilitate quantitative kinetic analysis. To avoid complications due to the ordering of polymer molecules in liquid crystalline domains, polymerizations were

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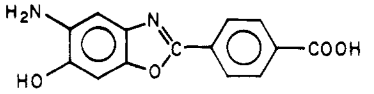
performed at concentrations of 0.5–2.0 wt % polymer. These concentrations were low enough that none of the reaction mixtures were birefringent when observed through crossed polars at room temperature, indicating that ordered domains were not present. A further advantage of dilute-solution polymerization is that the solution viscosity remains low enough for adequate stirring and for samples to be withdrawn throughout the reaction with a syringe and Teflon needle while preserving an inert atmosphere in the polymerization vessel. At this dilute concentration, the dihydrochloride monomer could be dehydrochlorinated within a few hours and the solution brought to the polymerization temperature by immersion in an oil bath controlled to ±0.1 °C. The reaction was begun with the addition of a stoichiometric quantity of finely divided terephthalic acid, followed by vigorous stirring.

Small reaction samples (~1 g) were precipitated in a 100-fold excess of water. The supernatant was analyzed for monomer content by UV absorption spectroscopy. Control experiments on mixtures of PBO and the monomers showed that the monomer remained in the supernatant fluid and could be easily detected. Larger samples (~20 g) were precipitated into a large excess of water, collected, and washed with water in a Soxhlet extractor for 12 h to remove residual poly(phosphoric acid). The polymer was then freeze-dried from water and dried under high vacuum before further analysis.

Intrinsic viscosity measurements were performed in Ubbelohde viscometers at 30 ± 0.01 °C. Vacuum-distilled methanesulfonic acid (MSA) and chlorosulfonic acid (CSA) were each used as the solvent. Capillaries were chosen to provide solvent flow times in excess of 150 s and no kinetic energy correction was needed. Measurements with several capillaries revealed no shear rate dependence.

Infrared absorption spectra were recorded on finely ground KBr pellets with a Perkin-Elmer 580 spectrometer. The ratio r of absorbance for the repeat group (benzoxazole, absorbing at 1630 cm^{-1}) and end group (carbonyl, absorbing at 1700 cm^{-1}) was used to compute the number-average molecular weight. Mixtures of terephthalic acid and 2,2′-diphenylbenzobisoxazole were used to obtain r over a range of benzoxazole to carbonyl ratios to evaluate the method and determine r_0 corresponding to the moiety



The results gave $r_0 = 4.35 \times 10^{-2}$. The number-average degree of polymerization, x_n, was obtained from the expression

$$x_n = r/2r_0$$

where the factor of $^1/_2$ is necessary because there are two benzoxazole rings per repeat unit and an average of one carbonyl end group per chain.

UV–vis absorption spectra of the supernatant from reaction precipitation and of polymer solutions in MSA and CSA were recorded with a Cary 14 spectrometer. Size-exclusion chromatography (SEC) characterization was performed with an instrument designed for use with solutions of polymers in strong acid solvents.[10] The effluent concentration was monitored by absorption at 425 nm, using a Spec-21 spectrometer. The data were interpreted by using a universal calibration in terms of intrinsic viscosity–molecular weight product, $[\eta]M$, as a function of elution volume, obtained with narrow molecular weight polystyrene standards in various solvents.

Molecular theories for the intrinsic viscosity of rigid rodlike molecules indicate that the molecular weight dependence of the intrinsic viscosity may be expressed as[11]

$$[\eta] = 5.81 \times 10^{20} d_H^{0.2} M_L^{-1} L^{1.8} \qquad (1)$$

or

$$M[\eta] = 2.70 \times 10^{-7} M^{2.8} \qquad (2)$$

obtained by substituting the appropriate values of the hydrodynamic diameter, d_H, and the mass per unit length, M_L, equal to the molecular weight M divided by the chain length L. Using eq 2, one can calculate from the chromatogram of $M[\eta]$ vs. (relative) concentration average molecular weights, the molecular weight distribution, and the intrinsic viscosity.

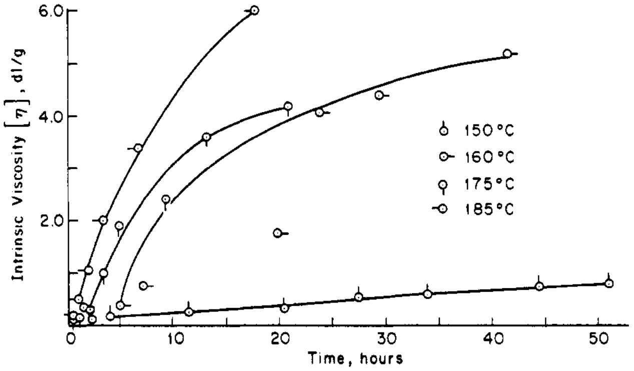


Figure 1. Intrinsic viscosity (MSA at 30 °C) vs. polymerization time for reactions at several temperatures as indicated; initial monomer concentration 1% by weight.

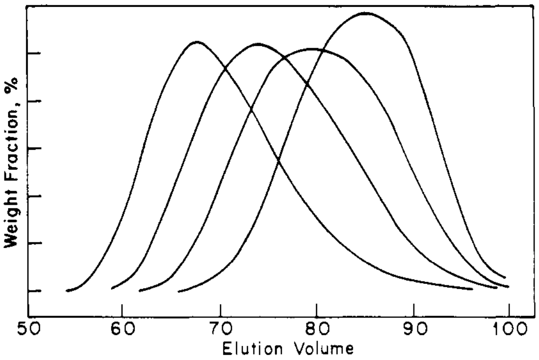


Figure 2. Size-exclusion chromatograms for aliquots obtained at reaction times of 1, 2, 3, and 7 h from right to left, respectively; polymerization at 185 °C, with initial monomer concentration 1% by weight.

In principle, the analysis would be enhanced by collection and concentration of the fractions from the SEC to permit measurement of molecular weight and intrinsic viscosity for each. Unfortunately, precipitation of this and other aromatic heterocyclic polymers leads to irreversible morphological changes preventing complete redissolution,[11,12] making such a tactic unreliable.

Results

The UV–vis absorption spectra of the supernatant fluid recovered on precipitation of an aliquot from the polymerization reaction did not contain absorption bands due to either monomer. Control experiments indicate that both monomers are quantitatively extracted from the water-insoluble polymer on precipitation. The minimum detectable concentration (0.01 absorbance) of DBD in aqueous solution is ~10^{-6} g/mL, which with our reaction workup (100-fold dilution) corresponds to a concentration in the reaction medium of 10^{-4} g/mL. The analytical procedures therefore are sensitive to monomer concentrations several orders of magnitude below that which would be expected for the conversions encountered in this study. The absorption spectra, which give zero absorbance for wavelengths greater than 240 nm, indicate the absence of soluble side products or incompletely cyclized, e.g., hydroxy amide, condensation products.

In typical polycondensation reactions, monomer molecules are the most prevalent species by number throughout the reaction. The enhanced consumption of monomer resulting from intrinsic reactivity differences has been observed in other systems,[4-6] but only in one system[4] has

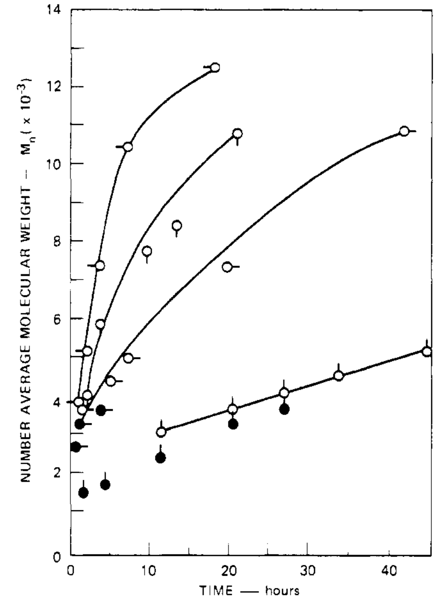


Figure 3. Number-average molecular weight vs. polymerization time for reactions at several temperatures as designated in Figure 1. M_n for SEC (○) and IR analysis (●).

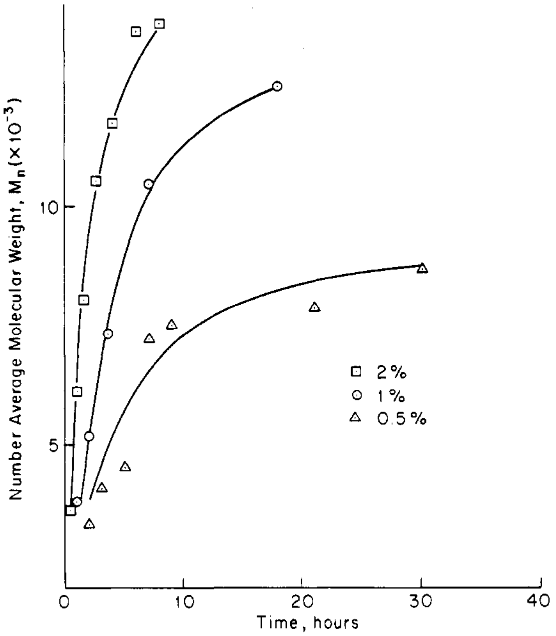


Figure 4. Number-average molecular weight (from SEC analysis) vs. polymerization time for reactions with initial monomer concentration as indicated; polymerization temperature 185 °C.

the complete consumption of monomer been observed at such a low extent of reaction.

The intrinsic viscosities in MSA of the samples produced in this study are shown in Figure 1 as a function of reaction time and temperature. Our experience with measurements of the intrinsic viscosity of PBO and other aromatic heterocyclic polymers has consistently shown that the data are very difficult to interpret. Both reversible and irreversible aggregation are thought to occur as a result of variations in concentration and solution history (e.g., workup of the polymerization reaction, reprecipitation, and trace quantities of moisture). These data may therefore be used as an indication of the extent of reaction, but they do not at this time warrant a quantitative analysis.

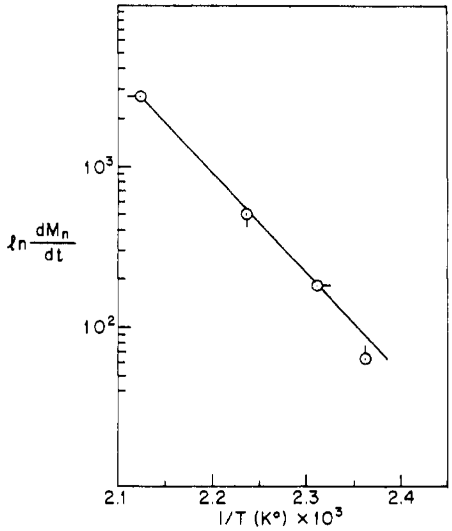


Figure 5. Plot of ln (dM_n/dt) vs. reciprocal temperature for data from the initial part of the reaction; initial monomer concentration 1% by weight.

Typical SEC results obtained for a series of polymerization aliquots are shown in Figure 2. Quantitative SEC analysis[13] requires that all polymers eluted at a specific elution volume share a constant $[\eta]M$ product. The molecular weight distribution may then be calculated with the use of a relation between $[\eta]$ and M, such as eq 1. Comparisons of M_n obtained by end-group analysis and SEC given in Figure 3 show general agreement between the two methods for M_n less than 4000. For larger M_n, data (not shown) consistently gave larger M_n by the IR method, probably owing to the difficulty of properly determining areas of the absorption bands when the carbonyl absorption is very weak. Nonetheless, the limited comparison is of value because the IR analysis is immune to the effects of aggregation that complicate the dilute-solution characterization. Molecular weights obtained by SEC analysis are plotted in Figures 3 and 4 as a function of reaction time, temperature, and concentration. Equation 2 is of the form $[\eta]M = KM^b$. Use of different values of K and b than those given by eq 2 to calculate M_n and M_w/M_n will vary the absolute numbers, but not the overall qualitative character of the results; calculation of M_w/M_n does not depend on K and is insensitive to b for reasonable values of b.

The presence of side reactions that consume reactive end groups could bring about the decreasing rate of growth in the molecular weight observed in Figures 3 and 4. The amine monomer is highly sensitive to oxidation, especially at these high temperatures. However, degradation products, which are readily detected because of their intense red color, were not present in any of these polymerization reactions. Moreover, amine monomer appears to be stable for periods of several days under reaction conditions. For example, analysis of UV–vis absorption spectroscopy of a 1% solution of DBD in PPA stirred at 150 °C for 48 h revealed neither the formation of degradation products nor the loss of more than 0.10% of the monomer.

Second-order reaction statistics, which should apply to condensation in acidic solvents, require that the rate of increase in the number-average molecular weight, dM_n/dt, be constant and proportional to the rate of polymerization:

$$x_n = [M]_0kt + \text{const} \qquad (3)$$

where $[M]_0$ is the initial monomer concentration and x_n

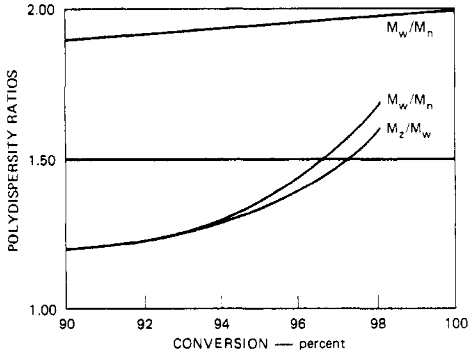


Figure 6. Polydispersity ratios as a function conversion for most-probable reaction statistics (straight lines) and experimental data.

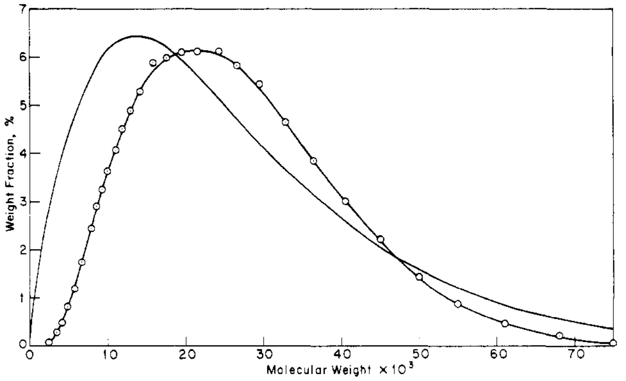


Figure 7. Experimental (⊙) and most-probable (—) molecular weight distributions at equal number-average molecular weights.

is the number-average degree of polymerization. The data in Figures 3 and 4 are clearly not consistent with a single-rate process. Early stages of the reaction, however, appear to be linear. The apparent rate constants $[M]_0k$ plotted vs. inverse temperature in Figure 5 yield an activation energy of 7.16 kcal/mol. This value is somewhat higher than the flow activation energy for PPA of 3.7 kcal/mol. Values of $[M]_0k$ determined at 185 °C for initial monomer concentrations of 0.5, 1.0, and 2.0 wt % (Figure 4) gave $k = 5.3 \times 10^4$ L mol^{-1} h^{-1} for each concentration, consistent with the assumed second-order kinetics.

Further evidence for a polymerization rate dependent on the molecular weight may be found in an analysis of the molecular weight distribution and polydispersity ratios. Figure 6 shows that throughout the polymerization, the polydispersity ratio, M_w/M_n, is consistently lower than that calculated on the basis of most-probable reaction statistics and only approaches the limiting value of 2.0 at extremely high conversions. Figure 7 shows comparison of the actual experimental molecular weight distribution for a sample with a degree of polymerization of 30 with one calculated for most-probable reaction statistics at an equal number-average degree of polymerization. An important feature is the depletion of components with very low and high chain lengths. It should be mentioned that SEC measurements over a wide range of conversion indicate that the column exclusion limits have not been approached, as shown by Figure 2.

Discussion

The observed effects on the rate of conversion and the molecular weight distribution can be understood in terms of a polymerization rate constant k_p that depends markedly on the chain lengths of the reactants. The rate of disappearance of components with chain length x_i is given by the relation

$$-\mathrm{d}[P_i]/\mathrm{d}t = [P_i]\sum k_p(i,j)[P_j] - (1/2)\sum k_p(i-j,j)[P_{i-j}][P_j] \quad (4)$$

where the sums extend over all components identified by degree of polymerization x_i and the total molal concentration $[P] = \sum[P_i]$. A coupled set of such equations is required to describe the polymerization kinetics. With flexible-chain polymers, k_p is independent of chain length (except for x_i less than about 3–4 in some cases), and k_p may be factored out of the sum. This condition is brought about by the effects of segmental motion, which renders the collision frequency of chain ends independent of the chain length, and by compensating effects on diffusion of the reactive ends into and out of the reactive transition state. With the latter, decreased molecular mobility increases the time required to form a transition state but lengthens the time such as state persists.[1]

A strongly chain length dependent diffusion constant will alter this situation. If the time τ_D required to form the transition state necessary for condensation is longer than the lifetime τ_E of that state (e.g., the time required for either reaction or separation of the end groups), the rate-limiting step is the formation of a transition state. The rate-limiting step is therefore not the rate at which molecules which have obtained the necessary collinear alignment successfully condense, but the rate at which that collinear alignment is formed. In the extreme, all molecules which achieve collinearity and proximity condense, and the polymerization rate is controlled by the rate at which that transition state is formed.

With PBO, the cyclization can only be completed if the rodlike chains are aligned collinearly; intermediate partially cyclized products have not been found and are presumably not stable in PPA. Because of this required collinearity, τ_D for PBO might be limited by the rotational time constant τ_R, which is proportional to x^3 for dilute solutions and is even more markedly dependent on x for moderately concentrated solutions.[14] Simple translation along the chain axis, with time constant τ_T about proportional to x, will suffice to destroy the transition state if reaction does not occur. An analogous situation is found in some bulk free radical polymerizations at high conversions, for which τ_D for formation of a transition state of a pair of macroradicals becomes very long compared to the lifetime of the transition states, causing the termination rate constant to decrease in comparison with the propagation rate constant. The latter is relatively unaffected by conversion, as the time to form a transition state of monomer and macroradical is controlled by monomer diffusion.

During the phase of the reaction studied for which the number-average degree of polymerization $x_n > 10$, it is found that (1) the quantity $\mathrm{d}x_n/\mathrm{d}t$ decreases rapidly with increasing conversion for x_n greater than about 20, (2) the molecular weight distribution is sharper than expected for an equilibrium step-growth polymerization, (3) the distribution is depleted in low molecular weight components, and (4) the apparent activation energy of the polymerization (7.16 kcal/mol) is comparable to that for viscous flow of the polymerization solvent. These observations are consistent with substantial dependence of $k_p(i,j)$ on the chain lengths x_i and x_j of the reactants. This seems reasonable in view of the low mobility of the reactant species, the extreme dependence of τ_R on x that is expected, and the disparity between $\tau_D \sim \tau_R$ and $\tau_E \sim \tau_T$.

Two additional features of the polymerization are noteworthy: no monomer was found in the polymerization aliquots (all taken after x_n had advanced to about 5) and the data for x_n vs. t do not extrapolate to dimer, as expected, unless the initial rate is allowed to be much greater than that observed for x_n greater than 10. The latter may reflect the postulated dependence of $k_p(i,j)$ on chain length, since $k_p(i,j)$ might be expected to decrease most rapidly with increasing chain length for small chain lengths. The rapid loss of monomer observed may involve intrinsic difference in the reactivity of the end group on the monomer as compared with those of oligomers. Such differences have been observed in the polymerization of flexible-chain polymers but usually have negligible influence beyond a chain length of 3–4 repeating units. The effects of protonation of the monomer and oligomers in PPA on the electronic state may play a role in any intrinsic difference in reactivity, as was suggested by similar behavior for polymerization of a heterocyclic flexible-chain polymer in PPA.[4] In that case, the rapid loss of monomer is not directly related to the subsequent effects on $\mathrm{d}M_n/\mathrm{d}t$ and M_w/M_n as functions of polymerization time.

A definitive analysis of the data given here would require a reaction rate theory to relate $k_p(i,j)$ to τ_E and τ_D and is beyond the scope of this study. It may be noted, however, that τ_D does not have to be excessively long on an absolute scale for the effects enumerated above to be observed but merely long compared with τ_E, and strongly dependent on x. Although these conditions are not met with flexible-chain polymers, the severely decreased mobility of the rodlike chains appears to foster conditions in which condensation proceeds through a mechanism which can not be modeled by equilibrium step-growth polymerization statistics. Numerical calculations by Peebles and coworkers[7] for polymerizations with $k_p(i,j) \propto x_i^{-r} + x_j^{-r}$ simulate some of the features observed here (e.g., a decreasing rate of polymerization with increased conversion and a narrowed molecular weight distribution), but the model appears too arbitrary to apply meaningfully to the limited results reported here.

The tendency noted in Figure 6 for M_w/M_n to approach the limit 2 expected of an equilibrium step-growth polymerization implies that the terms $k_p(i,j)[P_i][P_j]$ in eq 4 tend to become independent of the chain length of the reactants at high conversion. This is to be expected in that as chain lengths increase, their rotational diffusion constants asymptotically approach zero. The difference in the rate at which molecules reorient decreases, relative to the differences between smaller oligomers, and the conditions necessary for equal reactivity are approached.

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