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Notes

Polymerization Kinetics of Poly(*p*-phenylene-*cis*-benzobisoxazole)

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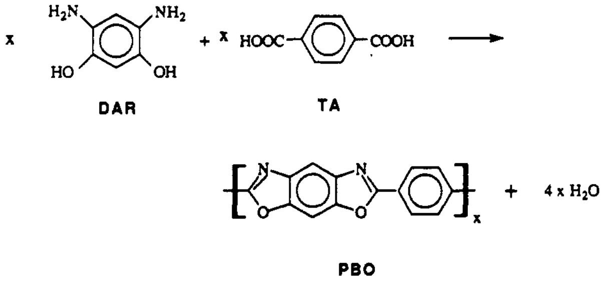
Introduction

Poly(1,4-phenylene-*cis*-benzobisoxazole) (*cis*-PBO) belongs to the new class of high-performance "rigid-rod" materials[1] ("PBZs"). It is formed by the polycondensation[2,3] of terephthalic acid (TA) and diaminoresorcinol (DAR) in polyphosphoric acid (PPA):



High levels of phosphorus pentoxide (P_2O_5) PPA composition (formal weight fraction of P_2O_5 in PPA) are required to drive the reaction and to keep the polymers in solution. When the reaction is carried out at sufficiently high monomer concentration (>6%), the solution becomes optically anisotropic when the molecules achieve sufficient length to form a liquid crystalline phase.

In polycondensation reactions of flexible coils, the reaction rates are found to be mostly independent of MW.[4a] This behavior conforms to the "equal reactivity" hypothesis used by Flory in his derivation of molecular size distribution in condensation polymers.[4b] For the case of rodlike polymers, however, this hypothesis may not be valid. Cotts and Berry[5] showed that the reaction rates were dependent on the degree of polymerization (X_n) for *cis*-PBO at low concentrations, where the solutions were in the isotropic state. They attributed the result to the control of the reaction rate by the slow rotational diffusion of the rods. Wolfe[6] reported an abrupt reaction rate increase as the solution entered the nematic phase from the isotropic state.

Later studies by Spencer and Berry[7] on poly(1,4-phenylene-2,6-benzobisthiazole) or *trans*-PBT, however, did not find the abrupt rate changes between reactions carried out in the isotropic *vs* the nematic phases, but the dependence of the reaction rate on MW was still observed in the nematic phase at high levels of conversion. They suggested that translational diffusion was the controlling factor of the reaction rate in the nematic phase. Their polymerizations, however, were conducted in sealed ampules with no agitation, a condition which may be more conducive to formation of concentration gradients and diffusion control.

Table I. PBO Intrinsic Viscosities (dL/g) and Corresponding Molecular Weights

sample	15 min	30 min	45 min	165 min
1	27.5 (114 000)	33.5 (147 000)	33.5 (147 000)	38.5 (178 000)
2	13.5 (51 700)	14 (53 700)	16 (61 600)	26.5 (109 000)

In this paper, we report a study of polymerization kinetics of DAR and TA in the nematic phase with intensive agitation. Earlier research efforts in this area encountered several difficulties: monomer purity, high mixture viscosities,[7] and the lack of a reliable [η]–MW relationship for PBO. The purity of the monomers used in the present studies is evidenced by the high [η]apos shown in Table I. The reactions were carried out in a reactor specifically designed to homogenize and mix under vacuum very viscous liquids.[1,2] Finally, our group recently established the [η]–MW relationship for *cis*-PBO by light scattering in methanesulfonic acid solutions[8] (MSA).

Experimental Section

The monomers were purified by recrystallization, and extreme care was taken to avoid contamination from ambient humidity. The formulation followed Wolfe's recipe[3] for solutions with 83.5% final P_2O_5 content in the PPA solvent and 14% PBO.

The polymerization runs were divided into two stages: An isotropic phase oligomerization was performed first in a kettle reactor; this was followed by a nematic phase polymerization in a piston-agitated reactor.[1,2] The kettle reactions were carried out at 160 °C under vacuum and were continued until the onset of "stir opalescence", indicating the appearance of the nematic phase.[6] At this point, stirring and heating were stopped and the reaction mixtures were transferred to the piston reactor to advance the polymerizations. The temperature in this phase of the process was 180 °C (±2 °C.) during the runs.

The reaction mixtures were sampled at several intervals during the second stage of the polymerization, and the conversion was monitored by measuring the sample intrinsic viscosities in methanesulfonic acid (MSA), as discussed elsewhere.[8,9]

Polymerization Rates and Conversion

The results are shown in Table I. The corresponding molecular weights are shown in parentheses. The MW_w's were computed using the relationship[8]

$$Y = -9.6758 + 3.5889X - 0.27504X^2 \qquad (1)$$

where $Y = \log\{[\eta]\}$, and $X = \log(\mathrm{MW})$. Equation 1 is consistent with the behavior of a semistiff wormlike chain model with persistence length $Q \approx 20$–25 nm. The deviation of *cis*-PBO from ideal rodlike behavior has been discussed elswhere.[10]

Figure 1 shows the intrinsic viscosities as a function of time for the runs, and Figure 2 shows the corresponding MW's as a function of time according to eq 1.

The plots have very different $t = 0$ extrapolations. This was caused by the difficulty in stopping the first part of the reaction exactly at the point of the appearance of the

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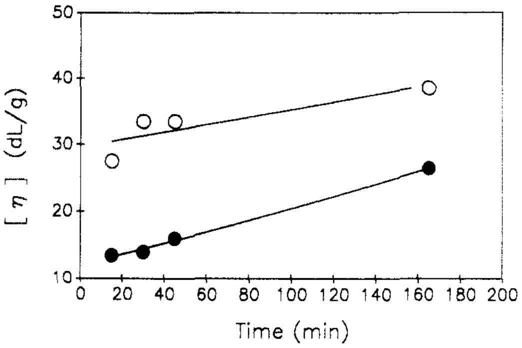

Figure 1. Intrinsic viscosity of two PBO dope samples as a function of reaction time in the piston reactor. The $t = 0$ extrapolations differ because sample 1 (open circles) was more advanced than sample 2 (filled circles) at the point of transfer from the kettle reactor to the piston reactor.

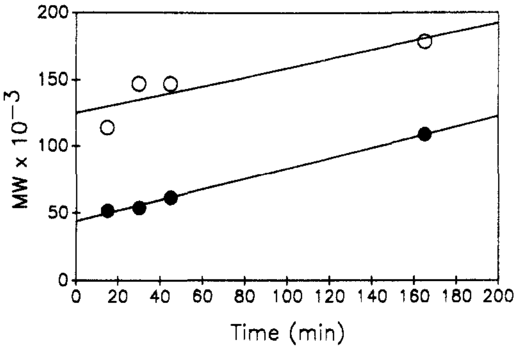

Figure 2. Weight-average molecular weights as a function of reaction time. Sample 2 (closed circles) shows a good linear fit (slope 0.39×10^3 Da/min). Sample 1 (open circles) shows considerable dispersion, but the overall slope (0.34×10^3 Da/min) is quite similar to that of the other sample.

nematic phase. This was done by visual observation of stir opalescence as described by Wolfe.[3] Besides this initial shift, the two runs show remarkably similar behavior: linear molecular weights increase with time, and the slopes appear to be in good agreement, although the data for sample 1 shows some uncertainty. The relevant point is that the linear relationship is maintained in this range. This is shown in Figure 3, where X_n is the number-average degree of polymerization, and the initial time t_0 of sample 1 was displaced by $t_0 = -206$ min to emphasize this feature. In Figure 3 we assumed Flory's most probable distribution,[5] $X_w = 2 X_n$, and $X_w = \mathrm{MW}/234$ to show the approximate degrees of chain extension. The MW distribution, however, is of little importance for the present discussion.

Summary

The kinetics of polymerization in the lyotropic phase appear to be independent of MW, in good agreement with

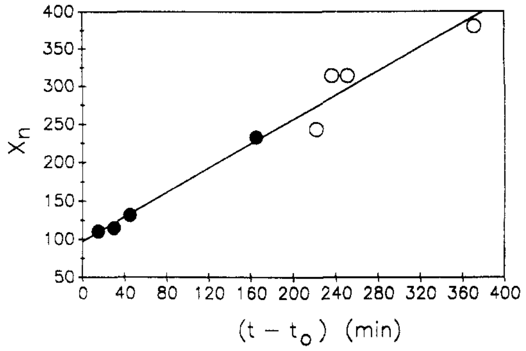

Figure 3. Number-average degree of polymerization X_n as a function of $t = t_0$. The data corresponding to 1 were shifted by $t_0 = -206$ min to emphasize the linear dependence. This behavior is in agreement with Flory's equal reactivity hypothesis.

Flory's equal reactivity hypothesis.[5] The present results suggest that, for well-mixed reactive mixtures, translational diffusion does not appear to control the polymerization rates of PBO.

Spencer and Berry also found that "...the polymerization of PBT (does not appear) to be controlled by diffusion at early polymerization times...". At higher conversions, however, their data fall off the linear range. While there are considerable differences between PBO and PBT, the results of this work suggest that mixing conditions are important during the later stages of the polymerization of these stiff chains.

References and Notes

(1) Ledbetter, H. D.; Rosenberg, S.; Hurtig, C. W. In *The Materials Science and Engineering of Rigid-Rod Polymers*, MRS Symposium Proceedings; Adams, W. W., Eby, R. K., McLemore, D. E., Eds.; Materials Research Society: Pittsburgh, PA, 1989; Vol. 134, p 253.

(2) Gregory, T.; Hurtig, C. W.; Ledbetter, H. D.; Quackenbush, K. J.; Rosenberg, S. U.S. Patent 5 089 591, 1992.

(3) Wolfe, J. F. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., et al., Eds.; Wiley: New York, 1988; Vol. 11, p 601.

(4) (a) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953, Chapter 3. (b) Flory, P. J. *J. Am. Chem. Soc.* **1936**, *58*, 1877.

(5) Cotts, D.; Berry, G. C. *Macromolecules* **1981**, *14*, 930.

(6) (a) Wolfe, J. F.; Arnold, F. E. *Macromolecules* **1981**, *14*, 909. (b) Wolfe, J. F.; Sybert, P. D.; Sybert, J. R. U.S. Patent 4 533 692, 1985.

(7) Spencer, C. P.; Berry, G. C. *Polymer* **1992**, *33*, 1909.

(8) Roitman, D. B.; McAlister, J.; Wessling, R. A. Submitted for publication to *Macromolecules*.

(9) Roitman, D. B.; McAlister, J.; Oaks, F. L. Submitted for publication to *J. Chem. Eng. Data*.

(10) Roitman, D. B.; McAlister, J.; McAdon, M.; Martin, E.; Wessling, R. A. Submitted for publication to *J. Polym. Sci., Polym. Phys. Ed.*