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Demonstration of the Liquid-Crystalline Behavior of a Rigid-Backbone Polyester in a Magnetic Field

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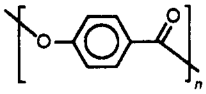
Rigid-backbone homopolyesters and copolyesters of hydroxy-substituted aromatic carboxylic acids such HBA (**1**) and HNA (**2**) are of considerable interest because of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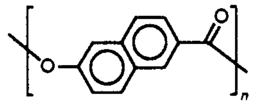
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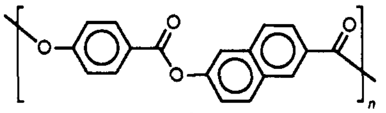
their superior thermal and mechanical properties.[1] On the basis of optical studies, it has been postulated that these rigid-backbone copolymers form a high-temperature liquid-crystalline phase.[2] However, there has been considerable discussion as to its nature and the role that molecular motions of the subunits might play in the solid → liquid crystal (S → LC) transition and how these are reflected in the thermal behavior of these polymers as monitored by differential scanning calorimetry (DSC).[1,3] The liquid-crystalline behavior in the high-temperature phase has previously been investigated by optical,[4] rheological,[5] and diffraction[8] studies. However, unlike the less rigid liquid-crystalline polymers were flexible spacer groups link the rigid moieties of the polymer, there has been no demonstration to date of magnetic field induced orientation of these materials. This is despite the possibility of even greater thermal and mechanical properties from molds or fibers prepared from a melt which has been oriented in the presence of a magnetic field. In the present paper we present such data on the random copolyester **3** of HBA and HNA.[7] Previous work on these materials has been restricted to ^{1}H NMR studies below 150 °C.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The samples were synthesized with deuterium incorporated in positions 4, 5, and 7 of the naphthalene ring (**3a**; see Figure 1A) and also with ^{13}C in the carbonyl group which is directly bonded to the naphthalene ring (**3b**; see Figure 1B). Figure 1A shows the deuterium NMR (^{2}H) spectra (61.4 MHz) of **3a** as a function of temperature. The room-temperature spectrum (25 °C) is representative of a rigid randomly oriented powder (i.e., rigid on the deuterium NMR time scale of ca. 0.25 MHz). By comparison, the spectrum at 218–228 °C shows considerable motional narrowing, indicative of a state in which the naphthalene rings are undergoing free rotation coupled with oscillations about the time-averaged long axis (director) of the polymer chain. It is important to note that these *rotational motions of the rings occur well below* the only observed endothermic transition (maximum at 257 °C) as observed by DSC for this sample.

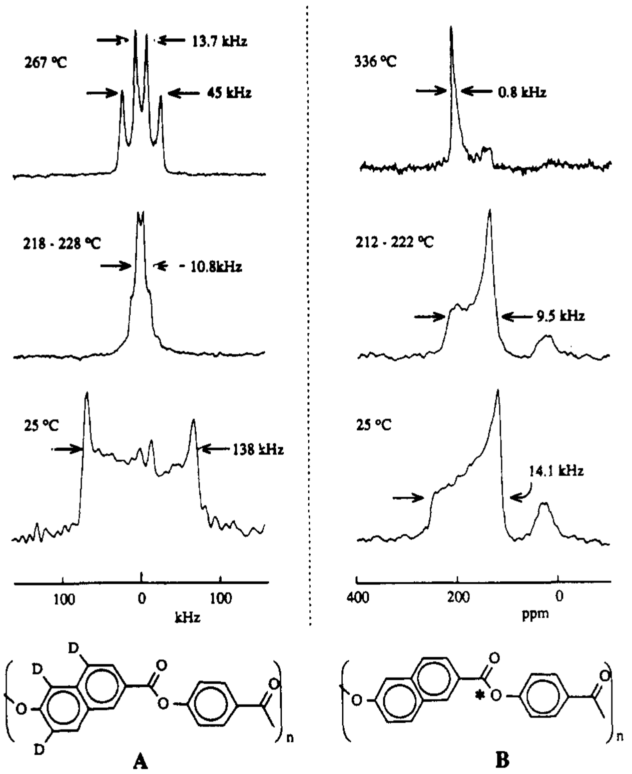

Figure 1. (A) Deuterium NMR spectra of p(HNA/HBA) (52:48) at the temperatures indicated. (B) ^{13}C NMR spectra of p(HNA-^{13}C/HBA) (30:70) at the temperatures indicated.

The two well-defined quadrupolar doublets in the spectrum at 267 °C for **3a** are characteristic of an *oriented liquid-crystalline compound* containing two type of nonequivalent deuterium nuclei. The 2:1 ratio of the inner doublet to the outer doublet is a result of the isotopic labeling, with the deuteriums in the 4 and 5 positions having identical C–D orientations. The quadrupolar splittings of 45 and 13.7 kHz observed for **3a** are typical for aromatic deuterons on oriented nonpolymeric liquid crystals and to our knowledge are the first to be observed for *rigid* main-chain thermotropic liquid-crystalline polymers.

While the ordering of the sample (i.e., the S → LC phase transition) occurs as the sample is heated through the endothermic transition observed for **3a** by DSC,[7] the above ^{2}H NMR results clearly demonstrate that the naphthalene rings are freely rotating well below the S → LC phase transition. In an effort to determine what additional motions might be occurring, the carbonyl carbon directly bonded to the naphthalene ring was labeled. It was felt that it was unlikely that this carboxyl group could freely rotate independent of the polymer chain (or at least large segments of the polymer chain) due to the sp^{2} hybridization (trigonal geometry) of the carbonyl carbon which necessitates motion of the whole ester group. Labeling the carbon directly bonded to the naphthalene ring allows for a direct comparison of the ring motions to the rest of the polymer backbone as there are no atoms separating the two moieties which could fortuitously decouple their respective motions.

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The corresponding cross-polarization ^{13}C NMR (100.6 MHz) spectra as a function of temperature for ^{13}C-enriched (90%) **3b** are shown in Figure 1B. The axially symmetric powder pattern (107–260 ppm) observed at room temperature is consistent with that of a rigid powder (on the ^{13}C NMR time scale of ca. 100 kHz). The signal intensity centered about 30 ppm is due to the probe background. While there may also be a small amount of signal intensity from natural-abundance ^{13}C in other positions in the polymer which is coincident with the spectral pattern observed for the carboxyl carbon, this contribution will be small and should not affect our conclusions.

The spectrum at 212–222 °C is somewhat motionally narrowed, indicating that the carboxyl group (and hence the polymer backbone) undergoes some motion below the phase transition observed by DSC for this compound (290–310 °C). The reduction in the width of the chemical shift anisotropy (CSA) pattern (from 153 to 125 ppm) is similar to that observed for the carboxyl carbon **1** as it is heated from room temperature to 360 °C.[3] In the case of **1**, it was concluded that the narrowing of the CSA pattern resulted from the carboxyl group undergoing discrete 180° jumps. Given the similarity of the two polymers as well as the similarity of the changes in their ^{13}C NMR spectra with heating, it is likely that the motion responsible for the narrowing of the spectrum at 212–222 °C for **3b** is also discrete 180° jumps of the carboxyl groups. This is in good agreement with the ^{2}H NMR spectra which showed a small degree of off-axis oscillations at this temperature which could easily be accounted for by 180° jumps of the carboxyl group. It should be noted, however, that there remains a fundamental difference between **1** and **3**. In the case of **1**, the onset of motion in the carboxyl group is accompanied by a phase transition, while there is no corresponding phase transition for **3**. This difference may result from a higher degree of disorder (*free volume*?) present in crystals of **3** caused by the presence of the naphthalene ring.

The spectrum at 336 °C is dominated by a narrow line at 212 ppm which results from the sample orienting the magnetic field as it is heated through the S → LC phase transition. The small amount of signal intensity centered at 146 ppm presumably results from natural-abundance ^{13}C. The chemical shift (212 ppm) of the narrow component is consistent with that of an oriented sample *with the director axis parallel to the magnetic field.* This conclusion is based on the assumption that the individual tensor elements in **3** follow that of a typical carbonyl carbon[9-11] with σ_{33} (direction of greatest shielding) perpendicular to the sp^2 plane of the carbon and σ_{22} (intermediate value of shielding) and σ_{11} (least shielded direction) in the sp^2 plane, with σ_{22} near-parallel to the C=O bond axis. The room-temperature powder pattern allows approximate values to be assigned to the individual tensor elements with $\sigma_{33} = \sigma_{22} = 107$ ppm and $\sigma_{11} = 259$ ppm. The oriented spectrum at 336 °C has a chemical shift of 212 ppm which is consisted with the assignment that the director axis of the molecule is parallel to the magnetic field (i.e., the chemical shift of the oriented polymer is dominated by σ_{11}). The predicted isotropic chemical shift for this system, based on the room-temperature powder pattern, is approximately 158 ppm, thereby eliminating the possibility that the sharp signal in the spectrum at 336 °C results from the sample being in an isotropic melt.

Thus, for the first time it is unambiguously demonstrated that **3** orients in the presence of an external magnetic field as it undergoes a S → LC transition at elevated temperatures and that this corresponds to the *endothermic* transition observed for these polymers by DSC in the 240–320 °C temperature range.[12] However, rotational motions of both the naphthalene ring and carboxyl group directly attached to the naphthalene ring occur at temperatures well below the S → LC transition, indicating that they alone are not responsible for the orientation of the polymer. It remains unclear precisely what additional motional freedom is gained by **3** as it is heated through the phase transition which allows it to orient. We are currently investigating complementary deuterium and ^{13}C labeling of the benzoic acid monomers (or repeat units) and carboxyl groups, respectively, and ^{17}O labeling of both carboxyl functionalities in an effort to more fully understand the nature and role of molecular motions in the orientation of this polymer and of both to the DSC data. Details of these results will be presented subsequently in a full paper.

Experimental Section. Materials: 4-hydroxybenzoic acid (Aldrich) was used without purification. 6-Hydroxy-2-naphthoic acid was a gift from Celanese Research Co., Summit, NJ. The labeling of HNA with deuterium and ^{13}C was carried out according to ref 13, and the polymers were prepared according to literature techniques.[14] Both deuterium spectra (using the quadrupolar-echo sequence) and ^{13}C spectra (cross-polarization conditions) were recorded on a Bruker MSL400 spectrometer.

NMR probe: The high-temperature broad-banded and double-tuned probe used to record the NMR spectra was home-built and consisted of a horizontal solenoid coil encased in a block heater with a noninductively wound chromel/alumel wire. The outer casing of the probe consisted of a water jacket to protect the magnet and room-temperature shims from the high temperatures involved.

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