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Crystalline and Liquid Crystalline Properties of Polyesters of Phenyl-Substituted 4,4′-Biphenol. 2. Copolymers with 4-Hydroxybenzoic Acid

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ABSTRACT: The results of X-ray diffraction, DSC, and optical microscopy are presented for a series of four copolyesters of either 3-phenyl-4,4′-biphenol (MPBP) or 3,3′-diphenyl-4,4′-biphenol (DPBP) with either terephthalic acid (TA) or 2,6-naphthalenedicarboxylic acid (NDA) and 30 mol % of *p*-hydroxybenzoic acid (HBA). The properties of the copolyesters resembled those of the Xydar family of polymers. The X-ray diffraction patterns of oriented samples drawn from the nematic phase of three of the four copolymers showed a series of aperiodic intensity maxima on the meridian, orientation, or fiber direction, which, in general terms, are consistent with that expected from a random sequence of monomers.

Introduction

Liquid crystalline wholly aromatic polyesters can form fibers and plastics of high strength and stiffness by melt spinning or injection molding in the liquid crystalline (LC) state. An example of a commercially important liquid crystalline polymer (LCP) is the copolyester of 4,4′-biphenol (BP), terephthalic acid (TA), and *p*-hydroxybenozic acid (HBA), which is commonly known as Xydar (Dartco Manufacturing Co., GA). This copolyester[1,2] has a melt-processing temperature in excess of 400 °C, which is rather high for melt processing in conventional molding equipment, so it was of considerable interest to synthesize and to characterize several copolyesters based on 3-phenyl-4,4′-biphenol (MPBP) and 3,3′-diphenyl-4,4′-biphenol (DPBP). These copolymers were found to have anisotropic behavior at temperatures lower than 400 °C.

The two aromatic diols studied, MPBP and DPBP, are potentially valuable monomers for the synthesis of relatively low melting thermotropic polyesters because the phenyl groups appendaged to the 4,4′-biphenol moieties sharply decrease the polymer melting temperatures, T_m, by structural effects that result in a property termed the "frustrated chain packing concept".[3] Many studies on the copolymerization of different mesogenic (LC-forming) monomers have demonstrated that this approach is an efficient method for the synthesis of polyesters with lower melting transitions.[4] In the present study copolyesters based on MPBP and DPBP with 30 mol % HBA were synthesized and examined. On copolymerization of these monomers with HBA, a random distribution of the *p*-oxybenzoate units should be obtained which would be expected to disturb the packing of the polymer chains, giving a lower melting transition. Copolymers with higher percentages of HBA units were not included in the study because such copolyesters might contain blocklike sequences[5,6] of HBA units, which would impart a higher melting transition.

The structures and designations of the copolyesters prepared for this study are given in Figure 1 together with the structure of a Xydar polymer for comparison.[7] The wholly aromatic polyesters prepared were examined by viscometry, polarized light microscopy, and differential scanning calorimetry (DSC). X-ray diffraction patterns of fibers drawn from the nematic fluid were obtained for three polymers of the series, but it was not possible for one, as discussed later.

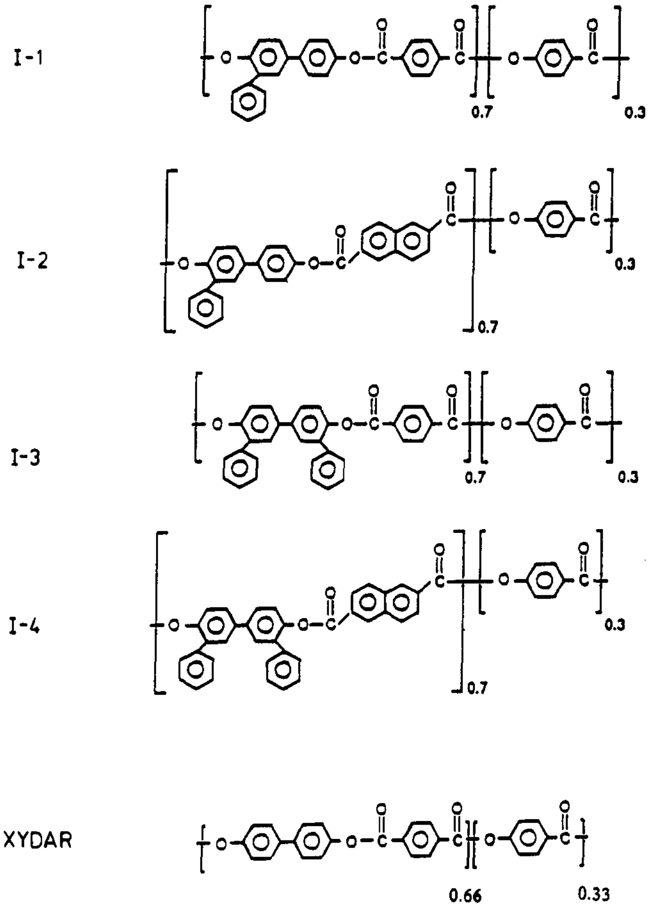

Figure 1. Structures of the four copolyesters investigated and a related Xydar polymer.

Experimental Section

Polymer Synthesis. All of the polyesters with 30 mol % HBA were prepared from *p*-acetoxybenzoic acid and the requisite amounts of the acetates of the two diol comonomers and the two dicarboxylic acids by melt polycondensation reactions without an added catalyst.[8] At the end of polymerization the solidified polyester was processed by either one of two procedures, as

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Table I
Physical Properties of Thermotropic Copolyesters of MPBP and DPBP

polymer	polymer composition	I.V. (dL/g)	T_g (°C)	$T_m{}^c$ (°C)	$T_f{}^d$ (°C)	texture by optical microscopy
I-1	(MPBP + TA) + (HBA) (0.3)	0.57	135	318[a]		nematic
I-2	(MPBP + NDA) + (HBA) (0.3)	1.34	152		235	nematic
I-3	(DPBP + TA) + (HBA) (0.3)	0.83	143	318[a] 302[b]		nematic
I-4	(DPBP + NDA) + (HBA) (0.3)	2.71[e]	140	338[a]		nematic

[a] First heating cycle. [b] Second heating cycle. [c] The crystalline melting transition, T_m, was determined from a DSC thermogram. [d] Fusion temperature, T_f, was determined from the temperature of onset of flow as observed on a hot-plate melting point apparatus and verified by polarizing light microscopy from observation of a typical nematic texture on the sample edge, the thinnest part of the sample. [e] Polymer I-4 had an I.V. value of 4.9 dL/g in TCE at 30 °C.

follows: (1) the product was chipped out of the reactor and ground and washed successively with either boiling n-propanol or isopropyl alcohol and acetone several times to remove any residual monomer, or (2) the product was dissolved in a mixture of p-chlorophenol and 1,1,2,2-tetrachloroethane, precipitated from solution with a 10-fold excess of ethanol, and washed several times with boiling ethanol. The copolyester products were either dried under vacuum at 95 °C for 24 h in the former case or dried for 72 h in the latter case. The usual polymerization time was 24 h, and the yield of copolymer generally varied between 80 and 90%.

Polymer Characterization. Inherent viscosities of the copolyesters prepared were measured in mixtures of p-chlorophenol/1,1,2,2-tetrachloroethane (60/40 by weight) either at 30 °C (for polymers I-1 and I-3) or at 50 °C (for polymers I-2 and I-4) at a polymer concentration of 0.2 g/100 mL with a Cannon–Ubbelohde-type viscometer. The inherent viscosity of polymer I-4 was also measured in 1,1,2,2-tetrachloroethane at 30 °C at a polymer concentration of 0.2 g/100 mL with the same type of viscometer. The molecular weight of polymer I-4 was estimated by the use of a Waters 804E GPC calibrated with monodisperse polystyrene standards through Ultrastryagel columns with 50-, 10^2-, 10^3-, and 10^4-nm pore sizes.

The phase-transition temperatures were measured on a Perkin-Elmer II DSC under a nitrogen flow with heating and cooling rates of 20 °C/min. The temperature of the DSC thermogram was calibrated prior to use with reference standards of high-purity indium, tin, and lead. Polymer samples usually weighing 5–10 mg were used for this analysis. The peak maximum of the phase-transition temperature was recorded from both the first and second heating cycles for all samples. The glass transition temperature was taken as the onset of that transition during either the first or second heating cycle, whichever was more prominent. For one sample (polymer I-2) there were no phase-transition temperatures in either the first or the second heating cycles, and, in this case, a fusion temperature, T_f, was reported for the temperature of onset of flow as observed for the sample on a hot-plate melting point apparatus and verified by use of a hot stage on a polarizing microscope from observation of a typical nematic texture on the edge of the sample, i.e., at the thinnest part of the specimen. The liquid crystalline textures of the copolyesters were observed on an optical microscope (Leitz, Model Ortholux) equipped with a pair of crossed polarizers and a hot stage (Mettler).

X-ray Diffraction. Samples were heated to above the isotropization temperature and allowed to cool to fixed temperatures in the mesophase range. Oriented fibers were pulled from the fluid and quench-cooled in cold water. The samples were X-rayed using pinhole collimation with a Statton camera, evacuated to backing pump pressure (~10^{-2} Torr). The radiation used was Cu Kα using a nickel filter, and the patterns were recorded on photographic film.

Results and Discussion

Viscometry, DSC, and Polarized Light Microscopy. The data in Table I show that all of the copolyesters had moderate to high molecular weights because their inherent viscosity, I.V., values were in the range of 0.57–2.71 dL/g. A solution of polymer I-4, which is soluble in TCE alone and which remained in solution on dilution with $CHCl_3$, was evaluated by GPC at room temperature. A single peak, as shown in Figure 2, with an average molecular weight ($\bar{M}_w$) of 124 000, compared with polystyrene standards, was obtained. Therefore, the thermal properties, optical textures, and other properties can be compared neglecting the effect of molecular weight on these properties.

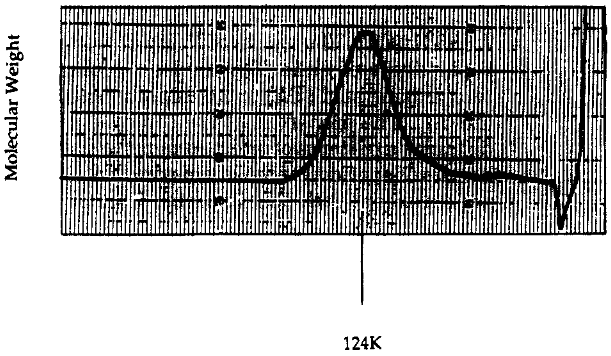

Figure 2. GPC plot for polymer I-4.

The copolymer of MPBP and TA with 30 mol % HBA, polymer I-1, exhibited a melting transition, T_m, at 318 °C in the first heating cycle of the DSC thermogram, which is lower than that of the Xydar copolyester of 4,4′-biphenol, TA, and 30 mol % HBA. Presumably this result is caused by the *internal copolymerization effect* of the unsymmetrically-substituted MPBP repeating units. This effect arises from the placement of the single phenyl group of MPBP in either a head-to-head or head-to-tail sequence along the polymer chain in a statistically random manner. In the second heating cycle there was no melting endotherm, which indicates that, on cooling at a rate of 20 °C/min, there was no development of any measurable amount of crystallinity.

In contrast to the TA copolymer, the copolymer of MPBP with NDA and 30 mol % HBA, polymer I-2, did not show any melting endotherm in either the first or second heating cycles of the DSC thermogram, but it fused to form a LC phase at a lower temperature (Table I). The different nature of the copolymer of NDA compared to that of TA may be related to the offset structure of the 2,6-ester linkage of NDA as compared to the collinear 1,4-ester linkage of TA. In that regard, the copolymer of symmetrically-substituted DPBP with TA and 30 mol % HBA showed a melting endotherm, T_m, in both heating cycles of the DSC thermogram (Figure 3), which is also lower than that of the equivalent Xydar copolymer containing 4,4′-biphenol. This copolymer, polymer I-3, formed an LC phase on melting, and on cooling under the conditions used a crystalline phase was readily formed, as indicated by the presence of a melting endotherm in the second heating cycle thermogram. Again, this behavior presumably results from the collinear arrangement of the terephthalate units and p-oxybenzoate units in the copolymer chain.

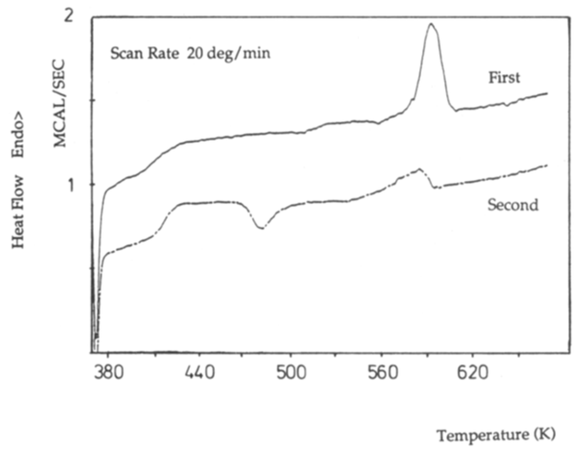

Figure 3. DSC thermograms for polymer I-3: (—) first heating cycle; (– · –) second heating cycle.

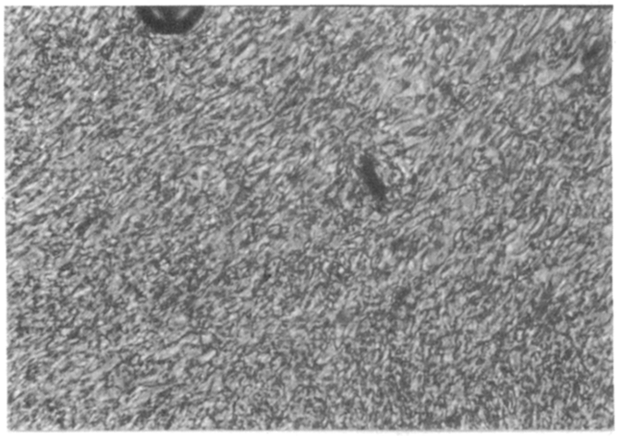

Figure 4. Photomicrograph of polymer I-3 quenched from 350 °C, taken with crossed polars (magnification 260×).

In contrast to the behavior of the TA copolymer, polymer I-3, the copolyester of DPBP with NDA and 30 mol % HBA, polymer I-4, had a melting endotherm at 338 °C in the first heating cycle but no melting endotherm in the second heating cycle, which indicates that on cooling from the melt no measurable development of crystallinity occurred under the conditions used. This behavior could result from the mismatching of the 2,6-naphthalenedicarboxylate units with *p*-oxybenzoate units in the polymer chain.

All the copolyesters listed in Table I formed turbid melts that showed strong shear opalescence. This property was taken as a preliminary indication of mesomorphic behavior. The polymers were also investigated by visual observation using a polarizing microscope, and all showed typical nematic textures which exhibited either highly threaded or schlieren textures depending on the thickness and thermal history of the sample. A typical example is shown in Figure 4.

X-ray Diffraction. Polymer I-1. The X-ray diffraction pattern obtained from a fiber drawn from the nematic melt is shown in Figure 5a. The spacings of the series of meridional arcs are listed in Table II. The spacings are aperiodic and compare quite well with the values reported for the closest copolymer of the Xydar series, that containing a 33/33/33 monomer ratio for BP/TA/HBA.[9] The basic features of the X-ray pattern are those for an oriented nematic phase with the aperiodic meridional series consistent with the convolution of the monomer residues[10] representing a random sequence.[9] Annealing the sample produced little improvement in the level of crystallinity, and it is useful to compare these results with those reported for the Xydar copolymers with a BP/TA/HBA ratio of 25/25/50 as reported by Field and co-workers,[7] who observed the development of crystallinity on annealing. In the present case a smaller amount of HBA is present in the copolymer to decrease the average sequence length of the BP/TA units, and in addition the random orientation of the BP units reduced the orderliness of the copolyester. Thus, the copolymer, polymer I-1, had a particularly useful nematic range, and it was sufficiently stereochemically frustrated to suppress crystallization and melt at approximately 320 °C.

Table II
X-ray Diffraction Spacings (nm)

polymer	spacing (±0.002)	description
polymer I-1	0.770[a]	meridional, strong
Figure 5a	0.598	meridional, weak, sharp
	0.450	meridional, weak and diffuse
	0.329	meridional, medium, broad
	0.208	meridional, strong
	0.450	equator, strong, diffuse
polymer I-3	0.745	off-meridional pair
Figure 5b	0.442	meridional, weak, diffuse
	0.328	meridional, medium, broad
	0.208	meridional, strong
	0.445	equatorial, diffuse
polymer I-4	0.817	off-meridional pair
Figure 5c	0.618	meridional, sharp
	0.475	meridional, weak, diffuse
	0.310	meridional, medium
	0.208	meridional, strong
	0.445	equatorial, diffuse
Xydar	0.770	meridional
BP/TA/HBA[b]	0.577	meridional
(33/33/33)	0.327	meridional
	0.287	meridional
	0.208	meridional

[a] This spacing may emanate from a pair of off-meridional diffraction arcs; a similar diffraction signal observed in polymers I-3 and I-4 clearly shows a pair of off-meridional diffraction arcs in the 0.75–0.82-nm region. [b] From ref 9.

Polymer I-2. It was not possible to obtain oriented fibers from this copolymer, which is consistent with the indications from DSC that the copolymer is amorphous and showed only a T_g and a fusion temperature, T_f. Although optical observations indicated that there is a small temperature range over which a nematic texture appears, it was not possible to obtain an oriented nematic sample, and so only unoriented X-ray diffraction patterns were obtained which did not change significantly on annealing.

Polymer I-3. The X-ray diffraction pattern of a fiber drawn from the nematic melt of this copolymer is shown in Figure 5b, and the spacings of the diffraction signals are listed in Table II. The usual strong and diffuse equatorial signal was observed centered on a value of 0.445 nm and respresenting the interchain spacing. The meridional series are aperiodic and are similar to both polymer I-1 and Xydar (with 33/33/33 composition), both of which are listed for comparison in Table II. There was no significant increase in crystallinity on annealing.

Polymer I-4. The X-ray diffraction pattern of fibers drawn from the nematic melt of this copolymer is shown in Figure 5c, and the recorded diffraction spacings are listed in Table II. There is a strong diffuse diffraction signal on the equator centered at 0.445 nm, and the meridional series is again aperiodic, indicating a random sequence of monomers. The values obtained differ from those of polymers I-1 and I-3 and Xydar as expected because of the replacement of TA with NDA. Certain diffraction signals remained constant, especially the 0.208-nm meridional spacing, which is an inherent feature

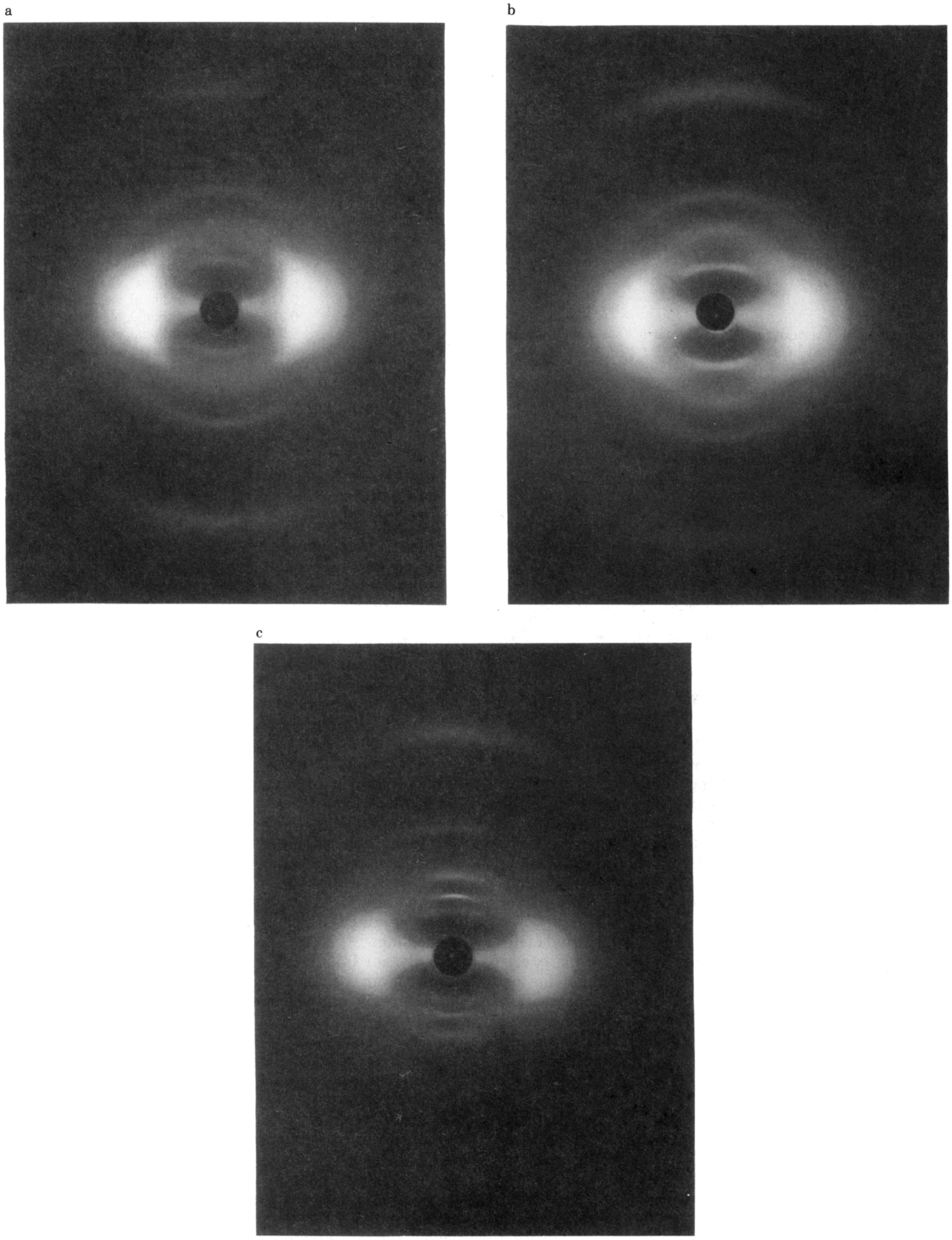

Figure 5. Oriented X-ray diffraction patterns obtained by drawing fibers from the nematic melt: (a) polymer I-1; (b) polymer I-3; (c) polymer I-4. The orientation axis is vertical in each case. The details of the structures and X-ray spacings are given in Figure 1 and Table II.

emanating from the atomic distribution in aromatic polyesters.[9] There was no significant increase in crystallinity on annealing.

These copolyesters, together with Xydar, are members of a family, and the results obtained enable us to assess the effect of variations in polymer structure on physical properties, with particular emphasis on the development of a nematic phase in an amenable temperature range and its implications for processing. If we chose Xydar as a standard, then the experimental data obtained show that the preservation of a phenyl group randomly substituted on the BP unit as in polymer I-1 (see Figure 1) lowered the melting point by approximately 80 °C, to 320 °C, suppressed the degree and apparently the rate of crystallization, and gave a copolyester with a useable nematic LCP behavior. In the symmetrically-substituted copolymer, polymer I-3, the properties were intermediate between polymer I-1 and Xydar. It had a lower melting temperature and lower crystallinity compared with Xydar, but it was more crystallizable than polymer I-1. Polymers I-2 and I-4 relate to polymers I-1 and I-3 by replacing the TA units with NDA units in which the two carboxyl groups were offset. The result in each case was to raise the melting temperature, in the case of polymer I-2, to above the fusion temperature and lower the crystallizability substantially.

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