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Liquid Crystals

Polymers with Terminally Cyanobiphenyl-Substituted Side Chains
A Re-Entrant Polymorphism N S_A N_{Re}

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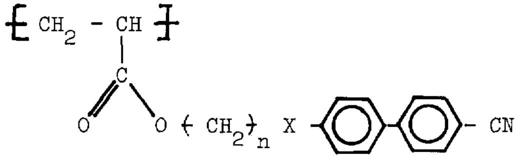
Summary

Two acrylate side chain polymers in which the mesogenic moiety is a 4'-cyano-biphenyl-4-yl group have been synthesized and characterized by d.s.c., optical microscopy and X-ray diffraction. If the mesogenic moiety is linked to the polymer backbone by a $-O-CO-(CH_2)_5$ group, the resultant polymer is nematic. For a $-O(CH_2)_6$ group, the unusual NS_AN_{re} sequence is observed. X-ray diffraction has shown that the S_A phase has a partially bilayer structure : the molecules are arranged in an antiparallel, overlapping interdigitated structure with a layer spacing of about 1.4 times the length of the side chains. Monolayer fluctuations are also observed in this S_A phase.

Introduction

Certain liquid crystals with a terminal cyano group exhibit the following complex sequence of phase transitions on cooling : isotropic → nematic → smectic A → nematic(1-3). The second nematic phase, which occurs at a lower temperature than the smectic phase is called the "re-entrant" nematic phase. The highly polar cyano group attached to one end of the molecules results in strong antiparallel near-neighbour correlations. As a consequence, the S_A phases of these materials often consist of "bilayers", the molecules arranged in an antiparallel overlapping interdigitated structure with a layer spacing of about 1.3 - 1.6 times the molecular length. As the temperature is varied, the molecular packing is slightly altered and the resulting subtle changes in the bilayer structure appear to be responsible for the occurrence of the reentrant nematic phase. This prompted us to synthesize the polymers of the general structure:



where n = 2-6 and X = -O-, -CO-O- (4). In the present paper we report on the synthesis and characterization of two polymers in which n = 6 and X = -O- (PO 6) and n = 5 and X = -CO-O- (PCO-O 5) respectively. The different mesomorphic phases were identified both by optical microscopy and X-ray diffraction.

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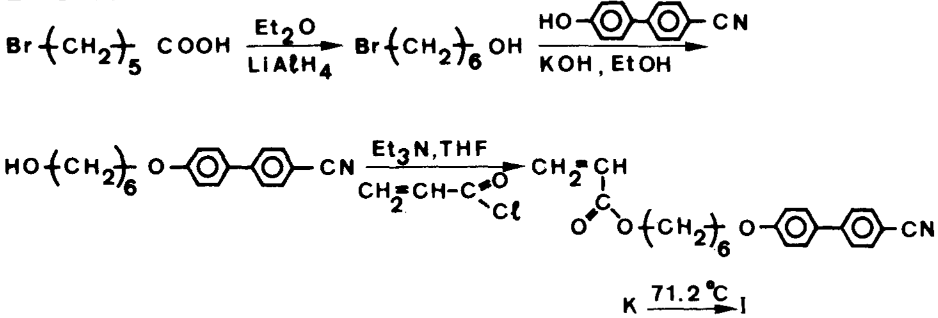
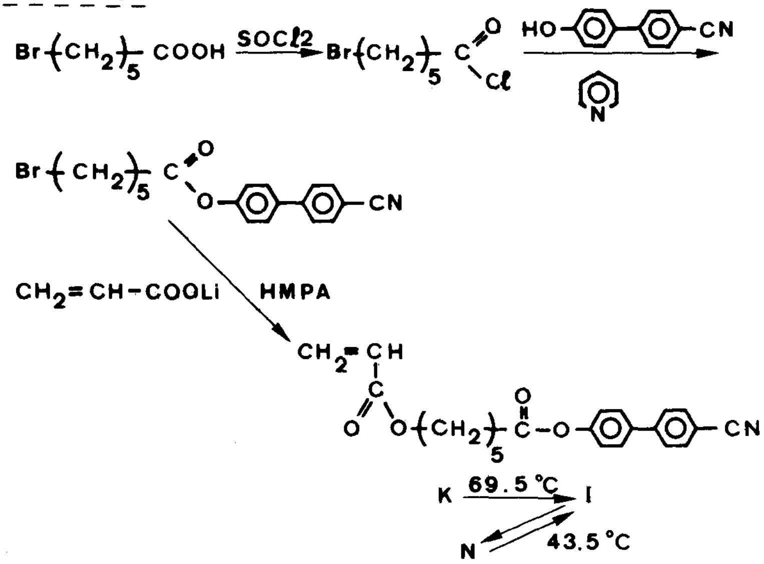
Experimental

The polymerizable monomers were prepared by standard methods as described in schemes 1 and 2. The structures of all compounds and synthetic intermediates were confirmed by infrared spectroscopy and ^{1}H n.m.r. (4).

Scheme 1



Scheme 2



The polymers PO 6 and PCO-O 5 were prepared by free radical polymerization in solution with the use of azo-bis-isobutyronitrile as initiator at 60°C (Table I). Purification was accomplished by two re-precipitations into methanol after which the polymers were dried in vacuo.

Table I - Polymerization of monomers

Monomer		Solvent	$\frac{[\text{Monomer}]}{[\text{AIBN}]}$	Reaction time (h)	Conversion %
X	n				
O	6	C_6H_5Cl	152	15	62
CO-O	5	THF	25	7	63

Molecular heterogeneities and weight average molecular weights were determined by G.P.C. using universal calibration (Table II)

Table II - Properties of polymers

Polymer	$\overline{M_w}$	$\overline{M_w}/\overline{M_n}$	Transition Temperature (°C)				
			Tg	N_{re}	S_{A_d}	N	I
PO 6	62,000	3.4	.32	.80	.124.5	.132	.
PCO-O 5	7,300	1.3	.30			.115	.

Thermal transitions in polymers were measured by means of a differential thermal analyser Du Pont 1090.

The transition characteristics were surveyed with a polarizing microscope (Olympus BHA-P) equipped with a Mettler FP5 hot stage.

X-ray diffraction patterns were recorded on flat films using Ni-filtered CuK_α radiation. The samples were contained in 1 mm Lindemann glass tubes which were mounted in an electrically heated oven, the temperature of which was controlled within 0.2 K using a platinum resistor as sensing element. Well oriented samples of PO 6 and PCO-O 5 were produced by drawing fibres out of the mesophase with a pair of tweezers.

Results and Discussion

The synthesized polymers are essentially non crystalline in character. Their transition temperatures are listed in Table II. Polarized light photomicrograph depicting the appearance of the mesophase of polymer PCO-O 5 show readily identifiable nematic threaded texture (Figure 1). The X-ray patterns obtained with unoriented samples in a temperature range 30-115°C are consistent with a nematic structure. At large diffraction angles they present a diffuse, broad ring which is related to the lateral interferences between the mesogenic cores and points out the lack of lateral periodic order. It corresponds to an average intermolecular spacing of approximately 4.3-4.4 Å. A second diffuse ring is seen at small angles. It corresponds to a distance of about 13 Å, which is approximately half the length of the side chains in their most extended conformation. The anisotropy shown in the X-ray patterns of stretching-oriented fibres clearly demonstrates the nematic structure of the mesophase. The outer ring is split into two crescents symmetrical about the equatorial plane which is perpendicular to the stretching direction : the mesogenic moieties are parallel to the fibre axis. At

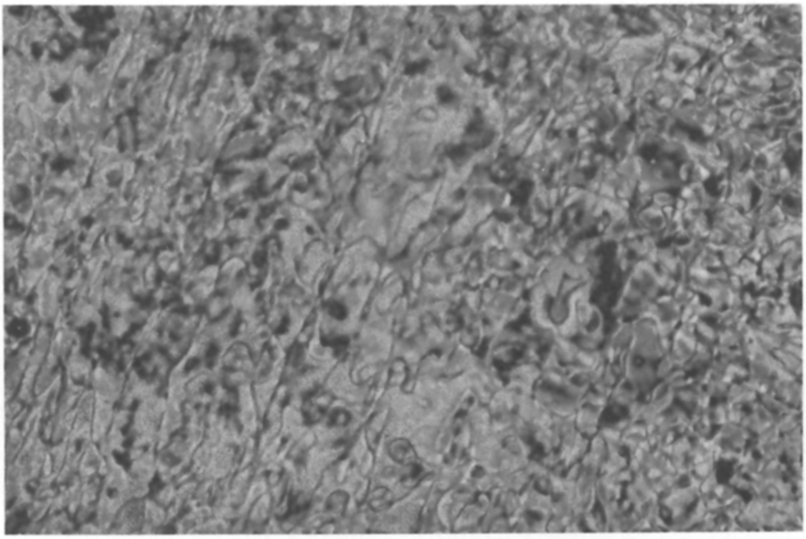


Figure 1 - Threaded texture of polymer CO-O 5 (crossed polarizers)

low angles, along the meridian line one can see diffuse lines whose periodicity corresponds to the length of the side chains.

On cooling from the isotropic state, the high-temperature mesophase of polymer PO 6 appears at 130°C as a Schlieren texture (Figure 2). From the observation of disclinations of strength ± 1/2 this mesophase can be unambiguously identified as a nematic phase (5). Further reduction in temperature produces at about 123-122°C a striated or myelinic texture with typical transition bars (Figure 3). Such a texture generally appears in the temperature range immediately below N/S_A or N/S_C transition (5). This texture changes on standing for some time into the stable simple focal conic and fan-shaped textures (Figure 4) which are consistent with a S_A phase. There is also some indication that polymer PO 6 forms a re-entrant nematic phase upon cooling from the S_A state : below 78°C either a Schlieren texture is progressively restored or a paramorphic fan shaped texture is formed (Figure 5). Recently, Kostromin et al. (6) reported for this polymer the same sequence of phase transitions : nematic → smectic A → re-entrant nematic.

Both nematic and smectic A phases give at large diffraction angles a diffuse ring which arises essentially from the intermolecular spacings perpendicular to the long axes of the side chains. The average intermolecular spacing varies from 4.6 Å at 120°C to 4.25 Å at room temperature which is consistent with most results reported so far.

At small diffraction angles the X-ray patterns of nematic and smectic A phases differ in their aspect. X-ray patterns of smectic A phase are characterized by a sharp ring and a weak second order reflection corresponding to a layer thickness of 33.6 Å, which is considerably in excess of the length of the side chains in their most extended conformation ($L \simeq 24$-25 Å). Thus,

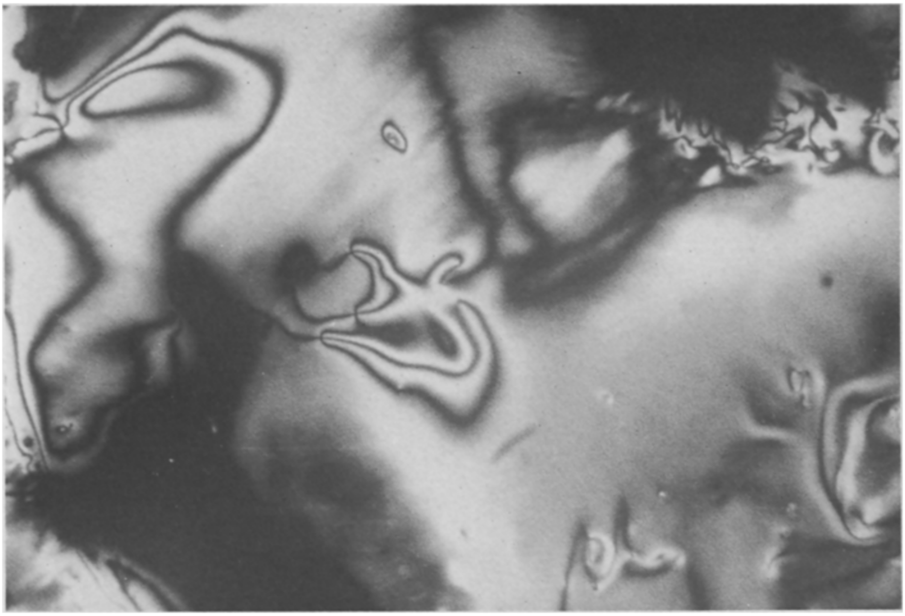


Figure 2 - Photomicrograph of high-temperature nematic phase from polymer PO 6 (crossed polarizers).

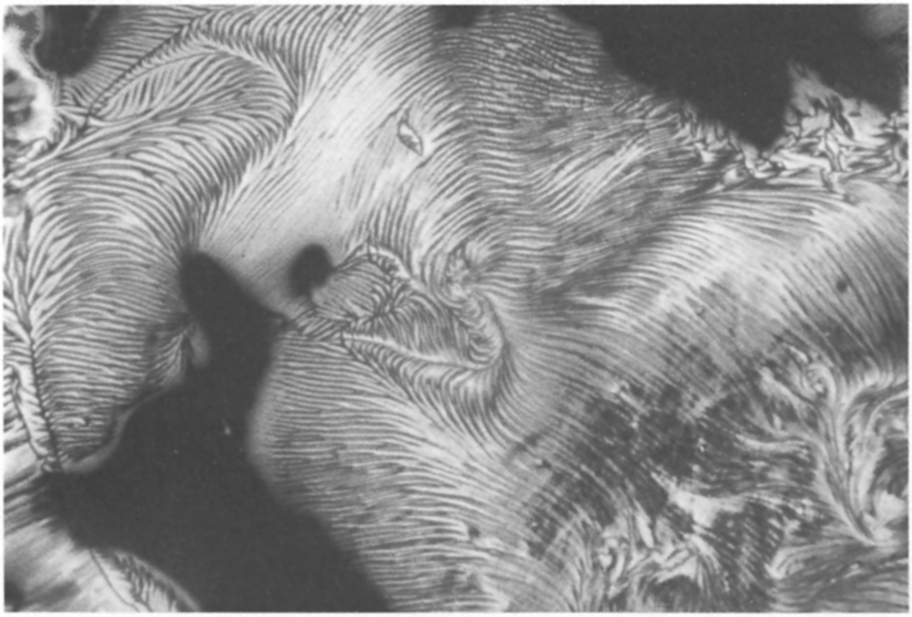


Figure 3 - The transition Nematic/Smectic A. (crossed polarizers).

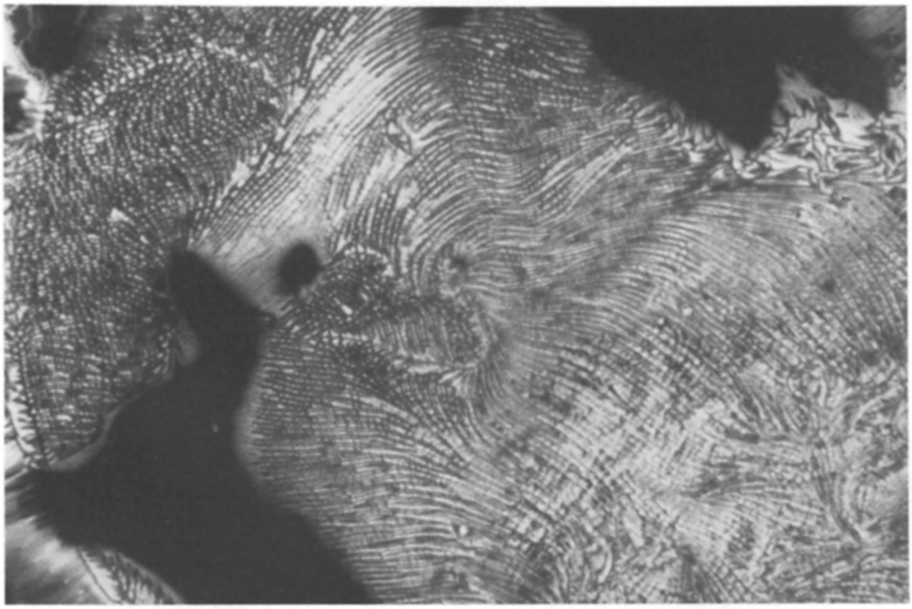


Figure 4 - Photomicrograph of smectic A phase from polymer PO 6 (crossed polarizers).

Figure 5 - Photomicrograph of re-entrant nematic phase from polymer PO 6 (crossed polarizers).

as observed for certain low molar mass cyano derivatives which exhibit S_{A_d} phases (7-9) some form of bilayer structure is implied, in which the molecules are partially overlapped. In addition, a diffuse ring can also be seen. It corresponds to a distance of 12.5 Å, which is approximately half the length of the side chains. This diffuse ring is related to local monolayer fluctuations away from the mean smectic organization. The variation of the modulation wave vectors as a function of temperature is shown in Figure 6.

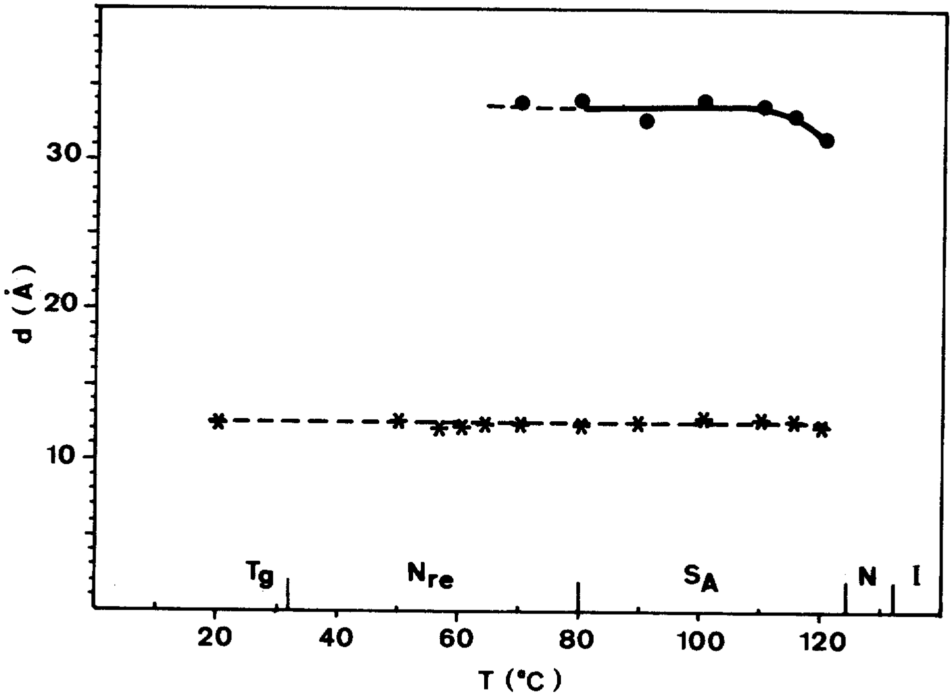


Figure 6 - Thermal evolution of the modulation wavevectors in polymer PO 6.
(---- diffuse rings)

In the temperature range 80-60°C, the X-ray patterns of re-entrant nematic are characterized by two diffuse rings at 33-34 Å and 12-12.6 Å, respectively. Therefore partially bilayer and monolayer fluctuations are present simultaneously. Below 60°C, however, only monolayer fluctuations remain.

Dielectric studies on the same polymer have shown that the activation energy for the flip-flop rotation of the side chains is higher for the nematic phases than for the S_A phase (10). Moreover, the activation energy turns out to be much higher for the re-entrant nematic than for the normal nematic, proving that the molecular associations in these two phases are significantly different. It is to be noted that a somewhat similar type of behavior has been reported for some low molar mass compounds with a terminal cyano group that exhibit re-entrant nematic phase (11, 12).

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