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Crystalline and Liquid Crystalline Properties of Polyesters of Phenyl-Substituted 4,4'-Biphenol. 1. Polymers from Terephthalic Acid and 2,6-Naphthalenedicarboxylic Acid

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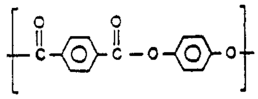
ABSTRACT: A group of six thermotropic aromatic polyesters was investigated using X-ray diffraction, DSC, and optical microscopy. The occurrence of nematic phases was examined, and its relationship to structural irregularities and crystallinity are discussed. The polyesters are based on 3-phenyl-4,4'-biphenol (MPBP) and 3,3'-diphenyl-4,4'-biphenol (DPBP) with terephthalic acid (TA) and/or 2,6-naphthalenedicarboxylic acid (NDA). The polymers studied form two series. In series I, MPBP was combined either with TA or with NDA to form homopolymers. In types of both polymers the randomness in the position of the substituent phenyl group depressed the melting transition and created a nematic state over a sufficiently wide temperature range to allow fibers to be drawn from the nematic melt. X-ray diffraction studies confirmed that the chain conformation is an extended ribbon with localized biaxial order. The random copolymerization of 50 mol % of each of the two acids, NDA and TA, with MPBP created an amorphous polymer as indicated by DSC and X-ray diffraction experiments. In series II, DPBP was combined either with TA or with NDA to form homopolymers. The symmetric arrangement of the two phenyl groups in the biphenol group led to fast rates of crystallization; indeed, the rates were so fast that it was not possible to draw fibers. The copolymerization (50%) of the two acids with DPBP introduced sufficient disorder to greatly depress the crystallinity and allow fibers to be drawn from the nematic fluid for examination by X-ray diffraction. In the entire group of six homopolymers and copolymers the two basic variables are the randomness of phenyl group substitution and the randomness induced by copolymerization. The results show that too much of both these elements of disorder suppressed nematic order, while too little of both increased the rate of crystallization to an extent that made the preparation of the oriented nematic state by fiber drawing technically difficult or even inaccessible.

Introduction

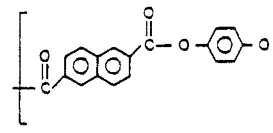
Thermotropic liquid crystalline polymers are of considerable interest scientifically and commercially with growing industrial applications and use. The wholly aromatic polyesters (where the connecting linkages are all at para positions) are of particular interest, especially so if they are able to form liquid crystalline (LC) nematic melts at manageable temperatures so that they can be processed into high-strength fibers and self-reinforced molded plastics.

Good candidates for all-aromatic LC polyesters, both for scientific investigations and for industrial applications, are shown in Figure 1. In these polymers, the nature of the chemical units and the linkage geometries would be expected to create extended, stiff chains which should lead to nematic liquid crystal formation, but in practice the requirement for more rigidlike structures needs to be combined with the requirement for such polymers to have accessible melting temperatures for processing. If the melting temperature is too high, chemical degradation takes place.

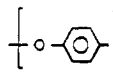
The high melting temperature of the stiff polymers is related to its low melting entropy, and many investigations are currently devoted to modifying the molecular composition and architecture of rigid polymeric systems in attempts to obtain more practical conditions for manipulating and processing such polymers. The general principles for modifying the architecture of rigid polymer systems have been discussed by Griffin and Cox.[1] They delineated three categories of modification, including (1) monosubstitution on the aromatic groups to frustrate chain packing, (2) flexible (especially aliphatic) links, and (3) nonlinear rigid links. The liquid crystalline polymers (LCPs) in this investigation fall into the frustrated chain-packing category.



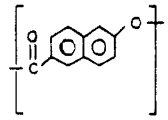
poly(p-phenylene terephthalate)



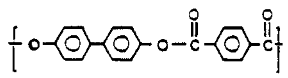
poly(p-phenylene naphthalene-2,6-carboxylate)



poly(p-oxybenzoate)



poly(2-oxy-6-naphthoate)



poly(4-4'-biphenylene terephthalate)

Figure 1. Typical all-aromatic LC polyesters.

In general, aromatic homopolyesters are highly crystalline, infusible, and insoluble in the known solvents. To

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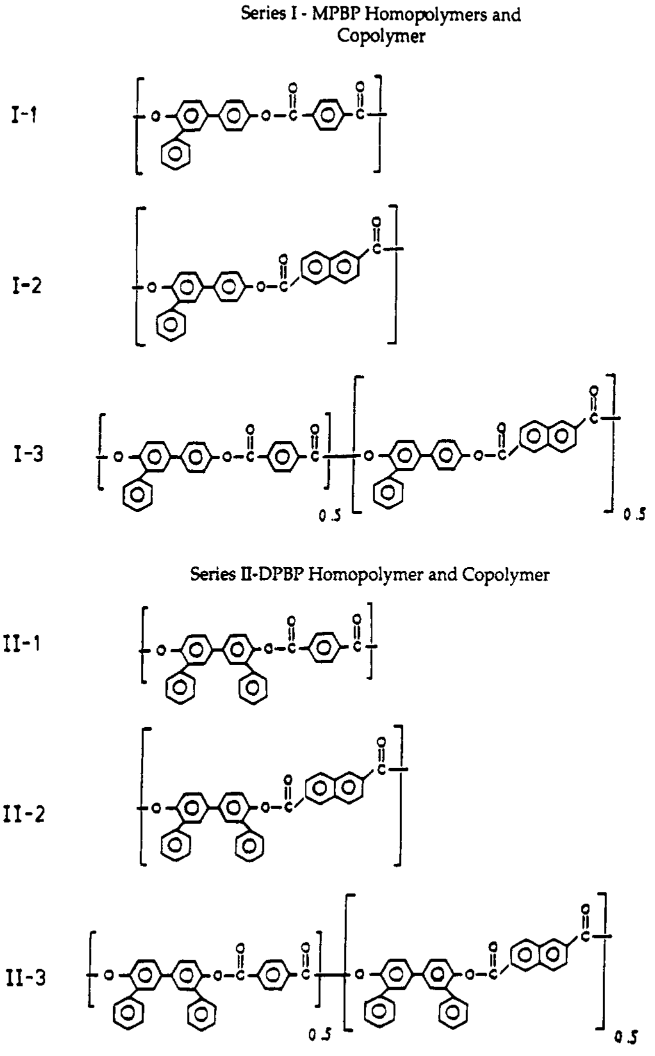

Series I - MPBP Homopolymers and Copolymer

Series II-DPBP Homopolymer and Copolymer

Figure 2. Structures of the series I polymers based on MPBP (3-phenyl-4,4'-biphenol) and of the series II polymers based on DPBP (3,3'-diphenyl-4,4'-biphenol).

reduce the crystallinity in these homopolymers, two approaches among several are usually found to be successful in decreasing the melting transitions, especially for wholly aromatic thermotropic polyesters, to an amenable temperature range. One approach is to use a monomer with a single bulky substituent such as phenylhydroquinone (PhHQ), which enters the polymer chain in a random head-to-tail orientation to prevent close packing and to frustrate chain organization into polymer crystals. Such an example is the homopolymer of terephthalic acid (TA) and PhHQ, which has a conveniently low melting transition, T_m, at 340 °C.[2,3] The second approach is the copolymerization of different mesogenic (LC-forming) monomers such as 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA), which form random copolymers with depressed melting transitions, T_m, as low as 345 °C.[7] These hydroquinone copolymers form the basis of the Vectra family of thermotropic LCPs.[4] Another example of this latter approach are the copolymers of 4,4'-biphenol(BP) and HBA, which form the basis of the Xydar family of thermotropic LCPs[5,6] and have a minimum T_m at 388 °C. To lower the T_m still further, for melt processing in conventional molding equipment, additional modifications on these polymers can be made. For example, monomers, such as carbonate groups, have been inserted in the latter polymers,[8] and other substitutions, for example, *tert*-butylhydroquinone,[9] have been added.

In this report we describe the characterization and analysis of the X-ray diffraction patterns of oriented samples of wholly aromatic polyesters based on 3-phenyl-4,4'-biphenol (MPBP) and 3,3'-diphenyl-4,4'-biphenol (DPBP), both of which form polymers that exhibit anisotropic behavior lower than 400 °C, which is the temperature usually needed for processing unsubstituted copolyesters. These diols are potentially useful for the synthesis of relatively low melting thermotropic polyesters because they both contain either one or two bulky substituent phenyl groups, which are expected to decrease T_m by frustrating the chain packing as discussed above.[1] In addition, copolymerization of these monomers with a mixture of 50 mol % TA and 50 mol % NDA should occur in a random manner and should cause additional lowering of T_m.

The structures and designations of the homopolymers and their copolymers prepared and characterized in this study are shown in Figure 2. The wholly aromatic polyesters prepared were examined by viscometry, polarized light microscopy, differential scanning calorimetry (DSC), and transmitted light intensity measurement. X-ray diffraction patterns were also obtained for some of the polymers in the nematic LC state, and the samples were subsequently annealed to investigate levels of induced crystallinity.

Experimental Section

Polymer Synthesis. All of the polyesters in this study were synthesized by the melt polycondensation reaction without an added catalyst from the diacetate derivatives of the biphenol monomer with TA and/or NDA.[10]

Polymer Characterization. Inherent viscosities of the polymers were measured either in *p*-chlorophenol (for polymers I-3, II-1, and II-3) or *p*-chlorophenol/1,1,2,2-tetrachloroethane (60/40 by weight) at 50 °C at a polymer concentrate of 0.2 g/100 mL, with a Cannon-Ubbelohde-type viscometer.

The thermal properties of the polymers were determined by differential scanning calorimetry on a Perkin-Elmer DSC-2 instrument. Polymer samples of about 10 mg each were examined under a nitrogen flow at both a heating rate and a cooling rate of 20 °C/min. Indium and lead were used for calibration of the phase-transition temperature which was recorded from both the first or 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 some samples there were no phase-transition temperatures in either the first or the second heating cycle of the sample. For these samples, a fusion temperaure, T_f, was reported as the temperature of onset of flow as observed for the sample on a hot-plate melting point apparatus. This property was verified by use of Mettler hot stage on a Leitz Ortholux polarizing microscope from observation of the formation of a typical nematic texture at the edge of a sample, i.e., at the thinnest part of the sample.

The transmitted light intensity scan[10] of a thin film of polymer I-2 as a function of temperature at a heating rate of 10 °C/min was recorded.

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 ($\sim 10^{-2}$ Torr). The radiation used was Cu Kα using a nickel filter, and the patterns were recorded on photographic film.

Results and Discussion

The data in Tables I and II show that all of the polyesters studied (except polymer I-1, which is insoluble both in *p*-chlorophenol and *p*-chlorophenol/1,1,2,2-tetrachloroethane (60/40 by weight)) had moderate to high molecular

Table I
Properties of Thermotropic Polyesters Based on MPBP

polymer no.	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		132	323[a] and 269[b]	369[a]	nematic
I-2	MPBP + NDA	1.86			260	nematic
I-3	$(MPBP + TA)_{0.5} + (NDA)_{0.5}$	7.16	160		285	nematic

[a] First heating cycle. [b] Second heating cycle. [c] Crystalline melting transition, T_m, was determined by DSC measurement. [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 a polarizing light microscope on observation of a typical nematic texture on the edge, the thinnest part of the sample.

Table II
Properties of Thermotropic Polyesters Based on DPBP

polymer no.	polymer composition	I.V. (dL/g)	T_g (°C)	T_m[c] (°C)	T_i[c] (°C)	texture by optical microscopy
II-1	DPBP + TA	0.48		341[a] and 353[b]	398[a] and 398[b]	nematic
II-2	DPBP + NDA	2.07		362[a] and 403[b]	423[a] and 415[b]	nematic
II-3	$(DPBP + TA)_{0.5} + (NDA)_{0.5}$	1.88	157	303[a]		nematic

[a] First heating cycle. [b] Second heating cycle. [c] Crystalline melting transition, T_m, and isotropization temperature, T_i, were determined by DSC measurement.

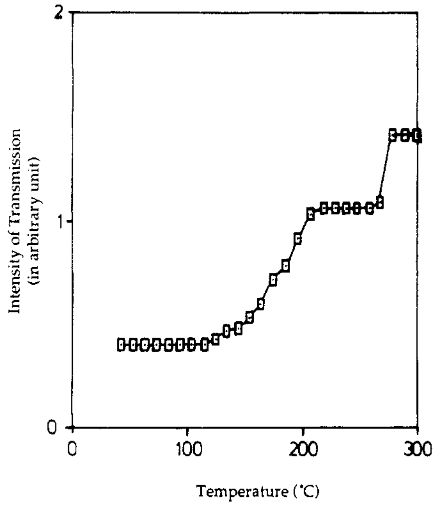

Figure 3. Transmitted light intensity as a function of temperature for polymer I-2 (heating rate 10 °C/min).

weights because their IV values were in the range of 0.48–7.16 dL/g. Therefore, the thermal properties, optical textures, and other properties of these polymers can be compared without referring to the effect of molecular weight on those properties.

All the polyesters listed in Tables I and II formed turbid melts that exhibited strong shear opalescence. These properties were taken as a first indication of their liquid crystalline behavior. For further information, especially about the melt morphology of these polymers, the polymers were studied by visual observation on a polarizing microscope. They all exhibited typical nematic textures, which were highly threaded mobile textures and/or Schlieren textures depending on the thickness of the sample and the temperature at which the photomicrograph was obtained, on the polarizing light microscope hot stage.

MPBP Polymers. The homopolymer of MPBP with TA, I-1, showed a much lower crystallinity and T_m than that of poly(4,4′-biphenylene terephthalate), which undergoes decomposition before its transformation into the LC state. The low crystallinity and low T_m of the former are not surprising because MPBP has an unsymmetrical structure with a single phenyl group in only one of the two rings of the biphenol moiety which serves a dual role in the suppression of the crystallinity and T_m of this homopolymer: first, by its large size and steric hindrance effect and, second, resulting from the random head-to-head or head-to-tail orientation of these moieties in consecutive repeating units along the polymer chain, which is termed the "internal copolymerization effect". Both of these effects can severely disrupt the packing of the polymer chains and can greatly reduce crystallinity and T_m.

The homopolymer of MPBP with NDA, I-2, did not exhibit a melting endotherm, T_m, in the DSC thermogram, but it did have a fusion temperature T_f, of 260 °C, presumably because of very little or no crystallinity in this sample. The amorphous nature of the NDA homopolymer in contrast to the TA homopolymer may result from the difference between the offset 2,6-ester linkage of NDA compared to the linear 1,4-ester linkage of TA. This result is consistent with that reported by Calundann and Jaffe.[11]

The transmitted light intensity scan[12] of a thin film of polymer I-2 as a function of temperature at a heating rate of 10 °C/min exhibited two transitions: one-transition from 155–215 °C and the other from 260–275 °C, as shown in Figure 3. The latter transition corresponding to the T_f value as observed by the onset of flow with the hot-plate melting point apparatus and verified with the polarized light microscope by observation of a typical nematic texture on the edge of the sample, which was the thinnest part. Unfortunately, the nature of the first transition observed by this method for the polymer is still unknown.

The copolymer with 50 mol % TA and 50 mol % NDA, I-3, also formed an anisotropic melt but at lower temperature than the TA homopolymers. Presumably this copolymer has a random distribution of the terephthalate and 2,6-naphthalene dicarboxylate units in the chains, so it is not surprising that is did not show any melting endotherm in the heating cycle or crystallization exotherm in the cooling cycle of the DSC thermogram, and it fused to form an LC phase at a considerably lower temperature than either homopolymer as shown in Table I.

DPBP Polymers. The data in Table II, in contrast to the behavior of the MPBP homopolymers, show that both of the homopolymers of DPBP, with either TA or NDA, II-1 and II-2, respectively, have observable melting transitions, T_m, and even isotropization endotherms, T_i. The high T_m values for these homopolymers as compared to that of I-1 is most likely a result of the symmetric structure of DPBP in contrast to the unsymmetric structure of MPBP. That is, the symmetric DPBP allows the units of its homopolymers to pack well, giving rise to high crystallinity and high T_m values for these homopolymers.

In addition, it also lacks the internal copolymerization effect. The homopolymer of DPBP with NDA, II-2, had a higher melting transition, T_m, and a higher isotropization temperature, T_i, as compared to those properties for the homopolymer of DPBP with TA, II-1. The high T_m value of the DPBP with NDA homopolymer, II-2, compared to that of the DPBP with TA homopolymer, II-1, may result from the ability of the 2,6-ester linkage of NDA to form a linear offset structure, which can accommodate the two symmetrically-substituted bulky phenyl groups in the resulting polymer in a more efficient manner than can the 1,4-ester linkage of TA.

The copolymer of DPBP with 50 mol % TA and 50 mol % NDA, II-3, showed only a melting endotherm, T_m, at 303 °C in the first heating cycle of the DSC thermogram. On melting it formed a LC phase, but on cooling at a rate of 20 °C/min there appeared to be no development of any appreciable amount of crystallinity as indicated by the absence of a melting endotherm in the second heating cycle of the DSC thermogram.

X-ray Diffraction. Series I Homopolymers. The X-ray diffraction patterns of oriented samples of polymer I-1 are shown in Figure 4. Fibers that were drawn from the polymer melt which showed nematic optical properties and quench-cooled gave patterns similar to those in Figure 4a. The X-ray pattern shows a series of layer lines (at least 10) with continuous but fluctuating intensity on each layer line which represented the molecular chain transform, together with a strong, but diffuse, equatorial diffraction signal. The pattern is typical of an oriented nematic LCP and confirms the interpretation of the optical and DSC results.

The layer line series index as orders of 1.63 nm, which is slightly less than the theoretical value for the fully extended repeating unit of 1.71 nm, and the diffuse interchain peak (equatorial diffraction spot in Figure 4a) centers on a spacing of 0.44 nm, similar to other rigid-rod-like aromatic polymers.[13] When the oriented sample was annealed at or near T_m, various degrees of crystallinity developed. The annealing time and annealing temperature were important. Generally, the higher the temperature, the shorter the time necessary to obtain a particular degree of crystallinity, but if the annealing temperature was too high, orientation was lost, making interpretation considerably more difficult.

Figure 4b shows an example of induced crystallinity. Discrete diffraction signals occur on the layer lines, row lines can be seen, and the strong, diffuse interchain equatorial diffraction signal segregates into a series of individual reflections. The spacings of the prominent diffraction signals are listed in Table III. The layer line spacing is the same as that found in the oriented nematic state, indicating that there is little, if any, change in the basic conformation in the chain as the polymer crystallizes.

The value of 0.44 nm for the interchain distance is interesting because it is only a little greater than the value of 0.428 nm reported previously for other aromatic polymers[13] and indicates that there is a predominance of face-to-face interaction of the ribbonlike chains. This observation infers partial restriction in the *localized* azimuthal rotation about the chain axis of groups of chains. In other words, this result is an indication of localized biaxiality which suggests the formation of a higher order nematic phase. This pattern of behavior seems appropriate for ribbonlike molecules, whereas the Friedelian classification focuses on rodlike entities and a simpler description of nematics. Strictly speaking, however, biaxiality is an optical phenomenon and would be appropriate if the chains in the whole sample had a preference for a particular azimuthal orientation. This arrangement is not the case in our samples where the preference of azimuthal orientation is localized to molecular dimensions. The term sanidic[14] has also been introduced as a possible

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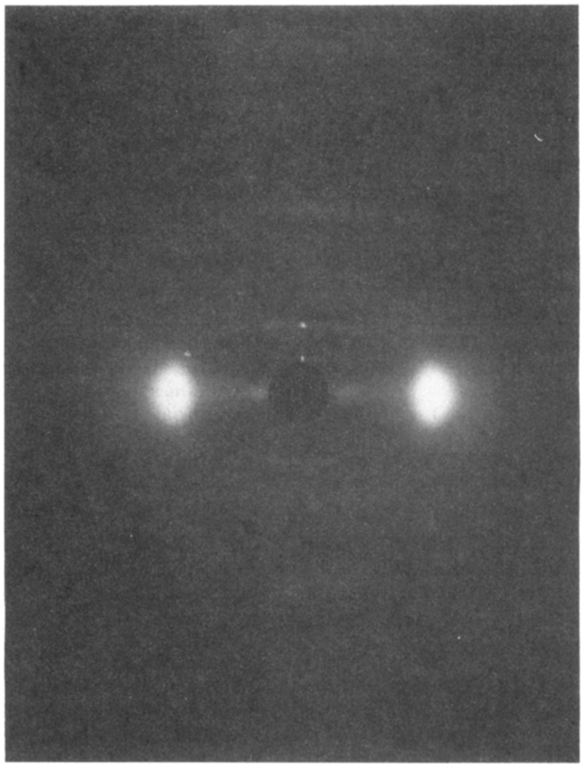

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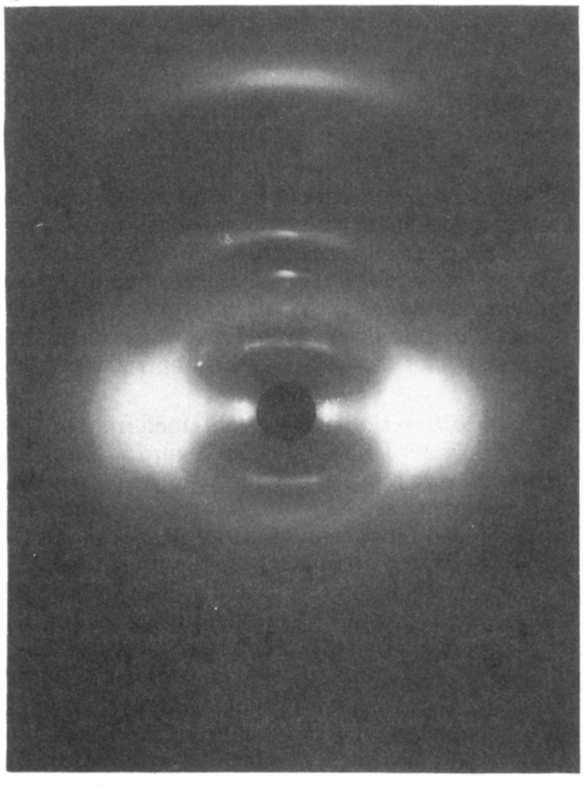

Figure 4. Oriented X-ray diffraction patterns from polymer I-1, orientation direction vertical: (a) obtained from a fiber drawn from the nematic fluid and quench-cooled in cold water (b) obtained by annealing the sample at elevated temperature. Prominent spacings are listed in Table III.

Table III
X-ray Diffraction Spacings (nm)

polymer I-1	spacing	description
Figure 4a	1.63	layer line spacing
(nematic)	0.44	equator, strong and diffuse
Figure 4b	1.63	layer line spacing
(crystalline part)	1.31	equatorial and row line
	1.11	equatorial and row line
	0.53	equatorial and row line
	0.45	equatorial
	0.41	equatorial
polymer I-2	spacing	description
Figure 5a	1.87	layer line spacing
(nematic)	0.45	equator, strong and diffuse
Figure 5b	1.87	layer line spacing
(crystalline part)	1.24	equatorial
	0.85	equatorial
	0.48	equatorial
	0.45	equatorial
	0.41	equatorial
polymer II-3	spacing	description
Figure 6a	1.83	nonperiodic layer line
(nematic)	0.88	nonperiodic layer line
	0.59	nonperiodic layer line
	0.44	nonperiodic layer line
	0.32	nonperiodic layer line
	0.20	nonperiodic layer line
	0.46	equatorial, strong and diffuse
Figure 6b (crystalline part)	nonperiodic layer lines as in Figure 6a	
	1.33	equatorial
	0.66	equatorial
	0.51	equatorial
	0.43	equatorial

nomenclature; see also ref 15 and 16 with regard to biaxiality.

One can envisage a spectrum of localized azimuthal restriction in polymers with ribbonlike geometries, especially as a function of temperature. A parameter(s), like an order parameter for orientation, is needed to estimate both the magnitude and extent of the azimuthal restriction. We believe it inappropriate to use the term biaxial nematic unless the extent of biaxiality enters the optical wavelength range.

The X-ray diffraction patterns obtained from oriented samples of polymer I-2 are shown in Figure 5. They show features similar to those of polymer I-1; the pattern from the nematic phase is shown in Figure 5a and the crystallinity induced by annealing can be seen in Figure 5b. The average interchain spacing in the nematic state is 0.45 nm, and the layer line spacing is 1.87 nm. The calculated length of a MPBP + NDA unit is ~2 nm, but the trans-linkage geometry of the NDA unit (see Figure 2) will cause a reduction, and so the value of 1.87 nm is again commensurate with an extended conformation. On annealing, a proportion of the sample crystallized and the resulting crystalline diffraction peaks overlaid the diminishing proportion of the nematic diffraction pattern. The spacings of the prominent row lines of the crystalline phase are listed in Table III.

Series II Homopolymers. We were unable to obtain X-ray diffraction patterns from oriented samples of polymers II-1 and II-2 although a nematic phase was observed using polarized optical microscopy. Most likely, the more symmetric nature of the DPBP units causes a fast crystallization. This was reported by one of us earlier as the formation of unoriented, highly crystalline X-ray patterns for these samples.[10] A specialized experimental arrangement would be necessary to obtain oriented samples of these polymers by suppressing the rate of crystallization of the *oriented* nematic state. The bulk unoriented nematic state is accessible, as observed with optical microscopy, but we have found that any induced orientation introduces too fast a rate of crystallization.

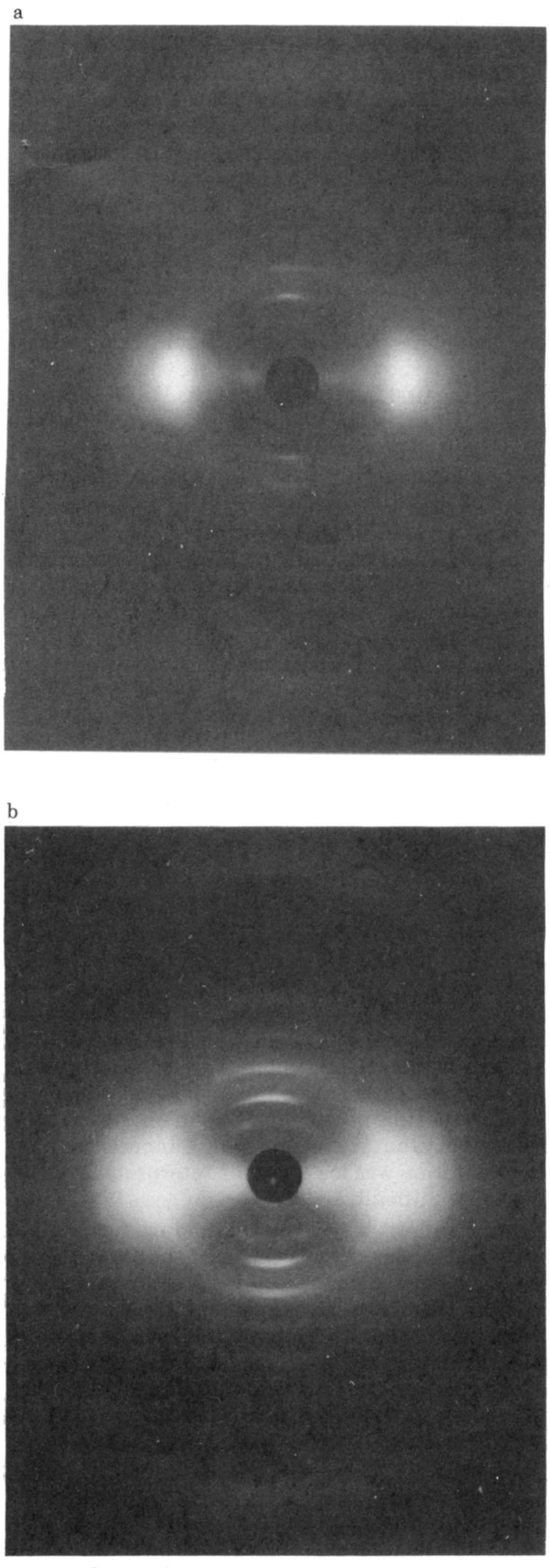

Figure 5. Oriented X-ray diffraction patterns from polymer I-2, orientation direction vertical: (a) obtained from a fiber drawn from the nematic fluid; (b) obtained on annealing at elevated temperature. Prominent spacings are listed in Table III.

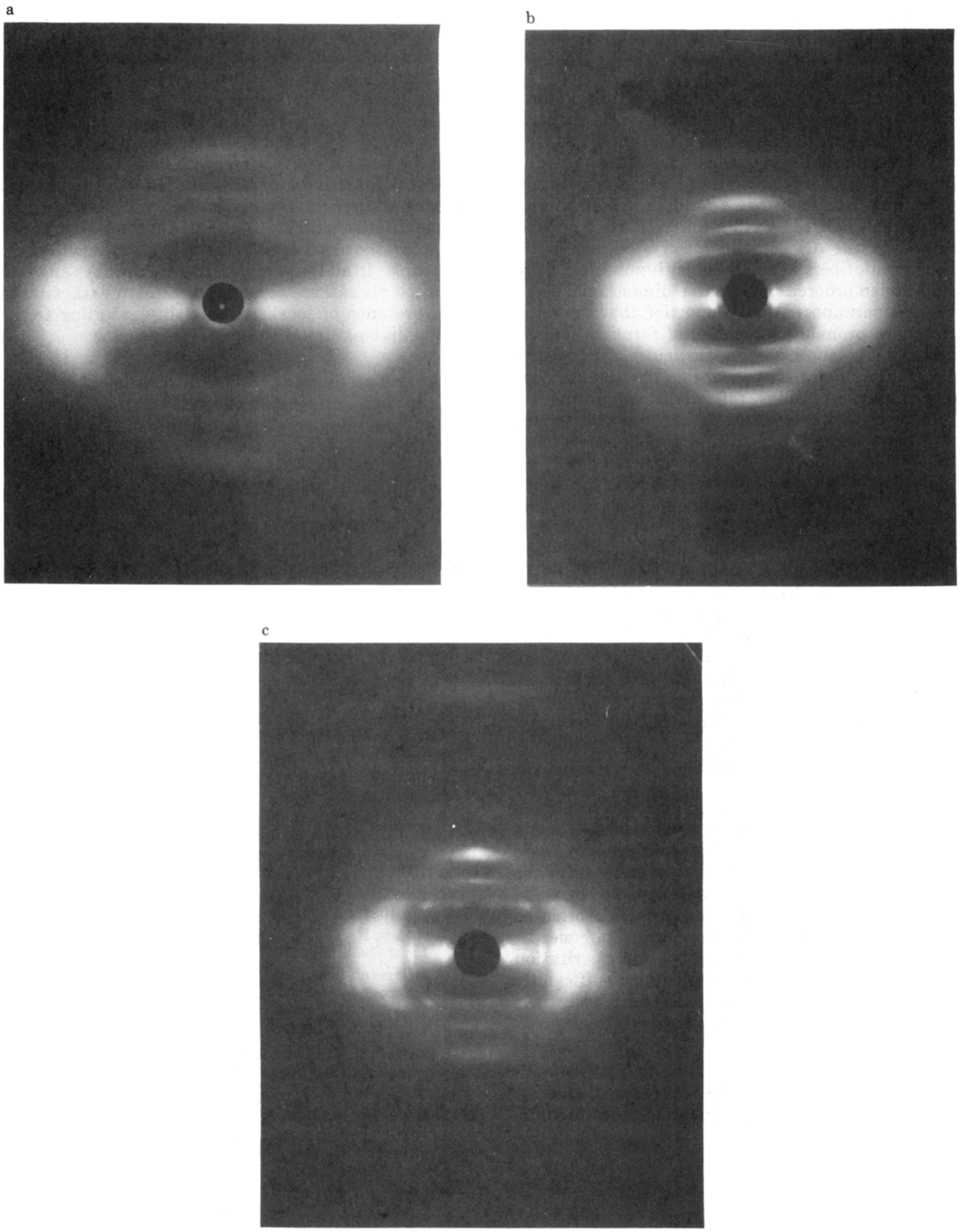

Figure 6. Oriented X-ray diffraction patterns from the copolymer containing DPBP (polymer II-3), orientation direction vertical: (a) pattern obtained from a fiber drawn from the nematic fluid and quench-cooled in cold water; (b) pattern obtained after annealing for 24 h at 280 °C; (c) same sample as (b) annealed for 4 days at 280 °C. Prominent spacings are listed in Table III; note also that the layer line spacings are nonperiodic.

Even in unoriented samples no X-ray patterns of a nematic state could be obtained.[10]

Copolymers. As mentioned above the copolymer of MPBP (polymer I-3) did not exhibit a melting endotherm, and DSC experiments indicate it was totally amorphous. We were also unable to obtain any oriented X-ray diffraction patterns. In contrast, the copolymer with DPBP (polymer II-3) had an observable melting endotherm and oriented X-ray diffraction patterns were obtained as shown in Figure 6. The oriented nematic phase is shown in Figure 6a. A series of broad layer line streaks are seen in this figure which do not index on a lattice, together with a very diffuse and strong equatorial signal centered at 0.46 nm. The polymer sample diffracted rather weakly, and a longer than usual exposure was needed to record the X-ray pattern. The photograph bears a resemblance to the X-ray patterns reported for other random copolymers of LCPs.[17]

The randomness of the copolymer structure does not allow the usual Bragg lattice reflections to occur, but a nonperiodic pattern was observed which emanates from the convolution of the Fourier transforms of the individual monomers.[18] The X-ray pattern of the copolymers confirms that the copolymer has a random substitution of DPBP + TA and DPBP + NDA units. Parts b and c of Figure 6 show the development of crystallinity as the oriented nematic fibers were subsequently annealed. Parts of the specimen ordered into a three-dimensional array, which was superimposed on a proportion that was reluctant, or more probably incapable, of forming a three-dimensional crystal. Note, in particular, the relative broadness of the remaining layer-line-like streaks compared with the crystalline reflections supporting the nonperiodic origin of this feature of the composite pattern. The spacings of the prominent diffraction signals are listed in Table III.

The series I MPBP homopolymers exhibit a nematic phase prior to isotropization. Although levels of crystallinity can be induced by annealing the nematic phase at elevated temperature, only a proportion of these polymers crystallized to form small crystalline domains (to ~0.25 nm resolution). Most likely, the random orientation of the phenyl substituent groups on successive biphenol units caused this suppression of crystallization. This behavior is consistent with the *frustrated chain packing* concept proposed and described by Griffin and Cox[1] for thermotropic, aromatic polyesters. The extra degree of randomness, or disorder, introduced in the copolymer (polymer I-3) of the MPBP series suppresses the level of crystallinity to below a reasonable level, so in that case the *frustration* level was too high.

The results show that the incorporation of the more symmetrical DPBP units in the series II homopolymers encouraged much faster rates of crystallization. These high rates made the process of fiber drawing from the nematic fluid difficult, and we were unable, in these investigations, to obtain a structural insight of the oriented nematic state. In the case of the copolymer (polymer II-3), the extra randomness introduced by copolymerization apparently slowed the rate of crystallization sufficiently to allow the oriented nematic state to be obtained by fiber drawing and to be examined using X-ray diffraction.

Conclusions

The results of the investigations from these two series of thermotropic, aromatic polymers provide useful information regarding the relationship between the structures of aromatic polymers and their ability to form the liquid crystal state. The results highlight in particular the subtle interaction of the disorder caused by randomly placed substituent groups (series I) with the additional disorder by random copolymerization. If the polymer is too regular, as in polymers II-1 and II-2, then the crystallization rates are too fast for conversion of the nematic state into the form of drawn fibers. The results highlight the frustrated chain packing concepts in a qualitative way but also provide a quantitative estimate of the levels of frustration necessary to access the nematic state in a useful way, such as by fiber drawing. In all the samples that did produce an oriented nematic phase there were structural features that indicated the presence of localized biaxiality resulting from the ribbonlike nature of these polymer chains.

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