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## Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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### X Ray Diffraction Study of Thermotropic Liquid-Crystalline Main-Chain Polyesters and Diester Model Compounds

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## X-RAY DIFFRACTION STUDY OF THERMOTROPIC LIQUID-CRYSTALLINE MAIN-CHAIN POLYESTERS AND DIESTER MODEL COMPOUNDS

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**Abstract** Two nematic liquid-crystalline polyesters were examined by x-ray diffraction following quenching from the nematic temperature in a magnetic field of 15 tesla. It was not possible to quench an aligned nematic glass; instead a polycrystalline phase showing some preferred orientation or an unoriented nematic glass was produced. Fibers drawn from the nematic melts yielded monodomain nematic diffraction patterns with one resembling that of a fiber (crystalline) photograph while the other showed good nematic alignment which could be enhanced slightly by annealing. A series of Siamese-twin diester model compounds also were examined at their respective nematic temperatures in a magnetic field of 2,000 gauss as well as in their crystalline phase at room temperature. All displayed well-aligned nematic monodomains above the crystallization point.

### INTRODUCTION

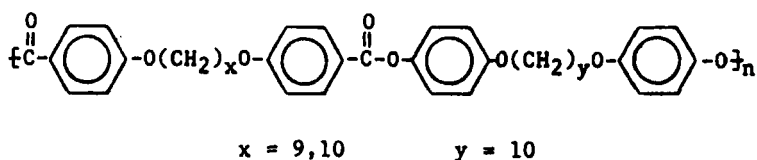
The interest in liquid crystalline polymers is increasing as more compounds are being synthesized and studied.<sup>1,2</sup> Two types of thermotropic liquid crystalline polymers

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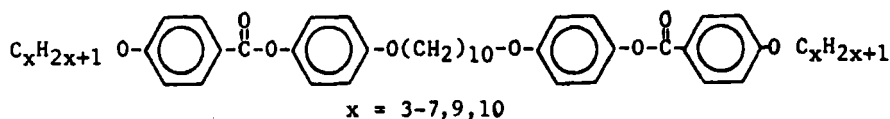
can be distinguished: Those in which the mesogenic units form a part of the polymer chain and those in which the mesogenic group is attached to the side of the polymer chain. The current study is limited to the analysis of main-chain liquid crystalline polymers and some of their model compounds.

Two nematic liquid crystalline polyesters<sup>3,4</sup> having the general structure



were examined by x-ray diffraction following quenching from the nematic temperature range<sup>4</sup> in a magnetic field of 15 tesla. Fibers also were drawn from the nematic melt in order to compare the degree of alignment induced magnetically and mechanically.

A series of Siamese-twin diesters<sup>5</sup> having the general structure



were examined in their respective nematic ranges<sup>5</sup> in a magnetic field of 2,000 gauss.

Powder photographs were recorded at room temperature in order to study the crystalline phases of these dimers and polymers. An attempt to fit likely molecular models inside the unit cells is currently in progress.

### EXPERIMENTAL

Thermal analysis (DSC) was used to check the transition temperatures (Table I) which agreed, within experimental error, with those reported previously<sup>4</sup> for the two polymers.

TABLE I. Transition temperatures for solid  $\rightarrow$  nematic (K-N) and nematic  $\rightarrow$  isotropic (N-I) transitions of polymers.

x	y	$T_{K-N}(^{\circ}\text{C})$	$T_{N-I}(^{\circ}\text{C})$
9	10	179.5	202.5
10	10	185.0	212.0

The polymers were packed inside glass capillaries having circular cross sections (1mm diam.). Several capillaries were placed inside a special furnace and heated to about 5-15°C above the nematic transitions ( $T_{K-N}$  in Table I) in a superconducting magnet (field strength 15 tesla) at the Francis Bitter National Magnet Laboratory at M.I.T. and, following several hours at that temperature, quenched by liquid nitrogen. Fibers were drawn directly from the nematic melts. All of these samples were examined using a Buerger precession camera equipped with a bent-crystal monochromator using Cu or Fe K $\alpha$  radiations, before

and after further annealing for several hours at 15-20°C below their nematic transitions.

The dimers were examined similarly to the polymers except that the camera was equipped with a magnet ( $H=0.2$  T) and a sample heating arrangement.<sup>6</sup> Photographs typical of nematic mesomorphs were obtained in the nematic range of temperatures, Table II.<sup>5</sup>

TABLE II. Transition temperatures for solid  $\rightarrow$  nematic (K-N) and nematic  $\rightarrow$  isotropic (N-I) transitions of dimers.

x	$T_{K-N}(^{\circ}\text{C})$	$T_{N-I}(^{\circ}\text{C})$
3	138.7	160.1
4	128.7	159.9
5	122.8	149.0
6	120.3	149.5
7	124.0	143.0
9	118.2	133.0
10	122.7	136.2

### RESULTS AND DISCUSSION

Cell constants listed in Tables III and IV were deduced from powder-photograph data of the dimers and polymers, respectively, in their crystalline phases using Ito's method.<sup>7</sup> Table III also lists the molecular length  $L$  of the dimer calculated in its most extended conformation using standard bond lengths, angles, and Van der Waals radii. Note that the  $a$  axis agrees closely with the length of the dimer  $L$  suggesting that the molecules are aligned parallel to this cell edge. By comparison, there is no clearly evident relationship in Table IV between the

TABLE III. Cell constants of dimers.

x	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\beta(^{\circ})$	$L(\text{\AA})$
3	40.82	10.50	7.80	90.8	42.57
4	44.79	11.04	7.62	94.7	44.67
5	44.63	10.43	7.40	99.2	46.78
6	50.10	10.66	7.33	93.7	48.88
7	51.40	10.31	7.43	93.9	50.99
9	45.30	10.10	7.50	92.7	55.20
10	57.82	10.31	7.59	91.6	57.31

length of the repeat unit in the polymer L and the cell constants in Table IV although  $a \approx L/2$ . Similarly, the anomalous value of  $a = 45.30 \text{ \AA}$  for the dimer with  $x = 9$  is not understood at present.

TABLE IV. Cell constants of polymers

x	y	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\beta(^{\circ})$	$L(\text{\AA})$
9	10	21.88	27.70	9.36	93.8	43.46
10	10	21.84	28.90	9.63	91.8	44.52

Two x-ray diffraction photographs of nematic dimers are shown in Fig. 1. All such photographs indicated well aligned nematic monodomains. Only the shortest chain ( $x=3$ ) and the longest chain ( $x=10$ ) are shown here. Note that an inner reflection appears along the meridian as the chain length increases, showing up first at  $x=5$  and growing in intensity as  $x$  increases, becoming most prominent at  $x=9$  and 10. The measured spacings for the equatorial and meridional reflections are listed in Table V.

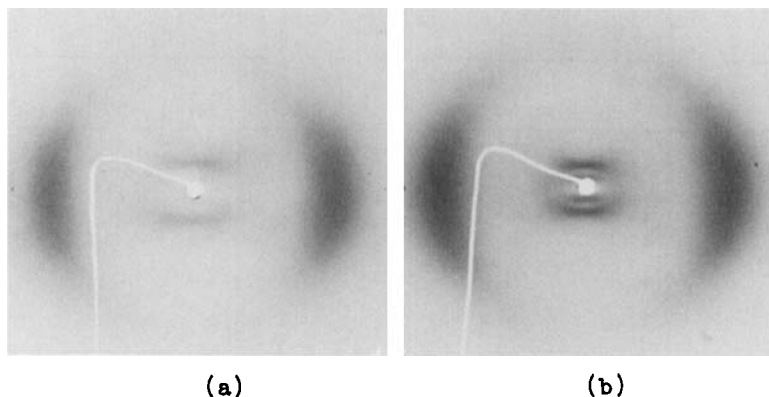


FIGURE 1. Normal-beam x-ray diffraction photographs of magnetically aligned dimers recorded with crystal monochromatized Fe K $\alpha$  radiation. (a) Dimer 3; (b) Dimer 10.

The meridional reflections in Fig. 1 record the average repeat distances parallel to the magnetic field direction and the molecular axes. The spacing increasing from 22.14 to 27.63 Å as  $x$  changes from 3 to 10 can be explained by two possible molecular models. If the dimers bend over to form "hairpins", the average repeat distance

TABLE V. Measured spacings of nematic dimers (Å).

$x$	equatorial	meridional	
3	4.68	22.14	-
4	4.66	22.92	-
5	4.64	23.61	?
6	4.69	24.35	58.29
7	4.65	25.22	61.52
9	4.57	27.05	60.56
10	4.61	27.63	63.02



becomes slightly less than  $L/2$  as the dimers align parallel to each other in the magnetic field. Because the monomers constituting these "Siamese-twin" dimers have virtually identical electron density distributions in the extended form of the dimers, however, a parallel alignment of extended dimers would appear to be indistinguishable by x-ray diffraction from a parallel array of monomers, each of length  $L/2$ . Thus x-ray data alone could not distinguish which array was actually present. The emergence of an inner reflection, however, suggests that the extended dimer is the correct model in the present case.

To understand the fact that the second meridional reflection in Table V is produced by a repeat distance that is longer than the length  $L$  of the dimer in its most extended configuration (Table III) it is necessary to posit a pairing of adjacent dimers in which the polar groups (positively charged carbon) at the centers of the aromatic portions of one dimer associate with negatively charged oxygens in the ether groups (at the ends of the aromatic portions) of an adjacent dimer, Fig. 2, so that the dimer "pair" has a length equal to  $L$  plus part of one end chain. For each pair of dimers, there should be a total of four such interactions. These dimer pairings are further stabilized by chain-chain interactions as the chain ends are extended, enabling overlaps of the adjacent end chains. The first hint of the formation of such pairs is evident in x-ray photographs when  $x=5$ . The relative intensity of the inner reflection grows progressively as  $x$  increases above  $x=6$ , becoming equivalent to the outer meridional reflection when  $x=10$ . Since such pairings are transitory in a liquid crystal, the relative intensities of the two meridional reflections indicate that the probability of such pairing

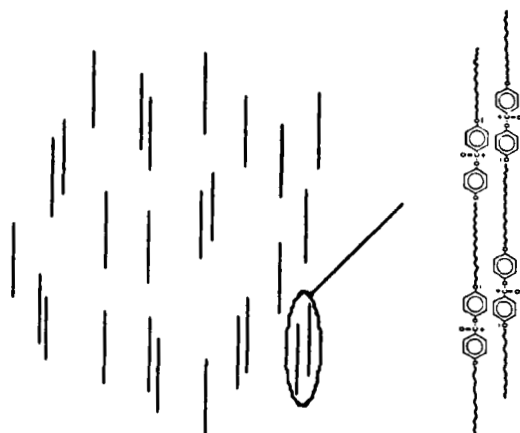
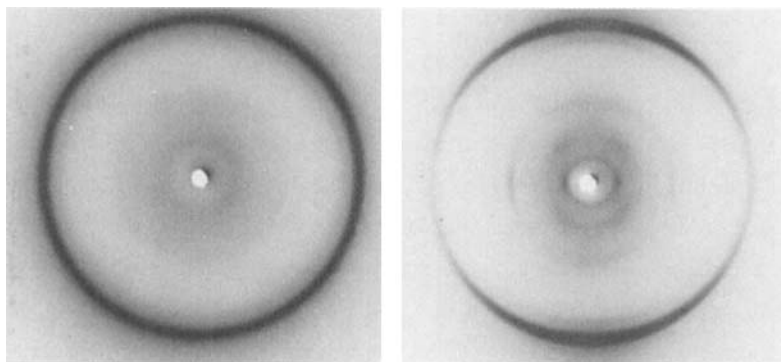


FIGURE 2. Structure of nematic dimers.

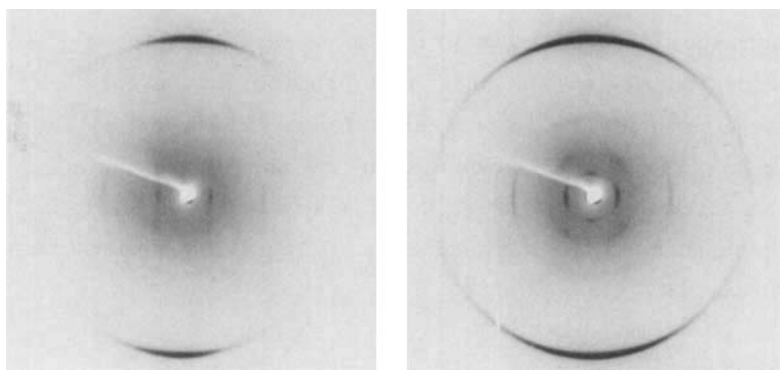
is highest when the lengths of the aliphatic chains at the ends of the dimers are longest. Thus two repeat distances along the magnetic field direction (meridian in Fig. 1) predominate, one proportional to  $L/2$  for the isolated dimers and the other proportional to the length of extended dimer 'pairs' (Fig. 2).

The x-ray diffraction photographs of the polymers following quenching from the nematic temperature in a magnetic field of 15 tesla are shown in Fig. 3. As can be seen therein, it is not possible to obtain a magnetically aligned monodomain in this way. Figure 3(a) shows that an unaligned nematic phase can be quenched in the 9,10 polyester whereas Fig. 3(b) is that of a polycrystalline aggregate displaying preferred orientation of the crystallites.

When fibers are mechanically drawn from the nematic melts of these polymers, Fig. 4(a) shows that a nematic



(a) (b)  
 FIGURE 3. Normal-beam x-ray diffraction photographs of polymers (filtered Cu K $\alpha$ ). (a) 9,10 polyester; (b) 10,10 polyester.



(a) (b)  
 FIGURE 4. Normal-beam x-ray diffraction photographs of drawn fibers (crystal monochromatized Fe K $\alpha$ ). (a) 9,10 polyester; (b) 10,10 polyester.

monodomain tends to form in the 9,10 polyester whereas the 10,10 polyester crystallizes rapidly, Fig. 4(b), to yield a fiber photograph not unlike the preferred orientation visible in Fig. 3(b). These trends could be enhanced (diffraction patterns sharpened) slightly by annealing the fibers for 12 hrs. at 10-20°C below the nematic transition temperatures (Table I). A further interpretation of these photographs should await completion of current attempts to determine the molecular arrays present in the crystalline phases of these polymers. It is quite probable, however, that the tendency to segregate the aliphatic and aromatic segments in adjacent molecules, already evident in the dimers, is responsible for the strong tendency to crystallization in the polymers.

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