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## Liquid Crystals

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# A comparative study of photo-optical behaviour of photosensitive chiral copolymers with cholesteric mesophases induced in nematogenic and smectogenic matrices

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The photo-optical behaviour of two series of chiral photochromic acrylic copolymers with a chiral nematic phase has been studied. These copolymers contain identical chiral photochromic units, but have different structures of the phenyl benzoate mesogenic side groups which are responsible for the development of LC phases. This approach allowed us to examine specific features of the photo-optical behaviour of the copolymers as a function of the nature of the LC 'matrix' in which the cholesteric phase was induced. The action of UV irradiation was shown to lead to the *E*–*Z* isomerization of the chiral side groups and, as a consequence, to untwisting of the cholesteric helix of the copolymers. For copolymers of both series, the effective quantum yields of this photochemical process were calculated. In the case of copolymers in which the cholesteric mesophase is induced in a smectogenic matrix, the corresponding values of the quantum yield are lower and depend slightly on temperature. A plausible explanation of the above phenomena is suggested.

## 1. Introduction

Recently, research and developments in photosensitive polymers which are capable of 'self-organization' and the formation of phases with different symmetry and degrees of ordering constitute one of the most promising new directions for the preparation of photochromic materials [1–5]. The great interest in such materials is primarily related to their possible application as photo-controllable media for data recording and storage, holography, optical electronics, the development of molecular photoswitchable units, and optical memory.

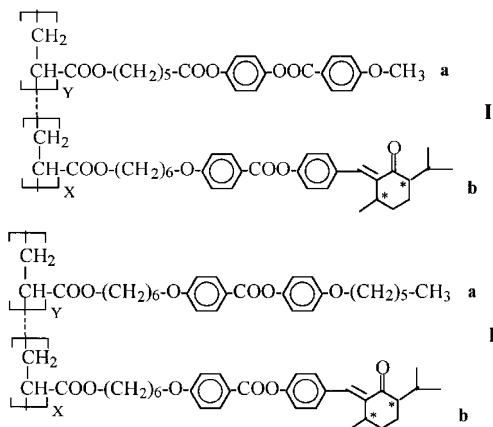
Recently, in our work and in that of the research group at the Philips company, a new approach in the development of cholesteric (chiral nematic) copolymers with irradiation-controlled pitch of the cholesteric helix was suggested [6–13]. Such copolymers contain combined chiral photochromic side groups (derivatives of menthone [6–10] or cinnamic acid [11]) which can undergo a light-induced *E*–*Z*-isomerization. As a result

of this process, the helical twisting power of these groups markedly decreases, and untwisting of the supramolecular helical structure is observed. In [6–8, 11], specific features of the kinetics of the light-induced process of helix untwisting were studied, and effective quantum yields of this photoprocess were calculated. In [10], the effect of the structure of the chiral photochromic benzylidene menthanone units on the phase behaviour, and the optical and photo-optical properties of such systems was examined.

However, copolymers containing similar chiral photochromic units, but having different structures of the achiral units producing a particular type of LC organization have also aroused considerable interest. In this work, as an LC matrix, we have used two types of mesogenic monomer based on phenyl benzoate from which the homopolymers are able to produce only nematic (**Ia**) [14, 15] or smectic SmC (**IIa**) mesophases [16, 17]. As a second chiral photochromic component, we selected an acrylic monomer containing an optically active photosensitive benzylidene-*p*-menthanone fragment which provides the possibility of helical twisting of the initial nematic

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(copolymers of series **I**) or smectic C (copolymers of series **II**) phases



The objective of the present work was to identify specific features of the photo-optical behaviour of the two series of menthone-containing copolymers as a function of the structure of the LC 'matrix' in which the cholesteric mesophase may be induced. In this investigation, we have tried to answer the question concerning the extent to which the rate of photoinduced untwisting of the cholesteric helix depends on the character of the LC ordering in the matrix and to understand the effect of temperature on this process.

## 2. Experimental

The synthesis of the chiral photochromic menthone-containing copolymers was described in [12, 13].

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

Selective light reflection by the chiral polymers was studied with a Hitachi U-3400 UV-Vis-IR spectrophotometer equipped with a Mettler FP-80 hot stage. The polymer samples with a thickness of 20  $\mu\text{m}$  were sandwiched between two flat glass plates. Prior to tests, the polymer samples were annealed for 20–40 min at appropriate temperatures.

Photochemical investigations were performed using an optical set-up [7] equipped with a DRSh-250 ultra-high pressure mercury lamp. Using filters, the 313 and 366 nm bands of the linear radiation spectrum of a mercury lamp were selected. To prevent heating of the samples due to IR irradiation from the lamp, a 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 intensities of UV irradiation were determined actinometrically [18] and were equal to  $1.0 \times 10^{-9}$  Einstein  $\text{s}^{-1} \text{cm}^{-2}$  ( $\lambda_{\text{ir}} = 313 \text{ nm}$ ) and  $1.1 \times 10^{-8}$  Einstein  $\text{s}^{-1} \text{cm}^{-2}$  ( $\lambda_{\text{ir}} = 366 \text{ nm}$ ).

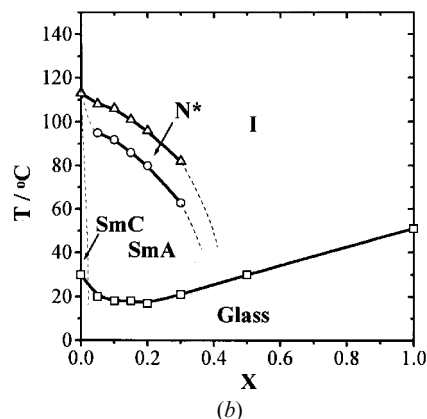
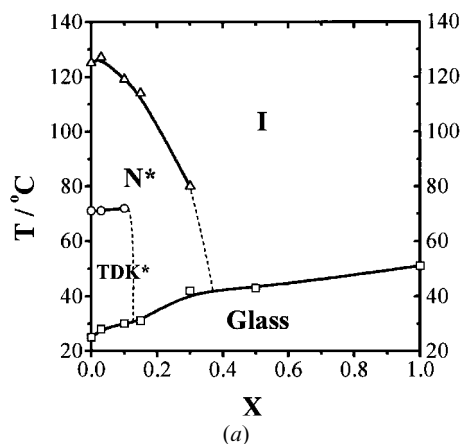


Figure 1. Phase diagrams for the copolymers of series **I** (a) and **II** (b).

Photochemical properties of the copolymers in the bulk were studied by illuminating the 10  $\mu\text{m}$  thick films at different temperatures. After a certain time of irradiation, the samples were annealed at a temperature 10–15°C lower than the isotropization transition temperature. During annealing, the selective light reflection spectra were recorded or values of the clearing temperature ( $T_{\text{cl}}$ ) were determined periodically by polarizing microscopy. The samples were annealed until no changes in the selective light reflection wavelength or in  $T_{\text{cl}}$  were observed (usually, about 40 min).

## 3. Results and discussion

Synthesis and a detailed description of the phase behaviour and optical properties of copolymers **I** and **II** have been reported in [13]. Let us emphasize that copolymers **I** and **II** are characterized by quite different phase behaviours: in the case of copolymers **I**, chiral nematic ( $N^*$ ) and ordered TDK\*† mesophases are developed; in the case of copolymers **II**,  $N^*$  and SmA mesophases are formed (figure 1). The different phase

†The structure of this phase is discussed in detail in [12].

behaviours of the copolymers also manifest themselves in different optical properties of the copolymers (figure 2).

Planar oriented films of the copolymers are capable of selective light reflection in the visible and IR spectral regions. In the case of copolymers **I**, as the temperature decreases, the selective light reflection wavelength ( $\lambda_{\max}$ ) slightly increases, figure 2(a); in the case of copolymers **II**, figure 2(b), one observes a dramatic untwisting of the cholesteric helix which is related to a pretransitional enhancement in the smectic order fluctuations [19–21].

For copolymers **II**, irradiation and subsequent annealing markedly shift the selective light reflection maximum to a long wavelength spectral region (figure 3). This trend is usually accompanied by broadening of the selective light reflection peak. This arises from a non-uniform distribution of Z-isomeric chiral units formed during irradiation in the film thickness [7]. Furthermore, as was shown earlier in [7], the rate of helix untwisting is a diffusion-controlled parameter and, hence, strongly depends on temperature.

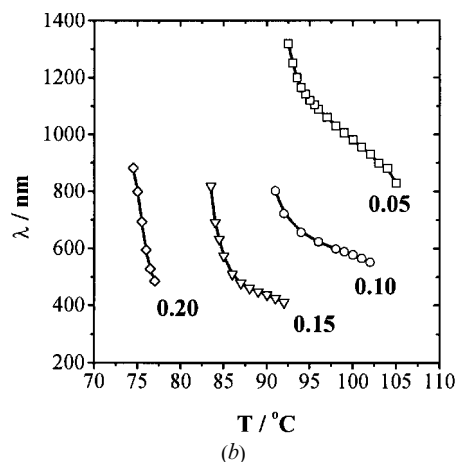
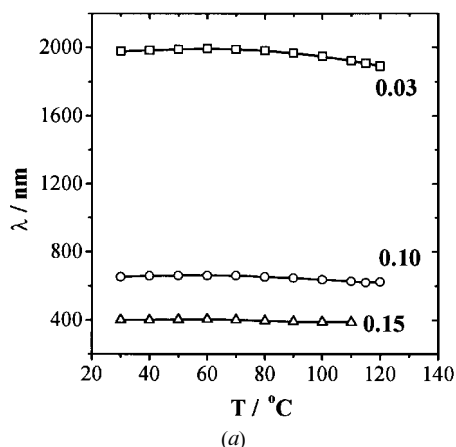


Figure 2. Temperature dependences of the selective light reflection wavelengths for copolymers of series **I** (a) and **II** (b) with different mole fractions of chiral units.

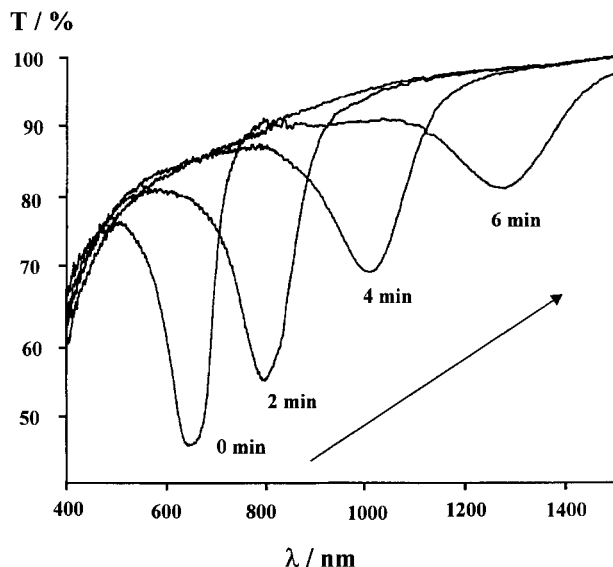


Figure 3. Changes in the transmission spectrum of copolymer **II** with 10 mol% of chiral photochromic units during UV irradiation (366 nm). Irradiation time is shown; temperature of irradiated sample is 94°C.

In the case studied, a very pronounced temperature dependence of the rate of increase in  $\lambda_{\max}$  is observed for copolymers containing nematogenic units **I**, figure 4(a). In the case of copolymers **II**, the rate of this process is almost independent of temperature, figure 4(b), and this presents a case of particular interest for further studies.

As a result of UV irradiation, the temperatures of phase transitions decrease by several degrees (4–10°C), and this trend is related to a certain decrease in the anisotropy of the chiral side units during irradiation. However, it is interesting to note that in this case the temperature interval of the existence of the N\* mesophase remains almost unchanged.

For a quantitative estimation of the efficiency of the above process, virtual quantum yields of the photo-process were calculated. To this end, the formula derived in [7] was used in its modified form:

$$\varphi'_E = (\varphi_E)_{t=0} = - \frac{\rho l}{MAI_0(1 - 10^{-D_\lambda})} \left( \frac{d\lambda_{\max}^{-1}}{dt} \right)_{t=0}$$

where  $\rho$  is the sample density ( $\text{g cm}^{-3}$ ),  $l$  is the sample thickness (cm),  $M$  is the average molar mass of the copolymer ( $\text{g mol}^{-1}$ ),  $A$  is the helical twisting power ( $\mu\text{m}^{-1}$ ),  $I_0$  is the incident light intensity ( $\text{mol s}^{-1} \text{cm}^{-2}$ ),  $D_\lambda$  is the optical density at a wavelength corresponding to particular actinic light wavelengths (313 and 366 nm),  $\lambda_{\max}$  is the selective light reflection wavelength ( $\mu\text{m}$ ), and  $t$  is the irradiation time (s).

Let us emphasize that values of the virtual quantum yields in this case strongly depend on the efficiency of

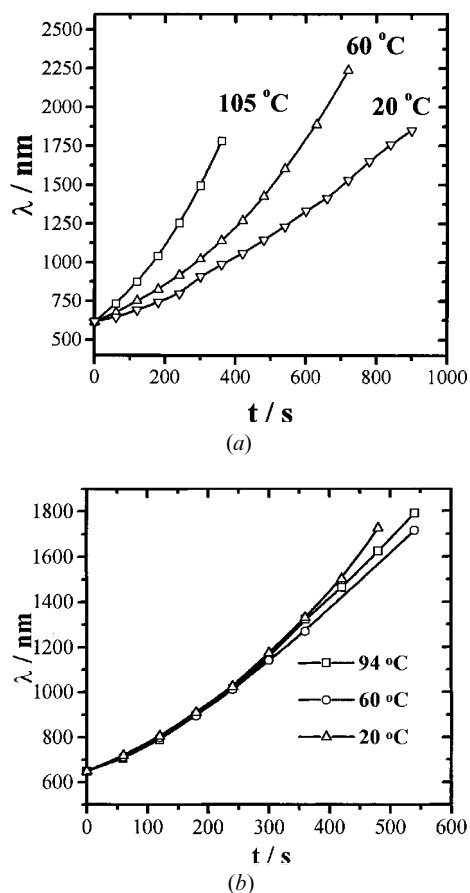


Figure 4. Helix unwisted during UV irradiation (366 nm) for copolymers **I** (a) and **II** (b) with 10 mol % of chiral photochromic units at different temperatures. Annealing temperature  $T_{N^* - 1} = 12^\circ\text{C}$ .

the diffusion mobility of the macromolecules in the copolymers. The calculations of the true quantum yields present a more complicated task [22, 23].

Figure 5 shows the temperature dependences of the virtual quantum yields for copolymers of both series and for different wavelengths of UV irradiation. Analysis of the above dependences allows us to outline a number of specific features.

First, upon irradiation of copolymers with a shorter wavelength (313 nm), the quantum yield appears to be several times lower. This trend is associated with a difference in the extinction coefficients for films of the copolymers as observed at the different wavelengths of 313 and 366 nm. At  $\lambda_{\text{ir}} = 313$  nm, incident light is completely absorbed in a thin surface layer; at  $\lambda_{\text{ir}} = 366$  nm, the optical density of the films is equal to about 0.15, and so the photochemical reaction proceeds throughout the whole film thickness. Evidently, in the latter case, the limiting effect of self-diffusion on the rate of helix untwisting is much lower, and the efficiency of irradiation is much higher.

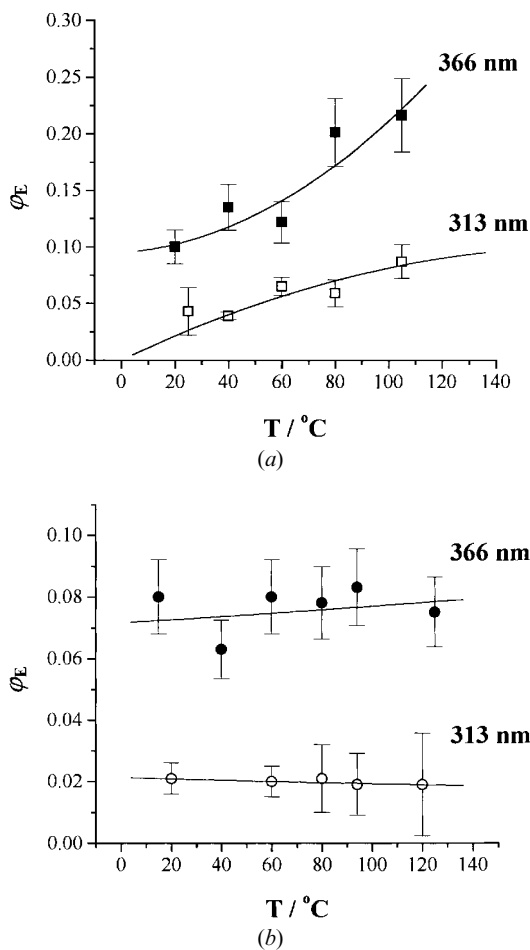


Figure 5. Dependence of apparent quantum yield on temperature for copolymers **I** (a) and **II** (b) with 10 mol % of chiral photochromic units on irradiation with UV light of different wavelengths.

Second, as was mentioned earlier, the second specific feature concerns the absence of any temperature dependence of the quantum yield for copolymers **II**. Furthermore, this trend is observed for both wavelengths of UV irradiation.

Finally, in the case of copolymers **II**, for both wavelengths  $\lambda_{\text{ir}}$ , the values of the quantum yield are much lower. As known from literature data, the efficiency of isomerization of derivatives of azobenzene [24–28] and, in particular, of stilbene [27, 28] strongly depends on the free volume existing in the polymer matrix and on the local viscosity of the system. In the case studied, the low values of the quantum yield of copolymers **II** are likely to be related to the presence of elements of smectic ordering in the smectogenic hexyloxyphenyl benzoate matrix which reduce the free volume content and increase the viscosity of the system. Hence, in the case studied, efficiency of untwisting of the cholesteric helix is controlled not only by the diffusion rate of the *Z*-isomeric

units that are formed, but probably also by the free volume content of the copolymers. However, this hypothesis evidently requires additional experimental verification.

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