Macromolecules 1991, *24,* 2829–2833

Synthesis and Properties of Needlelike Crystals (Whiskers) of Poly(6-hydroxy-2-naphthoic acid)

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Received June 29, 1990; Revised Manuscript Received November 19, 1990

ABSTRACT: Three samples of poly(6-oxy-2-naphthoate) were prepared under different reaction conditions, and long needlelike crystals (whiskers) were obtained in one case. The properties of all three samples were studied by means of WAXS measurements up to 470 °C, DSC measurements and optical microscopy up to 600 °C, IR spectroscopy, and thermogravimetric analyses. A reversible phase transition from an orthorhombic to a nearly pseudohexagonal chain packing occurs at 330–350 °C, and a second reversible transition associated with the change of rotational freedom of naphthalene rings occurs at 440–460 °C. Both phase transitions depend significantly on the reaction conditions used for the preparation of the sample. A melting process followed by side reactions, such as Fries rearrangement, was found at 540–550 °C. The formation of a nematic phase, postulated in the literature, could not be confirmed. The whiskers proved to be the chemically and physically most perfect form of all three poly(6-hydroxy-2-naphthoic acid) samples.

Introduction

6-Hydroxy-2-naphthoic acid plays an important role as the comonomer of meltable and processable thermotropic copolyesters of 4-hydroxybenzoic acid.[1,2] However, relatively few publications deal with the synthesis and properties of the corresponding homopolyester.[2–4] In a recent study of poly(6-oxy-2-naphthoate), Economy and co-worker presented DSC measurements showing two endotherms in the heating trace. The reversible transition at 338 °C was interpreted as change from an orthorhombic crystal modification to an one-dimensional plastic crystal. The second, likewise reversible transition at 450–455 °C was postulated to yield a nematic melt. Furthermore, the close analogy between the synthesis and properties of poly(hydroxynaphthoic acid) and poly(hydroxybenzoic acid) (poly(HNA) and poly(HBA)) was stressed.

In a previous paper, we have demonstrated that the phase transition and melting process of poly(HBA) single crystals (whiskers) significantly deviate from those described by Economy. This situation prompted us to attempt the synthesis of poly(HNA) single crystals and to investigate their properties.

Experimental Section

Materials. 2-Hydroxy-6-naphthoic acid was a gift of Hoechst AG. It was acetylated with an excess of acetic anhydride in refluxing toluene in the presence of a catalytic amount of pyridine. 6-Acetoxy-2-naphthoic acid was recrystallized from toluene/ligroin. The fraction used for the preparation of needlelike crystals was sublimed (after recrystallization). Marlotherm-S, a mixture of isomeric dibenzylbenzenes, was a gift of Hüls AG (Marl, FRG). It was used without purification, because it was found in experiments with 4-acetoxybenzoic acid that distillation (in vacuo) does not improve the results.

Polycondensations. (A) 6-Acetoxy-2-naphthoic acid (50 mmol) was dissolved in Marlotherm-S (120 mL) and heated rapidly under stirring to 350 °C. This temperature was maintained for 8 h, and the liberated acetic acid was removed with a slow stream of nitrogen. After cooling, the reaction mixture was diluted with acetone, and the precipitated polyester was isolated by filtration. The isolated polyester was extracted by refluxing acetone (1 h) and dried at 65 °C in vacuo. Yield 77%; DP > 200. Anal. Calcd for $C_{11}H_6O_2$ (170.17): C, 77.64; H, 3.55. Found: C, 77.38; H, 3.38.

(B) 2-Acetoxy-6-naphthoic acid (10 mmol) dissolved in Marlotherm-S (200 mL) was rapidly heated to 350 °C. This temperature was maintained for 8 h without stirring. Acetic acid was removed with a slow stream of nitrogen. After cooling, the precipitated material was worked up as described above. Yield 62%; DP ~ 160. Anal. Found for $C_{11}H_6O_2$: C, 77.46; H, 3.44.

A second condensation with a sublimed monomer sample was conducted analogously. The whiskers obtained in this way were 10–20% longer, but all other properties were identical.

(C) Trimethylsilyl 6-acetoxy-2-naphthoate (50 mmol) dissolved in Marlotherm-S (120 mL) was rapidly heated under stirring to 350 °C for 16 h. After cooling, the precipitated polyester was worked up as described for A. Yield 55%; DP ~ 100. Anal. Found for $C_{11}H_6O_2$: C, 77.15; H, 3.80.

Measurements. The DSC measurements were conducted with a Perkin-Elmer DSC-4 in aluminum pans at a heating (or cooling) rate of 20 °C/min. WAXS measurements were conducted with a Siemens D-500 powder diffractometer at room temperature using Ni-filtered Cu Kα radiation. WAXS measurements at variable temperature (heating rate = 20 °C/min) were conducted with synchrotron radiation ($\lambda = 1.50$) at HASYLABB (DESY, Hamburg).[5] The calibration of scattering angles differs by 0.15° in both methods.

IR spectra were measured on a Nicolet SXB-20 FT spectrometer by means of KBr pellets.

Thermogravimetric analyses were conducted with a Perkin-Elmer TGS-2 either at a heating rate of 10 °C/min in air or at a heating rate of 20 °C/min under nitrogen.

^{1}H NMR end group analyses were conducted in such a way that 20 mg of polyester was hydrolyzed in 5-mm-o.d. sample tubes with 4 N NaOH + CD_3OD (volume ratio 1:2). After hydrolysis, 100-MHz ^{1}H NMR spectra were recorded on a Bruker AC-100 FT spectrometer. 3-(Trimethylsilyl)deuteriopropionic acid served as the internal standard.

Results and Discussion

Syntheses. As demonstrated for 4-acetoxybenzoic acid,[6–9] the synthesis of high molecular weight poly(HBA) is best conducted in a high boiling inert reaction medium at temperatures ≥ 300 °C. The condensation of monomers in solution yields lamellar crystals of oligomers that precipitate from solution at DP's in the range of 5–7 depending on concentration and temperature.[8,10] The chain growth yielding higher molecular weights proceeds in the solid state, namely at the interface between oligomer lamellae staked on top of each other.[8–11] Crystalline aggregates of so-called slablike morphology are obtained in this way. The recent results of Economy and co-workers[4] suggest that the same sequence of chain growth and crystal growth processes is operating in the case of 6-acetoxy-2-naphthoic acid. However, it was also demonstrated in the

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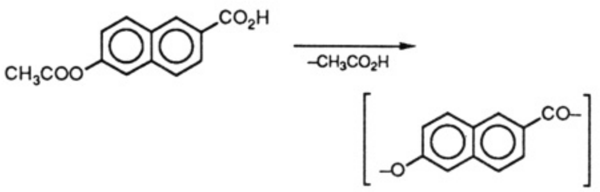
case of poly(HBA) that crystallites obtained in this way may be considerably disordered.[10] Furthermore, it will be demonstrated in a forthcoming paper[12] that the polycondensation of 4-acetoxybenzoic acid under standard conditions is accompanied by side reactions, and part of the byproducts (e.g., 3-acetyl-4-hydroxybenzoic acid) is bi- or trifunctional and, thus, incorporated into the polyester. In other words, poly(HBA) prepared under standard conditions is neither chemically pure not physically perfect. This aspect is of interest because it has been demonstrated that the thermostability of poly(HBA) depends on its chemical and physical perfection.[8] It has also been found that so-called whiskers, i.e., needlelike crystals, of poly(HBA) are chemically and physically more perfect than poly(HBA) prepared under standard conditions.[11-13]

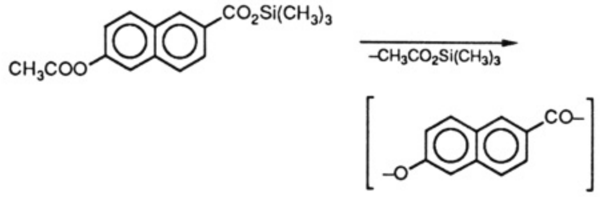
Due to this information on the synthesis and properties of poly(HBA), it seemed advisable to prepare poly(HNA) under two or three different reaction conditions and to attempt the synthesis of needlelike crystals (whiskers). Therefore, one condensation of 6-acetoxy-2-naphthoic acid (6,2-ANA) was conducted in a concentrated solution under stirring (eq 1), the reaction condition that was expected to yield slablike crystals[4] (procedure A). The poly(HNA) obtained in this way is denoted A.



(1)

A second condensation was conducted according to eq 1 in dilute solution without stirring (procedure B), and this polycondensation indeed yielded needlelike crystals as demonstrated by Figure 1A. When this synthesis was repeated with a monomer sample that was sublimed after recrystallization, whiskers were obtained that were 10–20% longer, whereas all other properties were identical (sample B). For two reasons, this result is not trivial. First, needlelike crystals of poly(HNA) have never been reported before. Second, attempts to prepare needlelike polyester crystals from other monomers, such as 3-acetoxybenzoic acid, 3-chloro-4-acetoxybenzoic acid, 3,5-dichloro-4-acetoxybenzoic acid, 3-methoxy- or 3,5-dimethoxy-4-acetoxybenzoic acid and 4′-acetoxybiphenyl-4-carboxylic acid, were not successful.

A third sample of poly(HNA), denoted C, was prepared by polycondensation of trimethylsilyl 6-acetoxy-2-naphthoate (eq 2, procedure C). This synthetic method has



(2)

the advantage that acidic protons that may cause side reactions are excluded. A detailed study on the polycondensation of silylated 4-acetoxybenzoic acid will be published separately.[12]

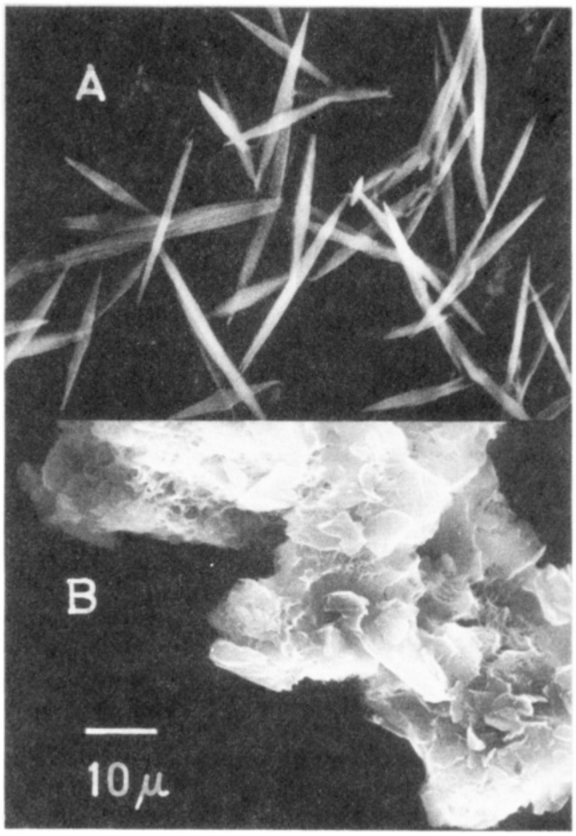


Figure 1. REM micrographs of poly(HNA): whiskers of (A) sample B, (B) sample C.

The results obtained by all three procedures were surprising for the following reasons. Procedure A yielded small whiskers instead of the expected slablike crystals. These whiskers were shorter by a factor of 20–40 than those obtained according to procedure B. In contrast, the morphology of poly(HNA) sample C resembles the slablike crystals of Economy[4] (Figure 1B) and not the whiskers of A and B. The fibrils reported by Economy were never observed. Furthermore, the DSC heating traces of all three products are different (see below).

Obviously, these different properties have nothing to do with low molecular weights. When average DP's were determined by ^{1}H NMR spectroscopic end group analyses of hydrolyzed samples, the following values were obtained: sample A, DP > 200; sample B, DP ~ 160; sample C, DP ~ 100. It was shown in the case of poly(HBA) that oligomers do not form whiskers.[13] Furthermore, the same temperature but longer reaction times were used than in ref 4.

DSC Measurements. DSC measurements of all three poly(HNA) samples were conducted at a heating rate of 20 °C/min up to 600 °C. These first heating traces revealed two remarkable aspects. In addition to the two endotherms around 320–330 °C (α-transition) and 440–460 °C (β-transition), a new and particularily strong endotherm was detected at 535–555 °C (Figure 2), which corresponds to the combined γ- and δ-transition of poly(HBA). This endotherm represents the final and irreversible melting process as evidenced by optical microscopy, IR spectroscopy, and WAXS measurements (see below).

Microscopic observation of individual whiskers under polarized light revealed that these crystals maintain sharp tips and edges up to a temperature in the range 540–550 °C. IR spectra of samples heated up to 500 °C are almost unchanged. However, short heating above 550 °C leads to a complete change of the chemical structure in analogy to poly(HBA)[14] (Figure 3). The "CO band" of the ester groups disappears almost completely, and a new CO band shows up at lower frequencies (1620 cm^{-1}). This band might originate from an aromatic ketone and the band at

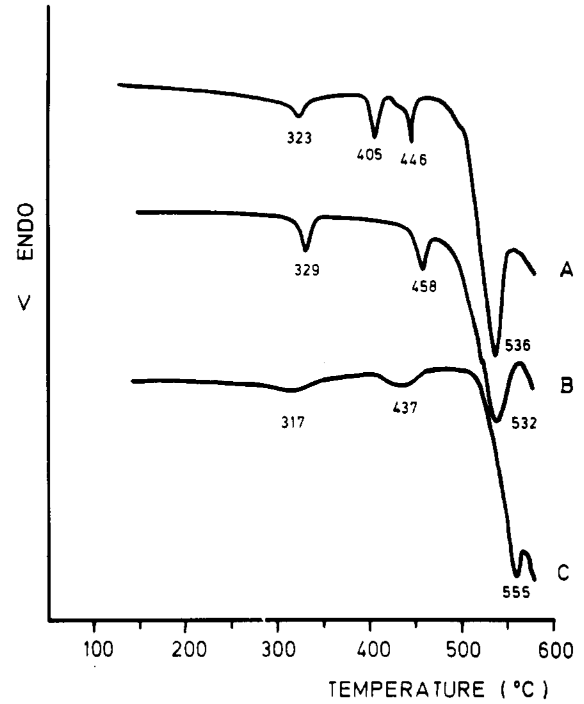


Figure 2. DSC measurements (first heating only) of poly(HNA) conducted at a heating rate of 20 °C: (A) sample A, (B) sample B, (C) sample C.

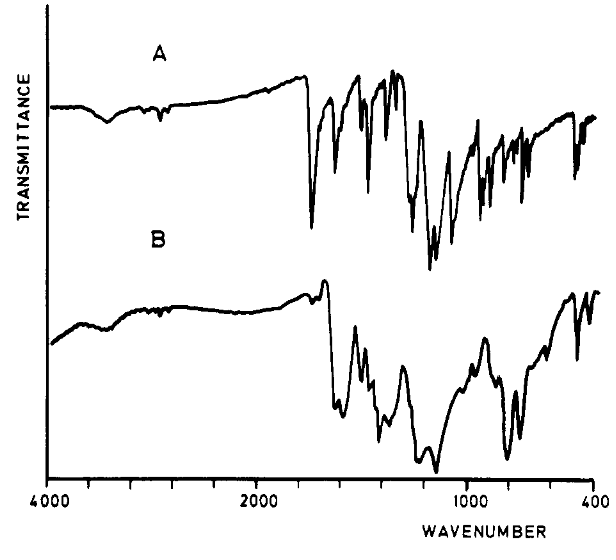


Figure 3. IR spectra of poly(HNA) measured from KBr pellets: (A) sample B, (B) polymeric residue obtained after heating (20 °C/min) to 580 °C under nitrogen.

1250 cm^{-1} from an aromatic ether group. In the case of poly(HBA), Fries rearrangement and formation of diphenyl ether groups is well documented.[6,14,15]

The second remarkable aspect of the DSC heating is the finding that all three samples differ considerably with regard to α- and β-transition (Figure 2). Not only are the temperatures different, but in the case of sample A, two endotherms show up at 405 and 446 °C. For the enthalpy change of both endotherms together, an average value of 4.75 kJ/mol (6.67 cal/g) was obtained from three measurements. This value fits in with an average value of 4.85 kJ/mol (6.82 cal/g) found for sample B and 4.40 kJ/mol (6.20 cal/g) for sample C. Thus, it is obvious that both endotherms together represent the β-transition, but an explanation for this splitting cannot be offered.

Furthermore, the different enthalpy changes of the α-transition are worth mentioning. An average value of 7.25 kJ/mol (10.15 cal/g) was found for sample B, but only values of 2.35 kJ/mol (3.30 cal/g) for A and 3.15 kJ/mol (4.42 cal/g) for C were found. Obviously the enthalpy change of the α-transition extends over a broader temperature range (Figure 2) and is more difficult to quantify than in the case of sample B. From these results and from the WAXS patterns discussed below, it may be concluded that the whiskers of B represent the highest state of three-dimensional order. Obviously, samples A and C contain a considerable degree of conformational and positional disorder, which due to the "crankshaft structure" of the 2,6-disubstituted naphthalene rings is more likely for poly(HNA) than for poly(HBA). A lower degree of order entails a greater free volume, and thus, the unfreezing of flip–flop motions that seem to be typical for the α-transition[14,16] may extend over a broader temperature range.

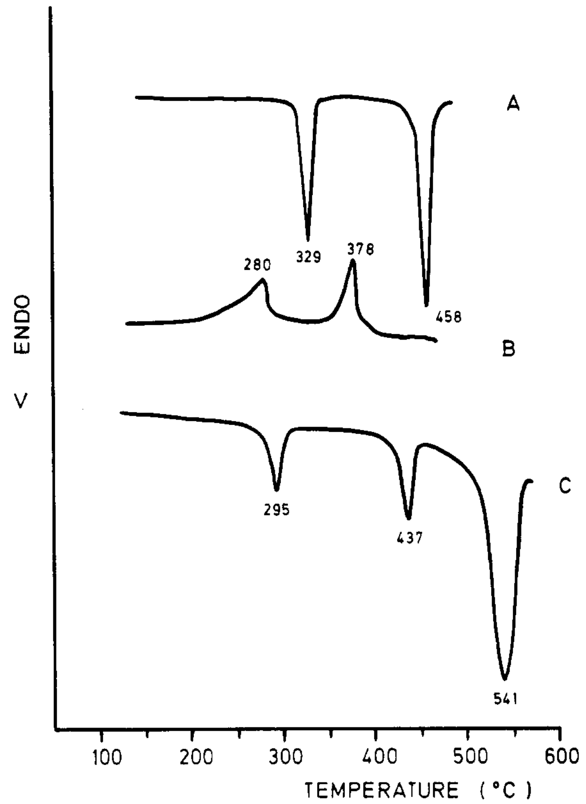


Figure 4. DSC measurements of poly(HNA) whiskers of B conducted at a heating and cooling rate of 20 °C/min: (A) first heating, (B) first cooling, (C) third heating following a second heating stopped at 480 °C.

Finally, it is worth mentioning that several heating/cooling cycles could be conducted up to temperatures of ca. 400 °C, without significant alteration of temperature and enthalpy change of the α-transition. However, repeated heating above the β-transition (up to 480 °C) led to remarkable changes of the positions of all endotherms, possibly due to gradual thermal degradation (Figure 4).

WAXS Powder Patterns. WAXS powder patterns of all three samples measured at room temperature display reflections that were identical with regard to number, scattering angle, and intensity ratio (Figure 5). However, all reflections of samples A and C were 30–50% broader than those of sample B. This observation indicates that the crystallites of sample B possess a higher degree of three-dimensional order, a result that agrees well with the above interpretation of the DSC measurements. Obviously the crystal growth in concentrated monomer solutions is so rapid that it entails a lower degree of conformational and positional order ("condis"/"posdis" crystals[17]).

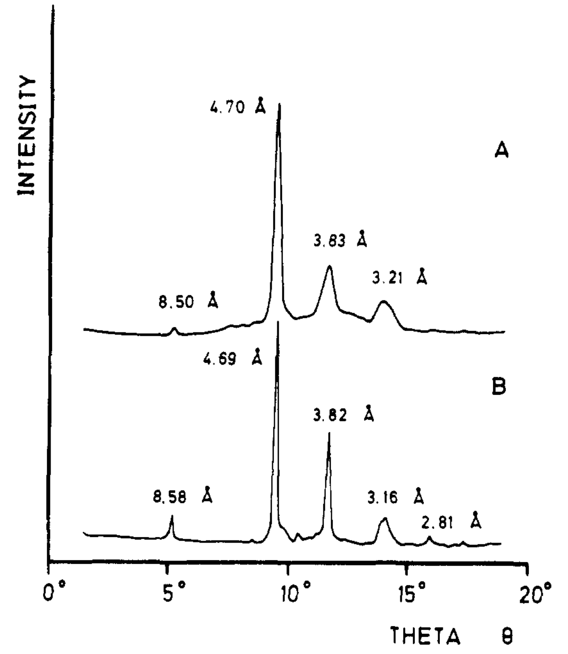


Figure 5. WAXS powder patterns of poly(HNA) measured at 20 °C: (A) sample A, (B) sample B.

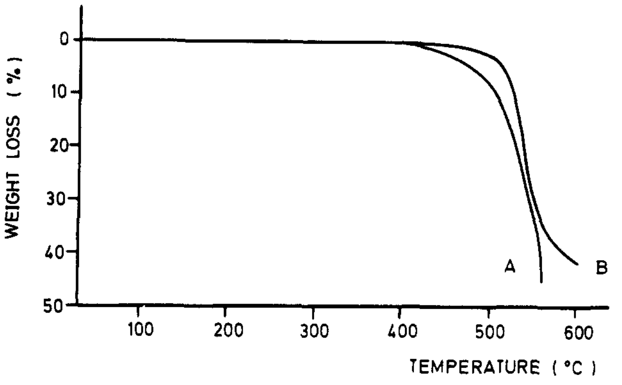


Figure 6. Thermogravimetric analyses conducted with a heating rate of 10 °C/min in air: (A) sample A, (B) sample B.

Interestingly, samples A and B (C was not measured) are also different with regard to their thermal stability (Figure 6). Since DSC, optical microscopy, and WAXS patterns agree in a way that an ordered super molecular structure exists up to the melting process around 550 °C, the access of oxygen and intramolecular degradation processes may depend on the extent of chemical and physical perfection of the crystallites. Another interesting result of these thermogravimetric analyses is the finding that measurements of B whiskers conducted with a heating rate > 10 °C/min will not be seriously affected by thermal degradation up to ca. 500 °C. This result is worth noting in connection with WAXS measurements conducted at a heating rate of 20 °C/min.

These measurements were conducted with synchrotron radiation ($\lambda = 1.50$ Å) up to 470 °C. For technical reasons, a higher temperature could not reached, but these measurements sufficed to monitor both α- and β-transition (Figure 7). The α-transition is characterized by the disappearance of the 3.8-Å reflection ($\vartheta = 11.6°$ at 25 °C), whereas a new reflection appears at $\vartheta = 12.8$. This reflection indicates that the chain packing above 350 °C is still orthorhombic, but close to hexagonal. This reflection and the strong reflection at 4.7 Å ($\vartheta = 9.45°$ at 25 °C) disappear at the β-transition, whereas the weak reflection at $\vartheta = 5.10°$ (at 25 °C) (8.75 Å) remains unchanged. This reflection corresponds to the length of a monomer unit (001 reflection) and suggests that the poly(HNA) chains maintain an extended conformation up to the final melting process. This 001 reflection decreases from 8.75 to 8.60 Å between 20 and 440 °C and drops down to 8.45 Å at the β-transition. These slight changes fit in with the postulated increase of rotational motions. A similar situation was found for poly(HBA).[14]

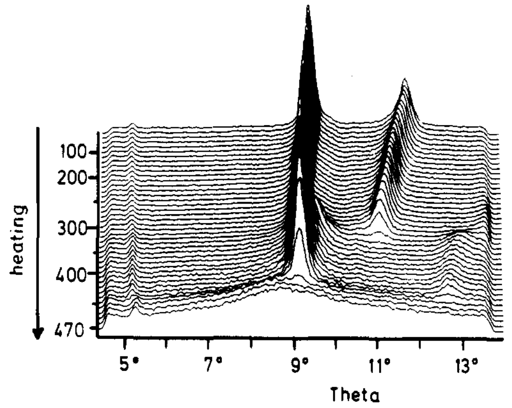
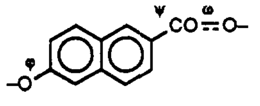


Figure 7. WAXS measurements of poly(HNA) needlelike crystals of sample B conducted with synchrotron radiation at a heating rate of 20 °C/min.

The disappearance of all but the 8.5-Å reflection at the β-transition may be interpreted as formation of a rotatory phase. Due to the crankshaft structure of HNA units, rotation about φ and ψ (formula a) may entail rotation of their center of gravity. Hence, an uncoordinated rotation of neighboring monomer units will bring about a complete loss of order in the *a*/*b* plane (the chain axis is denoted *c*). The shift of all reflections to lower scattering angles (with exception of $\vartheta = 5.2°$, Figure 7) demonstrates that increasing temperature entails the lateral expansion required for a higher freedom of rotation. In the case of poly(HBA), rotation of the benzene rings around φ and ψ (formula b) does not affect the center of gravity of the benzene rings. Hence, the 4.7-Å reflection representing the lateral distance in the hexagonal chain packing does not vanish, when the rotatory phase is formed at the β-transition[14] (Figure 8). Assumption of a rotatory phase above the β-transition not only gives a consistent interpretation of the WAXS patterns of both poly(HNA) and poly(HBA), but it also agrees with the DSC measurements of both polyesters. For the unfreezing of free rotations of naphthalene rings, a greater enthalpy (and entropy) change is expected than for the rotation of phenylene rings (around the para axis), and such a significant difference of the enthalpy changes was indeed found (4.9 ± 0.2 versus 0.35 ± 0.2 kJ/mol). In this case, it should be mentioned that a similar kind of rotatory phase characterized by a rotation of phenylene rings around the para axis has been reported for poly(*p*-xylylene)s.[18,19]



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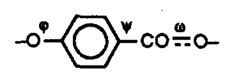

b

Conclusion

Under suitable reaction conditions, needlelike crystals (whiskers) may be prepared from 6-acetoxy-2-naphthoic acid, which represent a chemically and physically rather perfect form of poly(HNA). These whiskers are particularly useful for studying the thermal properties of poly-

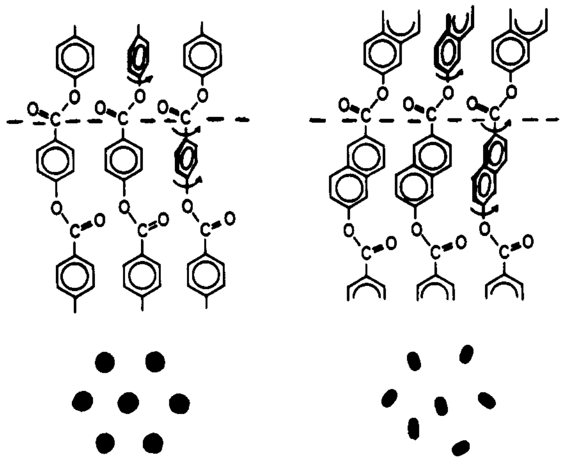

Figure 8. Scheme of the rotatory phase in the case of poly(HBA) and poly(HNA).

(HNA). All measurements demonstrate a close similarity between poly(HBA) and poly(HNA). The only conspicuous difference concerns the molecular order in the hypothetical rotatory phase above the β-transition (>440 °C). In the case of poly(HNA), it is likely that free rotation of naphthalene rings requires rotation of their centers of gravity, in contrast to para-substituted phenylene rings. If we look at the molecular order for a picosecond, the rotatory phase of poly(HNA) resembles a smectic A phase and that of poly(HBA) a smectic B phase. In neither case could the postulated nematic melt be found. However, it is conceivable that strong shear forces interrupt the layer structure of the rotatory phase (Figure 8), yielding a columnar mesophase with a texture similar to that of a nematic phase. In the absence of shear forces, a layered, more or less hexagonal chain packing is maintained up to temperatures around 540 °C, where rotation around the ω-bond of ester groups initiates a complete breakdown of any molecular order. This sudden increase of segmental mobility then entails rapid degradation and rearrangement processes, so that a stable, mobile melt is never observed.

Acknowledgment. We thank Dr. S. Buchner for the synchrotron WAXS measurements, Dipl.-Chem. C. Teasler (Tech. Universitat Harburg, FRG) for the SEM micrographs, and Prof. Dr. H. Cherdron (HOECHST, AG) for a gift of 6-hydroxynaphthalene-2-carboxylic acid.

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Registry No. 2,6-ANA (homopolymer), 87257-28-1; 2,6-ANA (SRU), 87257-45-2; 2,6-HNA, 16712-64-4; 2,6-ANA, 17295-26-0; trimethylsilyl 6-acetoxy-2-naphthoate (homopolymer), 133165-79-4.