**Registry No.** AZA9 (SRU), 82851-48-7; AZA9 (copolymer), 120667-64-3; DDA9 (SRU), 79079-27-9; DDA9 (copolymer), 120667-65-4.

## References and Notes

(1) Straley, J. P. *Phys. Rev.* **1974**, *A10*, 1881.

(2) Luckhurst, G. R.; Zannoni, C.; Nordio, P. J.; Segre, U. *Mol. Phys.* **1975**, *30*, 1345.

(3) Bergersen, B.; Palffy-Muhoray, P.; Dunmur, D. A. *Liq. Cryst.* **1988**, *3*, 347.

(4) Emsley, J. W.; Luckhurst, G. R.; Stockley, C. P. *Mol. Phys.* **1981**, *44*, 565.

(5) Bunning, J. D.; Crellin, D. A.; Faber, T. E. *Liq. Cryst.* **1986**, *1*, 37.

(6) Wu, B.-G.; Ziemnicka, B.; Doane, J. W. *J. Chem. Phys.* **1988**, *88*, 1373.

(7) (a) Ferreira, J. B.; Martins, A. F.; Galland, D.; Volino, F. *Proceedings of the 5th European Winter Conference on Liquid Crystals*, Borovetz, Bulgaria; *Mol. Cryst. Liq. Cryst.* **1987**, *151*, 283. (b) Galland, D.; Volino, F. *J. Phys. Fr.*, in press.

(8) Esnault, P.; Galland, D.; Volino, F.; Blumstein, R. B. *Proceedings of the 6th International Symposium on Liquid Crystals and Ordered Fluids*, ACS National Meeting; New Orleans, LA, 1987; *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.* **1988**, *157*, 409.

(9) Doane, J. W. In *Magnetic Resonance of Phase Transitions*; Owens, F. J., Poole, C. P., Farach, H. A., Eds.; Academic Press: New York, 1979; p 131.

(10) "Polymer Liquid Crystals". *Faraday Discuss. Chem. Soc.* **1985**, *no. 79*.

(11) Samulski, E. T. In ref 10, p 7.

(12) Blumstein, A.; Gauthier, M. M.; Thomas, O.; Blumstein, R. B. In ref 10, p 33 and references therein.

(13) Blumstein, A. *Polym. J. (Jpn.)* **1985**, *17*, 227.

(14) Emsley, J. W.; Luckhurst, G. R.; Shiltone, G. N. *Mol. Phys.* **1984**, *53*, 1023.

(15) Blumstein, A.; Thomas, O. *Macromolecules* **1982**, *15*, 1264.

(16) Blumstein, A.; Vilasagar, S.; Ponrathnam, S.; Clough, S. B.; Maret, G.; Blumstein, R. B. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 887.

(17) Blumstein, R. B.; Stickles, E. M.; Gauthier, M. M.; Blumstein, A.; Volino, F. *Macromolecules* **1984**, *17*, 177.

(18) (a) d'Allest, J. F.; Sixou, P.; Blumstein, A.; Blumstein, R. B.; (b) Kim, D. Y.; d'Allest, J. F.; Blumstein, A.; Blumstein, R.; (c) Esnault, P.; Gauthier, M. M.; Volino, F.; d'Allest, J. F.; Blumstein, R. B. *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.* **1988**, *157*, 273 (three consecutive papers).

(19) Martins, A. F.; Ferreira, J. B.; Volino, F.; Blumstein, R. B.; Blumstein, A. *Macromolecules* **1983**, *16*, 279.

(20) Volino, F.; Blumstein, R. B. *Mol. Cryst. Liq. Cryst.* **1984**, *113*, 147.

(21) Blumstein, R. B.; Poliks, M. D.; Stickles, E. N.; Blumstein, A.; Volino, F. *Mol. Cryst. Liq. Cryst.* **1985**, *129*, 375.

(22) Bothner-By, A. A.; Pople, J. A. *Annu. Rev. Phys. Chem.* **1965**, *16*, 43.

(23) Esnault, P.; Casquilho, J. P.; Volino, F. *Liq. Cryst.* **1988**, *3*, 1425.

(24) Adams, J. M.; Morsi, S. E. *Acta Crystallogr.* **1976**, *B32*, 1345.

(25) Elix, J. A.; Engskaninan, U.; Jones, A. J.; Raston, C. L.; Sargent, M. V.; White, A. H. *Aust. J. Chem.* **1978**, *31*, 2057.

(26) Hummel, J. P.; Flory, P. J. *Macromolecules* **1980**, *13*, 479.

(27) Bergès, J.; Perrin, H. *Mol. Cryst. Liq. Cryst.* **1984**, *113*, 269.

(28) The molecule being not flat, this equivalence can only be obtained by fast exchange between the actual conformation and the conformation deduced by symmetry with respect to a plane, by rotation around all the single covalent bonds (racemization).

(29) The referee has suggested a possible different explanation for the observed decrease of $\Delta\nu^*{}_1/S_{zz}$, namely, that $\langle\cos 2\phi_1\rangle$ is negative and decreases in such a way that it overcompensates the corresponding increase of $\eta_S$. Such a possibility is unrealistic since an increase of $\eta_S$ of $\sim$0.1 between low and high temperature (consistent with the magnetic results) implies a variation of $|\langle\cos 2\phi_1\rangle|$ larger than 1 in the same temperature range. Changing the convention concerning the sign of $\eta_S$ changes the meaning of the angle $\phi_1$ in eq 9 and the sign of $\Delta\chi_2{}^{(0)}$ in eq 8 but clearly not the physical situation.

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# Synthesis and Characterization of Poly(oxy-2,6-naphthalenediylcarbonyl)

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ABSTRACT: The synthesis of oligomeric and high molecular weight polyesters of 6-hydroxy-2-naphthoic acid in therminol is described. The polyesters are characterized by X-ray, DSC, TMA, light microscopy, and SEM. Close analogies are found to exist between the polycondensation reaction, thermal transitions, and solid-state structures of poly(oxy-2,6-naphthalenediylcarbonyl) and poly(oxy-*p*-phenylenecarbonyl). The composition versus $T_{c\to n}$ diagram for the copolyesters of 6-hydroxy-2-napthoic acid and 4-hydroxybenzoic acid is described.

## Introduction

The structure and properties of the copolyesters of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) have been examined by a number of different workers in considerable detail during the past few years.[1-10] Similarly, the homopolyester of HBA has been the subject of many investigations concerning its polymerization,[11,12] its crystal structure,[13-15] and the nature of its thermal transitions.[16,17] On the other hand, very little information has been published on the homopolyester of HNA other than preliminary studies by Calundann[18] and Cao and Wunderlich.[2] Much of the scientific interest in poly(HBA) arises from its tendency during polycondensation to precipitate out at a low degree of polycondensation ($\bar{P}_n$) in the form of single crystals.[11] The poly(HBA) has been shown to display two reversible transitions at about 350 and 440 °C.[17] The first has been characterized as a crystal–(one-dimensional) plastic crystal (or highly ordered smectic)[19] and the second as a crystal–nematic transition.[17]

Our attention was drawn to poly(HNA) from a study undertaken to characterize the kinetics of copolycondensation of the HBA/HNA system.[20] It was observed that HNA oligomers precipitated early in the polycondensation reaction in a manner similar to the HBA system. In addition, poly(HNA) displayed two transitions in the DSC very close to those of poly(HBA). Consequently, we undertook to synthesize and better characterize the HNA homopolyester and to establish more definitively the structure of the material and particularly the nature of the high-temperature transitions.

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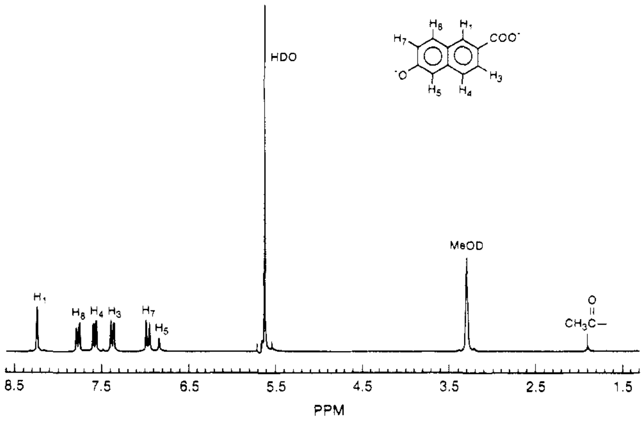

**Figure 1.** $^1H$ NMR of hydrolyzed poly(HNA) in $CD_3OD/D_2O/NaOD$ 12:3:1. The chemical shift scale is relative to internal TMS. Note: proton $H_5$ has exchanged partially with deuterium.

## Experimental Section

**Materials.** Therminol-66, a high-boiling aromatic hydrocarbon from Monsanto Co., was dried by passing a slow stream of argon through it at 320 °C. 6-Hydroxy-2-naphthoic acid (**1**) was kindly provided by Hoechst-Celanese Co., Summit, NJ, mp 255 °C. 6-Acetoxy-2-naphthoic acid (**2**) was obtained by acetylation of **1** in sodium hydroxide solution with acetic anhydride and recrystallized two times in acetone/water 4:1; mp 230 °C ($\Delta H$ = 131 J/g); crystal–crystal transition at 147 °C ($\Delta H$ = 22.1 J/g).

**Measurements.** Infrared Spectroscopy (IR) utilized an IBM Instruments IR/32 FT spectrometer. The absorption bands (below) are listed in wavenumbers ($cm^{-1}$) and their relative intensities are abbreviated with s (strong), m (medium), and w (weak).

Differential scanning calorimetry (DSC) was performed on a Du Pont 910 with a Du Pont 1090 data station. Samples, 4–14 mg, were heated in nitrogen at 10–40 °C/min. Thermogravimetric analysis (TGA) was performed on a Du Pont 951 with an 11-mg sample and heating rate of 20 °C/min. For the thermomechanical analysis (TMA), a Du Pont 943 instrument was used with a heating rate of 5 °C/min and 5-g load on an area of 0.64 $mm^2$. The sample was prepared by rapid (<90 s) compression molding of the fine powder of poly(HNA) at 460 °C under 8 kpsi pressure. Microscopic examination of compression-molded shapes formed at 460 °C indicates that the material is fused under these conditions. The sample thickness was measured on a Heidenhain CT 60 M to be 227 $\mu$m.

Transmitted polarizing light microscopy was performed on a Zeiss Photomicroscope III with a Linkam THM 600 hot stage and a PR 600 controller. The powder was held between thin microscope cover slips of small mass and area compared with that of the hotstage. To minimize in situ specimen polycondensation, the hot stage was preheated to the desired temperature, before the samples were mounted. Textures characteristic of a given temperature were quenched to room temperature to allow microscopy with high-resolution objectives.[17] All micrographs shown were obtained at room temperature. The preservation of textures in similar materials by quenching has been demonstrated previously.[21] Specimens that did not flow spontaneously when heated above their transition temperatures were subjected to shear by pressing on the upper cover slip with a dissecting needle. The scanning electron microscopy (SEM) analysis was performed on a JEOL 840A instrument. The samples were coated with gold/palladium.

**Molecular Weight Analysis.** The procedure introduced first by Kricheldorf and Schwarz[12] for the determination of the number-average molecular weight of oligomers and polymers of 4-hydroxybenzoic acid was used: 1–2-mg samples of oligo- or polyesters were hydrolyzed in methanol-$d_4/D_2O/NaOD$ 12:3:1 (by weight) at 50 °C and their $^1H$ NMR spectra measured on an IBM Instruments NR 250/AF spectrometer. Figure 1 shows, as an example, the spectrum of hydrolyzed poly(HNA) with $\bar{P}_n$ = 15. By comparison of the integrated intensity of the methyl group of acetic acid (chemical shift, 1.9 ppm relative to TMS) with the intensities of the six aromatic proton signals in the chemical shift range 6.8–8.3 ppm, the average degree of polycondensation ($\bar{P}_n$) and the number-average molecular weight ($\bar{M}_n$) were calculated. (Note, in the calculation of ($\bar{M}_n$), the partial exchange of proton $H_5$ was taken into account in determining the integrated intensity of the six aromatic protons.)

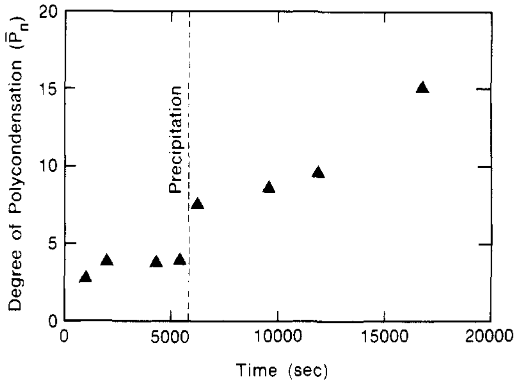

**Figure 2.** $\bar{P}_n$ versus time in the polycondensation reaction of 6-acetoxy-2-naphthoic acid; $T$ = 245 °C.

**Polycondensations.** General: The synthesis of poly(HNA) was performed similar to the synthesis of Ekonol, first described by Economy et al.[11]

**Preparation of Oligomers.** **2** (4.029 g, 17.5 mmol) and 20 mL of therminol-66 were placed in a 50-mL three-necked round-bottom flask equipped with mechanical stirrer, thermometer, and argon inlet and outlet. The flask was immersed in a preheated woods metal bath and kept at 245 °C while passing an argon stream (ca. 100 mL/min) through the reaction mixture. One-milliliter samples were taken between 33- and 280-min reaction time, quenched by pouring into cold acetone, filtered, washed with acetone, and dried at 120 °C for 24 h in vacuo (<0.01 Torr).

**Preparation of Polyesters.** **2** (1.20 g, 5.21 mmol) was placed together with 30 mL of therminol-66 in a 50-mL round-bottom three-necked flask equipped with magnetic stirrer, heating mantle, thermometer, argon inlet, and microdistillation apparatus. The mixture was heated slowly to 220 °C and kept at this temperature for 1 h and then heated slowly to 240 °C and kept at this temperature for 1 h. Afterward the temperature was raised 1 °C/min to 350 °C and kept there for 12 h under argon. After cooling to room temperature, poly(HNA) was scratched out of the vessel with a spatula, filtered, washed with acetone, and extracted 24 h with acetone/water 5:1 in a Soxhlet extractor. The polyester was dried 24 h at 120 °C in vacuo (<0.01 Torr). Yield, 78% (0.69 g).

**Characterization.** Anal. Calcd for $C_{11}H_6O_2$ polymer: C, 77.64; H, 3.55. Found: C, 76.90; H, 3.59. IR (KBr, $cm^{-1}$): 3072 w, 3048 w (C—H str), 1732 s (C=O str), 1629 s, 1603 s, 1505 m, 1470 s, 1340 m, 1260 s, 1181 s, 1074 s, 1014 s, 969 m, 940 s, 920 s, 889 s, 811 s, 764 s, 740 s.

## Results and Discussion

**Synthesis.** Typically the HBA/HNA copolyesters are prepared by melt polycondensation.[18] However, in the case of poly(HNA) because of the potential for solidification of the melt, it was decided to use the slurry technique originally developed for the polymerization of HBA.[11] The acetylated HNA was found to react initially in solution and then the reaction could be continued as a slurry once precipitation occurred ($\bar{P}_n \gtrsim 4$ at 245 °C). As shown in Figure 2, the reaction appears to proceed at about the same rate initially in solution and subsequently in the solid state at a given temperature.[20] Examination of poly(HNA) using scanning electron microscopy showed a well-ordered morphology very similar to that of poly(HBA).[15] At relatively low molecular weights ($\bar{P}_n \simeq 18$), one could isolate uniform slabs measuring ca. 1 $\mu$m in thickness and ca. 5–8 $\mu$m in width with a well-defined lamellar structure at the edge (see Figure 3a,b). At higher molecular weights ($\bar{P}_n \gtrsim 180$) the slabs had increased in thickness and the

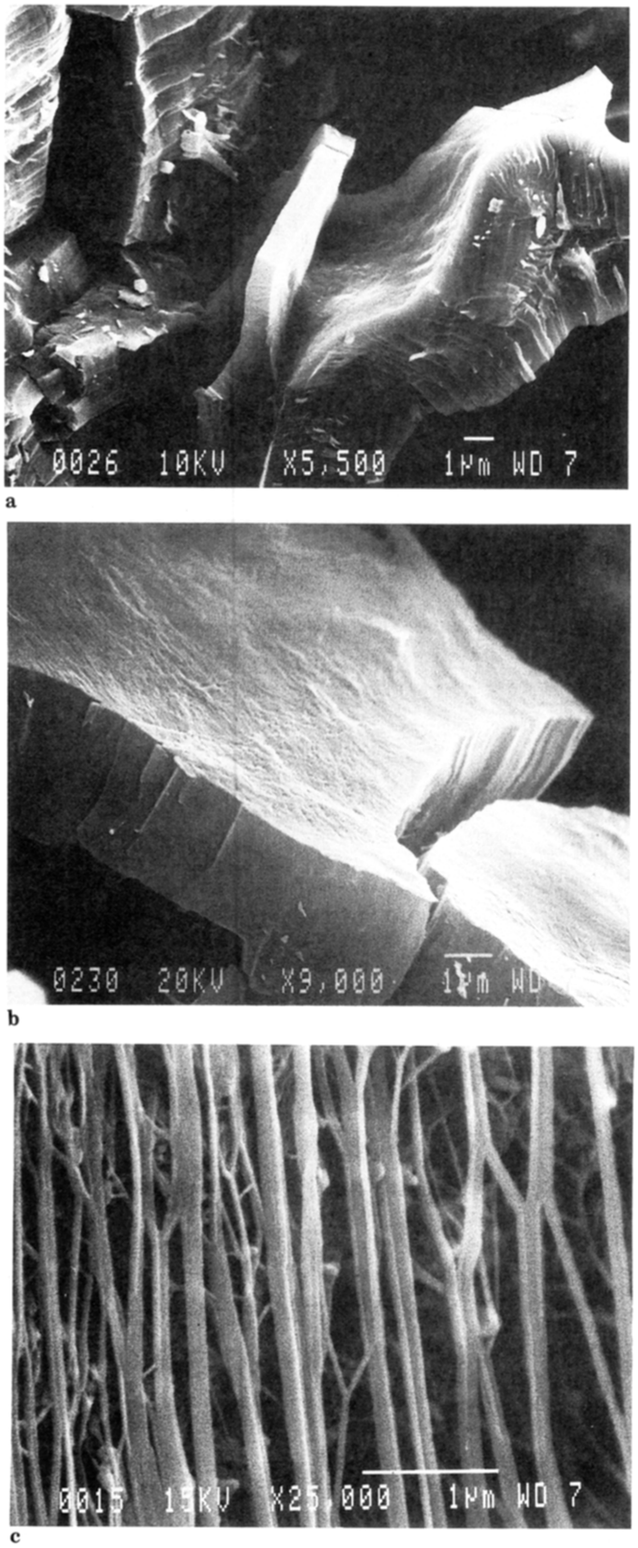

**Figure 3.** SEM of poly(HNA). (a) and (b) two different sections of $\bar{P}_n = 18.1$; (c) $\bar{P}_n \gtrsim 180$, annealed for 5 min at 370 °C.

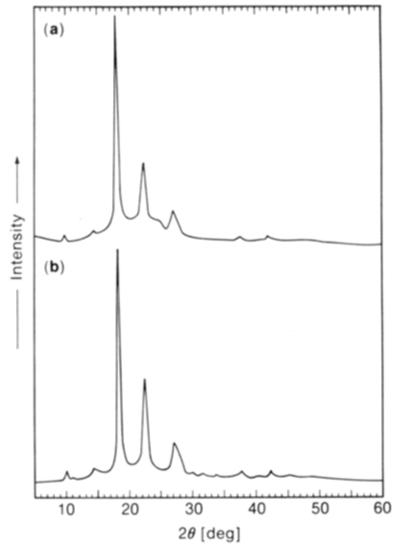

**Figure 4.** Wide-angle X-ray diffraction pattern (goniometer trace) of poly(HNA). (a) Not annealed; (b) annealed 24 h, 370 °C.

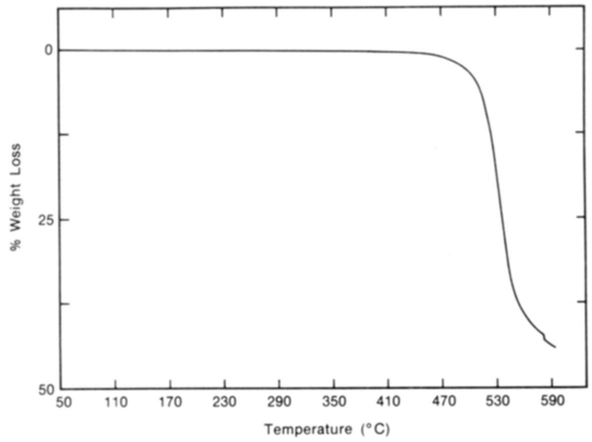

**Figure 5.** Thermogravimetric analysis of poly(HNA) in $N_2$; heating rate, 20 °C/min.

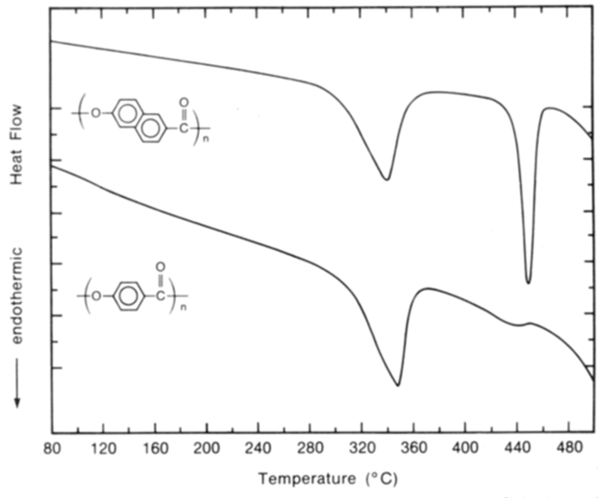

**Figure 6.** DSC thermograms; heating rate, 40 °C/min. (a) Poly(HNA), 5 min annealed at 370 °C; (b) poly(HBA), second heating (after initially heated to 450 °C and quenched).

tendency for the slabs to cleave into lamellae and fibrils was clearly apparent (see Figure 3c). Almost identical morphologies have been observed in poly(HBA), indicating a very close similarity in the two polycondensation processes. X-ray diffraction analysis of the high molecular weight poly(HNA) samples (see Figure 4) showed a high degree of crystallinity, in excess of 70% after annealing and comparable to that of poly(HBA). These results suggest that 6-acetoxy-2-naphthoic acid polymerizes by a mechanism similar to that of 4-acetoxybenzoic acid where the oligomers precipitate as thin slabs with a high degree of chain-to-chain regularity. Polycondensation continues within the slab as well as at the surface to yield a three-dimensionally ordered structure. Preliminary results from electron diffraction analysis indicate a pattern typical of a single-crystal structure with 2-fold symmetry in the basal plane and a two-monomer repeat along the chain direction of the unit cell. A detailed structure determination has

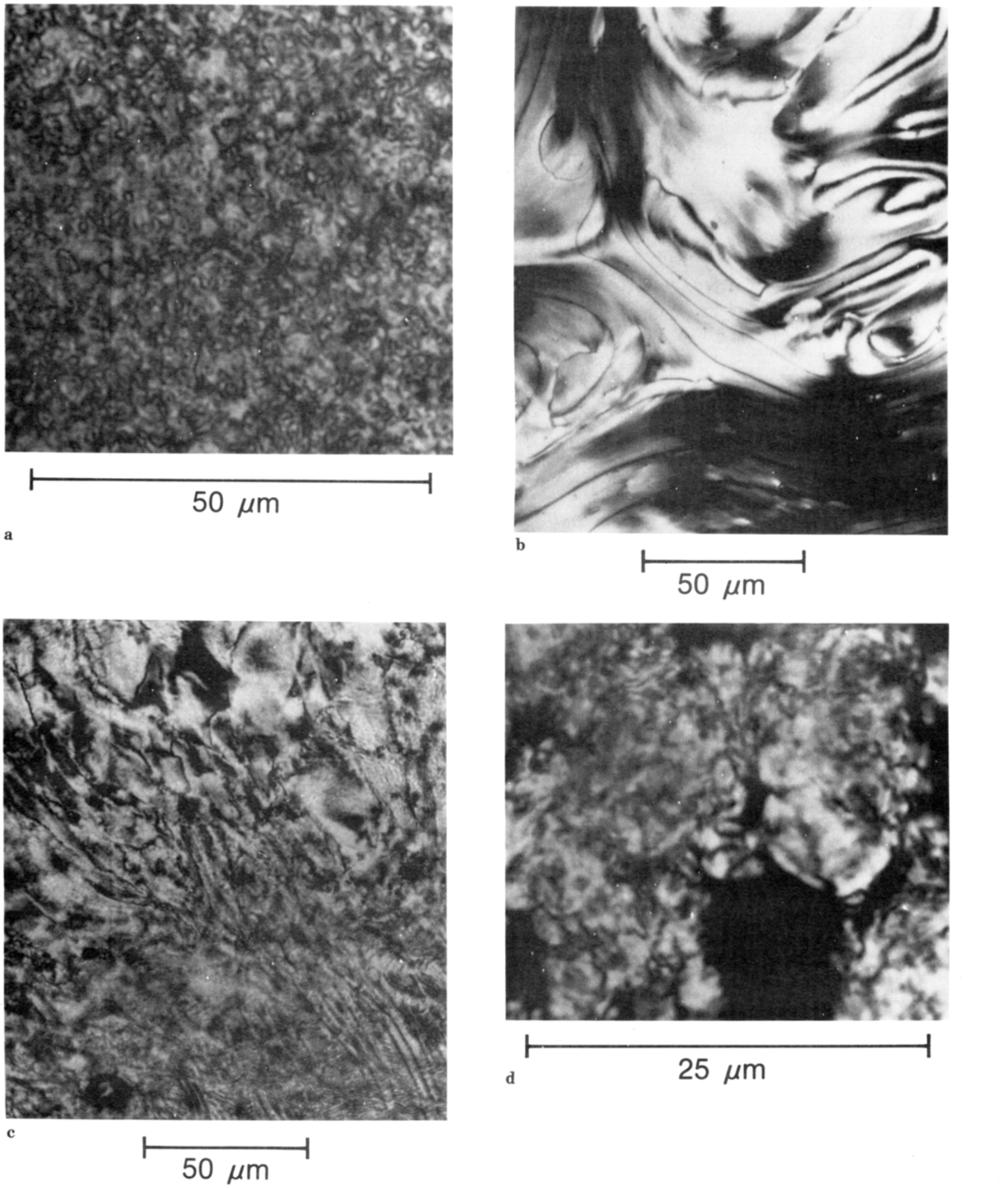

**Figure 7.** Polarizing micrographs of poly(HNA): (a) $\bar{P}_n = 18.1$, quickly heated to 350 °C, sheared and quenched; (b) $\bar{P}_n = 18.1$, quickly heated to 460 °C and quenched (no shear); (c) $\bar{P}_n = 18.1$, longer at 460 °C and quenched (no shear); (d) $\bar{P}_n \gtrsim 180$, heated to 460 °C, sheared, and quenched.

been carried out and will be reported.[22]

The tendency to form single crystals of poly(HBA) or poly(HNA) during polycondensation is unique and deserves further comment. Undoubtedly, the melt polycondensation of either monomer would initially proceed in the isotropic state and possibly continue to a nematic structure followed by solidification of the low molecular weight melt. Hence, one would not observe formation of single crystals. On the other hand, solution polycondensation leads to oligomers that do not have the necessary critical concentration to phase separate as a lyotropic phase. Because of the relatively low solubility of the oligomers and especially their rodlike nature, a mechanism is available for facile packing of these low molecular weight units into single-crystal assemblages. Polymerization continues within the crystal as well as at the surface, until internal stresses lead to cleavage into lamella and subsequently fibrils.

**High-Temperature Properties.** The HNA polymer displays excellent thermal stability on the basis of thermogravimetric analysis (see Figure 5). DSC analysis confirmed the presence of a reversible endotherm at 338 °C, reported earlier to be a disordering transition from crystalline to "condis-crystalline" state.[2] We could not

**Table I**
**Polycondensation Temperatures, Molecular Weight, Transition Temperatures, Enthalpies, and Entropies of Poly(HNA)**

| polyester | polycondensation[d] time, min | $\overline{\mathrm{DP}}$ | $\bar{M}_n$, g/mol | $T_1$,[a] °C | $\Delta H_1$[b] | $\Delta S_1$[c] | $T_2$,[a] °C | $\Delta H_2$[b] | $\Delta S_2$[c] |
|---|---|---|---|---|---|---|---|---|---|
| P1 | 200 | 9.6 | 1600 | 300, 358[f] | 1.19[g] | 2.08[g] | 449 | 1.84 | 2.54 |
| P2 | 280 | 15.0 | 2600 | 312, 357[f] | 1.36[g] | 2.32[g] | 451 | 2.47 | 3.41 |
| P3 | 1200 | >180 | >30K | 327 | 1.89 | 3.15 | 424, 435[f] | 5.63[g] | 7.94[g] |
| p(HNA)[e] | 1200 | >180 | >30K | 338 | 5.22 | 8.54 | 453 | 4.39 | 6.04 |
| p(HBA)[h] |  | >166 | >20K | 348 | 5.23 | 8.43 | 438 | 0.29 | 0.40 |

[a] Transition temperatures of first transition ($T_1$) or second transition ($T_2$). [b] Transition enthalpies in kJ/mol of oxynaphthalenediyl units. [c] Transition entropies in J/K·mol of oxynaphthalenediyl units. [d] At 245 °C; except P3 and p(HNA), 350 °C, 20 h. [e] After annealing P3 for 24 h, 370 °C. [f] Two transitions. [g] Sum of both transitions. [h] Transitions $\Delta H$ and $\Delta S$ are per oxyphenylene unit.

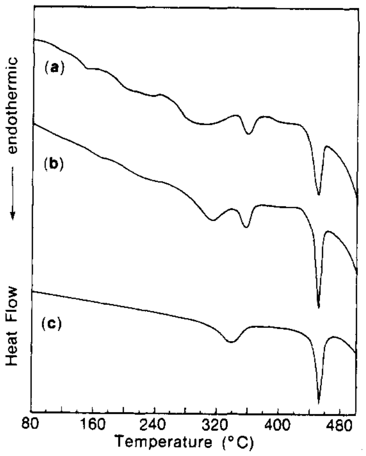

**Figure 8.** DSC of poly(HNA); heating rate, 40 °C/min: (a) $\bar{P}_n$ = 9.6; (b) $\bar{P}_n$ = 15.0; (c) $\bar{P}_n \gtrsim 180$, annealed 5 min, 370 °C. Note, for (a) and (b) the vertical scale range is one-fifth that of (c).

detect a crystal–crystal transition at 390 °C described earlier by Calundann.[18] A second transition was observed at 453 °C (heating rate 40 °C/min). In Figure 6, the two transitions in poly(HNA) are compared with those of poly(HBA). The poly HNA when rapidly heated to 460 °C and quenched showed a nematic texture similar to that of poly(HBA) under the polarizing microscope (see Figure 7d). Table I compares the transition temperatures, enthalpies, and entropies of poly(HBA) and poly(HNA). The two transitions occur almost at the same temperature for the two materials. The transition enthalpies of the first transition are nearly identical, while the enthalpy of the higher temperature transition in poly(HNA) is about 15 times larger than that of poly(HBA). This suggests that the poly(HNA) melt has a lower order parameter than the poly(HBA) melt. Attempts to determine the order parameters of the two homopolymers by optical methods or ordering in a magnetic field are complicated by the tendency for rapid degradation at these elevated temperatures. The first transition in the poly(HNA) may be described as a plastic crystal transition or a highly ordered smectic, in analogy to the interpretation for the poly(HBA).[17,19]

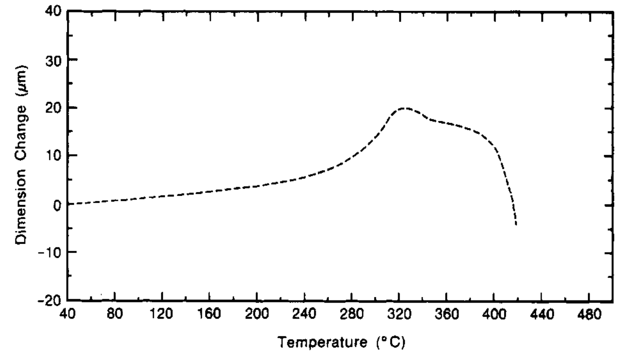

**Figure 9.** Thermomechanical analysis (penetration mode) of poly(HNA) ($\bar{M}_n \geq 30000$ g/mol), compression molded at 460 °C. Scan rate, 5 °C/min; loading, 5 g; initial sample thickness ($l_0$) = 276.8 μm.

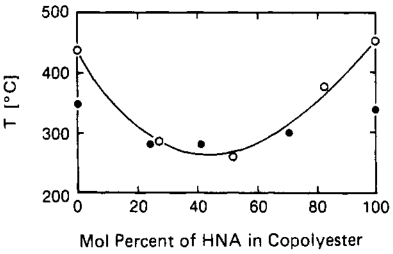

**Figure 10.** Composition versus $T_{c\rightarrow n}$ diagram of random copoly(HBA/HNA): (○) our data; (●) data given by Cao and Wunderlich.[2]

As part of this study, we also examined the high-temperature properties of the HNA oligomers with lower polymerization degrees (see Table I). The oligomers with $\bar{P}_n$ of 9.6 and 15 display DSC traces similar to those of the sample with $\bar{P}_n \gtrsim 180$ (see Figure 8), although the crystal–nematic transitions are somewhat lower. The transition at 338 °C for poly(HNA) appears to split into two peaks for the oligomers; one at 320 °C and the other at 360 °C. The presence of two peaks is not uncommon for DSC scans of as-prepared materials and may reflect the presence of different polymorphs of the same structure. On heating above the transition, the two peaks merge into one. Further characterization of this behavior is complicated by the fact that the oligomers continue to polymerize on thermal cycling, similar to the case of poly(HBA).[12,17]

When oligomers with $\bar{P}_n$ = 18.1 were heated above the 338 °C transition, one could induce flow with an applied shear to obtain a nematic-like texture (see Figure 7a). The same material heated to 460 °C and quenched without shear displayed a very coarse nematic texture (see Figure 7b). After 1 min at 460 °C, the texture changed dramatically to a very fine texture (Figure 7c) more typical of a higher molecular weight sample (see Figure 7d). Presumably the nematic texture observed at 350 °C with the sheared oligomer arises from a breakdown in the ester–ester dipole interactions between chains. This kind of behavior has been reported with the oligomers of HBA.[17]

Thermomechanical analysis of a compression-molded sample of poly(HNA) (see Figure 9) shows a rapid expansion beginning at ca. 280 °C and maximizing at ca. 320 °C; the probe easily penetrates the sample above 420 °C. Similar behavior has been observed in poly(HBA).[11,16] With the recent report of the poly(HBA) liquid-crystalline transition at 438 °C and now the poly(HNA) liquid-crystalline transition at 453 °C, one can define a composition versus $T_{c\rightarrow n}$ diagram for the HBA/HNA copolyester system (see Figure 10). This diagram is based on $T_{c\rightarrow n}$ transitions for the random copolyesters and corrects the transition temperatures for the homopolymers reported by Cao and Wunderlich[2] (these authors did not observe the higher transition temperature in either homopolymer and thus reported the value of the first transition in their diagram). One should recognize that a whole family of plots with higher $T_{c \to n}$ are possible for "blocky" or "alternating ordered" systems.

## Conclusions

Poly(HNA) has been characterized and shown to display crystal morphologies and thermal transitions almost identical with those reported for poly(HBA). This represents the second example of formation of single-crystal polymer morphologies starting with solution polycondensation. In analogy to poly(HBA), the first transition at 338 °C can be described as a plastic crystal or highly ordered smectic transition.[17,19] The argument in support of a highly ordered smectic structure requires a symmetry which permits retention of single-crystal morphology on cooling.[17] Since we have been unable to identify examples where any smectics (polymer or nonpolymeric) display this kind of behavior, we lean toward the concept of a one-dimensional plastic crystal where the naphthylene units have rotational freedom and the ester units, while having some motional freedom, still provide a three-dimensional framework.

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**Registry No.** 2 (homopolymer), 87257-28-1; 2 (SRU), 87257-45-2.

## References and Notes

(1) Chivers, R. A.; Blackwell, J. *Polymer* **1985**, *26*, 997.
(2) Cao, M. Y.; Wunderlich B. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 521.
(3) Blundell, D. J.; Buckingham, K. A. *Polymer* **1985**, *26*, 1623.
(4) Sawyer, L. C.; Jaffe, M. *J. Mater. Sci.* **1986**, *21*, 1897.
(5) Clements, J.; Humphreys, J.; Ward, I. M. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 2293.
(6) Takase, Y.; Mitchell, G. R.; Odajima, A. *Polym. Commun.* **1986**, *27*, 76.
(7) Kato, K.; Suzuki, S.; Inaba, N.; Murai, H. *Polym. J. (Tokyo)* **1987**, *19*, 815.
(8) Bechtoldt, H.; Wendorff, J. H.; Zimmermann, H. J. *Makromol. Chem.* **1987**, *188*, 651.
(9) Hanna, S.; Windle, A. H. *Polymer* **1988**, *29*, 207.
(10) Mühlebach, A.; Johnson, R. D.; Lyerla, J.; Economy, J. *Macromolecules* **1988**, *21*, 3115.
(11) Economy, J.; Storm, R. S.; Matkovich, V. I.; Cottis, S. G.; Nowak, B. E. *J. Polym. Sci. Polym. Chem. Ed.* **1976**, *14*, 2207.
(12) Kricheldorf, H. R.; Schwarz, G. *Makromol. Chem.* **1983**, *184*, 475.
(13) Geiss, R. H.; Street, G. B.; Volksen, W.; Economy, J. *IBM J. Res. Dev.* **1983**, *27*, 321.
(14) Lieser, G. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1611.
(15) Economy, J.; Volksen, W.; Geiss, R. H. *Mol. Cryst. Liq. Cryst.* **1984**, *105*, 289.
(16) Karis, T.; Siemens, R.; Volksen, W.; Economy, J. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 567.
(17) Economy, J.; Volksen, W.; Viney, C.; Geiss, R.; Siemens, R.; Karis, T. *Macromolecules* **1988**, *21*, 2777.
(18) Calundann, G. W., Celanese Corp., U.S. Patent 4,395,513, July 26, 1983.
(19) Economy, J.; Volksen, W. Structure and Properties of the Aromatic Polyesters of *p*-Hydroxybenzoic Acid. In *The Strength and Stiffness of Polymers*; Zachariades, A. E., Porter, R. S., Eds.; Marcel Dekker: New York, 1983; Chapter 7.
(20) Economy, J.; Lyerla, J.; Mühlebach, A., to be published. The kinetics of polycondensation are described in detail in this paper, and the reaction rates of the polycondensation reaction of the HBA and HNA homopolyesters are compared with that of the copolycondensation of HBA/HNA systems with different compositions.
(21) Viney, C.; Windle, A. H. *J. Mater. Sci.* **1982**, *17*, 1337.
(22) Geiss, R.; Economy, J.; Lyerla, J.; Mühlebach, A., manuscript in preparation.

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# Single-Chain Dimensions in Semidilute Ionomer Solutions: Small-Angle Neutron Scattering Study

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ABSTRACT: Small-angle neutron scattering has been used to measure individual chain dimensions in aggregates in ionomer solutions. Lightly sulfonated polystyrene was studied over a range of ionic substitutions and polymer concentrations in tetrahydrofuran. The molecular dimensions are compared with macroscopic solution viscosity measurements. Despite clear evidence in the viscosity data of interchain aggregation occurring at higher concentrations, the individual polymer chains preserve relatively constant dimension over the whole concentration range. In the free acid ionomer the interactions are not sufficiently strong to cause intermolecular aggregation and the individual chain dimensions are simply proportional to ionic content. These results clarify the role of interaction strength in associating polymer systems.

## Introduction

Associating polymer systems are known to assemble into aggregates at relatively low concentrations in appropriate solvents. When this assembly is driven by strong interactions between randomly located sites along the chain, as in the case of ionomer solutions, the resulting aggregate can be thought of as a microgel particle. Within such a particle, the polymer concentrations is locally semidilute and so the chain conformation must be governed by a balance between screening effects and strong site-specific interactions. It is therefore clearly of interest to determine the individual chain conformation within ionomer solutions over a range of compositions and concentrations.

Ionomers are a class of mainly linear hydrocarbon polymers containing up to 10 mol % salt groups which are usually randomly distributed along the chains. They have

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