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Poly(*p*-phenyleneterephthalamide) Chain Dynamics[13]

Poly(*p*-phenyleneterephthalamide) (PPTA) is a highly crystalline aromatic polyamide with exceptional thermal and mechanical properties. Structural studies utilizing X-ray diffraction have revealed that this polymer may adopt either of two crystal modifications, commonly referred to as the Northolt[1] and the Haraguchi[2] polymorphs, depending upon the precipitation conditions.[3] While the structures of both polymorphs have been characterized, detailed information concerning the nature of polymer chain motion at the molecular level and its relation to chain packing is controversial. Previous NMR studies[4-6] of PPTA have utilized ^1H and ^{13}C NMR primarily to investigate chain structure and packing. Additionally the authors have interpreted some of their experimental results, utilizing the implicit assumption of dynamic homogeneity (e.g., the motion of each chemically distinct site is considered to be essentially identical), to conclude that the aromatic rings exhibit very restricted motions; the results reported here indicate that these conclusions require revision. In this paper we present initial results[7] from a deuterium NMR investigation, designed to elucidate both the geometry and time scale of polymer chain motion in PPTA, that demonstrate the *dynamic heterogeneity* of this polymer; these results may be contrasted with structural data derived from X-ray diffraction.

Selectively deuterated PPTA used in this study was prepared by copolymerizing *p*-phenylenediamine and an equimolar mixture of terephthaloyl chloride and terephthaloyl chloride in *N*-methylpyrrolidone.[8] The inherent viscosity and number-average molecular weight were 4.28 dL/g and 16 000, respectively. The Northolt polymorph was obtained by coagulation in water from a sulfuric acid solution, while the Haraguchi polymorph was obtained via extraction of H_2SO_4 in chilled water from a PPTA/H_2SO_4 crystallosolvate.[3] X-ray diffraction experiments were subsequently performed to determine the polymorph composition of each preparation. The material precipitated from sulfuric acid was found to be an essentially pure Northolt structure, whereas, that prepared from the crystallosolvate was found to be approximately $^3/_5$ Haraguchi polymorph and $^2/_5$ Northolt polymorph. ^2H NMR experiments from −79 to 228 °C were performed on a Bruker MSL 200 spectrometer operating at a resonance frequency of 30.722 MHz. Spectra were obtained by using a quadrupolar echo pulse sequence with a delay time between 90° pulses of 40 μs.

The quadrupolar echo line shape for the Northolt polymorph at 50 °C is shown in Figure 1a and illustrates the general features, which we attempt to simulate. It can be seen that the line shape appears to be a composite of a rigid Pake-like powder pattern and a smaller fraction exhibiting anisotropic reorientation. The observed splitting between the outermost singularities is characteristic of a relatively rigid phenyl ring with a quadrupolar coupling constant of approximately 180 kHz. The splitting of the two central singularities, on the other hand, is characteristic of 180° flips about the 1,4 axis of the phenylene rings and cannot be simulated by flips or librations of substantially smaller amplitude. However, if an attempt is made to

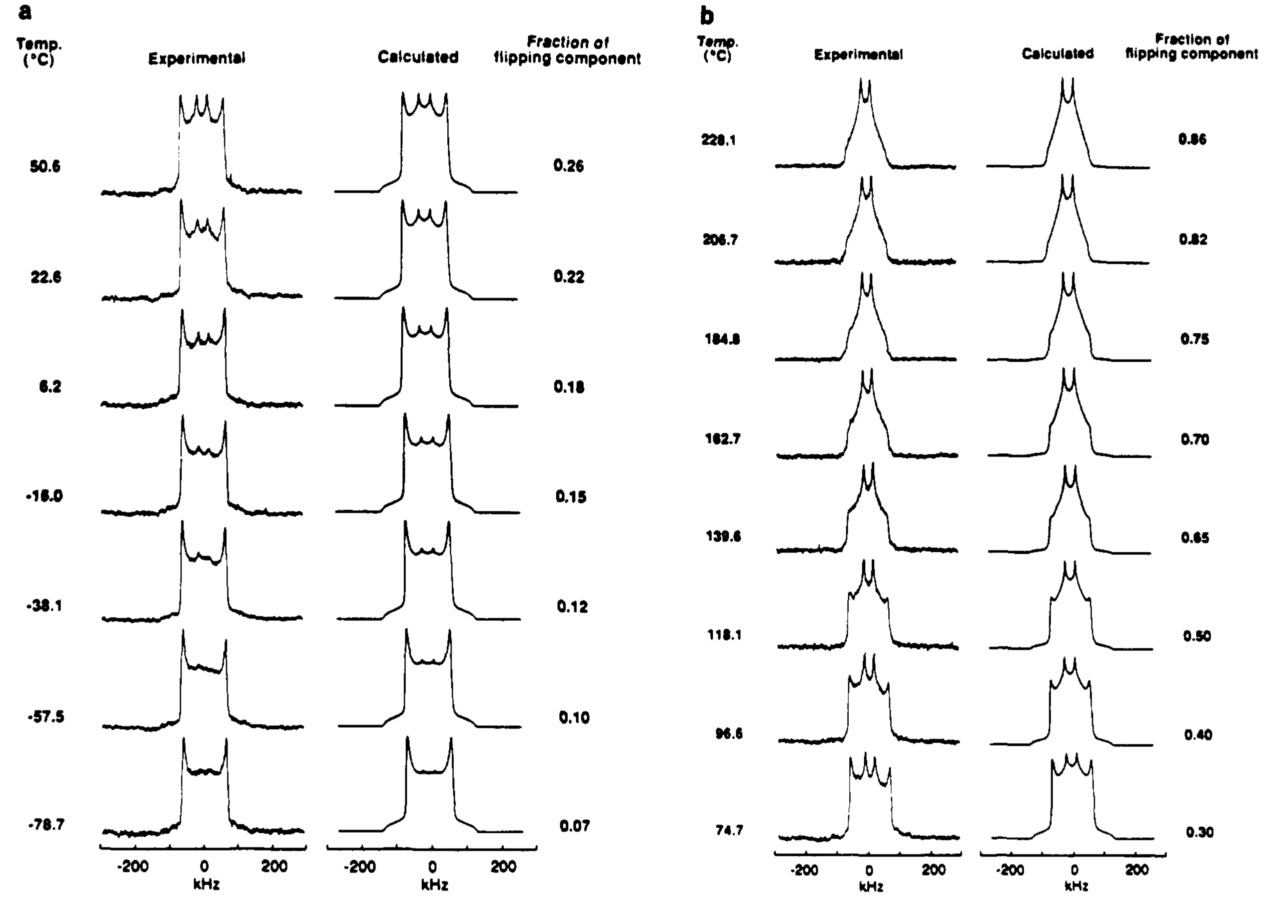

Figure 1. Experimental ($\tau = 40\,\mu$s) quadrupole echo ^2H NMR line shapes as a function of temperature for PPTA selectively deuterated in the terephthaloyl moiety over the temperature ranges of (a) −79 to +50.6 °C and (b) 74.7–228 °C. Calculated line shapes are generated with a bimodal model: one component which only librates with a mean librational angle of $\langle \Delta\theta \rangle = 10.3°$, and a second component, which executes 180° flips with $\tau_c = 10^{-10}$ s and a mean librational angle $\langle \Delta\theta \rangle = 19.8°$.

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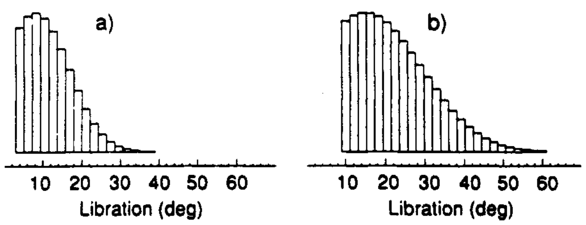

Figure 2. Gaussian distribution of librational amplitudes for (a) nonflipping component and (b) flipping component.

simulate the experimental line shapes over the entire temperature range based on this simple basis set, only very qualitative agreement is found. The most serious discrepancies occur at high temperature where it is found that the addition of librational motion about the 1,4 axis to the 180° flips is required to match the narrowing in the mid-signal-intensity region of the spectra. Further, it was found that, in the low to intermediate temperature spectra, the addition of libration motion to the nonflipping component was necessary to best fit the signal intensity near the center of the line shape. The rapid librational motions are modeled by Gaussian distributions of amplitudes ($\langle\Delta\theta\rangle$) of libration.[9] The distributions are illustrated in Figure 2. A comparison of calculated and experimental line shapes over the temperature range studied is made in Figure 1. At low temperatures, the spectra are dominated by the nearly rigid component while at higher temperatures an increasing contribution from the component that both flips and librates is seen. As indicated in Figure 1, the fractional contribution from the more mobile component ranges from 7% to 86% over the temperature range of $\sim$-80 to +230 °C. Additional support for the types of motion introduced in the NMR line-shape simulations comes from molecular dynamics simulations where extensive librational and ring-flipping motions are observed.[10]

The model used to simulate the experimental data assumes a bimodal distribution of correlation times for the ring-flipping process wherein the less mobile component is assigned a $\tau_c > 0.1$ s for flipping and the mobile component a $\tau_c < 1 \times 10^{-9}$ s. A distribution of flipping rates with a significant population density in the $\tau_c = 10^{-5}$–10^{-7}-s range would necessitate a τ dependence to the quadrupole echo line shapes. The experimental line shapes are observed to be independent of τ over the range of 20-160 μs. However, a distribution of flipping rates is a possible alternative model if the distribution is sufficiently broad that the population density near a flipping rate of 1 MHz is undetectably small (<10%). Analysis[11] of the temperature dependence of the population of flipping rings indicates that the data are consistent with a symmetric distribution of activation energies centered at $\sim$12 kcal/mol with a full-width at half-maximum of $\sim$8 kcal/mol; this leads to a temperature-dependent distribution of correlation times sufficiently broad to have an undetectable τ dependence. Last, the librational motion is assumed to be fast for both components of the line shape, and, once again, the absence of a τ dependence supports this assumption.

Experimental line shapes for the sample containing $\sim{}^3/_5$ Haraguchi polymorphs and $\sim{}^2/_5$ Northolt polymorph are quite similar to those observed for the pure Northolt polymorph. The only apparent difference is that the mixed-phase sample appears to have a slightly higher fraction of flipping rings at most temperatures. The unit cells of these two polymorphs are somewhat different, but their densities are quite similar, perhaps accounting for the similarity in the dynamic heterogeneity.

The data for both polymorphs illustrate that the fraction of phenyl rings that are able to flip at an appreciable rate increases slowly and monotonically with temperature. This behavior is not attributable to a uniqe relaxation process or a first-order phase transition but rather is indicative of a large degree of dynamic heterogeneity for PPTA in either polymorph. As in nylon 66 crytals,[9] the *dynamic heterogeneity* may correlate with the *structural heterogeneity* of the polymer crystals. The structural heterogeneity in the present case could arise from a variety of chain conformations being compatible with the unit cell[12] or simply a distribution of small crystallite sizes. The latter possibility is currently under investigation.

References and Notes

(1) Northolt, M. G. *Eur. Polym. J.* **1974**, *10*, 799.
(2) Haraguchi, K.; Kajiyama, T.; Takayanagi, M. *J. Appl. Polym. Sci.* **1979**, *23*, 915.
(3) Roche, E. J.; Allen, S. R.; Gabara, V.; Cox, B. *Polymer* **1989**, *30*, 1776.
(4) English, A. D. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 805.
(5) Hong, J.; Harbison, G. S. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1990**, *31*, 115.
(6) Fukuda, M.; Kawai, H.; Horii, F.; Kitamaru, R. *Polym. Commun.* **1988**, *29*, 97.
(7) Cain, E. J.; Gardner, K. H.; Gabara, V.; Allen, S. R.; English, A. D. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1990**, *31*, 518.
(8) Tanner, D.; Fitzgerald, J. A.; Phillips, B. R. *Adv. Mater.* **1989**, *51*, 151.
(9) Hirschinger, J.; Miura, H.; Gardner, K. H.; English, A. D. *Macromolecules* **1990**, *23*, 2153.
(10) Wendoloski, J. J. Private communication.
(11) Rössler, E.; Taupitz, M.; Börner, K.; Schulz, M.; Vieth, H. M. *J. Chem. Phys.* **1990**, *92*, 5847.
(12) Rutledge, G. C.; Suter, U. W. *Macromolecules* **1991**, *24*, 1921.
(13) Contribution No. 5815.

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