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Thermotropic liquid-crystalline polymers. XXVII. Reentrant nematic phase of side chain liquid-crystalline polymers and their optical properties

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Thermotropic liquid-crystalline polymers†

XXVII. Reentrant nematic phase of side chain liquid-crystalline polymers and their optical properties

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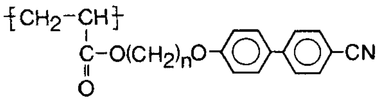
The phase diagrams of side chain liquid-crystalline acrylic copolymers with cyanobiphenyl mesogenic groups are described. These copolymers are shown to form a reentrant nematic phase. The main regularities of the reentrant behaviour of polymer systems are studied. Certain peculiarities of the electric field induced orientation phenomena are discussed.

1. Introduction

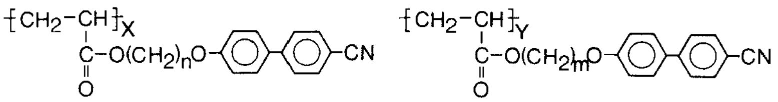
The side chain liquid-crystalline polymers have been found to exhibit thermotropic polymorphism [1]. The reentrant nematic phase known for low molar mass liquid crystals [2–5] has been discovered first for polymers in nitrile containing side chain liquid-crystalline polymers [6]. Later reentrant polymorphism has been described in other polymers [7, 8]. Here we discuss the main peculiarities of reentrant polymorphism for macromolecules of homopolymers and copolymers having the structure

Homopolymers



(1) $n = 6$. (2) $n = 5$. (3) $n = 4$.

Copolymers



(4) $n = 6$. $m = 4$. (5) $n = 6$. $m = 5$. (6) $n = 4$. $m = 5$.

2. Experimental

The polymers were prepared as previously described [9, 10]. The copolymer composition was considered to be equal to that of the monomer mixture. The initial unfractioned polymer 1 with the phase transitions (N_R 83°C S_A 118°C N 132°C I)

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† Part XXVI: KOSTROMIN S. G., SHIBAEV V. P., and PLATÉ, N. A., 1987, *Liq. Crystals*, **2**, 195.

was fractioned from a 1,2-dichloroethane/methanol mixture. The ratio of weight—average molar mass ($\bar{M}_w$) to number average molar mass ($\bar{M}_n$) of fractions, determined by the combined G.P.C.—light scattering technique (Waters-401; Milton Ray, USA) was 1·19–1·35. The viscosities of polymer solutions were measured at 30°C using a Ubbelohde viscometer. The phase diagrams were obtained for polymer samples with the $[\eta] > 0{\cdot}07$ ($\bar{P}_w > 100$–150) using D.S.C. and polarizing microscopy. The optical measurements were made with the aid of a polarizing microscope equipped with a heating stage. X-ray diffraction patterns were recorded using a flat camera with nickel-filtered CuK_α radiation. For electro-optical measurements the usual electrooptical cell [11] was used.

3. Results and discussion

3.1. *Reentrant polymorphism in polymers*

The influence of the molar mass of the polymers studied on their transition temperatures is of considerable interest. The increase in the degree of polymerization ($\bar{P}_w$), as shown in figure 1 leads to some narrowing of nematic region whereas the temperature range of the smectic phase increases slightly. In the sample with $\bar{P}_w > 100$–150 ($[\eta] > 0{\cdot}07$) the transition temperatures depend very slightly on the length of the polymer chain. These temperatures are listed in table 1.

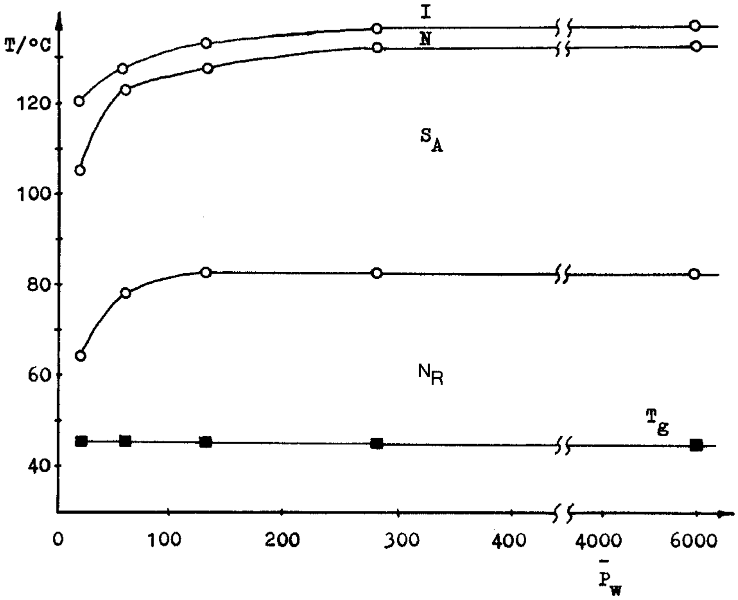
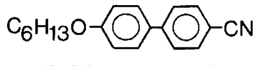


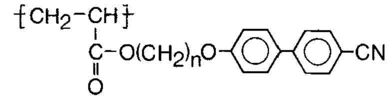
Figure 1. Phases, phase transitions (○) and glass transition temperatures (■) of polymer fractions with different $\bar{P}_w$.

In order to compare the reentrant phenomena in low and high molar mass liquid crystals the phase diagram of the unfractioned sample of polymer 1 and 4-*n*-hexyloxy-4′-cyanobiphenyl (6OCB) its low molar mass analog, with the formulae



has been studied. With increasing 6OCB content the smectic A range is decreased (see figure 2). For compositions containing more than 25 mole per cent of 6OCB the

Table 1. Mesophase types and phase transitions of homopolymers.



n	Polymer	T_g/°C	Mesophase types and phase transitions
6	1	35	N_R 84°C S_A 133°C N 136°C I
5	2	40	S_A 128°C I
4	3	45	N 124°C I

N_R, N, S_A, I—reentrant nematic, nematic, smectic A and isotropic phases respectively.

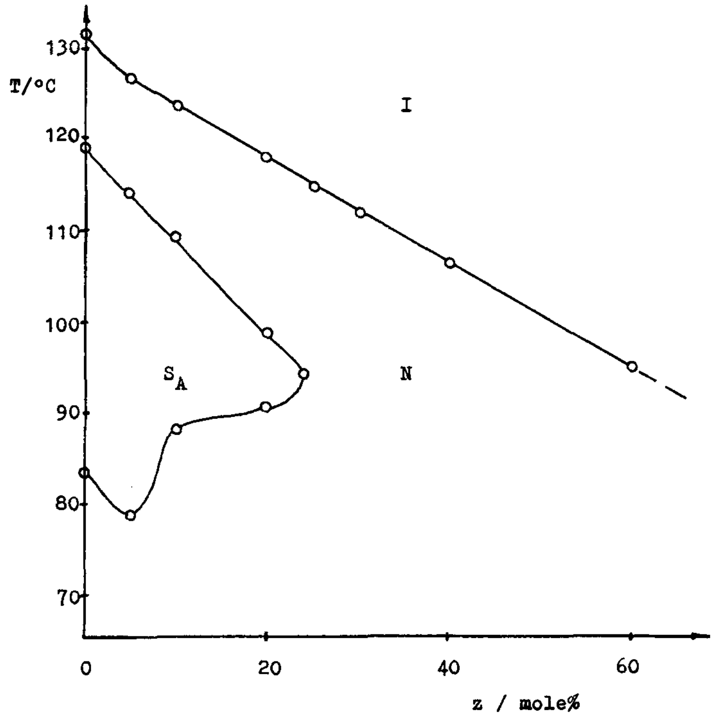


Figure 2. Phase diagram for the mixture of polymer 1 (non-fractionated sample) with the low molar mass liquid crystal 4-*n*-hexyloxy-4′-cyanobiphenyl. *Z*, the 6OCB content of the mixture.

smectic A phase disappears and the continuous transition from the high temperature nematic to reentrant phase is clearly seen. Such a phase diagram is identical to that for mixtures of low molar mass liquid crystals forming a reentrant nematic phase [12]. But at concentrations higher than 60 per cent of 6OCB phase separation takes place and complete miscibility in the whole concentration range may be achieved by using the copolymerization approach.

Two groups of copolymers were synthesized accordingly to the two types of mesogenic units being nematogenic for $m = 4$ (copolymer 4) and smectogenic for $m = 5$ (copolymer 5) incorporated into the macromolecules of polymer 1. Let us compare their phase behaviour (see figures 3, 4) with that of the polymer—6OCB

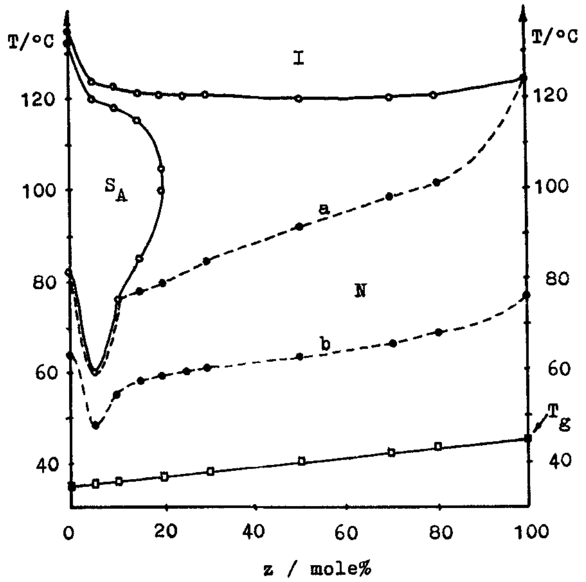


Figure 3. Phases, phase transitions (○), glass transition temperatures (□) and the temperature for the appearance of the birefringence (T_{tr}) in homeotropically oriented samples of copolymer 4 in an electric field at 0 (*a*) and 200 V (*b*). $Z = (y/(x + y))100$.

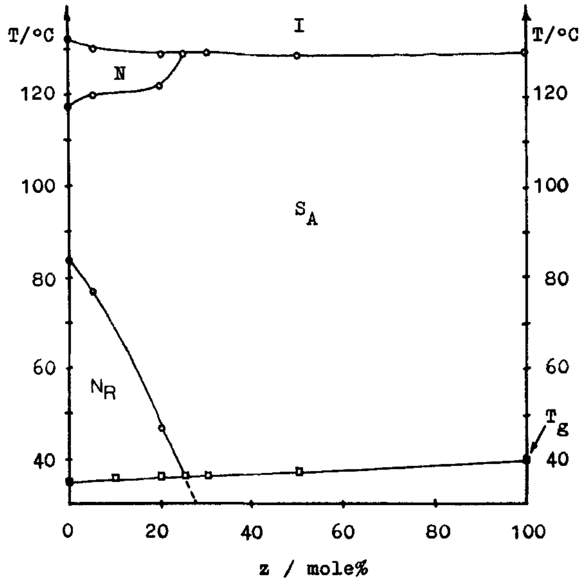


Figure 4. Phases, phase transitions (○) and glass transition temperatures (□) of copolymer 5. $Z = (y/(x + y))100$.

mixture mentioned (see figure 2). The copolymers 4 (figure 3) containing less than 50% of the monomer units with $m = 4$ behave like a mixture (see figure 2): the S_A region disappears in the same concentration range of nematogenic units as for 6OCB. Above 20 per cent of 3 units content the S_A phase is absent and a broad range of the nematic phase is seen.

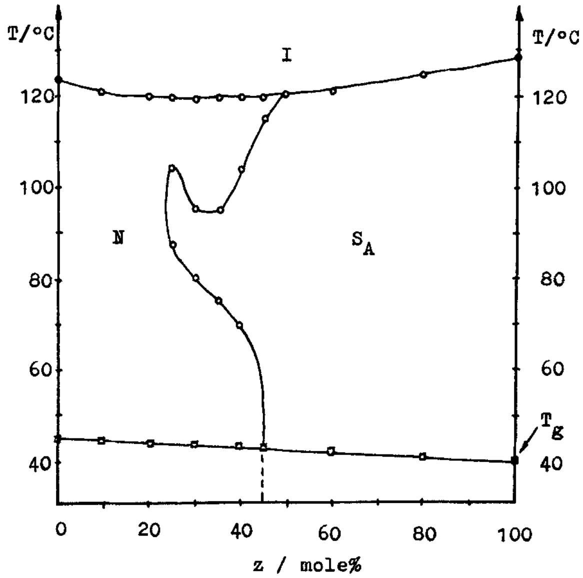


Figure 5. Phases, phase transitions (○) and glass transition temperatures (□) of copolymer 6. $Z = (y/(x + y))100$.

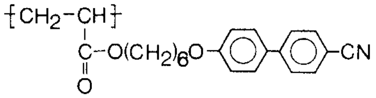
In contrast to such systems in copolymer 5 with smectogenic units ($m = 5$) the smectic phase prevails (see figure 4). With the incorporation of more than 20 mole per cent smectogenic units in polymer 1 the N_R phase disappears. However the latter may be induced in smectic polymer 2 by the incorporation of nematogenic units, such as 3. The reentrant nematic phase is absent in homopolymers 2 and 3 but exists in the corresponding copolymer 6 containing 60–80 mole per cent of nematogenic units (see figure 5).

Thus by varying the composition and structure of the copolymers units not only can we increase or decrease the temperature range of the reentrant phase but we can also induce reentrant polymorphism in side chain liquid-crystalline polymers which do not exhibit reentrant behaviour alone.

3.2. *Optical properties of samples oriented with an electric field*

All of the acrylic homo- and copolymers with cyanobiphenyl containing side chain groups can be easily oriented in an a.c. electric field [13]. In accord with their positive dielectric anisotropy ($\Delta\varepsilon > 0$) the side chains are aligned parallel to the field forming an optically uniaxial (homeotropic) texture. This is characterized by zero transmittance between crossed polarizers. In smectic polymers this texture may be frozen in the solid state by cooling below the glass transition temperature, T_g. Both in nematic polymers and in polymers with a reentrant nematic phase the freezing of the homeotropic texture in the glassy state of a polymer is not possible [14, 15]. On cooling oriented films of a nematic polymer a sharp increase of the optical transmittance is observed corresponding to the appearance of birefringent regions. This texture transformation proceeds in a very narrow temperature range and is reversible in the electric field on changing the temperature. This leads us to suggest that the texture change is a structural transition with the transition temperature (T_{tr}) depending

Table 2. The molecular characteristics of fractions of homopolymer 1.



Number of fraction	$\bar{P}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w$	$[\eta]$/dl g^{-1}
1	6500	–	2×10^6	0·40
2	380	1·32	$1{\cdot}33 \times 10^5$	0·12
3	130	1·19	$4{\cdot}63 \times 10^4$	0·08
4	60	1·15	$2{\cdot}21 \times 10^4$	0·06
5	30	1·39	$8{\cdot}53 \times 10^3$	0·04

$[\eta]$, intrinsic viscosities of polymer solutions.

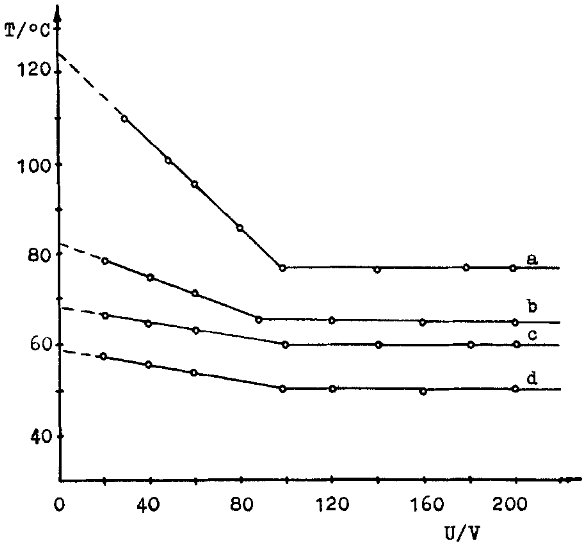


Figure 6. The temperature for the appearance of the birefringence as a function of electric field strength for oriented sample 3 (*a*), 1 (*b*), 5 with $z = 40$ per cent (*c*), 4 with $z = 5$ per cent (*d*) (sample thickness—10 μm).

strongly on the electric field intensity. The values of T_{tr} are shifted to a low temperature range with an increase in the voltage. This is clearly seen for all the systems studied (see figure 6).

For polymers with a reentrant nematic phase the extrapolation of the initial linear part of the curve $T_{tr} = f(U)$ to zero voltage gives the transition temperature values coinciding with the temperature of the reentrant nematic–smectic A transition. In the nematic homopolymer 3 the same procedure results in the clearing temperature being obtained. The optical behaviour of the homeotropically oriented copolymers 4, 5, and 6 may be controlled both by a voltage change and by variation of copolymer composition. For example in copolymer 4 T_{tr} is increased by an increase of the fraction of nematic ($m = 4$) monomer units. This is clearly seen from the dotted lines in the phase diagram (see figure 3) showing the shift in T_{tr} for zero ($U = 0$ (dotted line a)) and high voltage field ($U = 200$ V (dotted line b)).

The nature of this transition is not yet clear. On the one hand the change in the optical properties of the polymer oriented by the electric field may be induced by a conformational change of the polymer backbone resulting in a distortion of the macroscopic orientation. On the other hand it can be considered as a transition from a uniaxial nematic structure to a biaxial one although this is unusual for thermotropic liquid crystals. The possibility of a sharp increase of the elastic constants just above T_g must be also taken into account. In this case the increase of the threshold voltage as well as of the voltage necessary to stabilize the homeotropically oriented structure may be observed. To make a clear choice between these possibilities is the subject of further experiments.

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