Polymorphism in a Liquid Crystalline Polyester Based on 4,4′-Biphenol, Terephthalic Acid, and *p*-Hydroxybenzoic Acid (1:1:2)

N. D. Field,* R. Baldwin, R. Layton, P. Frayer, and F. Scardiglia

Dartco Manufacturing Inc, P.O. Box 5867, Augusta, Georgia 30906.

Received October 9, 1988

ABSTRACT: The polyester from 1 mol of 4,4′-biphenol, 1 mol of terephthalic acid, and 2 mol of *p*-hydroxybenzoic acid, synthesized by the acidolysis condensation reaction of the acetylated mixture, was studied by using wide-angle X-ray diffraction and differential scanning calorimetry (DSC). X-ray diffraction demonstrated a reversible crystal–crystal transition at about 100 °C. The transition was also observed with DSC as a small endotherm. The most prominent calorimetric feature is an endotherm at about 427 °C corresponding to the crystal–nematic transition. There is also a small endotherm at about 472 °C which may correspond to the nematic–isotropic transition. On cooling from 450 °C at 10 deg/min, there is observed about 40 deg of supercooling before crystallization occurs. Further cooling proceeds through the crystal–crystal transition. Rapid cooling from the melt produces a quenched solid which does not demonstrate the crystal–crystal transition. Annealing at elevated temperatures converts this metastable form to one which does demonstrate the reversible crystal–crystal transition.

Introduction

Thermotropic liquid crystalline polymers are of considerable interest, not only from a theoretical but also from a commercial point of view. Of special interest are completely aromatic polyesters wherein the connecting linkages are all para. These have high melting points, exhibit liquid crystalline properties in the melt, and demonstrate very high moduli in fabricated form. This paper will deal with the polymer from 4,4′-biphenol (BP), terephthalic acid (TA), and *p*-hydroxybenzoic acid (PHBA) in the molar ratio 1:1:2.

Earlier papers described a 1:1:2 polymer made by heating the acetates of BP and PHBA with TA in an inert, high-boiling liquid.[1-3] The molecular weight of the polymer was increased by further heating under vacuum at 320–340 °C, accompanied by raising of the melting point. The polymer was reported as having a melting point of around 430 °C, as measured by differential scanning calorimetry (DSC), with an endotherm of about 17 J/g. Low molecular weight polymer readily crystallized from the melt. High molecular weight polymer, on the other hand, did not show an exotherm on cooling from the melt at a rate of 10 deg/min, i.e., no tendency to crystallize. Polymer, quenched from the melt after shearing, exhibited high birefringence. No evidence for any other transition was presented. Solution properties could not be measured for lack of a solvent.

Wide-angle X-ray measurements disclosed reflections at 4.5 (vs), at 3.9 (s), and at 4.2 Å (w). The 4.5 spacing was attributed to the distance between chains. The supercooled form also displayed a peak at 4.5 Å but of appreciably less intensity and subtantially broadened. Measurements, utilizing ^{13}C NMR, located the PHBA-derived mers in two regions, one more ordered than the other. This was interpreted as demonstrating that the polymer sequence distribution was of a blocky nature.

Experimental Section

The 1:1:2 polyester was prepared by methods reported in the literature.[4-6] To summarize, 1 mol of BP, 1 mol of TA, 2 mol of PHBA, and excess acetic anhydride were refluxed to assure acetylation, in situ, of the phenolic hydroxyl groups. The slurry temperature was gradually raised with simultaneous distillation to remove the acetic acid formed in the acetylation reaction as well as that formed in the acidolysis polymerization reaction.

Melt polymerization was continued until an oligomer of 2000–3000 number-average molecular weight was formed. The melt was then cooled to a solid which was ground to a powder. Polymerization, in the solid state, was then continued under a nitrogen sweep until high molecular weight was attained as indicated by DSC. The number-average molecular weight of the polymer of this study is estimated from end group analysis to be about 25 000.

Diffractometer data were recorded in the reflection mode by using a Philips PN 3550 diffractometer equipped with a Paar HKT high-temperature attachment and a Philips XRG-3000 X-ray generator. A nitrogen atmosphere was used. A copper X-ray tube was used at 40 kV and 30 mA, and the Kα line was isolated by a curved graphite monochromator. Diffractometer angle, sample temperature, and data acquisition were programmed by means of an IBM PC-XT equipped with a Keithley System 570 data acquisition workstation and a centroid motion controller. All software was written in-house for this application. Wide-angle X-ray diffraction photographs were obtained with a flat film camera using Kodak Direct Exposure Film on the Philips XRG-3000 X-ray generator.

DSC determinations were made utilizing a Du Pont 1090 instrument.

Results

DSC Determinations. In order to minimize the effect of the previous thermal history, as-synthesized polymer was heated in the DSC apparatus to 450 °C at 20 deg/min, under nitrogen, followed by cooling at 10 deg/min. The specimen was then subjected to a second heating/cooling cycle and the data were plotted. Results are shown in Figure 1. The most prominent features of the heating scan are the small endotherm at around 100 °C with an enthalpy change of around 2 J/g and the appreciably larger one at 427 °C with an enthalpy change of about 10.5 J/g. Cooling from 450 °C, at 10 deg/minute, resulted in supercooling of about 40 deg, the exotherm starting at about 384 °C. Cooling at a controlled rate below the indicated temperature cutoff was difficult in our apparatus, but, nevertheless, it was apparent from other data that the lower temperature transition on cooling resulted in a small exotherm. Figure 2 shows the result of heating to 530 °C. A small endotherm, with an enthalpy change of about 1.5 J/g, appears at about 472 °C, indicating a third transition. This is followed by extensive decomposition.

Wide-Angle X-ray Diffraction. Flat plate powder diagrams (Figure 3), on the as-synthesized material, re-

---

* To whom correspondence should be addressed at Elkins Park Polymer Associates, 373 Linden Drive, Elkins Park, PA 19117.

0024-9297/88/2221-2155$01.50/0

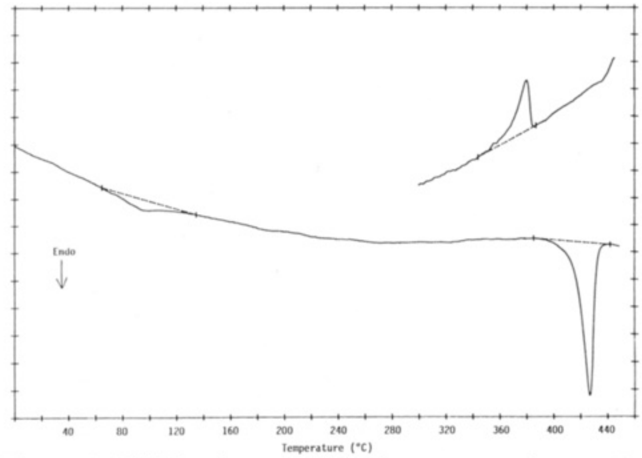

Figure 1. DSC heating trace in a nitrogen atmosphere at 20 deg/min (lower curve) and cooling trace in nitrogen at 10 deg/min (upper curve) for the BP/TPA/PHBA copolyester in the molar ratio 1:1:2 after preheating the as-synthesized polymer to 450 °C at 20 deg/min and then cooling at 10 deg/min in nitrogen.

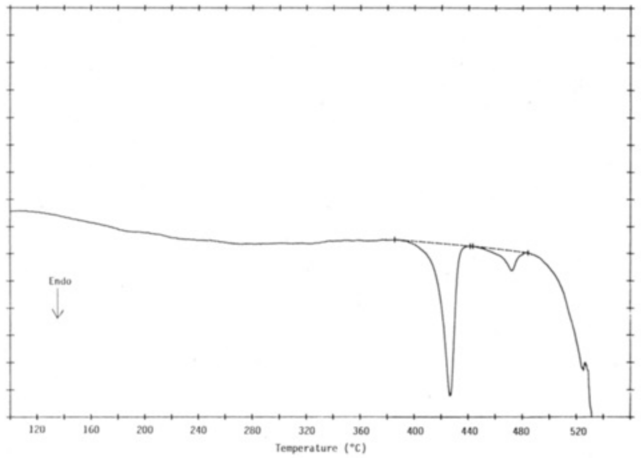

Figure 2. DSC heating trace only to 530 °C at 20 deg/min in nitrogen.

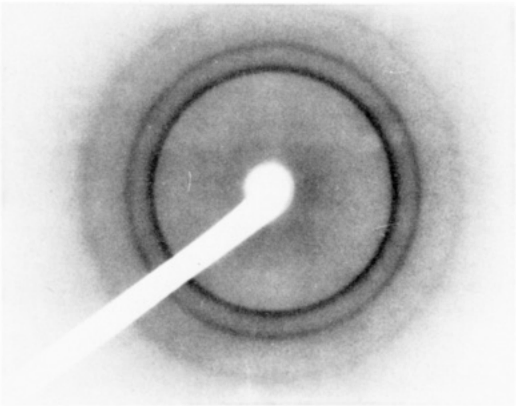

Figure 3. Flat plate powder X-ray diffraction diagram for the as-synthesized polymer.

vealed an appreciably crystalline pattern with several sharp rings. The three most prominent rings were at approximately 4.5, 3.9, and 3.1 Å. When the X-ray picture was taken at 150 °C, it appeared that the "3.9" ring had disappeared. The ring reappeared on cooling to room temperature. At higher temperatures than 150 °C, the "3.1" ring appeared to be gradually vanishing, especially at over 250 °C.

As long as the temperatures of the flat plate X-ray experiments were below that of the large endotherm, cooling back to room temperature resulted in X-ray diffraction patterns that appeared to be the same as the starting one. If, however, the sample temperature was raised to 450 °C and quenched abruptly to room temperature, the resulting picture revealed the absence of the "3.9" spacing and the prominence of a ring with a slightly smaller d-spacing than the original "4.5" one. When the sample was held at 400 °C, the original pattern was recovered on cooling to room temperature.

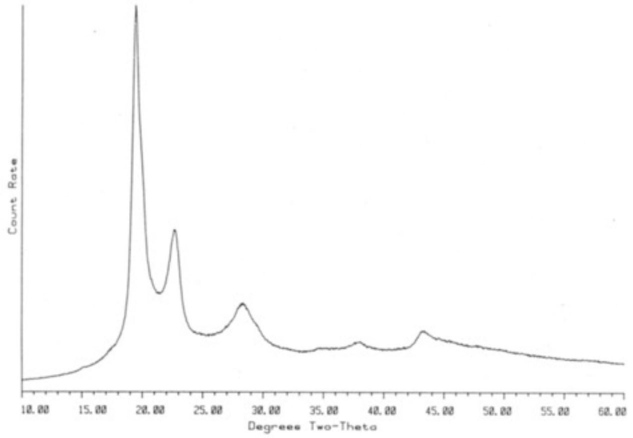

Figure 4. Diffractometer scan of intensity versus 2θ for the as-synthesized polymer.

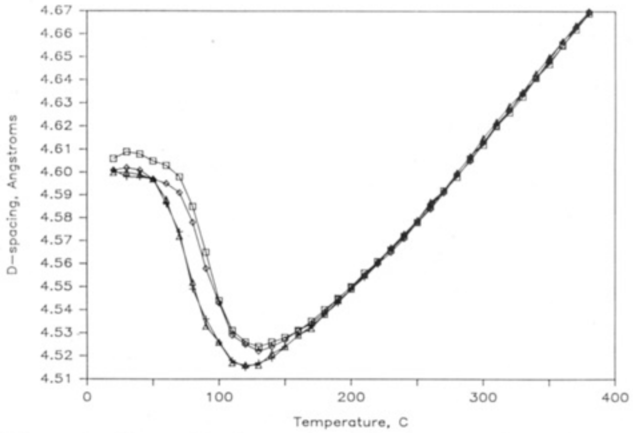

Figure 5. Change in the powder diffractometer d-spacing for the 4.5 Å peak during two successive heating and cooling cycles between room temperature and 380 °C: (□) first heating cycle; (+) first cooling cycle; (◇) second heating cycle; (△) second cooling cycle.

More precise data were obtained by using goniometer plotting methods. Figure 4 is a plot of intensity versus 2θ for the starting as-synthesized polymer. Peaks are seen to be present at 4.61 (vs), 3.94 (m), 3.17 (w), 2.4 (vvw), and 2.1 Å (vw). Data were also collected via X-ray scanning at 10-deg temperature intervals during heating from room temperature to 380 °C and on cooling back to ambient. The time for each scan was approximately 21 min. Figure 5 is a plot of the d-spacing of the "4.5" peak through two successive heating/cooling runs starting with as-synthesized polymer. Figure 6 is a plot of the "4.5" intensities for these runs. Figures 7 and 8 are the same plots for the "3.9" peak. Figure 9 is composed of plots of intensities at temperatures in the vicinity of the melting point versus 2θ. Figure 10 shows the comparable room temperature plots on quenching from each of the above temperatures.

An isometric view of the topography of a three-dimensional plot of 2θ, intensity, and temperature was simulated by slightly displacing each incremental (10 deg) temperature scan. Figure 11 is such a plot for heating a previously

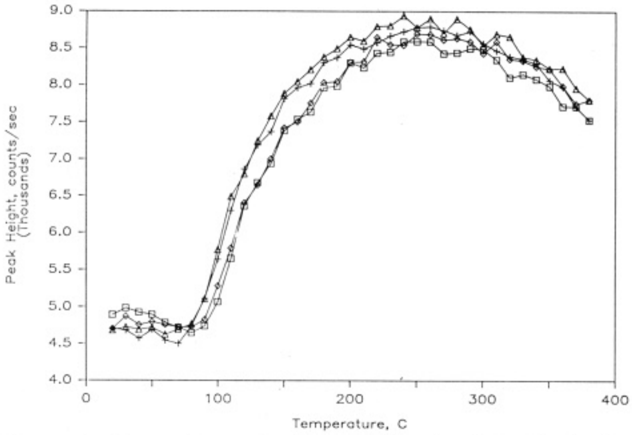

Figure 6. Change in powder X-ray diffraction intensity for the 4.5 Å peak during two successive heating and cooling cycles between room temperature and 380 °C: (□) first heating cycle; (+) first cooling cycle; (◇) second heating cycle; (△) second cooling cycle.

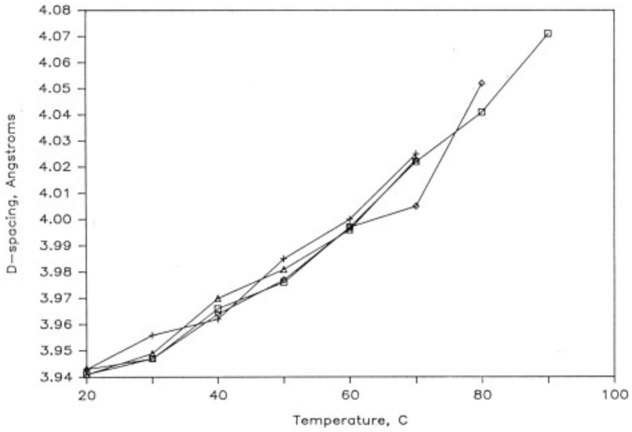

Figure 7. Change in the d-spacing for the 3.9 Å peak during two successive heating and cooling cycles: (□) first heating cycle; (+) first cooling cycle; (◇) second heating cycle; (△) second cooling cycle.

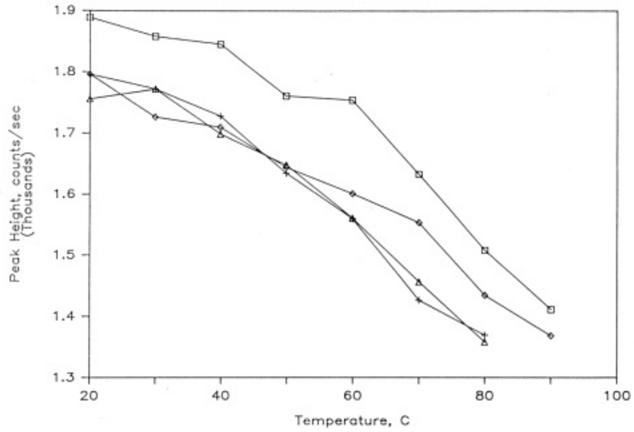

Figure 8. Change in intensity for the 3.9 Å peak during two successive heating and cooling cycles: (□) first heating cycle; (+) first cooling cycle; (◇) second heating cycle; (△) second cooling cycle.

heated sample from room temperature to 380 °C. The two peaks at 2θ of about 39.4 and 46 deg are due to the platinum support. Another sample of polymer was heated above its melting point, to 450 °C, and quenched rapidly to room temperature. Figure 12 portrays the heating of this sample to 380 °C. This was followed by cooling to room temperature. Figure 13 portrays the cooling data. Figure 14 is a plot of the “4.5” d-spacing versus temperature and Figure 15 is a plot of the intensity versus temperature corresponding to the heating/cooling regimen just described.

Figure 16 is a portrayal of the fiber diagrams, at room temperature and at 150 °C, of a highly oriented sample obtained by injection molding.

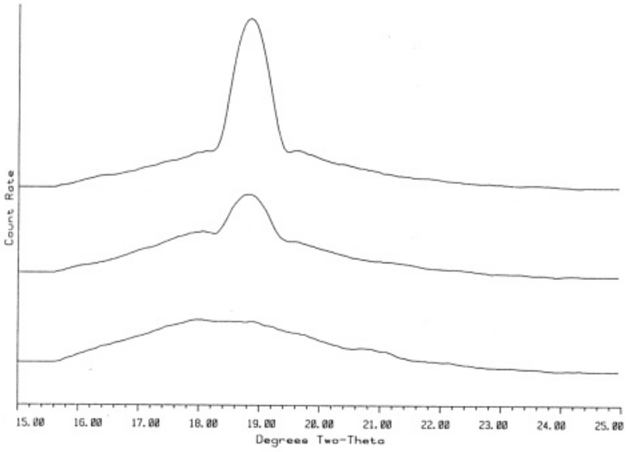

Figure 9. X-ray diffractometer scans of intensity versus 2θ in the vicinity of the melting point: upper curve run at 420 °C, middle curve run at 440 °C, and lower curve run at 460 °C.

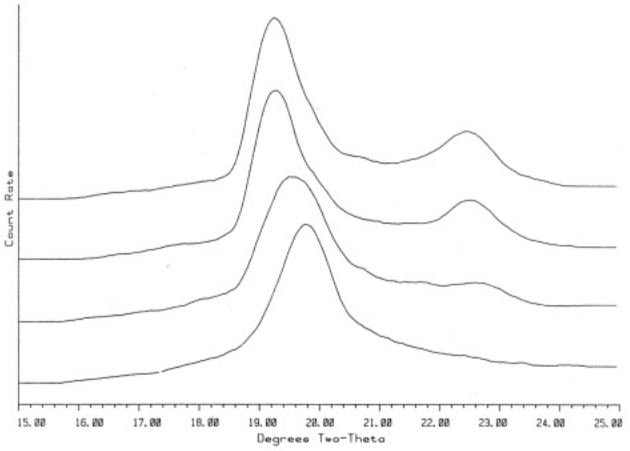

Figure 10. X-ray diffractometer scans of intensity versus 2θ run at room temperature after exposure to elevated temperature: uppermost curve with no heat history, upper middle curve after heating to 420 °C and quenching to room temperature, lower middle curve after heating to 440 °C and quenching to room temperature, and lowest curve after heating to 460 °C and quenching to room temperature.

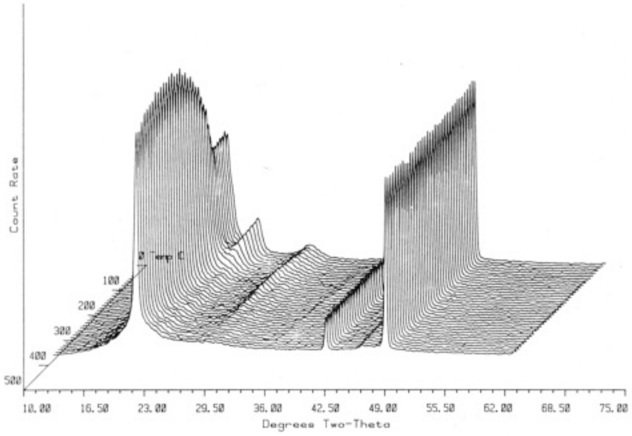

Figure 11. Three-dimensional, isometric view of diffractometer scans versus temperature for the heating of a sample previously heated to 380 °C.

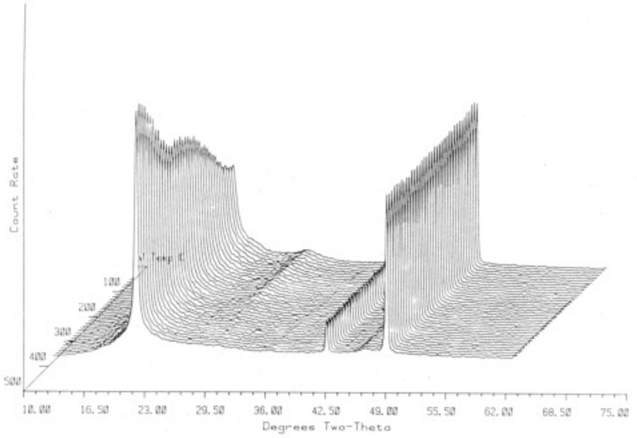

Figure 12. Three-dimensional, isometric view of diffractometer scans versus temperature for the heating of a sample previously heated to 450 °C and quenched rapidly to room temperature.

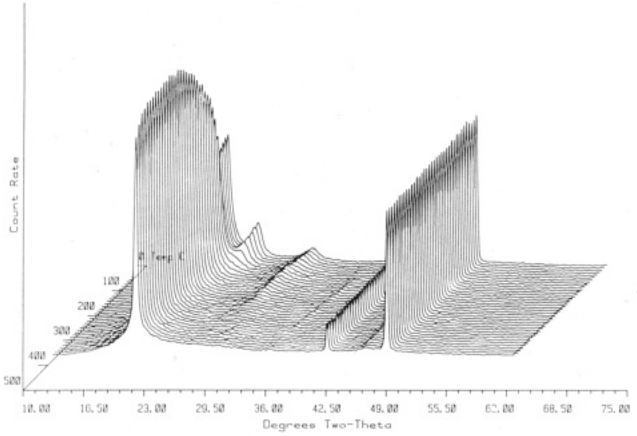

Figure 13. Three-dimensional, isometric view of diffractometer scans versus temperature for the cooling of the sample of Figure 12.

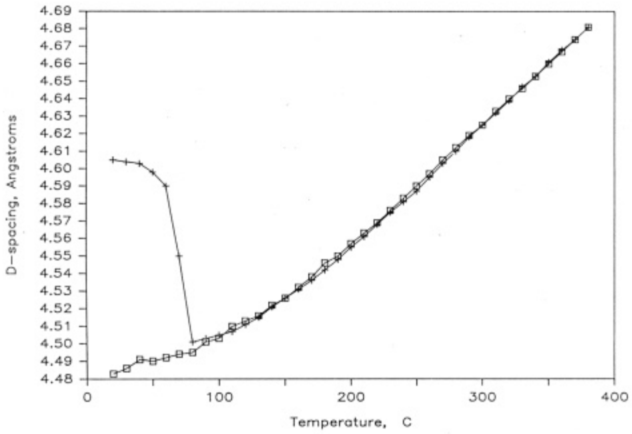

Figure 14. Plot of the 4.5 Å peak d-spacing versus temperature for a sample previously heated from room temperature to 450 °C and quenched to room temperature: (□) heating to 380 °C; (+) cooling to room temperature.

Discussion

Transitions Observed with DSC. The polyester of this study appears to be different in a number of features from the one reported earlier.[1-3] The latter showed little tendency to crystallize while the present polymer readily crystallizes albeit with supercooling of about 40 deg when cooled at a rate of 10 deg/min (Figure 1). In addition, the present polymer demonstrates a small endotherm at around 100 °C (Figure 1) and a small endotherm at 472 °C (Figure 2), neither of which were reported earlier.

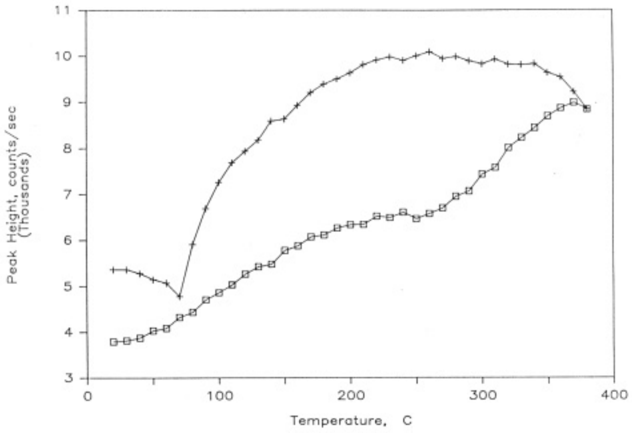

Figure 15. Plot of the 4.5 Å peak intensity versus temperature for the same sample as in Figure 14: (□) heating to 380 °C; (+) cooling to room temperature.

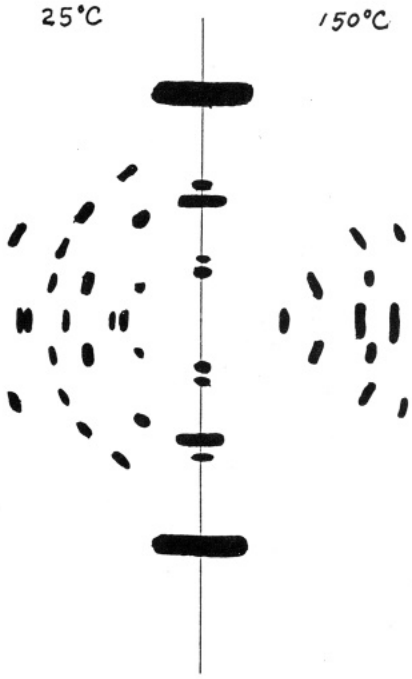

Figure 16. Schematic representation of the flat plate X-ray diffraction fiber diagrams at room temperature and at 150 °C for a highly oriented sample taken from the core of an injection-molded plaque.

The earlier investigators reported an endotherm at 430 °C with a value of about 17 J/g while the present value is 10.5 J/g. It should be noted, however, that the 10.5 J/g value is determined on the second DSC pass. The first DSC pass does show an endotherm comparable to the earlier reported value which reflects the thermal history of the polymerization. Because of the relatively long period of time required at elevated temperatures during polymerization in the solid state, crystal perfection is enhanced. On the other hand, the opportunities for ester–ester interchange scrambling, which would decrease any tendency to crystallize, are enhanced in the melt. Hence, on melting, cooling, and recrystallization and then upon reheating, the endotherm would be expected to be smaller.

The earlier polymer was reported as being liquid crystalline in the melt on the basis of birefrigence observed in a sheared, quenched sample. In the present authors' hands, optical measurements in the melt proved difficult because of potential damage to the microscope optics at the high temperatures required. However, when low melting point "prepolymer" (low molecular weight) was melted between cover slips and allowed to polymerize to higher molecular weight in the melt on a hot bar, the quenched sample demonstrated a multiplicity of colors when observed by using a microscope equipped with cross polars. The above, together with the X-ray observations and a consideration of the very rigid linear structure expected from an all-para aromatic polyester, plus the observations on model compounds,[7] confirm the assignment of a crystal–nematic transition (C to N) to the endotherm observed at 427 °C (Figure 1). The small peak observed at about 472 °C (Figure 2) is reproducible and probably corresponds to the nematic–isotropic transition (N to I). Other observers of liquid crystallinity in pertinent model compounds[7] and in all-para aromatic backbone polyesters have reported comparable temperature differentials between the crystal–nematic melting point and the nematic–isotropic melting point.[7,8]

Wide-Angle X-ray–Temperature Studies. Wide-angle X-ray at room temperature (Figures 3 and 4) generally confirms the earlier reported observations.[1-3] To gain insight, however, into the observed DSC behavior, an X-ray–temperature study was conducted.

Figures 5 and 6 portray the effect of temperature on the highest intensity ("4.5") Å reflection for successive heating/cooling cycles between room temperature and 380 °C, starting with as-synthesized polymer. The difference between the first and the second heating behavior reflects the polymerization thermal history. The remaining curves are very reproducible. Some hysteresis is evident between heating and cooling at the low-temperature ends.

It is clear that a crystal–crystal transition occurs at about 100 °C, consistent with the DSC behavior. On heating through the transition, a decrease of about 0.1 Å occurs, followed at higher temperatures by a uniform expansion. The reverse occurs on cooling. At the same time, the intensity of the reflection begins to increase rapidly, becoming maximum at about 250 °C. The "3.9" Å reflection parallels the "4.5" behavior except that the crystal–crystal transition is manifested in the disappearance of the former on heating above the transition temperature and its reappearance on cooling (Figures 7 and 8). The crystal form below the transition temperature, with d-spacings of 4.61 and 3.94 Å, and the form above the transition temperature, with d-spacing of ~4.5 Å (and larger) and no ~3.9 Å spacing, will be referred to, respectively, as the A and B forms. Figure 11 is a more dramatic portrayal of the transition.

Quenching and Annealing. From Figures 9 and 10, it appears that the solid phase present before melting as well as during the melting process, on rapid quenching, is unchanged. It cools down in the B form until the crystal–crystal transition temperature is reached hereupon it transforms into A. On the other hand, the liquid portion of the melt, on quenching, becomes a metastable crystalline form, B_q, which demonstrates a room temperature d-spacing of 4.47 Å. Moreover, B_q does not manifest a crystal–crystal transition on heating either by X-ray or DSC. Thus, polymer which is completely melted, on quenching, reflects only at 4.47 Å, while polymer which is at a temperature below the onset of melting, on quenching, reflects only at 4.61 and 3.94 Å at room temperature. Polymer in the midst of melting, on quenching, demonstrates a combination of these reflections.

When quenched melted polymer is heated, it is apparent from Figures 12–15 that the B_q form converts to the B form at temperatures beginning at about 260 °C with the process becoming rapid at above 350 °C. This is evidenced by the increase in the intensity of the "4.5" reflection on heating above 260 °C, by the huge hysteresis effects on heating to 380 °C and subsequent cooling, and by the dramatic B to A transition. These effects are not seen when the experiment is limited to heating and cooling from 260 °C. The intensity curves on heating and cooling are essentially the same, with no evidence of the B to A transition in the d-spacing versus temperature curve. Of considerable importance is the observation that above the crystal–crystal transition temperature, the "4.5" spacing and its coefficient of linear expansion (slope) are identical for the B and B_q forms (Figure 14). This suggests that B_q is a somewhat disordered B form (hence the symbol B_q rather than Q).

Interestingly, starting polymer demonstrates a shoulder at ~4.5 Å below the 100 °C transition and a displaced "ridge" above (Figure 11). When the polymer was melted, quenched, and annealed, the room temperature shoulder and the high-temperature "ridge" disappeared. Apparently, the as-synthesized polymer is largely in the A form with some "frozen-in" structure present, perhaps of the B_q type. The B_q may be related to quenching of the melt prior to the solid-state polymerization. The latter may also have introduced some blocky character which scrambles on melting.

Oriented A and B Forms. It has been observed that injection molding can lead to sections of core demonstrating highly oriented "annealed" structures, as observed by wide-angle X-ray.[9] At room temperature, the form present appears to be the highly oriented A. The skin, on the other hand, appears to be a very oriented "quenched" form. The core structure undergoes a reversible crystal–crystal transition at about 100 °C to the highly oriented B form. Figure 16 diagramatically portrays the flat plate pictures taken at room temperature and at 150 °C. The X-ray pictures are clearly those of highly crystalline polymer. Multilayer lines are evident. Orthorhombic pseudo unit cells have been proposed for the A and B forms with the "*c*" axis consisting of an average dimer.[10]

A random mer sequence along the polymer backbone is concluded from an analysis of the aperiodic meridional reflections.[11] In the light of this apparent random structure, the highly three-dimensionally crystalline X-ray patterns pose an interesting theoretical problem.

We have also been able to prepare fibers from the polymer. The "as-spun" fiber appears to be "quenched" and, on annealing, appears to convert to the A form when cooled to room temperature.[12]

Conclusions

To summarize, the polymer sample of this study can be described by the following scheme:

$A \rightleftharpoons B$	rapidly reversible at ~100 °C
$B \rightarrow N$	at ~427 °C (MW dependent)
$N \rightarrow B$	supercools ~40 °C
$N \rightarrow B_q$	rapid quench
$B_q \rightarrow B$	anneal at 260+ °C, preferably 350+ °C
$N \rightleftharpoons I$	at 472 °C

Acknowledgment. We are grateful to Dr. J. Cleary for synthesizing the polymer studied and to T. Dougherty for conducting the DSC scans.

Registry No. (BP)(TA)(PHBA) (copolymer), 31072-56-7.

References and Notes

(1) Economy, J.; Volksen, W.; Geiss, R. H. *Mol. Cryst. Liq. Cryst.* **1984**, *105*, 289.
(2) Volksen, W.; Lyerla, J. R., Jr.; Economy, J.; Dawson, B. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2249.

(3) Economy, J.; Storm, R. S.; Matkovich, V. I.; Cottis, S. G.; Nowak, B. E. *J. Polym. Sci. Polym. Chem. Ed.* **1976**, *14*, 2207.
(4) Cottis, S. G.; Layton, R.; Field, N. D. U.S. Patent 4 563 508, 1986.
(5) Duska, J. J.; Finestone, A. B.; Maher, J. B. U.S. Patent 4 626 557, 1986.
(6) Cottis, S. G. U.S. Patent 4 639 504, 1987.
(7) Jackson, W. J. *Br. Polym. J.* **1980**, *12*, 154.
(8) Dicke, H.; Lenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2581.
(9) Field, N. D.; Baldwin, R.; Scardiglia, F.; Duska, J.; Frayer, P. Topical Workshop on "Flow Deformation and Molecular Reorganization in Polymers with Crystalline and Liquid Crystalline Order", Montreal; American Chemical Society, Division of Polymer Chemistry, April, 1986.
(10) Frayer, P., unpublished results.
(11) Blackwell, J.; Cheng, H.-M.; Biswas, A.; Field, N. D.; Layton, R.; Frayer, P. *Structure Development During Molding of the Thermotropic Copolyester XYDAR*; Paper presented at the 3rd Polymer Processing Society Meeting Stuttgart, W. Germany, April 1987.
(12) We are grateful to Prof. J. Blackwell for the X-ray fiber diagrams.

Lignin 24 Ultrafiltration and Light-Scattering Evidence for Association of Kraft Lignins in Aqueous Solutions

Douglas L. Woerner† and Joseph L. McCarthy*

Department of Chemical Engineering, University of Washington, Seattle, Washington 98195. *Received November 12, 1987; Revised Manuscript Received January 7, 1988*

ABSTRACT: Ultrafiltration and light-scattering evidence is presented pointing to the growth of large, stable associated complexes from smaller lignin moieties as the alkalinity of an aqueous kraft lignin (KL) solution is decreased. Ultrafiltrates showed a decrease in the number of small molecules available to permeate the membrane as the solution alkalinity was decreased from pH 13.8 to 8.5. Light-scattering measurements indicated a large increase in the weight-average molecular weight (i.e., from about 3500 to 200 000) when the alkalinity was reduced. The association was found to be reversible and rapid. A model of the association is proposed in which the controlling step is presumed to be the protonation of phenolic hydroxyl groups. Association seems to explain the difficulties experienced in fractionation of KL on a molecular weight basis by use of incremental precipitation by acidification of alkaline solutions.

Introduction

Lignins are phenylpropane type polymers that make up about one-fourth of the mass of all woody plant tissue. Structural features of native soft-wood lignins have been proposed by Adler.[1] Characteristics of lignins have been described by Sarkanen and Ludwig.[2]

Several investigators have reported that kraft lignins (KL), which are extracted from wood by action of aqueous sodium hydroxide–sodium sulfide solutions at elevated temperatures and are schematically pictured in Figure 1 according to Marton,[3] may associate in aqueous solution to form complexes. Changes in diffusion coefficients with changes in concentration or alkalinity have been observed by Benko.[4] Increases in specific viscosity with decreases in alkalinity have been found by Yaropolov and Tishchenko[5] and also by Lindstrom,[6] who proposed that association occurs as a result of hydrogen bonding between carboxylic acid and phenolic hydroxyl groups. Shifts in molecular weight distributions (MWD), as estimated by size exclusion chromatography (SEC), have been seen in this laboratory by Sarkanen et al.,[7] who suggested that the complexes may arise as a result of HOMO–LUMO bonding of the π orbitals of benzene rings.

With this background, the now-reported research was undertaken[8] to assemble more information about the phenomenon of association of kraft lignins in aqueous solutions.

Experimental Section

Solutions. The KL studied was Indulin AT, a purified southern pine lignin solid obtained from the Westvaco Co. This KL was dissolved in sufficient aqueous sodium hydroxide to yield a solution (160 g L^{-1}, pH 9.2) which was then filtered through Whatman number 1 paper. The filtrate was divided into five aliquots, and each was adjusted to a different alkalinity by the addition of carbonate-free, saturated sodium hydroxide solution or by the removal of sodium by ion exchange. Solutions at pH 8.5, 9.2, 11.0, 12.0, and 13.6 were identified as KL85, KL92, KL11, KL12, and KL14. These were aged under nitrogen for about 1 month at room temperature and, before use, were passed through a fine-sintered glass filter. No precipitate was observed on the filter surface. The ionic strength of each solution was approximately 0.2 M.

Ultrafiltration Procedures. Experiments were conducted in a stirred ultrafiltration cell (Model 202, Amicon Co.) modified so that the stir bar was situated about 2.5 cm above the membrane surface. Polysulfone membranes from DDS, Ltd. (Denmark), and from the Amicon Co. were used. Three sets of experiments were performed to determine the effects of alkalinity on the concentration of solutes in the permeates. A fourth experiment was conducted to explore the effects of association on the molecular weight distribution.

For set UF-1, individual 160 g L^{-1} KL solutions were ultrafiltered separately at three different randomly chosen transmembrane pressures (134, 268, and 536 kPa) through a DDS GR8P membrane with stirring at 145 rpm. The initial 10 mL of permeate was discarded, and a 2-mL permeate sample was then collected. Lignin concentration was determined in each permeate. Between runs at different alkalinities, the membrane was washed by using an acid–base–detergent procedure described by Woerner.[8]

In UF-2, the KL92 solution (160 g L^{-1}, pH 9.2) was placed in an ultrafiltration cell and titrated with a saturated sodium hydroxide solution to yield several alkalinity levels and finally pH 13. Solutions were allowed to stand for 2 h between alkaline additions. Ultrafiltrations (GR8P membrane) were conducted at each alkalinity level with the transmembrane pressure and the stirring rates held constant at 134 kPa and 145 rpm, respectively. The initial ionic strength was approximately 0.2 M.

---

† Present address: Department of Chemical Engineering, University of Maine, Orono, ME 04468.

0024-9297/88/2221-2160$01.50/0