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## Liquid Crystals

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# Phase diagrams and optical properties of new menthyl-containing LC copolymers forming chiral mesophases

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New comb-shaped LC copolymers based on phenyl benzoate and menthyl-containing monomers were synthesized. Phase behaviour, optical properties and structure of the synthesized copolymers with different compositions were studied. Specific features of the development of helical nematic and smectic mesophases ( $N^*$ ,  $N_B^*$ ,  $N_{yb}^*$ ,  $N_e^*$ ,  $SmA^*$ ,  $SmF^*$ , blue phases) were revealed. Special attention was paid to studying the structure and optical properties of the new chiral  $N_B^*$  mesophase. For this unusual type of mesophase, a model accounting for the arrangement of the mesogenic group is suggested. It is stressed that the subscript B does not mean biaxial (a biaxial N phase is usually denoted  $N_b$ ) and B refers to the hexagonal ordering of the side groups, similar to that in a SmB phase. An alternative nomenclature would be  $N_h$ , where subscript h refers to hexagonal as in  $Col_{h0}$  for a hexagonally ordered columnar phase of a discogen.

## 1. Introduction

For many years, helical (chiral) liquid crystal phases produced by optically active molecules, or induced by the introduction of minor amounts of chiral additives to LC systems, have constituted a subject of special attention for many physicists and chemists involved in the study of LC compounds. Peculiar structural features of such mesophases involve the existence of a three-dimensional helical supermolecular packing of molecules and are responsible for their unique properties, provided by the ability of a helical structure to change its parameters easily (for example, helix pitch) under the action of various external factors such as temperature, electrical fields, and mechanical stress.

Chiral comb-shaped LC polymers combine the advantages of low molecular mass liquid crystals and high molecular mass compounds with their film-forming properties. In this connection, these compounds are of great scientific and practical interest. Such systems 'allow' one to fix the helical structure in a solid body at temperatures below the glass transition [1–4].

Despite evident progress in studying chiral low molecular mass and polymer liquid crystals, so far most attention has been focused only on cholesterol-containing compounds (usually called cholesterics), widely studied in recent years in connection with chiral smectic  $C^*$  ( $SmC^*$ ) phases with ferroelectric properties [5]. Meantime, for low molecular mass materials and

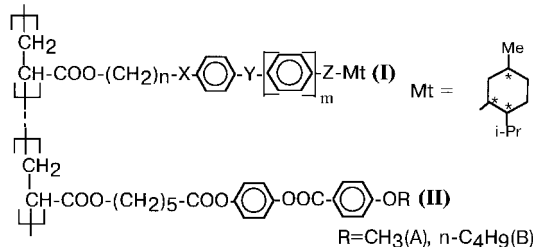
polymer compounds, new types of chiral helical mesophases with some elements of layer order (so-called TGB phases) and chiral ordered smectics, SmI and SmF phases, were being discovered [6–9]. These findings were inevitably associated with many new problems concerning not only their structural organization, but also the conditions of their formation [10]. For low molecular mass chiral liquid crystals, more and more publications have appeared, reporting attempts to construct a general theory accounting for the development of helical mesophases or, at least, containing systematic studies establishing a certain correlation between the molecular structure of chiral compounds and their ability to produce a given type of supermolecular helical modification [11, 12]. However, for chiral LC polymers, no such information is available.

As mentioned earlier, among chiral LC polymers, cholesterol-containing polymers have been most characterized [1–3, 13]. However, the 'drawback' of these polymers is associated with a very pronounced tendency of cholesterol fragments to produce layer structures even in the cholesteric mesophase [6]. This particular fact makes studying their structural organization and optical properties more difficult. Hence, compounds without any tendency to produce such translational order would make good candidates for further studies.

In connection, in this work we have studied menthol derivatives, which themselves usually do not produce mesophases, but are considered to be rather active chiral dopants in their compositions with low molecular

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mass nematics [14, 15]. One may assume that, being incorporated into the composition of a macromolecular as monomer units in a nematogenic polymer, these chiral fragments will act similarly to cholesterol fragments and serve as 'twisting agents' but without any structuring effect. On this basis we synthesized new menthyl-containing homopolymers as well as copolymers based on menthyl-containing (I) and nematogenic phenyl benzoate units (II). The general formula of the compounds is presented below:



The structure of the chiral units (I) was varied over a wide range by changing the length of the spacer ( $n = 5, 6, 10$ ) and the size of the rigid aromatic fragment ( $m = 0-2$ ), as well as the group Z joining the aromatic fragment with the menthyl group. Changing the length of the terminal substituent in the phenyl benzoate side groups (II) allowed one to control the phase behaviour of the polymer matrix, passing from a nematic phase in the case of a short terminal substituent ( $R = \text{CH}_3$ ; g 25 N<sub>B</sub> 60 N 125 I) to a more complex type of polymorphism in the case of the butyl terminal group ( $R = n\text{-C}_4\text{H}_9$ ; SmF 70 N<sub>re</sub> 115 SmA 138 N 148 I) (°C) [16, 17].

This choice of structure of the copolymers allows one to study the development of helical supermolecular organization in phases with different levels of ordering and symmetry: N, N<sub>B</sub>, N<sub>re</sub>, SmA, SmF and to reveal the character of changes in the optical properties and phase state as a function of the structure of chiral units in copolymers.

## 2. Experimental

All the new menthyl-containing monomers were prepared according to the procedure described in reference [18]. The copolymers were synthesized by radical copolymerization of monomers in benzene solution at 60°C; AIBN was used as initiating agent. All the synthesized copolymers were purified by repeated precipitation with methanol and dried in a vacuum.

Phase transitions for the copolymers were studied by differential scanning calorimetry (DSC) with a scanning rate of 10 K min<sup>-1</sup>. The experiments were performed using a Mettler TA-400 thermal analyser and a LOMO P-112 polarizing microscope. Selective light reflection of the chiral polymers was studied using a Hitachi U-3400 UV-Vis-IR spectrophotometer equipped with a Mettler

FP-80 hot stage. The polymer samples, with a thickness of 20 μm, were sandwiched between two flat glass plates; prior to tests, they were annealed for 20–40 min.

X-ray diffraction analysis was carried out using a URS-55 instrument (Ni-filtered CuK<sub>α</sub> radiation,  $\lambda = 1.54 \text{ \AA}$ ).

## 3. Results and discussion

### 3.1. Menthyl-containing homopolymers

Table 1 shows the structural formulae and glass transition temperatures for the menthyl-containing homopolymers prepared in this work. As evidenced by the data from DSC polarizing microscopy, all the synthesized homopolymers are amorphous. Comparison of their glass transition temperatures indicates that, as the length of the spacer increases, the glass transition temperature decreases (intramolecular plasticization [1]), whereas, with increasing length of the rigid fragment, quite the opposite tendency is observed, and the glass transition temperature  $T_g$  increases.

Note that even the homopolymer with a rather long system of conjugated bonds [three benzene rings, polymer PM-6,3(est.), table 1] shows no mesophase. The reason for this behaviour is likely to be associated with the disruption of the anisotropy by the chiral side group because of the presence of the bulky menthyl fragment. Since all the synthesized menthyl-containing homopolymers are amorphous, this allows one to assume that the phase behaviour of the copolymers based on chiral and nematogenic monomer units is primarily controlled by the properties of the 'nematogenic matrix'.

### 3.2. Chiral copolymers of series PM-*n,m*(*eth. or est.*)/AX ( $R = \text{CH}_3$ )<sup>‡</sup>

#### 3.2.1. Structure and phase behaviour

Let us consider the effect of the constitution of the chiral side fragments, namely the length of the rigid aromatic fragment, on the phase behaviour of the copolymers. Figures 1(a)–1(c) show the phase diagrams obtained from polarizing microscopy, DSC and X-ray analysis data. As follows from figure 1(a), for the copolymers with a single-ring chiral monomer, the existence of low temperature ordered N<sub>B</sub><sup>\*</sup> phase is observed over the entire concentration region of mesophase existence (up to 40 mol% of chiral units).<sup>‡</sup> As shown in previous papers [3, 17–19], this mesophase is characterized by a hexagonal order in the arrangement of the mesogenic

<sup>‡</sup> In this paper the superscript asterisk denotes a phase in which there exists a helicoidal supramolecular structure. Thus SmA<sup>\*</sup> is a twisted SmA and N<sub>cyb</sub><sup>\*</sup> is a chiral nematic phase which is twisted and has some elements of layer ordering. The asterisk does not here mean simply a mesophase consisting of or containing a proportion of chiral molecules.

<sup>‡</sup>  $X$  is the molar fraction of chiral fragments in the copolymers.

Table 1. Glass temperatures of menthyl-containing homopolymers. PM- $n,m$ (eth.) and PM- $n,m$ (est.) are acronyms for the homopolymers: M corresponds to the menthyl group existing in the polyacrylate;  $n$  is the spacer length;  $m$  is the number of benzene rings in the side group; eth. and est. correspond to the ether and ester groups which connect the menthyl group with the aromatic fragment.

Structure of homopolymer	Homopolymer	$T_g/^\circ\text{C}$
$\begin{array}{c}   \\ \text{CH}_2 \\   \\ \text{CH-COO-(CH}_2\text{)}_{10}\text{-COO-C}_6\text{H}_4\text{-COOMt} \end{array}$	PM-10,1(est.)	13
$\begin{array}{c}   \\ \text{CH}_2 \\   \\ \text{CH-COO-(CH}_2\text{)}_n\text{-OOC-C}_6\text{H}_4\text{-OMt} \end{array}$	$n = 5$ , PM-5,1(eth.) $n = 10$ , PM-10,1(eth.)	28 -6
$\begin{array}{c}   \\ \text{CH}_2 \\   \\ \text{CH-COO-(CH}_2\text{)}_6\text{-O-C}_6\text{H}_4\text{-COO-C}_6\text{H}_4\text{-COOMt} \end{array}$	PM-6,2(est.)	53
$\begin{array}{c}   \\ \text{CH}_2 \\   \\ \text{CH-COO-(CH}_2\text{)}_6\text{-O-C}_6\text{H}_4\text{-COO-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-COOMt} \end{array}$	PM-6,3(est.)	65

groups, and no translational order along the long axes of mesogenic groups is observed. Figure 2 shows the effect of the copolymer composition on the selective reflection wavelength. In this case, minimum light transmission corresponds to the maximum selective light reflection, which indicates a helical supermolecular organization of the  $N_B^*$  phase.

Figure 1(a) clearly shows that, on increasing the fractional content of chiral groups, the isotropization temperature quickly falls, whereas the temperature corresponding to the  $N_B^*-N^*$  transition remains almost unchanged. We have tried to rationalize this intriguing fact by resorting to the concepts of microsegregation. As the temperature decreases to about 60°C, copolymers with a relatively high content of chiral units (more than 15 mol %) experience microphase separation induced by a poor compatibility between the non-mesomorphic menthyl-containing groups and the nematogenic matrix. This microphase separation is accompanied by the development of 'domains' of untwisted  $N_B$ -phase produced by the mesogenic groups of the nematogenic monomer. Another microphase region contains the phenyl methoxybenzoate groups and chiral units, which provide the helical organization of  $N_B^*$  mesophase in the menthyl-containing copolymers.

Hence, we deal with a two-phase (with respect to a single macromolecule) system. In the copolymer, two components which are incompatible at lower temperatures are chemically attached to the backbone. As a result, no macroscopic phase separation takes place (as in the case of low molecular mass systems or polymer

blends), but separation proceeds at a microscopic level, i.e. the dimensions of the 'domains' of the phases are limited by the initial structure of the copolymer and depend on various factors, such as composition, distribution of different chain units, composition inhomogeneity, etc. The structure of the  $N_B^*$  phase in the menthyl-containing copolymers may thus be represented schematically (figure 3).

At the present time, this structural model is rather hypothetical in character and is not unambiguous. To construct a more correct model of this unique phase, detailed X-ray studies are required. A certain analogy between the local structure of this phase and well-established 'blue phases' [20–24], and the newly found TGB phases [9], which are also two-phase (at the microscopic level) systems, is evident.

For the copolymers with two-ring chiral fragments [copolymers PM-6,2(est.)/AX, figure 1(b)] containing more than 15 mol % of menthyl component, as well as for the copolymers with a three-ring chiral monomer [figure 1(c)] no  $N_B^*$  phase is observed. It seems likely that, with increasing length of the aromatic fragment, a marked improvement in compatibility of chiral component and nematic matrix takes place, and no microsegregation takes place.

The copolymers with three-ring chiral units are characterized by quite a unique phase behaviour. In this case, the development of a SmA phase is observed, even though neither of the homopolymers is characterized by the presence of translational order, and smectic ordering is observed only in the copolymers [figure 1(c)]. In this

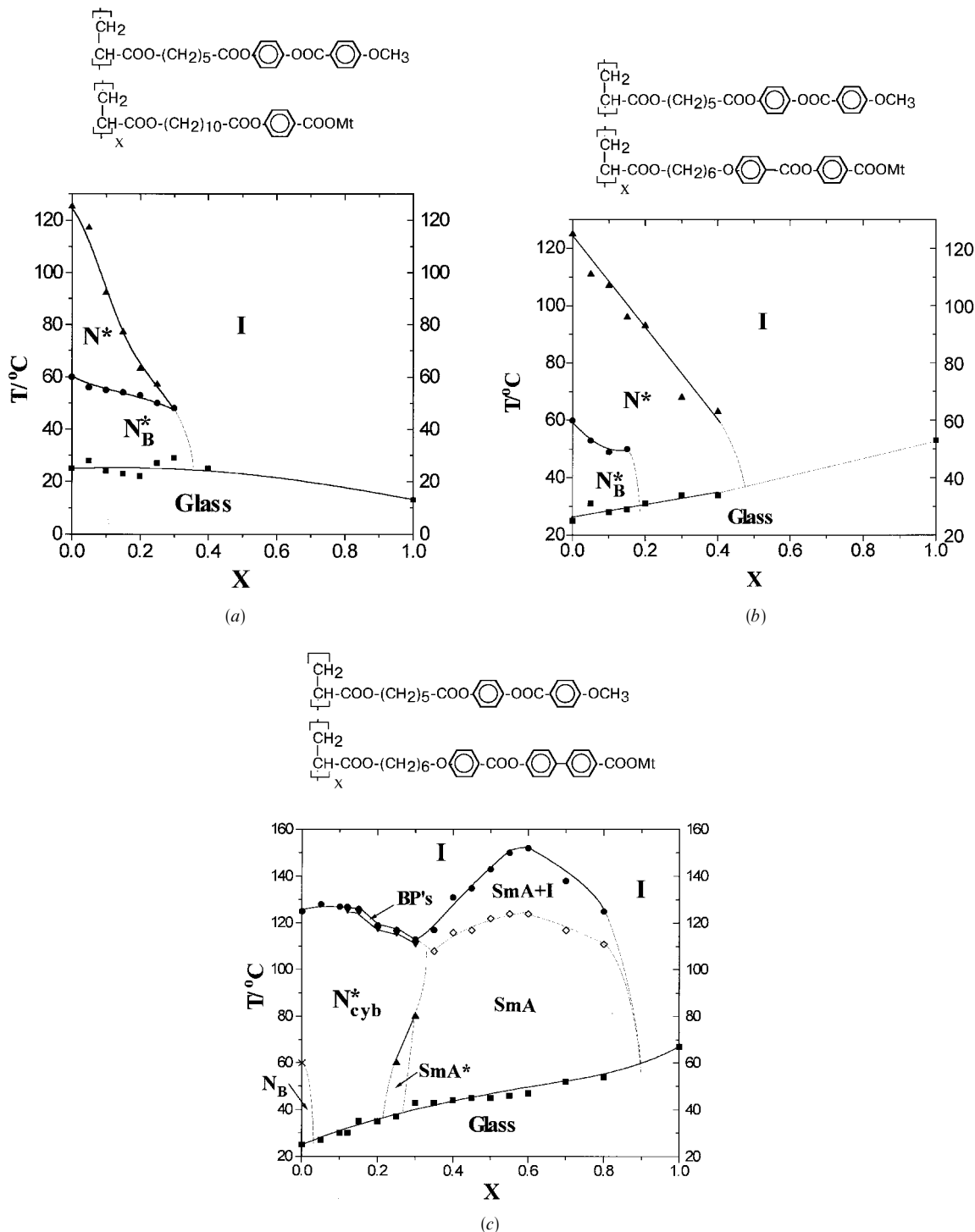


Figure 1. Structural formulae and phase diagrams for copolymers PM-10,1(est.)/AX (a), PM-6,2(est.)/AX (b) and PM-6,3(est.)/AX (c), ( $X$  is the mol fraction of chiral units).

mesophase, the interplanar distance  $d_{001} = 66 \text{ \AA}$  corresponds to twice the length of the chiral side fragment. This allows one to conclude that the copolymers are characterized by a bilayer packing of the side groups (figure 4).

The development of the SmA phase may be explained by assuming that the menthyl-containing monomer shows 'a potential smectogenicity', which is enhanced by a long aromatic fragment. In the chiral homopolymer, anisotropy is disrupted by the presence of the bulky

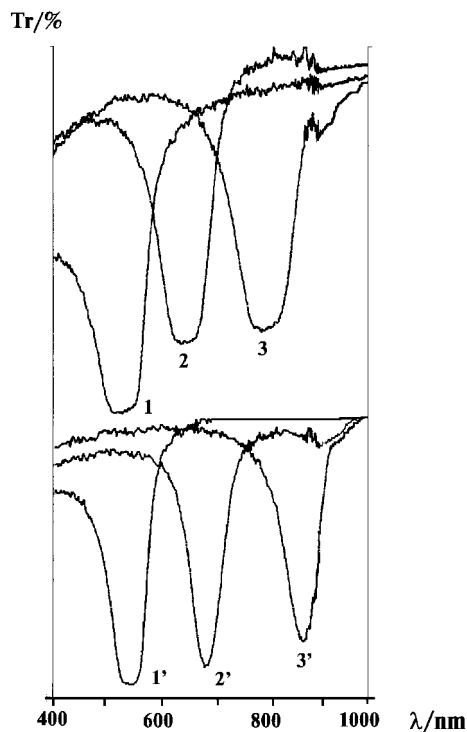


Figure 2. Transmittance spectra for copolymers PM-6,2(est.) / AX containing 20 (1,1'), 15 (2,2') and 12 (3,3') mol% of chiral groups. 1–3 =  $N_B$  mesophase at 25°C; 1'–3' =  $N^*$  phase at  $0.9T_{C1}$ .

terminal menthyl group, and the LC state is not observed. Introduction of the phenyl benzoate mesogenic groups into the system makes it more 'dilute' and offers free volume for the menthyl-containing units. Due to the steric conformity of the different groups, the copolymers adopt a dense packing as in a SmA phase (figure 5).

For copolymers of the same family containing more than 10 mol% of chiral units, the development of a *platelet texture* is observed (figure 6). This platelet texture is typical of blue phases BPI and BPII [20–24]. The temperature interval of existence of these phases is narrow (in this case, about 1–2°C). However, as compared with the low molecular mass blue phases, in the case studied, the platelet texture could be fixed or frozen in by rapid cooling.

### 3.2.2. Optical properties

Let us consider the effect of the chemical structure of the chiral groups on the optical properties of the helical mesophases induced in the copolymers. Figure 2 shows a typical profile of the transmission spectra for three copolymers of the series PM-6,2(est.) / AX (in the cases studied, a minimum of light transmission corresponds to the maximum of selective light reflection of circularly polarized light). Figure 7 shows the typical temperature

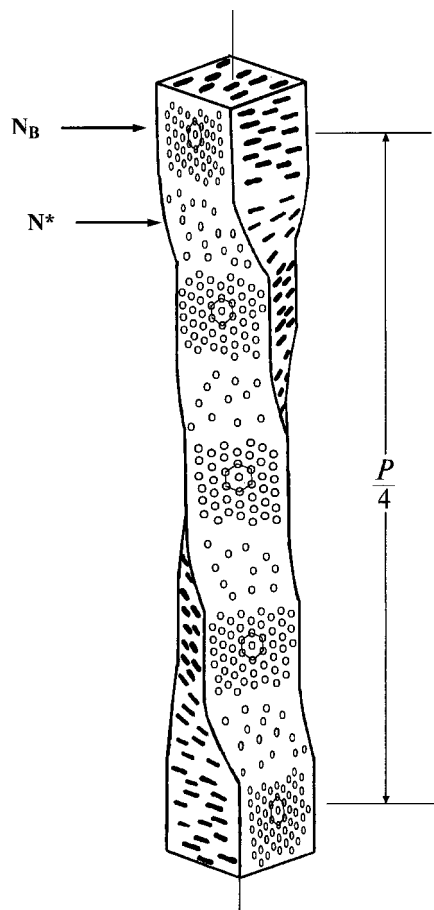


Figure 3. Schematic representation of the supramolecular structure of the  $N_B$  mesophase ( $P$  = helix pitch; main chains are omitted for simplicity).

dependences of the selective reflection wavelengths for copolymers of the series PM-10,1(est.) / AX.

The most interesting fact is that the transition to a more ordered  $N_B^*$  phase is associated with just a slight increase in helix pitch. In this case, transition to a more ordered phase is not accompanied by a pronounced pre-transitional increase in helix pitch as observed for the  $N^* \rightarrow$  SmA transition. Let us emphasize once more that, at the present time, among low molecular mass compounds, no analogues of mesophases  $N_B$  and  $N_B^*$  have been found, and these types of mesophase are realized only for 'polymer' systems [16–19].

The dependences presented in figure 7 agree with the model speculations developed by Finkelmann and Stegemeyer [25], and Lisetskii and co-workers [14, 26] for chiral molecules without anharmonism of their rotational vibrations. (In particular, they showed that for such systems,  $d\lambda_{\max}/dT > 0$ , i.e. with increasing temperature, untwisting of the helix is observed.) The temperature dependence of the selective light wavelength is described by the value of  $(1/\lambda_{\max})(d\lambda_{\max}/dT)$  which,

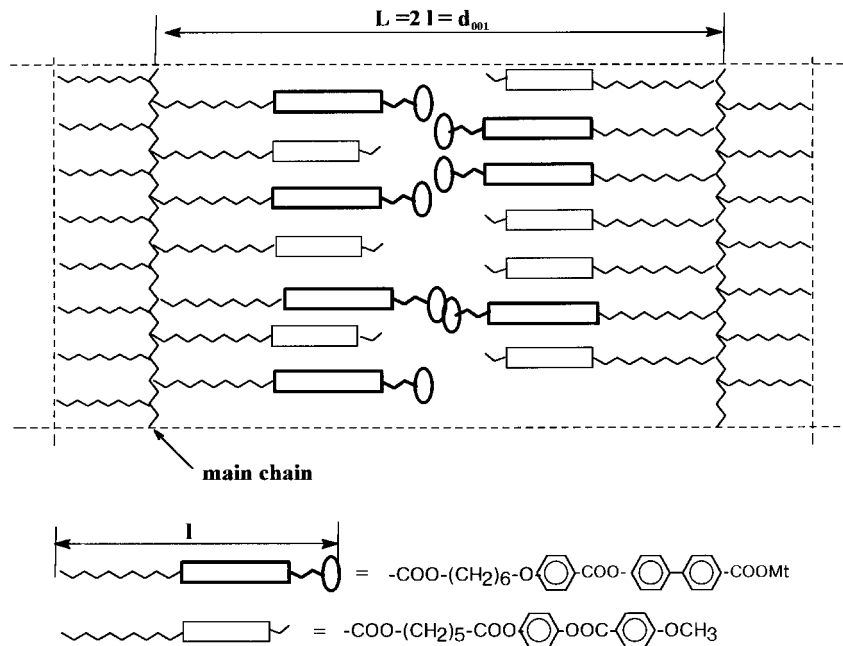


Figure 4. Scheme of molecular packing of the mesogenic groups in the SmA mesophase for copolymers of the series PM-6,3(est.)/AX.

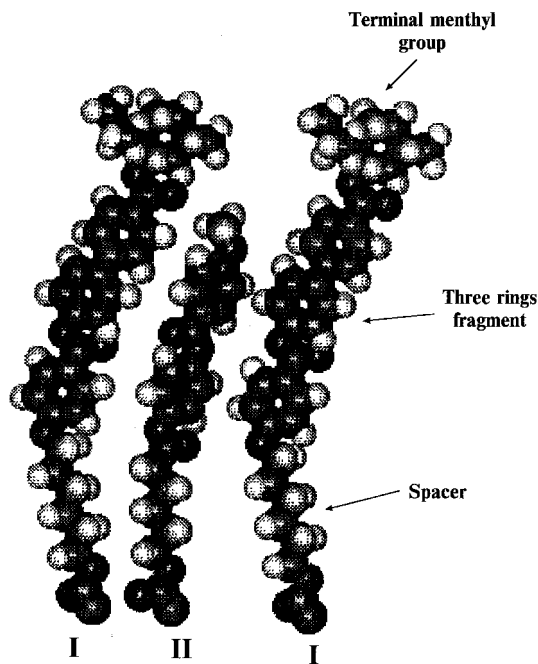


Figure 5. Arrangement of the neighbouring side groups in the induced SmA phase of copolymers of the series PM-6,3(est.)/AX. I = menthyl-containing side group; II = phenyl benzoate side group.

as calculated by Lisetskii, was equal to 0.004. In the case now studied, this parameter also lies within the region of (0.004–0.006).

For copolymers of series PM-6,3(est.)/AX, as the content of chiral component increases, the temperature coefficient of the selective reflection wavelength decreases

(figure 8), and this behaviour is accounted for by smectic fluctuations in such copolymers.

Similar behaviour was observed for cholesterol-containing copolymers forming an  $N^*$  phase [27]. In this case  $(1/\lambda_{\max})(d\lambda_{\max}/dT)$  was equal to 0.001–0.002, i.e. this value was three- to four-times smaller than theoretical estimates. In our opinion, this behaviour is likely to be associated with the smectogenic character of cholesterol-containing side groups and their tendency to give smectic order. Note that low and even negative values of  $(1/\lambda_{\max})(d\lambda_{\max}/dT)$  are usually observed for cholesteric copolymers when at least one of the comonomers exhibits elements of smectic order.

For copolymers of series PM-6,3(est.)/AX containing more than 15 mol % of chiral units,  $d\lambda/dT < 0$ , i.e. with decreasing temperature, the helix pitch  $P$  increases (figure 9). This profile of temperature dependence of  $\lambda$  is accounted for by untwisting of the helix, which is observed during the transition from  $N^*$  to SmA and SmA\* phases.

As mentioned earlier, for the copolymers of the same series containing more than 12 mol % of chiral units, polarizing microscopic observations revealed the existence of a blue phase (BP). The selective light reflecting properties of this mesophase were studied, and to this end, we prepared samples (by prolonged annealing for 12 h at the temperature of development of the platelet texture) with the 'frozen-in' blue phase, which was obtained by rapid cooling to temperatures below the glass transition temperature.

Only in the case of the copolymer containing 15 mol % of chiral units did we manage to identify the existence

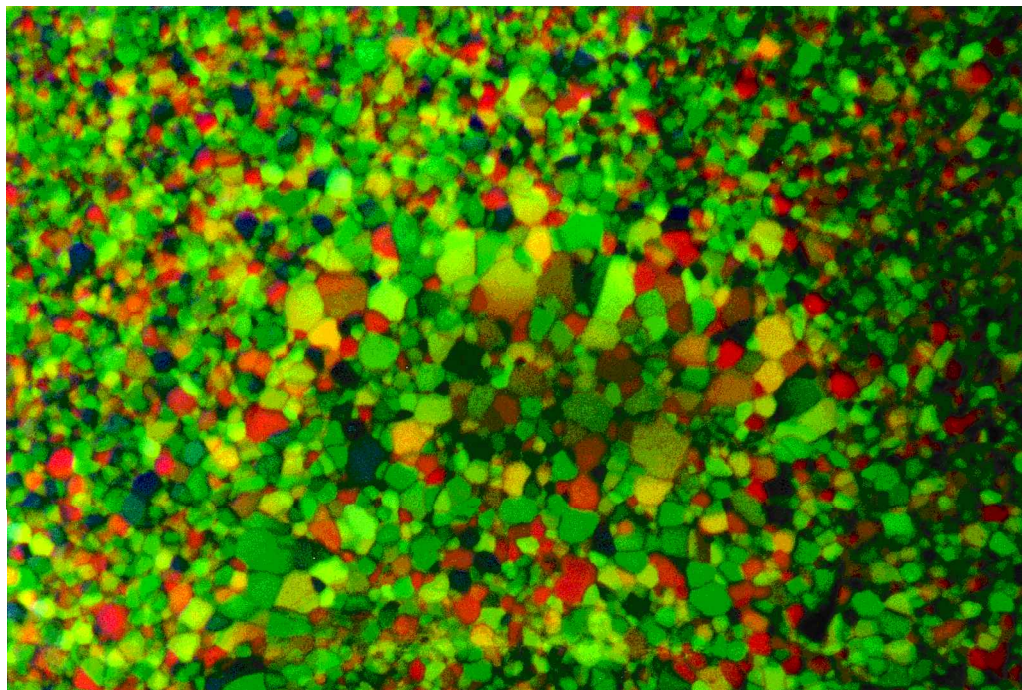


Figure 6. Platelet texture of the blue phase of copolymer PM-6,3(est.)/A15, obtained by prolonged annealing of the sample at 124.2°C followed by rapid cooling to ambient temperature (magnification  $\times 64$ ).

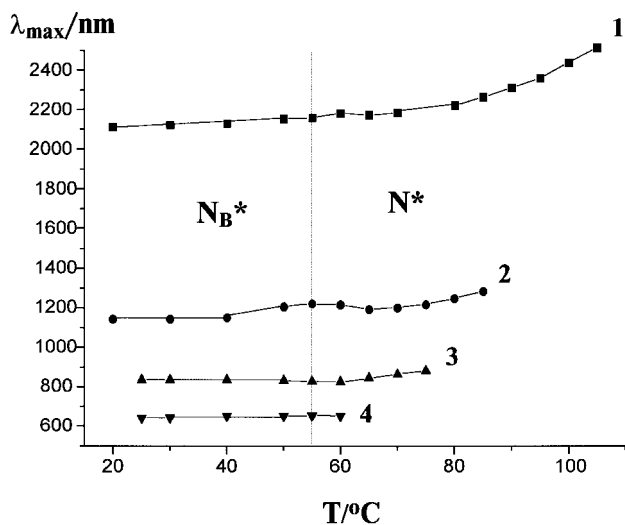


Figure 7. Temperature dependence of  $\lambda_{\max}$  for copolymers of the series PM-10,1(est.)/AX containing 5 (1), 10 (2), 15 (3) and 20 (4) mol % of chiral units.

of three low-intensity spectral peaks, two of which correspond to light diffraction from planes of the cubic structure— $\{h k l\} = \{1 1 0\}$ ;  $\lambda_{110} = 2^{1/2} \lambda_{200}$  (figure 10). However, these results are preliminary and require thorough verification; the analysis of such spectra is very difficult.

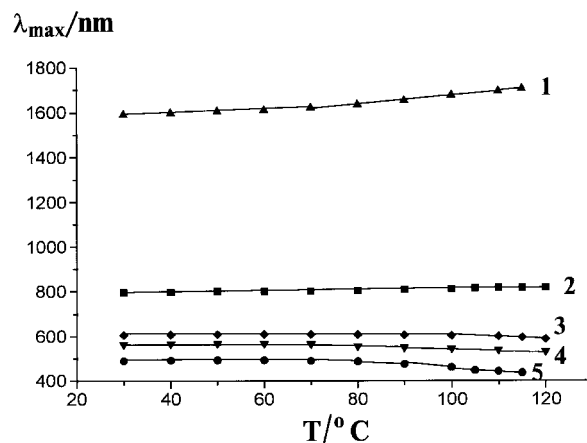


Figure 8. Temperature dependence of  $\lambda_{\max}$  for copolymers of the series PM-6,3(est.)/AX containing 5 (1), 10 (2), 12 (3), 15 (4) and 20 (5) mol % of chiral units.

### 3.3. Chiral copolymers of series PM- $n,m$ (est.)/BX ( $R = n-C_4H_9$ )

#### 3.3.1. Phase behaviour

Copolymers of these families were prepared by incorporation of menthyl-containing fragments into macromolecules of the phenyl benzoate polymer which produces a smectic F phase, a nematic phase N, as well as a high temperature smectic A phase (SmF 70 N<sub>re</sub> 115 SmA 138 N 148 I). As follows from figure 11 (a)–11 (c),



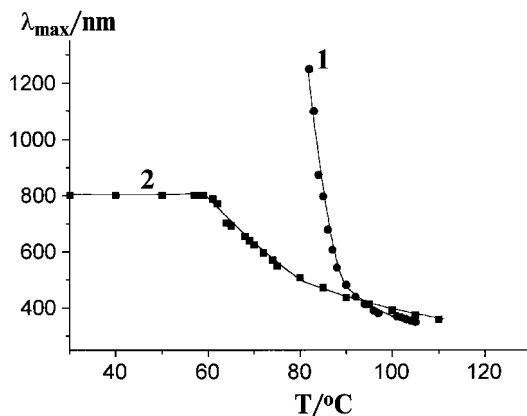


Figure 9. Temperature dependence of  $\lambda_{\max}$  for copolymers of the series PM-6,3(est.)/AX forming a low temperature SmA mesophase containing 30 mol % (1) and a SmA\* mesophase containing 25 mol % (2) of chiral units.

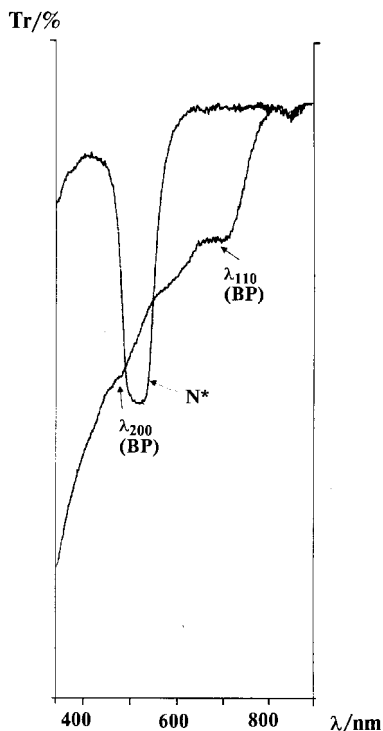


Figure 10. Transmittance spectra of copolymer PM-6,3(est.)/A15 displaying N\* and blue phases at ambient temperature. The texture of the blue phase was obtained by annealing the sample for 12 h at 124.2°C followed by rapid cooling to below  $T_g$ .

in general these copolymers are characterized by the same phase polymorphism as that of the phenyl benzoate homopolymer, into which helicity of the phases is induced. At room temperature, almost all the copolymers are characterized by the existence of a chiral SmF\* phase with a tilted arrangement of the mesogenic groups in the smectic layers (data from DSC, X-ray analysis

and spectrophotometry). However, in the case of copolymers containing two-ring and three-ring chiral units [PM-6,2(est.)BX and PM-6,3(est.)/BX] with relatively high contents of the chiral component, degeneration of this mesophase into the orthogonal SmA phase is observed, and this degeneration is driven by an increased 'affinity' between the side groups of the copolymer. In the case of copolymers with three-ring chiral units, an important role is likely to be attributed to the above-mentioned steric conformity of the different side groups. Note that the thermal stability of the non-helical SmA phase (fanlike texture with coexistence of regions of homeotropic orientation) markedly increases with increasing fractional content of chiral units in the copolymer [figure 11(b) and 11(c)].

### 3.3.2. Optical properties

A complex phase behaviour of the above copolymers manifests itself in quite different profiles of the temperature dependences of the selective light reflection wavelengths: this difference depends not only on the chemical nature of the chiral component, but also on the copolymer composition (figure 12). In all cases, in the region of the phase transitions ( $N_{\text{yb}}^* \text{--} \text{SmA}$ ,  $N_{\text{yb}}^* \text{--} \text{SmA}^*$ ,  $N_{\text{yb}}^* \text{--} \text{SmF}$ ,  $N_{\text{yb}}^* \text{--} \text{SmF}^*$ ), a complete or partial untwisting of the supermolecular helix is observed.

Examination of the phase behaviour and optical properties of the synthesized copolymers allows one to draw the following general conclusions:

- (1) For copolymers containing mesogenic and chiral non-mesogenic units, at a relatively low content of chiral units (up to 15–20 mol %), the phase polymorphism is completely controlled by the properties of the 'matrix'; the presence of the optically active groups leads only to helical twisting of the mesophase.
- (2) For copolymers with single-ring chiral units, with increasing content of chiral component the clearing temperature decreases. In this case, the temperature interval of existence of low temperature ordered phases remains almost unchanged with changing concentration of chiral component (to a certain critical concentration). This behaviour may be explained by the concept of microsegregation, three aspects of which are noted below.

First, microsegregation may be observed at the level of one single molecule having dissimilar fragments as the terminal groups. This reasoning may be invoked to explain the development of ordered smectic structures in thermotropic liquid crystals as well as in micellar, lamellar, etc.—lyotropic systems [28–30].

The second type concerns the microphase separation described in this work and observed for LC copolymers,

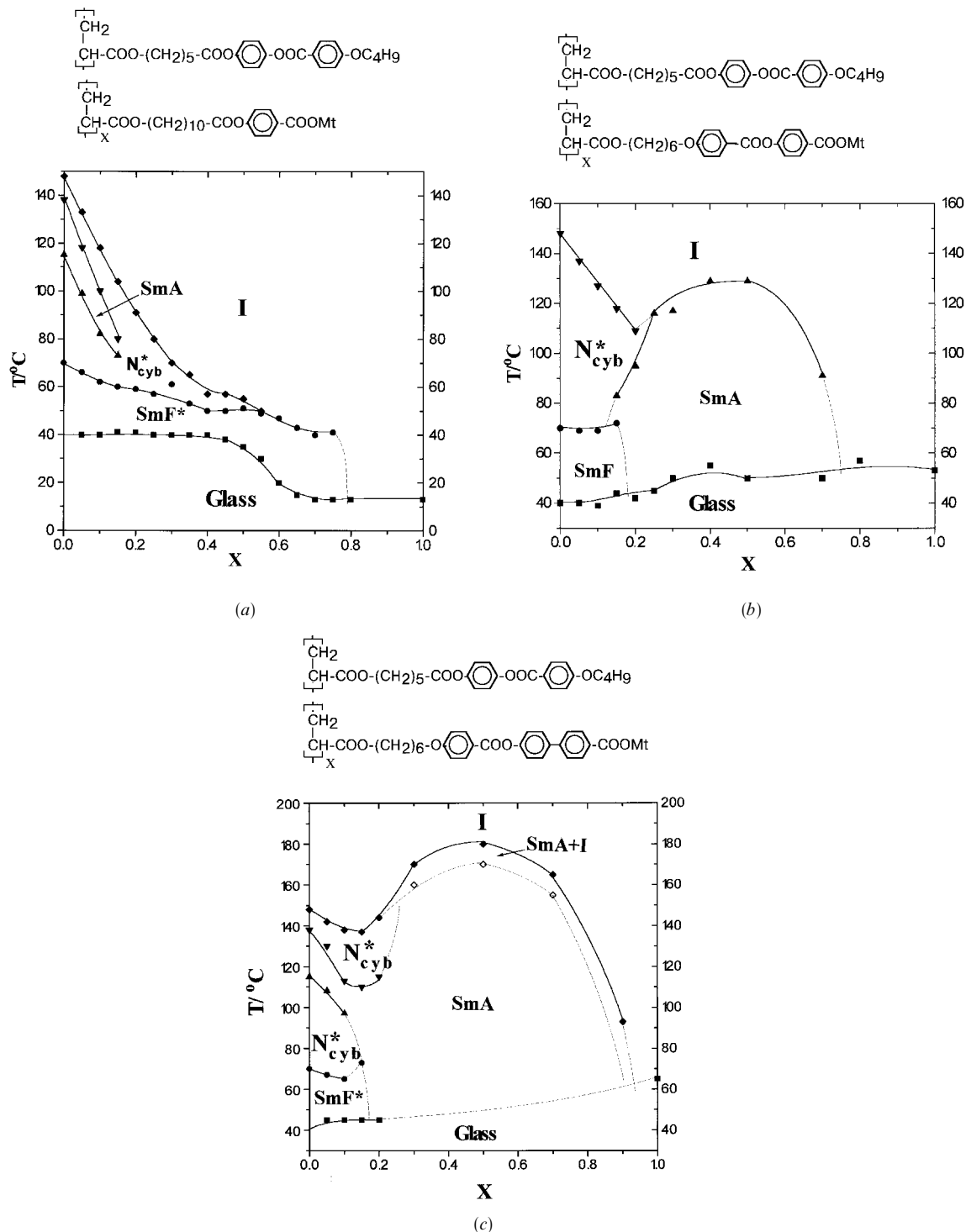


Figure 11. Structural formulae and phase diagrams for copolymers PM-10,1(est.)/BX (a), PM-6,2(est.)/BX (b) and PM-6,3(est.)/BX (c);  $X$  is the mol fraction of chiral units.

in which one of the comonomers is non-mesomorphic [31, 32]. Chemical binding of the two different components (one of which tends to produce ordered phases) into one polymer chain does not allow the system to

separate into two or more easily identified (for example, using polarizing microscopy) phases. Nevertheless, examination of phase diagrams and structure allows one to suggest the coexistence of two microphases with different

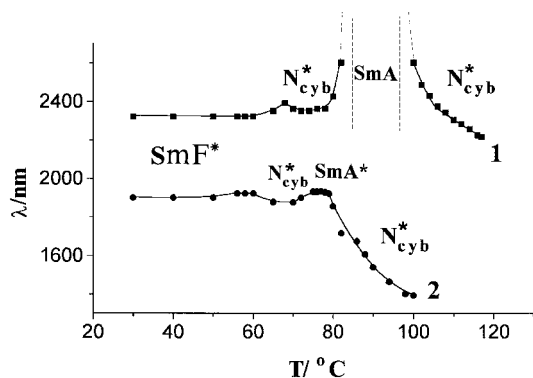


Figure 12. Temperature dependence of  $\lambda_{\max}$  for copolymers of the series PM-10,1(est.)/BX containing 10 (1) and 15 (2) mol % of chiral units.

degrees of ordering and symmetry within one macromolecule. Furthermore, microphase separation in comb-shaped copolymers has been predicted theoretically [33].

The third, well-studied and common type of microsegregation phase separation in poorly compatible mixtures of different compounds [34–37]. Usually, in this case identification of two or more phases (for example, by polarizing microscopy) is rather easy, and a great number of publications is devoted to studying mixtures of liquid crystal materials with non-mesomorphic compounds, where phase separation takes place.

Hence, in this work, the effect of the length of the aromatic fragment of chiral units on the phase behaviour of copolymers was studied. For copolymers with single-ring chiral units, microsegregation is observed. This microsegregation is accompanied by the coexistence of two microphases with different degrees of ordering. Increasing the length of the ‘mesogen’ improves the compatibility between the two components; as a result, degeneration of low temperature ordered mesophases takes place.

### 3.4. Helical twisting power

A chiral LC system is characterized by a very important parameter, the helix-induction force (or helical twisting power)  $\beta$ , which is given by the following formula [38]:

$$\beta = n(d\lambda_{\max}^{-1}/dX) \quad (1)$$

where  $n$  is the mean refractive index and  $X$  is the molar fraction of chiral component in the copolymer.

Helical twisting power depends on the geometry of the chiral component as well as on the nature of the ‘nematogenic matrix’ [11, 12, 25, 38]. To reveal the correlation between the chemical structure of chiral groups and their twisting power, the dependences of  $\lambda_{\max}^{-1}$  on the molar fraction of chiral fragments in various

copolymers were plotted (figure 13). In this work, the values of  $n$  were not estimated, and the helical twisting power value was determined from the slope of the linear region of the relation:

$$A = d\lambda_{\max}^{-1}/dX. \quad (2)$$

As follows from figure 13, in some cases the experimental points fit a straight line, whereas in other cases, a marked deviation from linearity is observed. We advance the following function for approximation of the experimental values:

$$\lambda_{\max}^{-1} = AX/(1 + BX) \quad (3)$$

where  $A$  is the helical twisting power, and  $B$  is a parameter which allows one to estimate quantitatively the deviation of the experimental data from linear dependence. A non-zero value of the parameter can be explained by the effect of specific lateral interactions or decrease in the order parameter  $S$ .

Comparison of  $A$  and  $B$  values (table 2) for copolymers of different series leads to the following conclusions:

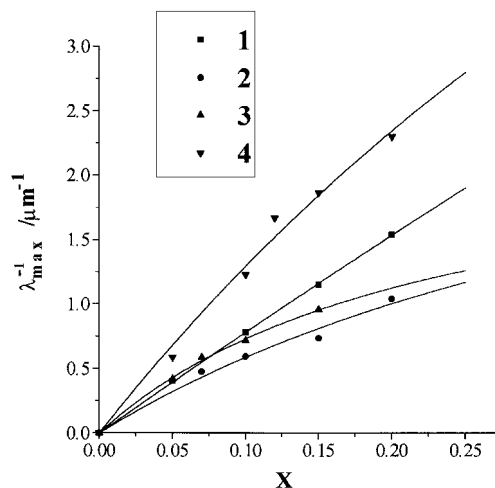


Figure 13. Dependence of  $\lambda_{\max}^{-1}$  on the molar fraction of chiral component for copolymers of the series PM-10,1(est.)/AX (1), PM-10,1(eth.)/AX (2), PM-5,1(eth.)/AX (3) and PM-6,3(est.)/AX (4).

Table 2. Helical twisting power  $A$  and parameter  $B$  for some copolymers [see equation (3)].

Name	$A/\mu\text{m}^{-1}$	$B$
PM-10,1(est.)/AX	7.9	0.2
PM-10,1(eth.)/AX	7.1	2.1
PM-5,1(eth.)/AX	8.6	2.5
PM-6,2(est.)/AX	13.9	1.0
PM-6,3(est.)/AX	14.7	1.6
PM-10,1(est.)/BX	4.5	0.2
PM-6,2(est.)/BX	7.2	1.1
PM-6,3(est.)/BX	12.0	2.7

- (1) With increasing length of the rigid fragment of the chiral monomer [copolymers of series PM-10,1(est.)/AX, PM-6,2(est.)/AX and PM-6,3(est.)/AX], the corresponding copolymers are characterized by an increase in helical twisting power (earlier this phenomenon has been described for low molecular mass mixtures [39]) and coefficient  $B$ , is accounted for by manifestation of the 'smectogenic character' of chiral monomer M-6,3(est.) with a long aromatic fragment.
- (2) With decreasing length of the spacer [compare PM-10,1(eth.)/AX and PM-5,1(eth.)/AX], parameter  $A$  increases, and this increase is associated with an increase in the rotational order parameter  $D = \cos 2\psi$  ( $\psi$  is the rotation angle about the long axis of chiral group) as a result of hindered rotation of chiral side groups about their axes. Earlier, this phenomenon was observed by Finkelmann and Rehage [40, 41] for homopolymers and copolymers with chiral groups based on cholesterol and *S*(-)-2-methylbutan-1-ol.
- (3) As a result of substituting the ester group connecting the rigid fragment to the chiral group by an ether linkage [compare PM-10,1(est.)/AX and PM-10,1(eth.)/AX, table 2], twisting power decreases. Most probably the order parameter decreases, and 'untwisting' of the helix is observed. Relatively high values of  $B$  support this reasoning.
- (4) Twisting power in a nematogenic matrix II [table 2, copolymers of series PM-10,1(est.)/BX, PM-6,2(est.)/BX and PM-6,3(est.)/BX] is much lower, and this behaviour is accounted for by the presence of elements of smectic order in the matrix.

Hence, in this work, a systematic synthesis of new chiral monomers and related LC copolymers has allowed us to characterize thermal and optical properties of the polymer chiral nematic phase as a function of the chemical nature of the optically active side groups. The conditions for the development of the new chiral ordered  $N_B^*$  mesophase have been studied, physicochemical and optical properties of this mesophase investigated, and a model accounting for the structure of this mesophase has been advanced.

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