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SHORT COMMUNICATION

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# Induction of a chiral nematic phase in smectic polymers

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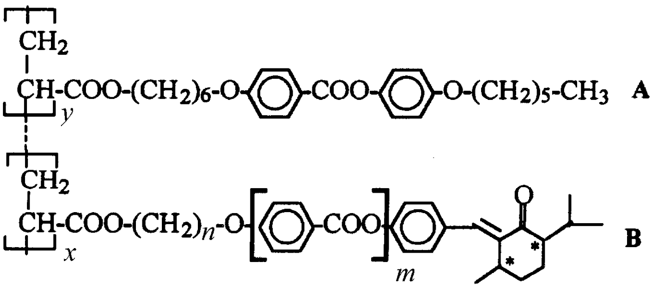
**Abstract** A number of new photosensitive copolyacrylates of different composition were obtained by the copolymerization of chiral photochromic benzilidene-*p*-menthane-3-one acrylic monomers with a smectogenic monomer containing a hexyloxyphenylbenzoate mesogenic group. The chiral, photochromic monomers differ by the length of the aliphatic spacer and the aromatic fragment. It was found that the introduction of a small number of chiral units into the copolymers (5 mol%) leads to the "degeneration" of the smectic C phase, which characterizes the hexyloxyphenylbenzoate homopolymer, and to the formation of the smectic A phase. An unusual effect of chiral nematic phase induction was observed for copolymers containing chiral side groups with two ring aromatic fragments. It should be pointed out that the chiral nematic phase does not occur in the case of the homopolymers of both initial comonomers. An explanation of this effect, based on the consideration of the chemical structure of the chiral and hexyloxyphenylbenzoate units, was suggested. The optical properties of cholesteric copolymers were investigated; the helical twisting power of the chiral groups of different structures was calculated. The possibility of using such copolymers as new photosensitive materials was demonstrated.

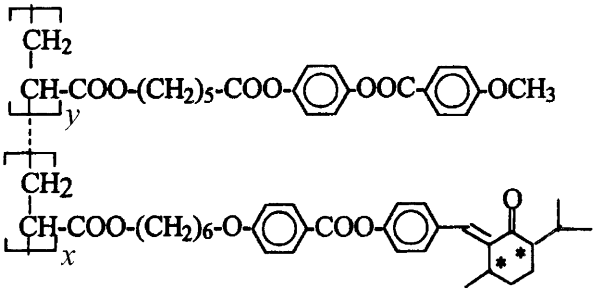
**Key words** Induction of chiral nematic phase · Liquid-crystalline copolymers · Photosensitive materials

## Introduction

A large number of low-molar-mass and polymeric mixtures, as well as copolymers, in which specific interaction and steric effects lead to the induction of more ordered mesophases, are known at the present time [1–13]. The most well-known examples are related to the systems where the initial components do not form smectic mesophases, but their mixing results in the appearance of the Smectic A (SmA) phase over a large concentration–temperature range [1–13]. Less work has been devoted to the investigation of the induction of less-ordered nematic or cholesteric mesophases in low-molar-mass smectic mixtures [14–16]. Finally, there are very few reports which consider the effect of such induction in smectogenic copolymers [17–19]. At the present moment, we do not have enough information to allow us to draw a conclusion about the possible causes of such abnormal behaviour. That is why in this work we made it our task to clarify the influence of the structure of chiral nonmesogenic side groups on the possibility of the "degeneration" of the layer order, i.e. the induction of the chiral nematic mesophase in the smectogenic matrix. For this purpose, copolymers with chiral side groups of different structure were synthesized:



According to the literature [20, 21] hexyloxyphenylbenzoate homopolymer **A** only forms the Smetic C (SmC) mesophase. The structure of chiral units **B** was varied over a wide range in order to reveal the peculiarity of its influence on the phase behaviour of the copolymers. It should be stressed that the presence of a double C=C bond in the chiral units makes such copolymers very attractive, for example, for their photo-optical properties [22–24]. As was shown before [22–24] for cholesteric copolymers **IV** containing the same chiral photochromic units and phenylmethoxybenzoate nematogenic groups, UV irradiation leads to an *E*-*Z* isomerization of the chiral units and, as a result, to the untwisting of the cholesteric helix.



**IV**

It was shown that such systems may be used for unique colour data recording on a coloured background [22–24]. That is why the synthesis and the investigation of these copolymers are of interest not only from the point of view of revealing the chiral nematic phase's induction conditions in a smectogenic matrix but also for enlarging our knowledge of the peculiarities of the phase behaviour of chiral liquid-crystalline copolymers in order to use them as new photosensitive materials.

## Experimental

### Synthesis of monomers

The hexyloxyphenylbenzoate smectogenic monomer was prepared according to the procedure described in Ref. [20]. The synthesis of the chiral, photochromic monomers is described in Ref. [24].

### Synthesis of homo- and copolymers

The polymers were synthesized by radical polymerization of monomers using the initiating agent 2,2′-azobis(isobutyronitrile) (AIBN) in benzene solution at 60 °C. For example, 100 mg chiral monomer and 1 mg AIBN were placed in a glass ampule and dissolved in 1 ml dry benzene. The solution was purged with dry argon for 20 min and the ampule was sealed. Then, the ampule was kept at 60 °C for 30 h; subsequently it was opened and the contents were poured into 15 ml methanol. The precipitated solid was purified by repeated precipitation from chloroform into methanol and outgassed in a vacuum.

### Techniques

The average molecular weights and the polydispersity of the polymers were determined by gel permeation chromatography (GPC) and are presented in Table 1. The GPC analyses were carried out with a Waters GPC-2 instrument equipped with an LC-100 column oven and a Data Modul-370 data station. Measurements were made using a UV detector, tetrahydrofuran as the solvent (1 ml/min, 40 °C), a set of columns of 100, 500 and $10^3$ Å and a calibration plot constructed with polystyrene standards.

The phase transitions in the copolymers were studied by differential scanning calorimetry (DSC) with a Perkin Elmer DSC-7 thermal analyser (a scanning rate of 10 K/min; prior to the DSC measurement the samples were annealed for 1 month at 45 °C).

The polarizing microscope investigations were performed using a Mettler TA-400 thermal analyser and a LOMO P-112 polarizing microscope.

The 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 $\mu$m were sandwiched between two flat glass plates. Prior to the tests, the polymer samples were annealed for 20–40 min at appropriate temperatures.

**Table 1** Yields and molecular weights of copolymers

| $X$[a] | $M_n$ ($10^3$) | $M_w/M_n$ |
|---|---|---|
| Copolymers of series **I** | | |
| 0.00[b] | 10.8 | 1.98 |
| 0.10 | 7.67 | 1.73 |
| 0.20 | 8.01 | 1.95 |
| 0.30 | 7.28 | 2.63 |
| Copolymers of series **II** | | |
| 0.05 | 7.35 | 1.47 |
| 0.10 | 7.76 | 1.67 |
| 0.15 | 7.55 | 1.97 |
| 0.20 | 7.29 | 1.54 |
| 0.30 | 5.68 | 1.75 |
| Copolymers of series **III** | | |
| 0.05 | 8.05 | 1.72 |
| 0.10 | 6.65 | 1.83 |
| 0.15 | 7.40 | 1.75 |
| 0.20 | 6.33 | 1.46 |
| 0.30 | 7.69 | 1.89 |
| 0.45 | 9.58 | 1.95 |
| 0.60 | 10.01 | 2.01 |

[a] $X$ is the content of chiral photochromic groups
[b] Data from Ref. [21]

X-ray diffraction measurements were carried out in a URS-55 instrument (Ni-filtered Cu $K_\alpha$ radiation, $\lambda = 1.54$ Å) with a flat-film camera at a distance of 56.7 mm from the sample.

Photochemical investigations were performed using a special instrument [23] equipped with a DRSh-250 ultra-high-pressure mercury lamp. Using filters, the 366-nm band of the linear radiation spectrum of the mercury lamp was selected. To prevent heating of the samples due to IR irradiation of the lamp, water filter was used. To obtain a plane-parallel light beam, a quartz lens was used. During irradiation, the constant temperature of the test samples was maintained using a Mettler FP-80 heating unit. The intensity of the UV irradiation was determined actinometrically [25] and was 4.1 mW/cm$^2$.

The photochemical properties of the copolymers in the condensed state were studied by illuminating the 10-$\mu$m-thick films at different temperatures. After a certain time of irradiation, the samples were annealed at a temperature 30 °C higher than the glass-transition temperature. During annealing, the spectra of the selective light reflection were recorded. The samples were annealed until no changes in the selective light reflection wavelength were observed (usually for about 40 min).

## Results and discussion

### Phase behaviour

According to the literature [21] a SmC mesophase with bilayer packing of mesogenic groups characterizes the hexyloxyphenylbenzoate homopolymer.

Polarizing optical microscopy shows that copolymers with one ring chiral unit (**I**), at a concentration up to 40 mol%, form smectic mesophases with a fan-shaped texture.

In X-ray patterns of oriented fibres of all three series of copolymers one can observe a diffuse halo at wide scattering angles ($\theta$ ˜ 20°). The splitting, typical of the SmC mesophase, is not observed in that case. Small-angle reflexes correspond to interlayer distances of about 36 and 24 Å. It seems, that these reflexes can be indexed as {0 0 2} and {0 0 3}, respectively. The {0 0 1} reflex cannot be observed, due to limited apparatus resolution.

The calculated length of the hexyloxyphenylbenzoate side group is about 35 Å; this allows a conclusion to be drawn about the formation in the copolymers of a SmA mesophase with bilayer packing of mesogenic side groups.

Thus, for all three series of copolymers the introduction of only 5 mol% of chiral units leads to the mesogenic groups' tilt "degeneration" (Fig. 1), i.e. to the formation of a SmA mesophase with the same type of packing (bilayer).

However, the most interesting fact is induction in the case of copolymers with two ring chiral side groups **II** and **III** of the chiral nematic phase (N$^*$, Fig. 1b, c). The assumption of its existence was made on the basis of polarizing optical microscopy data (on cooling the samples from an isotropic melt, a focal conic texture is formed, which easily transforms to a planar texture by shear deformation of the film). The formation of the N$^*$ mesophase is proved by DSC: in this case, the high-temperature endothermic peaks split into two peaks (Fig. 2).

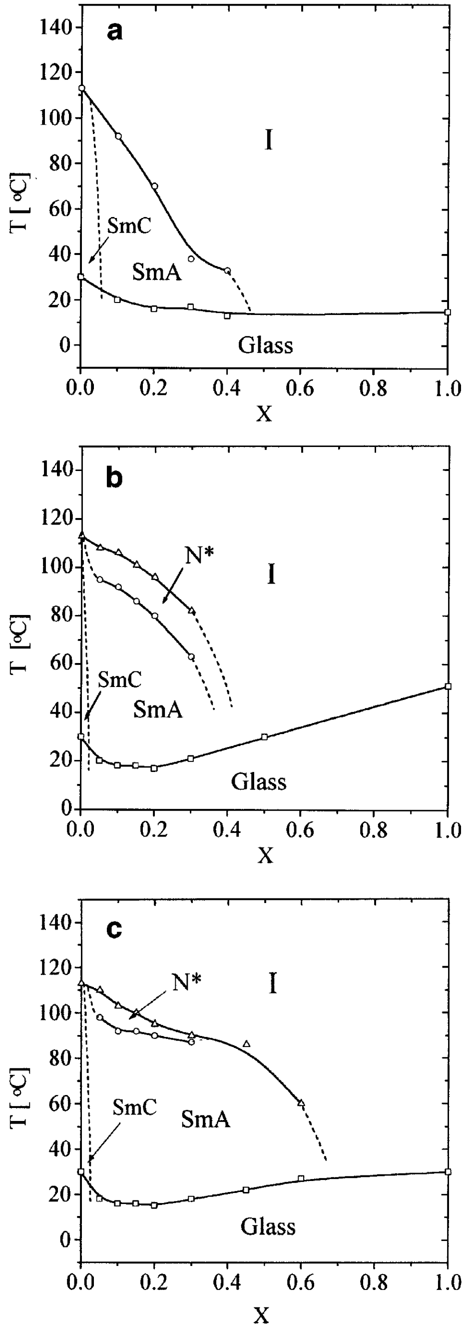


**Fig. 1** Phase diagrams for the copolymers of **a** series **I**, **b** series **II** and **c** series **III**

It is to be noted that the lengthening of the flexible spacer from 6 to 10 methylene units in the chiral side group leads to the narrowing of the temperature range of the N$^*$ mesophase.

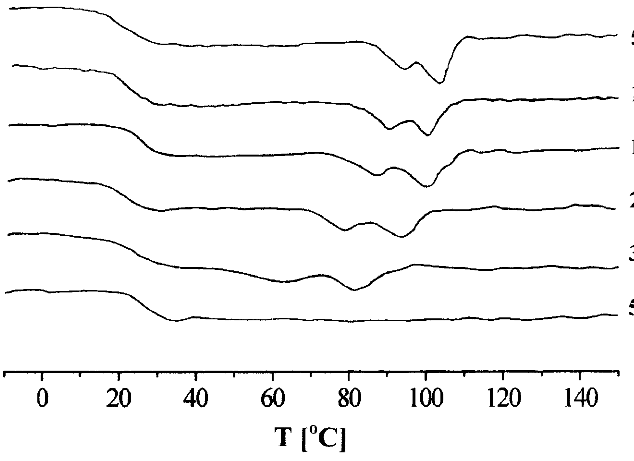


**Fig. 2** Differential scanning calorimetry curves for copolymers of series **II** with different content of the chiral units. (Contents in mole percent are shown in the figure; the heating rate was 10 °C/min, second heating scans.)

The formation of the chiral nematic phase is proved by the presence of selective reflection of light which is discussed in detail later.

While considering the possible causes of such abnormal phase behaviour of the copolymers, it should first be underlined that the maximum effect (i.e. the widest temperature range of the induced chiral nematic phase) is observed in the case of copolymers of series **II**. In that case, the side groups have the most similar chemical structure because they have a spacer of the same length and identical phenylbenzoate aromatic fragments. This indicates that the main cause of the $N^*$ phase induction is the structural similarity of the side groups. It seems that in the case of copolymers of series **II** and **III** the chiral side groups are very "compatible" with the hexyloxyphenylbenzoate smectogenic matrix and try to "penetrate" into the smectic layer, and thus they "destroy" it because of their bulky menthone groups. This breaks the translational order, but the orientational order remains unchanged. In contrast, in the case of copolymers with one ring chiral side group, menthone-containing groups are "pushed out" from the smectic layer and are located in the "poorly ordered" microphase, which is formed by the main chain and flexible spacers. Though this explanation may seem rather absurd, in our opinion, it is the only possible one.

## Optical properties

The transmittance spectra proved the induction of the $N^*$ mesophase in copolymers **II** and **III**: planar oriented films have selective light reflection in the visible and the IR spectral ranges (Fig. 3). Close to the point of the $N^*$-SmA transition, a sharp growth of the selective light reflection wavelength ($\lambda_{max}$), which is due to the pretransitional untwisting of cholesteric helix, is observed (Fig. 3) [26–28]. In order to calculate the helical twisting power of the chiral units in the copolymers, the dependencies of the inverse selective

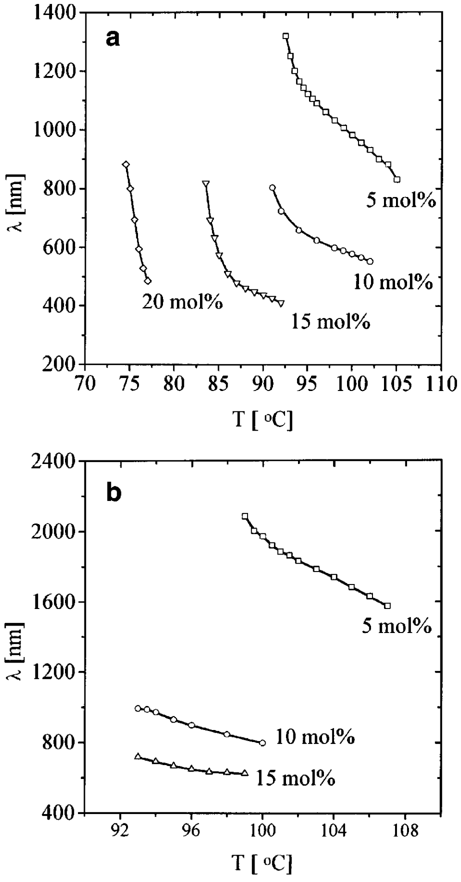


**Fig. 3** Temperature dependencies of selective light reflection wavelengths for copolymers of **a** series **II** and **b** series **III** with different chiral unit contents

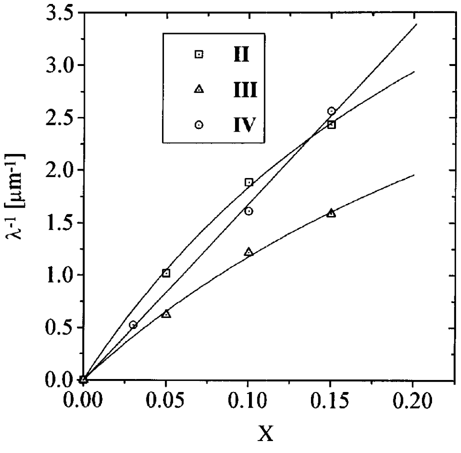


**Fig. 4** Dependence of $\lambda^{-1}$ on the molar fraction of chiral units (at $T = 0.95\, T_{N^*-I}$) for copolymers **II**, **III** and **IV**

**Table 2** Values of the helical twisting power (*A*) and parameter *B* of Eq. (1) for chiral, photochromic copolymers of different series

| Series of copolymers | A ($\mu m^{-1}$) | B |
|---|---|---|
| **II** | 24.67 ± 1.52 | 3.40 ± 0.71 |
| **III** | 14.85 ± 1.25 | 2.60 ± 0.89 |
| **IV** | 16.85 ± 0.50 | 0.0 ± 0.5 |

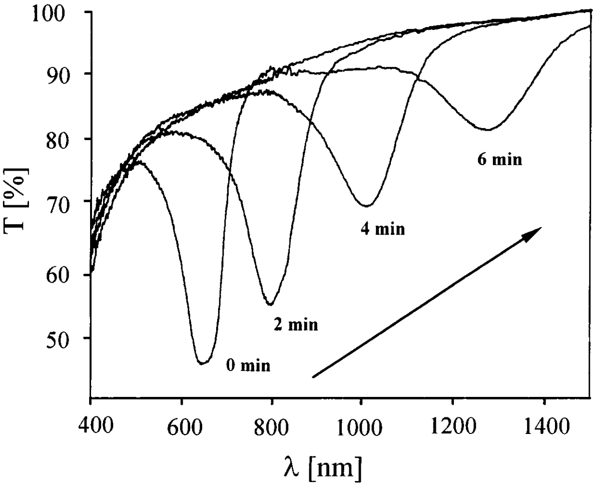


**Fig. 5** Changes in transmission of copolymer **II** with 10 mol% chiral, photochromic units during UV irradiation. The *irradiation time* is shown in the figure; temperature of irradiated sample −94 °C

light reflection wavelength on the mole fraction of the chiral component were plotted (Fig. 4). The dependencies were approximated by a function (Eq. 1) which we have used before [29, 30].

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

where *A* is the helical twisting power and *B* is a parameter characterizing the deviation of this plot from linear character.

The calculated values of *A* and *B* are presented in Table 2. For comparison, in Table 2 values of these parameters are presented for copolymers of series **IV** [24], which contain nematogenic phenylmethoxybenzoate groups.

As seen from the values of the helical twisting power in the case of smectogenic copolymers **II**, the helical twisting power is much greater than in the case of copolymers **IV**. It is interesting to note that the inverse situation is more common: the helical twisting power of a dopant or chiral side group in a smectogenic matrix is always lower than in a nematogenic one [30]. The causes of such behaviour need further investigation.

In our case, the lengthening of the spacer in the chiral side units leads to a considerable decrease in the helical twisting power; this may be explained by the decrease in a rotational order parameter [30, 31] as well as by a larger smectogenity of the system, because the temperature range of the $N^*$ phase becomes smaller with the lengthening of the spacer. For a copolymer with hexyloxyphenylbenzoate side groups the values of the *B* parameter are much higher than in the case of copolymers **IV**.

As we have already mentioned in the Introduction, UV light action on these copolymers must lead to *E-Z* isomerization of chiral benzilidene-*p*-menthane-3-one fragments. Such a process must be accompanied by a decrease in the helical twisting power and an untwisting of the cholesteric helix. As seen from Fig. 5, UV irradiation followed by annealing leads, in fact, to a shift of the selective light reflection peak to the long-wavelength region of the spectrum.

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