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E. B. Barmatov Corresponding author; M. V. Barmatova

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Induction of the chiral nematic phase in hydrogen-bonded blends of smectic copolymers and low molar mass dopant

E. B. BARMATOV* and M. V. BARMATOVA
Chemistry Department, Moscow State University, 119899 Moscow, Russia

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A new approach for the preparation of chiral nematic materials is described. The induction of a chiral nematic phase in hydrogen-bonded blends of smectic comb-shaped LC copolymers containing alkyloxy-4-oxybenzoic acid fragments with a low molar mass chiral dopant (a derivative of pyridine) was observed.

1. Introduction

The covalent attachment of chiral molecules as side chains of comb-shaped polymers provides a well known and traditional method for the preparation of chiral nematic phases (N*) in polymeric systems. This approach involves copolymerization of two monomers where one co-monomer is nematogenic (and its homopolymer shows the nematic phase), while the second co-monomer contains asymmetric carbon atoms, which are responsible for the development of a supramolecular twisted structure by the copolymer.

An alternative approach to achieving the N* phase involves the preparation of blends based on nematic polymers and low molecular mass chiral dopants. The phase compatibility of blends may be improved by the formation of hydrogen bonds between the low molecular mass chiral additive (derivatives of pyridine, carboxylic acid or stilbazole) and a polymer matrix containing carboxylic groups [1, 2].

To obtain the N* phase via the formation of hydrogen bonds, the polymer matrix should meet the following main criteria. First, the polymer should exhibit the nematic phase; second, it should contain an appreciably high fraction of carboxylic acid groups (30–50 mol%), which are necessary for the formation of hydrogen bonds with the pyridine fragment of the chiral additive. The optimal structure is provided by functional LC copolymers containing both mesogenic groups responsible for the formation of an LC phase and carboxylic groups, which are capable of hydrogen bonding.

We note that both approaches are based on using nematic polymer matrices but their choice is rather limited as in most cases, LC polymers tend to exhibit smectic phases. This trend is pronounced for functional LC copolymers because their acidic monomer units are capable of forming smectic phases. As a rule, copolymers containing more than 25–30 mol% of acidic units form a SmA phase [3]. Therefore, copolymers with a relatively high fraction of carboxylic groups appear not to be useful in the development of chiral nematic materials by this approach.

As we show for the first time here, however, a chiral nematic phase may in fact be exhibited in the hydrogen-bonded blends of smectic polymers and low molecular mass chiral dopants. The importance of this finding is primarily related to the application of smectic polymer matrices in the preparation of N* materials.

In this work, we studied the phase behaviour of blends of smectic functionalized LC copolymers containing a high fractional content of carboxylic acid groups (41 and 48 mol%) with low molecular mass pyridine-containing chiral dopants. The chemical formulae of the smectic LC copolymers P1, P2 and the chiral dopant PyChol are shown in the Scheme.

2. Experimental

Monomers M1, A6, A9 and the dopant PyChol were synthesized according to procedures described earlier [3].

M1: ^{1}H NMR ($CDCl_3$): δ 7.97 (d, 2H, Ph, $J = 8.85$ Hz); 7.67 (d, 2H, Ph, $J = 8.55$ Hz); 7.62 (d, 2H, Ph, $J = 8.51$ Hz); 7.51 (d, 2H, Ph, $J = 8.81$ Hz); 6.35 (dd, 1H, $C\underline{H}_2$–CH–, $J = 1.65$, 17.65 Hz); 6.12 (dd, 1H, CH_2–C$\underline{H}$–, $J = 10.3$, 17.31 Hz); 5.81 (dd, 1H, $C\underline{H}_2$–CH–, $J = 1.65$, 10.3 Hz); 4.21 (t, 2H, O–$C\underline{H}_2$); 4.02 (t, 2H, –$C\underline{H}_2$–O); 1.89 (4H, –$C\underline{H}_2$–$C\underline{H}_2$–).

A6: ^{1}H NMR ($CDCl_3$): δ 7.95 (d, 2H, Ph, $J = 8.82$ Hz); 6.93 (d, 2H, Ph, $J = 8.82$ Hz); 6.35 (dd, 1H, $C\underline{H}_2$–CH–, $J = 1.65$, 17.65 Hz); 6.12 (dd, 1H,

*Author for correspondence;
e-mail: barmatov@genebee.msu.su

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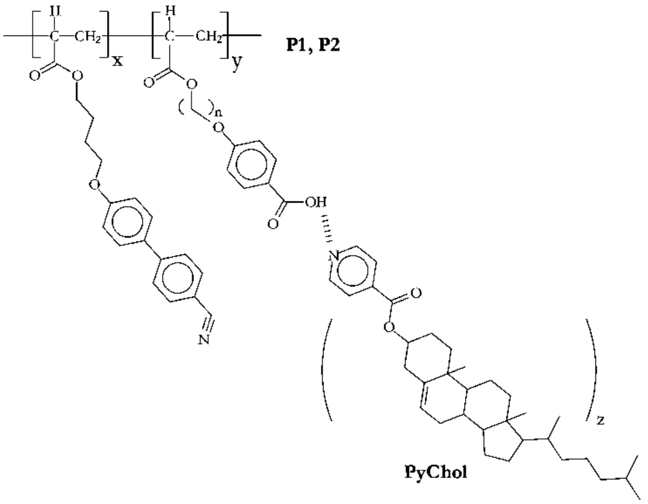

Scheme. Blends I: copolymer P1 ($n=6$, $y=48$ mol%) and dopant PyChol ($z=2$–19 mol%). Blends II: copolymer P2 ($n=9$; $y=41$ mol%) and dopant PyChol ($z=2$–23 mol%).

CH_2–C$\underline{H}$–, $J=10.3$, 17.31 Hz); 5.81 (dd, 1H, C$\underline{H}_2$–CH–, $J=1.65$, 10.3 Hz); 4.3 (t, 2H, O–C$\underline{H}_2$–); 4.12 (t, 2H, –C$\underline{H}_2$–O); 1.3–1.9 (8H, –C$\underline{H}_2$–).

A9: ^{1}H NMR ($CDCl_3$): δ 7.95 (d, 2H, Ph, $J=8.82$ Hz); 6.93 (d, 2H, Ph, $J=8.82$ Hz); 6.35 (dd, 1H, C$\underline{H}_2$–CH–, $J=1.65$, 17.65 Hz); 6.12 (dd, 1H, CH_2–C$\underline{H}$–, $J=10.3$, 17.31 Hz); 5.81 (dd, 1H, C$\underline{H}_2$–CH–, $J=1.65$, 10.3 Hz); 4.31 (t, 2H, O–C$\underline{H}_2$–); 4.12 (t, 2H, –C$\underline{H}_2$–O); 1.2–1.9 (14H, –C$\underline{H}_2$–).

PyChol: ^{1}H NMR ($CDCl_3$): δ 8.76 (d, 2H, Ph), 7.84 (d, 2H, Ph), 5.42 (d, 1H), 4.85 (m, 1H), 2.45 (d, 2H), 1.99–0.68 (overlapping peaks from cholesterol groups –CH_2–and –CH_3).

Copolymers were obtained by free radical copolymerization of M1, A6 and A9 monomers in absolute THF; AIBN was used as the initiator. The copolymers were purified by repeated precipitation from THF solutions with hexane. Phase transitions in the LC copolymers were studied by differential scanning calorimetry (DSC) at a scanning rate of 10 K min^{-1}. All experiments were performed using a Mettler FP90 thermal analyser and a Zeiss polarizing microscope.

Relative molecular masses (M_w and M_n) of the polymers were determined by gel permeation chromatography (GPC) using a GPC-2 Waters instrument equipped with an LC-100 column oven and a Data Modul-370 data station. Measurements were made by using a UV detector, with THF as solvent (1 ml min^{-1}, 25°C), a set of PL columns of 100, 500 and 10^3 Å, and a calibration plot constructed with polystyrene standards.

Selective light reflection of the chiral polymers was studied with a Hitachi U-3400 UV-Vis-IR spectrometer equipped with a Mettler FP-80 hot stage. The 20 µm thick samples were sandwiched between two flat glass plates, and the thickness of the test samples was determined by Teflon spacers. A planar texture was obtained by shear deformation of the samples, which were heated to temperatures above the glass transition temperature. Prior to testing, the samples were annealed for 20–40 min.

Table. Molecular mass characteristics and phase behaviour of the functionalized LC copolymers P1, and P2 and of the chiral dopant PyChol.

Sample	M_w	M_w/M_n	Phase behaviour/°C
P1	4000	1.34	Glass 45 SmA 116 I
P2	5700	1.60	Glass 36 SmA 112 I
PyChol			Cr 122 N 173 I

3. Results and discussion

Two smectic copolymers, P1 and P2, containing 41 and 48 mol% of 4-oxybenzoic acid were used for preparation of the hydrogen-bonded blends. The synthesis of the LC copolymers was described in [3]. The table shows the molecular mass characteristics and phase behaviour of P1, P2 and the chiral dopant PyChol. The blends of copolymers P1 and P2 with PyChol were prepared by dissolution of the components in THF and vacuum drying at 90°C.

Figure 1 shows the phase diagrams of the blends containing 2–24 mol% of PyChol. Both mixtures show similar phase diagrams. As the content of the chiral dopant is increased, the clearing temperature increases by 44 and 18°C for blends I and II, respectively. One may also observe a slight increase in the glass transition temperatures of the blends by 6–8°C. When the content of the dopant in the blends varies from 4 to 12 mol%, in addition to a SmA phase, a chiral nematic phase is formed.

The formation of the chiral nematic phase is confirmed on the basis of polarizing optical microscopy studies as well as by the presence of selective refection of light in the NIR spectral range, which is discussed in detail later. Blends with dopant contents 4–11 mol% form an oily streak texture shown in figure 2. Figure 2 also shows the transmission spectra of the samples with planar orientation. Selective light reflection half-width changes from 50 to 80 nm. The efficiency of the reflection depends on temperature and is about 40–45% on average. Figure 3 shows the temperature dependence of the maximum selective light reflection wavelength. On cooling, the selective reflection peak shifts to longer wavelengths, and this may be associated with the growth of smectic fluctuations. A further decrease in temperature leads to the destruction

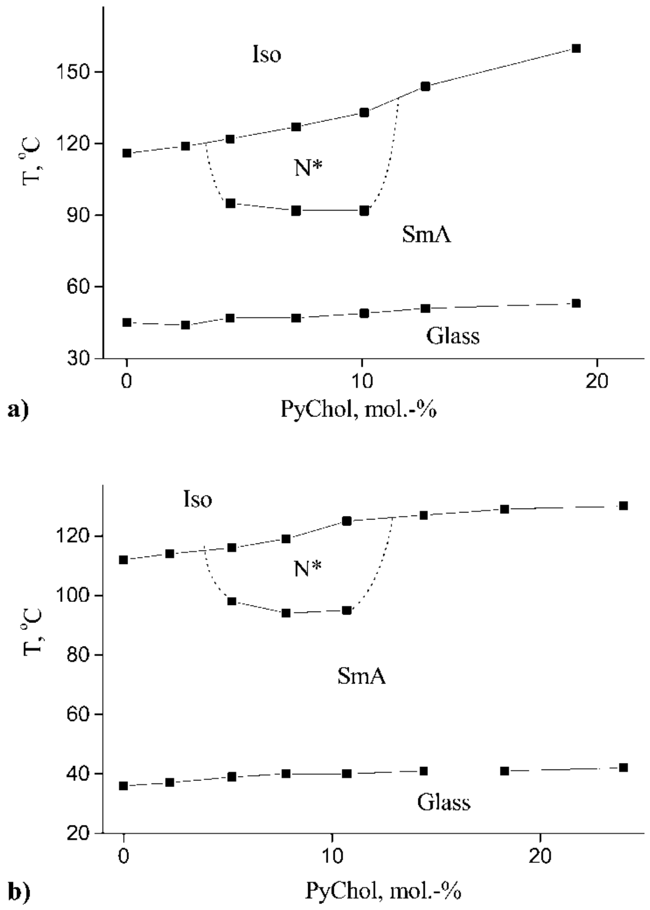

Figure 1. Phase diagram of (*a*) blends I and (*b*) blends II.

of the planar N* texture due to the appearance of the SmA phase.

To calculate the helical twisting power β, the reciprocal selective light reflection wavelength $\lambda_{\max}$ (at temperature $\tau = T/T_C = 0.97$) was plotted against the molar fraction X of the chiral component, see figure 4.

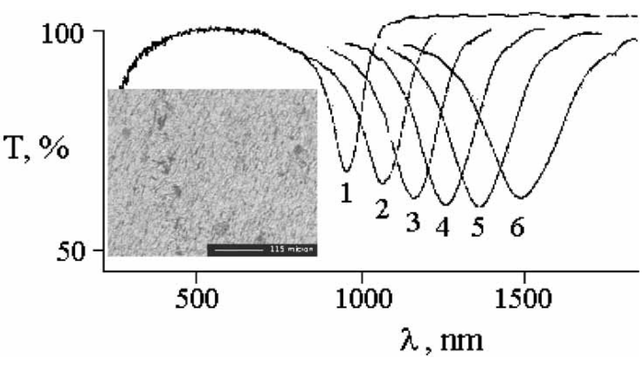

Figure 2. Transmittance spectra for blends II containing 10.7 mol% of chiral dopant at a temperature of (1) 120, (2) 115, (3) 110, (4) 105, (5) 102, and (6) 100°C, and the optical texture for the N* phase.

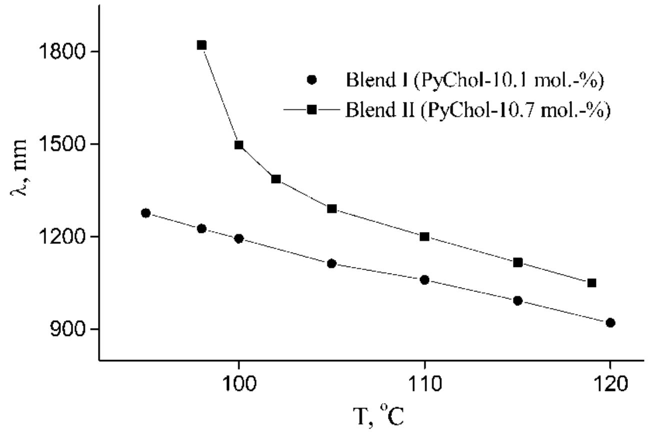

Figure 3. Temperature dependence of the maximum selective light reflection wavelength for blend I and II.

The helical twisting power was calculated approximating experimental data through the following function: $1/\lambda_{\max} = \beta X/(1 + BX)$, where B is the parameter that characterizes the deviation from linearity. Parameter B may be associated with defects in the mesophase due to the bulky dopant, or with the presence of elements of smectic order. The apparent helical twisting power of the pyridine-containing dopant PyChol is equal to $17.8 \pm 2.1\,\mu\mathrm{m}^{-1}$, with $B = 7.8 \pm 1.9$ for blend I; and $15.2 \pm 2.0\,\mu\mathrm{m}^{-1}$, with $B = 6.5 \pm 1.6$ for blend II. Analysis of our experimental data shows that blend II has a slightly lower value of the helical twisting power than blend I.

The formation of the N* phase in a smectic polymer matrix is related to the specific effect of the pyridine-containing dopant on the structure of the hydrogen-bonded compositions. As we previously reported [3], various compositions of functionalized smectic copolymers with pyridine-containing dopants show two types of phase sequences: SmA–N–I and $\mathrm{SmA_{Re}}$–N–SmA–I. In other words, blends of smectic polymers with

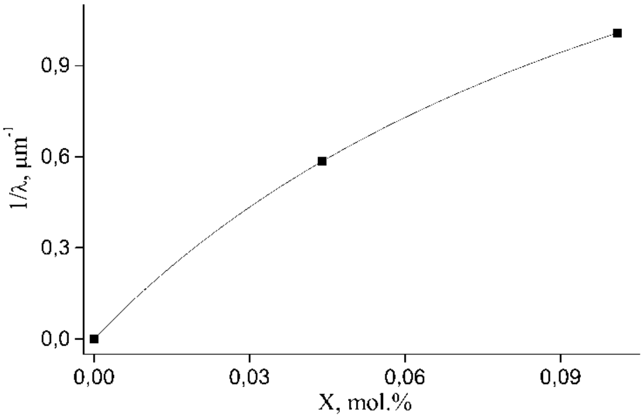

Figure 4. Dependence of $\lambda_{\max}^{-1}$ on the mole fraction of chiral units, X, for blend I.

dopants are able to exhibit the nematic phase. The reason for this phase behaviour was described in detail elsewhere [3, 4]. It was shown that the formation of an extended hydrogen-bonded fragment leads to a change in the smectic packing parameters and to the appearance of defects in the layered structure due to the difference in length of the cyanobiphenyl and hydrogen-bonded mesogenic groups. The increase of these defects in the packing of the side groups results in the destruction of the lamellar structure and the formation of a nematic phase.

Thus, the pyridine-containing dopant PyChol serves a dual function: (i) it disrupts the smectic packing of side group mesogenic units of the functionalized LC copolymer and (ii) 'twists' the resulting nematic phase due to the optically active cholesteric radical. In this work, therefore, the fragment problem associated with the preparation of chiral nematic materials by using smectic polymer matrices has been solved.

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