

The Induced S_A Phase in New Menthyl-Containing CopolymersA. Yu. Bobrovsky,[†] N. I. Boiko,[†] V. P. Shibaev,^{*,†} D. Wolff,[‡] and J. Springer[‡]

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ABSTRACT: A number of the new chiral side-chain menthyl containing copolymers were synthesized. Phase behavior, optical properties, and structures of the synthesized copolymers with different compositions were studied. For the first time a specific mesophase induction in side-chain copolymers, containing nonmesomorphous side groups, was proved to be possible due to the steric correspondence between different side units.

Introduction

Investigations concerning multicomponent blends of liquid crystals and LC copolymers are of considerable importance to understand the processes taking place at the molecular level and to produce mesophases with different degrees of order. Furthermore, varying the ratio between the components in blends or the ratio between the monomer units in copolymer allows one to control in a wide range such practically important parameters such as viscosity, electrooptical and magneto-optical properties, helix pitch (in the case of helical mesophases), etc. This approach makes it possible to prepare LC materials with the desired properties.^{1–3} However, at the present time, there is a number of systems, whose mixing behavior is far from ideal: these are the blends with so-called specific noncovalent intermolecular interactions.

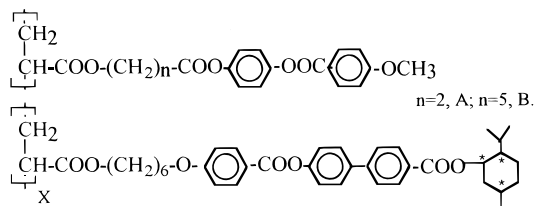
The presence of hydrogen bonds, donor and acceptor interactions,^{4–9} and strong dipole–dipole interactions often leads to the development of additional induced mesophases in such systems. The most common case concerns the development of the S_A phase in the blends of nematogens with strong polar, donor–acceptor interactions between the components.^{6–9}

For example, the development of the induced S_A phase proceeds in polymer systems where one comonomer is a donor and another comonomer is an acceptor.¹⁰ The development of the induced S_A phase is also observed for the copolymers and blends of homopolymers in which the initial components are nonmesomorphic.¹¹

However, not only specific intermolecular interactions may be responsible for the formation of “additional” mesophases. For example, Demus et al.^{12–15} studied blended compositions of nematics with liquid crystals bearing bulky and heavily branched terminal groups. Examination of the structural data allows one to conclude that, in such systems, the formation of the induced S_A mesophase is provided by the steric correlation between the different components. Shorter molecules of the nematic “occupy” the space produced by mesogens with two heavily branched aliphatic terminal groups. This arrangement favors the development of a relatively dense layered packing of mesogenic groups in blends.

In this work, we demonstrated the first example of this behavior for the comb-shaped copolymers. The objective of our investigation involves studying the formation of induced phases in the copolymers, in which no additional noncovalent interactions between the different units exist.

In this work, we studied copolymers composed of phenyl benzoate and menthyl-containing chiral units. The menthyl-containing chiral units involve a rigid aromatic fragment and a bulky terminal group, which prevents the development of the LC phase in the corresponding homopolymers:^{16,17}



The choice of phenyl benzoate monomers for copolymers may be rationalized by the following reasoning. Homopolymers of such monomers containing the spacer with five methylene units are known to be nematogenic.^{18–20} At the same time, in this work, we synthesized a phenyl benzoate monomer containing short spacer ($n = 2$), which polymerizes to yield an amorphous homopolymer. Hence, copolymerization of the menthyl-containing monomer with phenyl benzoate monomer will make it possible to reveal the possibility of the formation of more ordered phases in the systems containing units of different chemical nature.

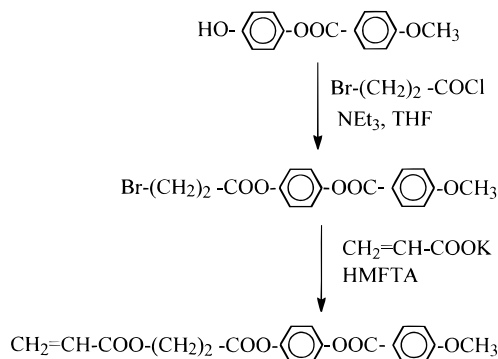
Experimental Section

Materials. 3-Bromopropionic acid (95%, Fluka), acrylic acid (99%, Fluka), 4-hydroxy-4'-methoxybenzoate (98%, Reakhim). 2,2'-Azobisisobutyronitrile (AIBN) was freshly recrystallized from methanol. Benzene used in the radical polymerization was first refluxed over sodium and then distilled under nitrogen.

Synthesis of 1-menthyl-4'-(4-(6-acryloyloxyhexa-1-yl-oxy)benzoyloxy)biphenyl Carboxylate. This monomer was synthesized as previously reported:¹⁶ mp 86 °C. IR (cm^{-1}): 2980, 2890 (CH_2), 1740 (CO in $\text{CH}_2=\text{CHCOOR}$), 1725 (CO in ArCOOMt), 1710 (CO in ArCOOAr), 1640 (C=C), 1600 (C–C in Ar), 1260 (COC). $[\alpha]_D^{22} = -45.0^\circ$; $[M] = -282^\circ$

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Scheme 1. Synthesis of Phenyl Benzoate Monomer with the spacer containing 2 methylene units.


(in CHCl₃). ¹H NMR (CDCl₃, TMS): δ 0.8–2.0 (m, 26H, CH₂=CHCOOCH₂(CH₂)₄CH₂COO–, protons of menthyl group), 4.07 (t, 2H, –CH₂CH₂OAr), 4.20 (t, 2H, –CH₂CH₂OOCCH=CH₂), 4.97 (m, 1H, CHCOO–), 5.82 (dd, 1H, CH₂=CH– trans), 6.13 (dd, 1H, CH₂=CH– cis), 6.41 (dd, 1H, CH₂=CH), 6.99 (d, 2ArH, ortho to OCH₂–), 7.32 (d, 2H, aromatic), 7.65–7.70 (2d, 4H, aromatic), 8.15 (2d, 4ArH, ortho to –COO–).

Synthesis of 4-(6-acryloyloxypropionyloxyphenyl)-4'-methoxy Benzoate. This substance was prepared according to the procedure described elsewhere:¹⁸ mp 83 °C. IR (cm⁻¹): 2985, 2889 (CH₂), 1740 (CO in CH₂=CHCOOR), 1710 (CO in ArCOOAr), 1640 (C=C), 1600 (C–C in Ar), 1260 (COC). ¹H NMR (CDCl₃, TMS): δ 1.44–1.86 (m, 6H, CH₂=CHCOOCH₂(CH₂)₃CH₂COO–), 2.58 (t, 2H, CH₂CH₂COOAr), 3.84 (s, 3H, –PhOCH₃), 4.18 (t, 2H, –CH₂CH₂OOCCH=CH₂), 5.80 (dd, 1H, CH₂=CH– trans), 6.11 (dd, 1H, CH₂=CH– cis), 6.40 (dd, 1H, CH₂=CH–), 6.97 (d, 2ArH, ortho to OCH₃), 7.10–7.25 (2d, 4H, aromatic), 8.14 (d, 2ArH, ortho to –COO–).

Synthesis of 4-(6-bromopropionyloxyphenyl)-4'-methoxy Benzoate. The synthesis of this substance was performed according to the reaction pathway outlined in Scheme 1. To a solution of 0.03 mol of 4-hydroxy-4'-methoxy benzoate in 150 mL of purified THF was added 0.04 mol of pure triethylamine followed by a dropwise addition of 0.04 mol of 6-bromopropionyl chloride, with stirring for 4 h. Then 100 mL of ether was added, and the solution was washed with water many times and dried with anhydrous MgSO₄. After removal of solvent, the white crude product was recrystallized twice from methanol. Yield: 60%. Mp: 105 °C. IR (cm⁻¹): 2989, 2890 (CH₂), 1710 (CO in ArCOOAr), 1600 (C–C in Ar), 1260 (COC), 650 (C–Br).

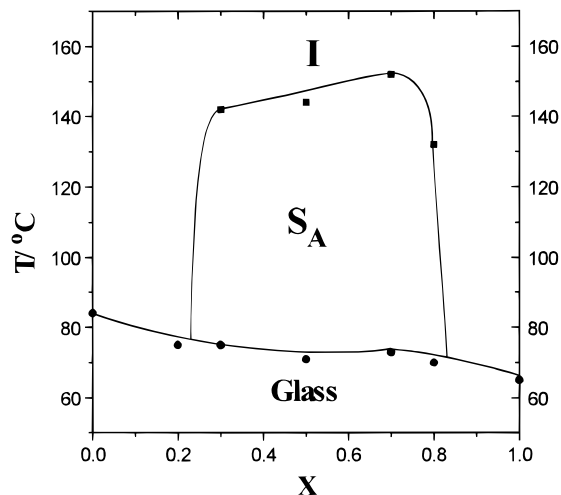
Synthesis of 4-(3-acryloyloxypropionyloxyphenyl)-4'-methoxy Benzoate (Scheme 1). 0.03 mol of 4-(6-bromopropionyloxyphenyl)-4'-methoxy benzoate was dissolved in 30 mL of hexamethylphosphoramide; then 0.04 mol of sodium acrylate was added by stirring, and stirring was continued for 6 h at room temperature. Then 100 mL of ether was added to the mixture, and the solution was washed with water and dried with MgSO₄. After removal of solvent, the crude product was purified by column chromatography using benzol/ethyl acetate (9:1) mixture as the eluant. The pure monomer was obtained as white crystals. Yield: 65%. Mp: 125 °C, IR (cm⁻¹): 2989, 2890 (CH₂), 1740 (CO in CH₂=CHCOOR), 1710 (CO in ArCOOAr), 1640 (C=C), 1600 (C–C in Ar), 1260 (COC). ¹H NMR (CDCl₃, TMS): δ 2.62 (t, 2H, CH₂CH₂COOAr), 3.85 (s, 3H, –PhOCH₃), 4.22 (t, 2H, –CH₂CH₂OOCCH=CH₂), 5.81 (dd, 1H, CH₂=CH– trans), 6.11 (dd, 1H, CH₂=CH– cis), 6.39 (dd, 1H, CH₂=CH), 6.97 (d, 2ArH, ortho to OCH₃), 7.10–7.25 (2d, 4H, aromatic), 8.14 (d, 2ArH, ortho to –COO–).

Synthesis of Homo- and Copolymers. The polymers were synthesized by radical polymerization of monomers using as initiating agent azobisisobutyronitrile (AIBN) in benzene solution at 60 °C. For example, 100 mg of chiral monomer and 1 mg (1 wt % of the monomer) of AIBN were taken in a glass ampule and dissolved in 1 mL of dry benzene. The solution was purged with dry argon for 20 min and sealed. The ampule was then kept at 60 °C for 30 h; subsequently, it was

Table 1. Phase Behavior, Thermal Properties, and Molecular Weights of Homopolymers and Copolymers of Series AX

X ^a (mol%)	phase transitions ^b	M _n × 10 ⁻³	M _w /M _n
0	amorphous, T _g = 84 °C	11.9	3.1
20	amorphous, T _g = 75 °C	12.3	3.6
30	g 75 S _A 142 (–) ^c I	10.1	4.3
50	g 71 S _A 144 (–) ^c I	14.8	4.3
70	g 73 S _A 152 (1.3) I	19.7	1.5
80	g 70 S _A 132 (1.2) I	12.0	1.2
100	amorphous, T _g = 65 °C	8.8	1.8

^a X is the chiral groups content. ^b Phase transition temperatures in °C are presented (in parentheses—enthalpies of the phase transition in J/g). ^c Endotherms were not clearly visible in the thermograms.


Figure 1. Phase diagram for copolymers AX (X, mole fraction of the chiral units).

opened, and the contents were poured into 15 mL of methanol. The precipitated solid was purified by repeated precipitation from chloroform into methanol and outgassed in a vacuum.

Techniques. IR spectra were recorded on a Bruker IFS-88 spectrophotometer using KBr pellets. Optical rotations were measured at 22 °C on a A-1 EPO polarimeter with chloroform as solvent for all compounds. ¹H NMR spectra were recorded on Bruker WP-200 (200 MHz) spectrometer using CDCl₃ as solvent.

Relative molecular weights of polymers were determined by gel permeation chromatography (GPC). GPC analyses were carried out with 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, THF as solvent (1 mL/min, 40 °C), a set of PL columns of 100, 500, and 10³ Å, and a calibration plot constructed with polystyrene standards.

Phase transitions of the copolymers were studied by differential scanning calorimetry with a Perkin-Elmer DSC 7 thermal analyzer (scanning rate was 10 K/min) and by polarizing microscopy using a LOMO P-112 polarizing microscope. Selective light reflection was studied using a Hitachi U-3400 spectrophotometer equipped with a Mettler FP-80 hot stage. The test samples with a thickness of 20 μm were sandwiched between the flat glass plates. Prior to tests, each sample was annealed for 20–40 min.

X-ray diffraction was carried out in a custom-made temperature-controlled (ΔT=K) vacuum chamber with a flat film camera at a distance of 81 or 84 mm from the sample. Ni-filtered Cu Kα-radiation (λ = 1.54 Å) was focused by a glass capillary. The samples of racemic copolymer were oriented inside the chamber in a magnetic field (2.4 T) perpendicular to the incident beam.

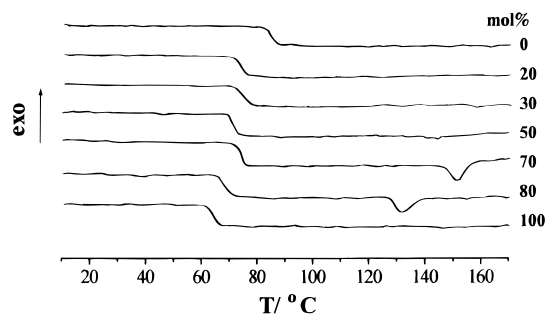
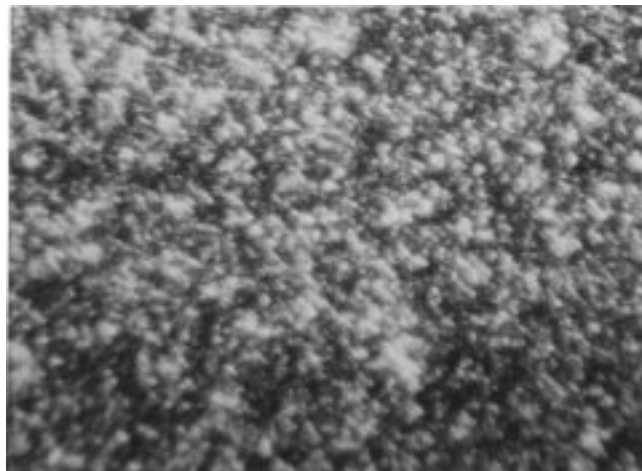


Figure 2. DSC curves for copolymers AX with different content of the chiral units. (Contents in mol% are shown in the figure. Heating rate was 10 °C/min, second heating scans.)



a



b

Figure 3. Polarized optical micrographs of the SA mesophase textures observed after annealing for 1 h upon cooling copolymers from the isotropic melt: (a) 140.0 °C, copolymer AX with 70 mol % of the chiral units; (b) 120.0 °C, copolymer BX with 60 mol % of the chiral units (200 \times).

Results

1. Phase Behavior of a series of Copolymers A.

Let us consider the phase behavior of the copolymers prepared by copolymerization of two monomers, the corresponding homopolymers of which are known to be amorphous polymers (Table 1). As follows from the phase diagram (Figure 1), copolymerization leads to an unexpected result, that is, in a wide range of temperatures and concentrations, LC phase is produced.

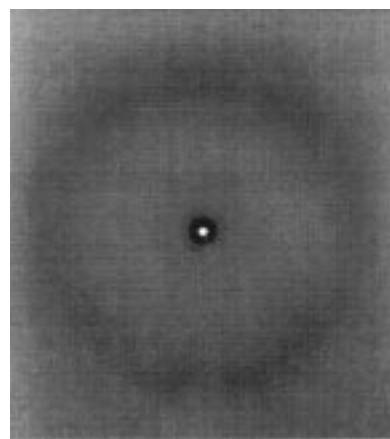


Figure 4. X-ray pattern for copolymer of series AX with 70 mol % of the chiral units (room temperature).

Table 2. Properties of Homopolymers and Copolymers of Series BX

X (mol %)	phase transitions	λ (nm) ^a	$M_n \times 10^{-3}$	M_w/M_n
0	g 25 N _B 60(7.0) N 125(1.0) I		23.1	3.2
5	g 27 N* 128(0.9) I	1704	14.3	3.0
10	g 30 N* 127(0.6) I	815	9.9	2.5
12	g 34 N* 120.5 BP 121.9 (0.7) I	600	12.8	2.2
15	g 35 N _{cyb} * 124.0 BP 124.5 (0.8) I	537	13.3	2.7
20	g 35 N _{cyb} * 116.7 BP 117.6(0.9) I	435	9.1	2.5
25	g 37 S _A * 65 N* 113.5 BP 114.0(0.6) I	383	11.6	3.0
30	g 43 S _A 83 N _{cyb} * 113(0.5) I	390	19.2	2.8
35	g 43 S _A 108-117(1.4)I		18.4	3.2
40	g 44 S _A 116-131(4.1) I		13.5	2.0
45	g 45 S _A 114-135(4.7) I		9.3	1.7
50	g 45 S _A 122-143(5.4) I		10.7	2.3
55	g 46 S _A 124-150(4.0) I		11.9	2.4
60	g 47 S _A 124-152(2.1) I		10.2	2.3
70	g 52 S _A 117-138(2.0) I		18.4	2.1
80	g 54 S _A 111-125(1.7) I		20.8	2.2
100	amorphous, $T_g = 65$ °C		8.8	1.8

^a λ : selective reflection of light wavelength at $T = 0.9T_{Cl}$.

The DSC curves of the copolymers containing less than 20 and more than 80 mol % of chiral units experience only one second-order transition (Figure 2) corresponding to glass transition temperature. These copolymers exhibit no birefringence and are amorphous, similar to the corresponding homopolymers. In the case of the copolymers containing 25–80 mol % of chiral units, the DSC curves show the glass transition temperature and an endothermic event (Figure 2) corresponding to the transition of LC phase into the isotropic melt. All copolymers, which produce LC phase, are characterized by fine-grained birefringent texture (as evidenced by microscopic observations, Figure 3a). However, the values of interplanar distances $d_{001} = 62$ Å corresponding to the small-angle reflections in the X-ray patterns (Figure 4) suggest the formation of a smectic A phase with bilayer packing of mesogenic groups. Note that this interplanar distance is independent of the concentration of chiral component and is equal to the double length of the menthyl-containing side fragment ($L = 31$ Å).

2. Phase Behavior and Optical Properties of Copolymers B. Let us consider the properties of copolymers B, in which phenyl benzoate side fragments

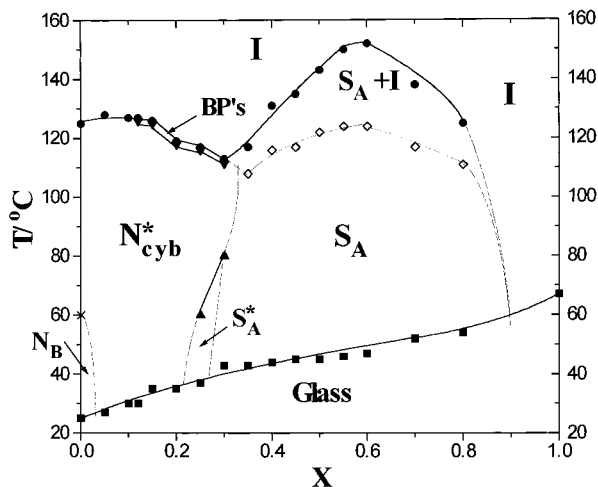


Figure 5. Phase diagram for copolymers BX.

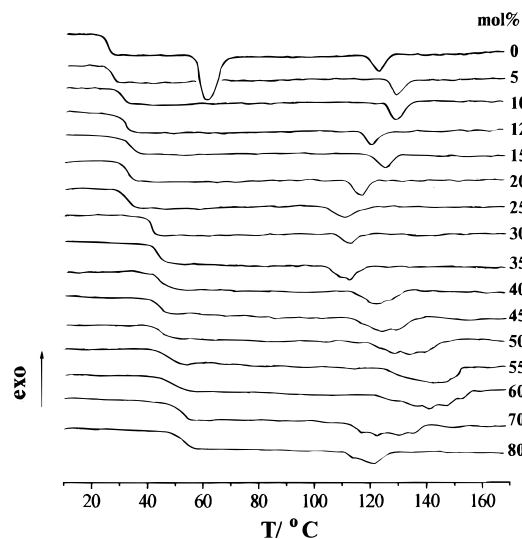


Figure 6. DSC curves for copolymers BX with different content of the chiral units. (Contents in mol % are shown in the figure. Heating rate was 10 °C/min, second heating scans.)

with a spacer containing five methylene fragments are nematogenic.

As follows from the above-mentioned data (Table 2 and Figure 5), in copolymers containing up to 20 mol % of chiral units, the formation of the chiral N^* mesophase is observed over a wide temperature range. The DSC curves of copolymers show the glass transition temperature and an endothermic event (Figure 6) corresponding to the transition of LC phase into the isotropic melt. The planar texture of the N^* phase shows selective light reflection in visible and near-IR region (Figure 7). With an increasing content of chiral units, in addition to the N^* phase, the copolymers display a smectic mesophase (S_A^* or S_A) in the narrow concentration region (25–30 mol %). This mesophase is not typical of the corresponding homopolymers. This character of polymorphic transformations has a certain effect on the optical properties of the system studied. Near the transition to smectic mesophase, a partial or complete untwisting of the cholesteric helix is observed (Figure 8). Note that copolymers B do not produce an ordered N_B phase, which was earlier observed for the nematogenic homopolymer.^{18–20} The reason for the “degeneration” of this phase is likely to be associated with the strong effect of chiral units containing a bulky terminal menthyl group.

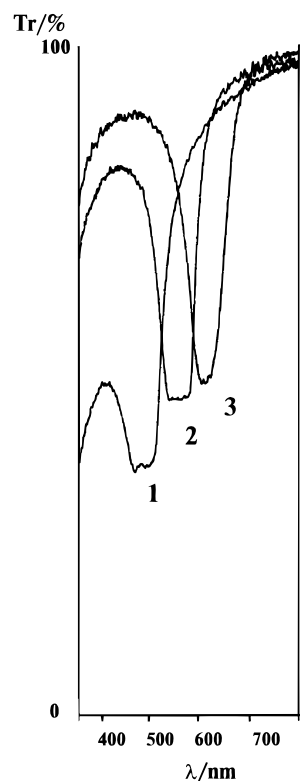


Figure 7. Transmittance spectra of planar texture of copolymers BX containing 20 (1), 15 (2), and 12 (3) mol % of the chiral units.

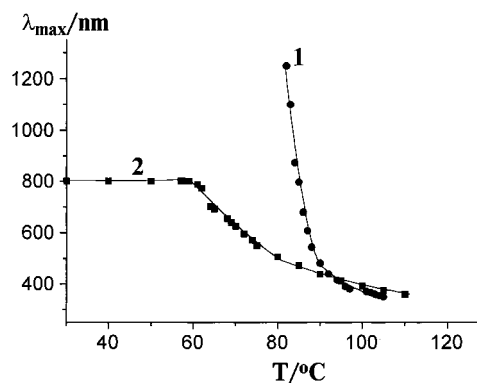


Figure 8. Temperature dependence of λ_{\max} for copolymers of the series BX forming low-temperature S_A -mesophase (30 mol % of the chiral units) (1) and S_A^* -mesophase (25 mol % of the chiral units) (2).

When the content of chiral units is higher than 30 mol %, the copolymers display a smectic A phase (with a typical fanlike structure as observed by polarizing microscope, Figure 3b), which is characterized by high thermal stability (T_{cl} achieves 152 °C at a content of chiral units of 60 mol %). As evidenced by X-ray data, interplanar distance corresponding to the small-angle reflection in the X-ray pattern (Figure 9a) is equal to 62 Å, that is, a double length of the chiral side units. The structure of the induced phase is completely the same as that of S_A phase of copolymers A, which were discussed in the preceding section. For copolymers with the relatively low content of menthyl units, the intensity of the (001) reflection d_{001} is much lower. This observation may be rationalized by a partial degeneration of a bilayer packing into a single-layered packing (Figure 9b,c).

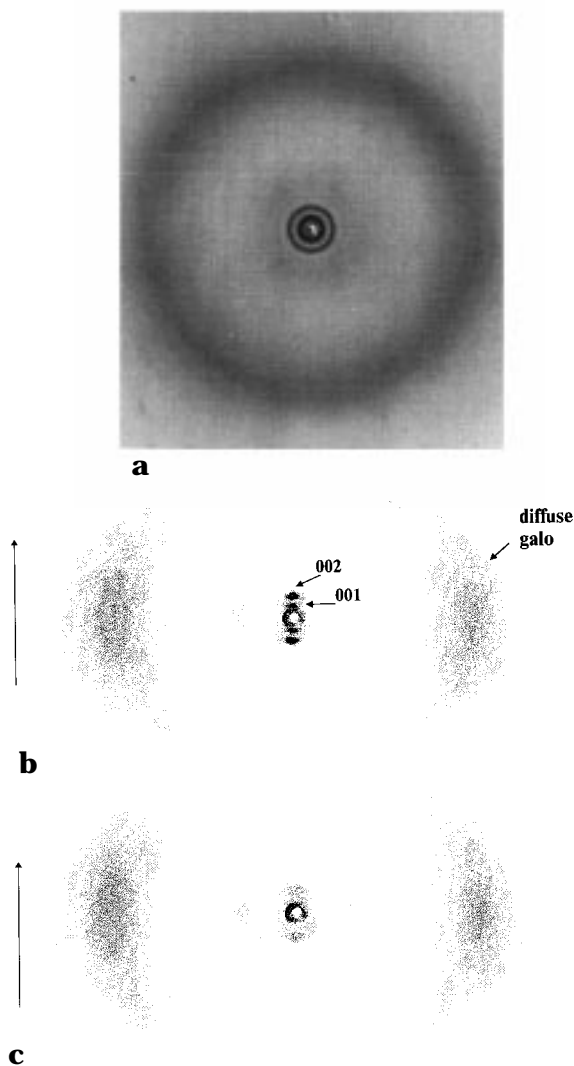


Figure 9. X-ray patterns: (a) copolymers of series BX containing 50 mol % of the chiral units; (b) copolymer with 30 mol % of the racemic menthyl containing units (room temperature, S_A phase); (c) the same copolymer in the N_{cyb} phase at 83 °C. (Arrow indicates the magnetic field direction.)

Discussion

Let consider in brief the possible reasons responsible for the abnormal behavior of the above copolymers, namely, the reasons responsible for the development of the more ordered smectic A phase. According to the X-ray data, the induced mesophase in both copolymers is characterized by a bilayer packing of side units, whose schematic representation is shown shown in Figure 10. Note that neither phenyl benzoate nor menthyl-containing units have groups with a strong dipole moment. Therefore, the following explanation of the abnormal behavior may be advanced. The chiral menthyl-containing homopolymer with a long aromatic fragment is potentially "smectogenic"; however, a rather large terminal menthyl group prevents the development of mesophase. Phenyl benzoate side units occupy the space between the bulky chiral fragment that leads to the dense packing of mesogenic groups of the copolymers (Figure 10). Just this steric correspondence is respon-

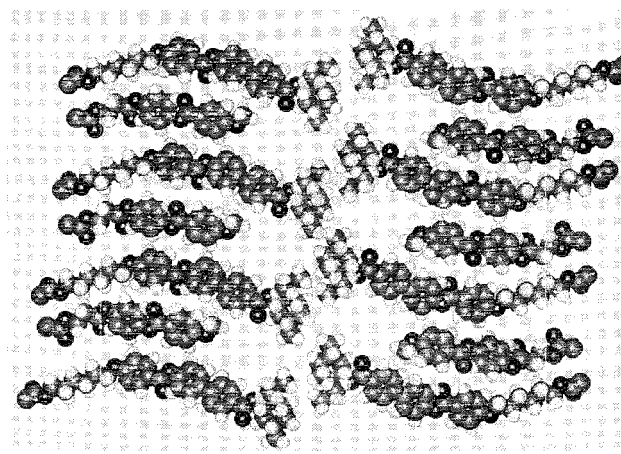


Figure 10. Hypothetical scheme of molecular bilayer packing of mesogenic groups in the S_A -mesophase (for copolymer AX with 50 mol % of chiral units).

sible for the development of the additional more-ordered phase in the copolymers. Note that, for the polymer systems, the new induced mesophase provided by the steric correspondence between different side units was developed for the first time in this work.

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