

A new approach to photorecording based on hindering a phase transition in photochromic chiral liquid crystalline polymers

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The phase transition from an 'isotropic smectic phase' to the proper SmA^* phase in a new photochromic chiral copolymer can be prevented by illumination with non-polarized white light of low intensity. On the basis of the effect observed, a novel photorecording technique is suggested, so that the shadow image appears as a white scattering texture of the SmA^* phase on the background of the transparent, optically isotropic TGB_A -like phase. Optical, DSC, and X-ray studies of the polymer are reported, the photorecording set-up is described, and the first written photoimage is presented.

1. Introduction

Recent years have been marked by a considerable interest in the synthesis and study of liquid crystalline (LC) and amorphous polymers containing azo dye fragments in the side chains. These polymers were convincingly shown to be applicable for reversible, optical, high density data recording and for data storage systems with optical memory [1–6].

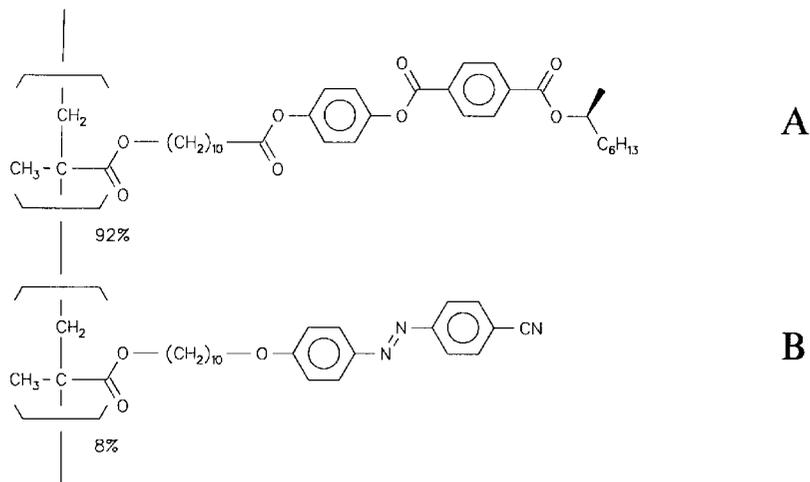
The principle of photo-optical recording is based on the activation of photochromic azo dye side branches of various homo- and co-polymers under the action of light with a certain wavelength. These azo dye fragments undergo a series of photochemical transformations (*trans*–*cis*-isomerization) which cause configurational changes: the rod-like azobenzene groups in the *trans*-configuration rearrange to the *cis*-isomers having a bent (broken) form. Such transformations lead to local changes in orientation of not only photochromic monomer units, but also of the neighbouring non-photochromic mesogenic side groups. The probability of light absorption by photochromic fragments is different, so the photochromic side branches must acquire a predominant orientation due to their photoselection. If polarized light is used, the azo fragments are oriented in such a way that the long axes of the dye fragments are perpendicular to the electric vector of the light (or laser illumination). This process is accompanied by orientation of the neigh-

bouring side groups in amorphous polymers and the reorientation of neighbouring mesogenic groups in LC polymers; in other words, a cooperative orientation of photochromic and non-photochromic groups takes place. Thus, the light acts as a 'controlled external field' permitting us to regulate the supramolecular structure of the polymer and to obtain highly oriented polymer materials at ambient temperature.

The orientation of asymmetric side fragments of amorphous and LC polymers results in a significant appearance of photoinduced birefringence, Δn_{ind} . The values of Δn_{ind} essentially depend on the initial structural organization of the polymer matrix: the higher the degree of mesogenic groups ordering, the lower are the values of the photoinduced birefringence, since the orientational order in the LC state most probably restricts the reorientation of side groups and, therefore, that process is probably more effective in the less ordered medium.

In our preceding papers and the publications of other authors [1–9], mainly nematic and smectic photochromic azo dye-containing copolymers have been used for photo-optical investigations. In this work we have focused our attention on the synthesis, structure, and photo-optical study of the chiral photochromic copolymer SK8, consisting of chiral phenyl benzoate mesogenic side groups and photochromic azobenzene dye fragments linked to the main chain via aliphatic spacers of equal length. The general formula of the copolymer SK8 is as follows:

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Two aspects make this copolymer especially attractive. First, the copolymer is one of the new representatives of *chiral* photochromic polymers, the study of which is of a great interest from both structural and photo-optical points of view; we should note that the number of the chiral photochromic polymers described in the literature is limited to only a few examples [10]. Second, the chiral homopolymer (A) forms the unusual 'isotropic smectic phase' described recently by one of us [11, 12] in the framework of a TGB_A-like structure; the isotropic character of that mesophase could predetermine the easy orientation of the mesogenic fragments of the copolymer SK8 under the action of light irradiation according to the data mentioned above and also in [5].

Having in mind that elucidation of the relationship 'molecular structure–optical properties–photo-optical behaviour' for chiral photochromic polymers practically does not exist up to date, we associate the goal of the present publication and future work in that field with the synthesis of new types of chiral photochromic LC polymers and with a systematic study of their thermal and structural properties, as well as their photo-optical behaviour.

2. Experimental

2.1. Synthesis of monomers and copolymerization

The chiral methacrylic comonomer A was synthesized according to the method described in [11]. Synthesis of the methacrylate with the 4-cyanoazobenzene group, i.e. comonomer B, was carried out according to a method reported earlier [13]. Copolymerization of the corresponding methacrylic monomers occurred in dry benzene (10% solution) during 72 h at 60°C using AIBN as initiator (0.1 wt %). The copolymer batch (0.3 g) was reprecipitated 3 times from chloroform into methanol and washed several times with 50 ml of boiling methanol.

The composition of the copolymer has been assumed to be equal to that of the monomer mixture used due to the almost identical chemical structures of the comonomers. In the present paper, the properties, structure, and photo-optical behaviour are presented only for the copolymer containing 8 mol % of the photochromic monomer B.

2.2. Methods

DSC curves were recorded with a Perkin-Elmer DSC-2C calorimeter at various heating/cooling rates from 1.25 to 10 K min⁻¹. The temperatures of phase transitions reported below are the values reduced to zero cooling rates.

Microscopic textures were observed using a Leitz polarizing microscope equipped with a Mettler FP-82 heating stage and videorecording system.

X-ray scattering curves were measured for samples in 2 mm capillaries by a modified STOE STADI 2 diffractometer using CuK_α radiation and a PSD linear position scanning detector [14]. For evaluation of the peak maxima, the curves were fitted with the split Pearson VII function (small angle range) and Lorentz function (wide angle range).

VIS spectra and linear dichroism of the copolymers were studied using Cary 17 and Hitachi U3400 spectrophotometers. Circular dichroism curves were obtained with a JASCO 500C spectropolarimeter from a 6 μm thick polymer film.

The photorecording was carried out with light from a 60 W incandescent lamp or an 11 W saving lamp of the same light flux from ~10 cm distance. SZS-21 and FS-6 colour glass filters were used for selective irradiation within the wavelength ranges 400–500 and 300–400 nm, respectively. To estimate the illumination intensity used for the photorecording, a Melles Griot broadband power/energy meter 13PEM001 was used.

3. Results and discussion

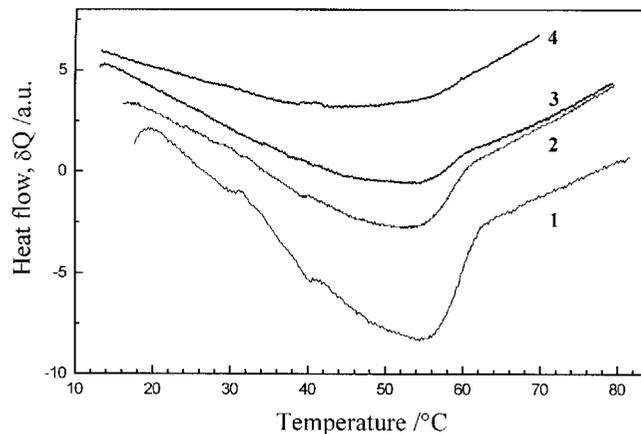
Before we start to consider the phase behaviour of the chiral photochromic copolymer synthesized in the present work, let us briefly recall the structural parameters of the corresponding homopolymers—the chiral homopolymer **A** and the azobenzene homopolymer **B**. Phase transitions for these homopolymers are summarized in the table. The homopolymer **B** (named CABO-10-OM in [13]) forms below its clearing point a standard SmA phase which is frozen into a glass at room temperature. For homopolymer **A** (named P8*M in [11]) the DSC, X-ray, and broad line PMR data give evidence of a phase transition at 64°C and indicate a layered smectic structure below that temperature, but no optical birefringence has been observed. Later, a TGB_A-like structure with extremely short helical pitch (less than the wavelength range of visible light) was suggested for that ‘isotropic smectic phase’ [12].

3.1. Phase behaviour and structural features of the copolymer SK8

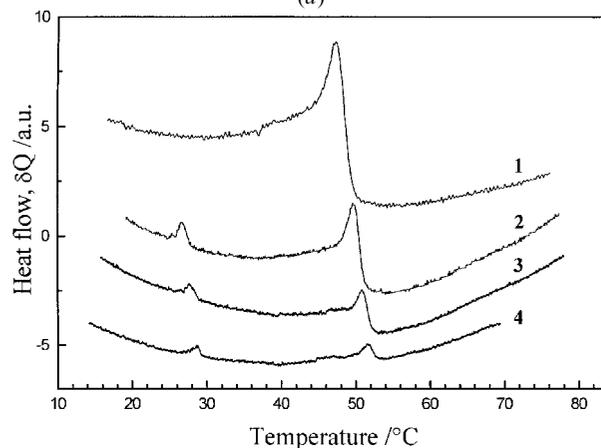
The DSC curves of the copolymer show only one broad peak on heating, but the shape of the corresponding curve on cooling depends on the cooling rate (figure 1). As seen from the figure, only one peak is observed on fast cooling to room temperature. When the cooling rate is lower than 5 K min⁻¹, a second peak appears.

The DSC data are supported by visual observations and X-ray measurements. When the copolymer is being cooled fast from the isotropic melt, no visual changes occur, and the resulting texture appears at room temperature as a uniform, highly transparent, optically isotropic texture and shows neither birefringence nor visible light scattering. However, the X-ray diffraction pattern from that phase (figure 2, curve 1) gives evidence of a layer structure: three peaks in the small angle range correspond to a single lattice with the period $d_0 \sim 65 \text{ \AA}$ which is close to the value for the TGB_A-like phase of the homopolymer **A**. Therefore, the same TGB_A-like structure has been suggested for the ‘isotropic smectic phase’ of the copolymer SK8.

We should emphasise here that there is no conclusive proof yet for assigning the ‘isotropic smectic phase’ as a TGB_A phase, i.e. no miscibility studies with known materials forming that phase. On the other hand, the combination of properties observed for the ‘isotropic smectic phase’ (layered structure, high optical activity,



(a)



(b)

Figure 1. DSC curves for copolymer SK-8 on heating (a) and on cooling (b), in both cases at 10 K min⁻¹ (1), 5 K min⁻¹ (2), 2.5 K min⁻¹ (3) and 1.25 K min⁻¹ (4).

and the complete absence of birefringence within the visible wavelength range) cannot be explained otherwise in terms of any known smectic phase from SmA to SmQ. Also, the chemical structure of the chiral mesogenic side groups of the homopolymer P8*M and of the copolymer SK8 meet perfectly the conditions favouring formation of the conventional TGB_A phase, as formulated by Goodby *et al.* [15].

When the copolymer SK8 is cooled slowly (at 2.5 K min⁻¹ or less), a phase transition occurs at $\sim 30^\circ\text{C}$, and the polymer sample appears at ambient temperature

Table. Phase transitions of the homopolymers.

Homopolymer	M_w	M_w/M_n	Phase transitions/°C	Layer thickness $d/\text{\AA}$	Ref.
A	99000	2.7	g 30 TGB _A -like 64 I	63.3	[11, 12]
B	23200	4.3	g 35 SmA 161 I	43.0	[13]

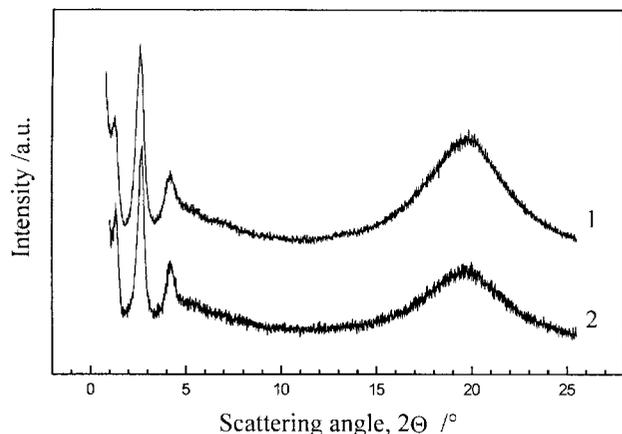
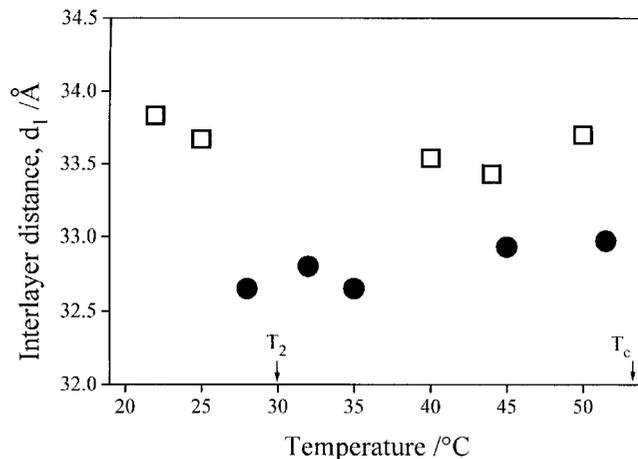


Figure 2. X-ray curves of SK8 at room temperature for polymer samples of different prehistory: (1) the TGB_A-like phase, (2) the SmA* phase.

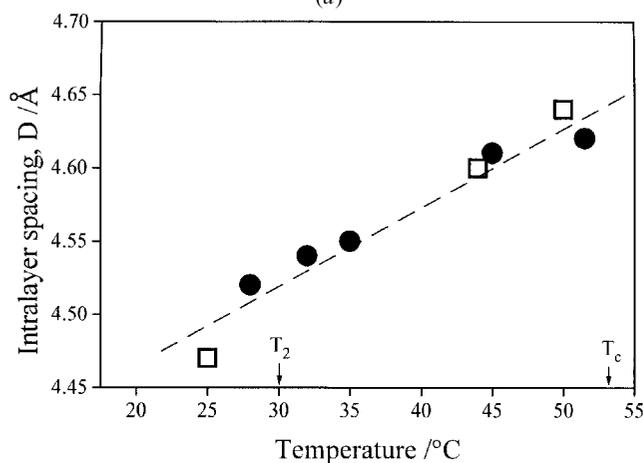
as a turbid, highly scattering, fine grained, confocal texture typical for proper smectics (figure 3). The X-ray scattering curve from the latter phase (figure 2, curve 2) is similar to curve 1, but the first scattering peak is much better resolved and the corresponding interlayer distance is somewhat higher, $d_0 \sim 67 \text{ \AA}$. (For both X-ray curves, the second order reflection $d_1 = d_0/2$ is more intense than the first, probably due to the particular distribution of the electron density along the mesogenic side group, as has been suggested for other LC polymers with phenyl benzoate side chains [16, 17].) We should note that Goodby *et al.* [18] report a similar change in the X-ray curves for a low molar mass liquid crystal at the transition from TGB phase to conventional smectic phase: the first X-ray peak grows, and the corresponding layer thickness decreases somewhat.

The 'proper smectic phase' of the copolymer, as obtained by slow cooling below 30°C , shows no ferroelectric switching, and the d_0 value estimated from the series of small angle scattering peaks shows no prominent temperature dependence, thus indicating an orthogonal smectic structure. The broad peak of the wide angle X-ray scattering of the mesophase is typical for disordered smectic phases. We can therefore suggest a SmA* structure for the low temperature 'proper smectic' mesophase of the copolymer SK8.

Figure 4(a) presents the layer spacing $d_1 = d_0/2$, estimated from the second X-ray peak of maximum intensity, as a function of temperature; figure 4(b) shows the temperature dependence of the distance between neighbouring side groups within the layer, D , measured from the wide angle peak. We should recall here, that a copolymer sample can appear at any temperature below the clearing point $T_c = 53.3^\circ\text{C}$ in the 'isotropic smectic phase' (when heated from the TGB_A-like amorphous



(a)



(b)

Figure 4. The position of the small angle peak of maximum intensity, d_1 (a), and the in-layer spacing, D (b), versus temperature, for the TGB_A-like phase (open squares) and the SmA* phase (filled circles).

glass), as well as in the proper smectic phase (when heated from the SmA* glass).

As seen from figure 4(a), the d_1 value for either mesophase remains practically constant with temperature, but the 1.5 \AA difference between the d_1 values for the two mesophases is statistically significant and without experimental error. On the other hand, the D values follow the same straight line for both mesophases. We can therefore conclude that the 'isotropic smectic phase' and the SmA* phase of the polymer differ in the ordering of the smectic layers, but not in the ordering of the side groups within the layers.

Figure 5 presents molecular models for the chiral mesogenic side groups **A** and the azobenzene dye side groups **B** in their most elongated conformations. The thickness of smectic layers for copolymer SK8 is between once and twice the length of the chiral side chain **A**,

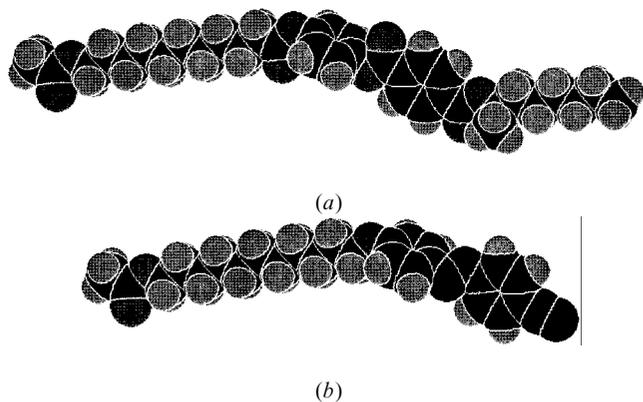


Figure 5. Molecular models of the mesogenic side groups: (a) chiral side group **A**, (b) photochromic side group **B** in *trans*-configuration.

$l \sim 39.5 \text{ \AA}$, but it should not be influenced much by the shorter dye mesogenic chains **B**, $l \sim 29.5 \text{ \AA}$, due to the small concentration of the latter.

The only reasonable structure of the mesophase layer must include mutual penetration of the chiral terminal groups of the side chains (figure 6), similar to that in the layer packing suggested for the homopolymer **A** [11]. The overlapping is somewhat deeper in the proper SmA^* phase ($d_0 \sim 65 \text{ \AA}$) than in the TGB_A -like phase ($d_0 \sim 67 \text{ \AA}$). Figure 7 summarizes the proposed scheme of phase transitions for the copolymer: the monotropic TGB_A -like phase formed on cooling from the true liquid phase (above 53.3°C) can be frozen in a glass before the TGB_A -like to SmA^* phase transition occurs, if the cooling rate is fast enough.

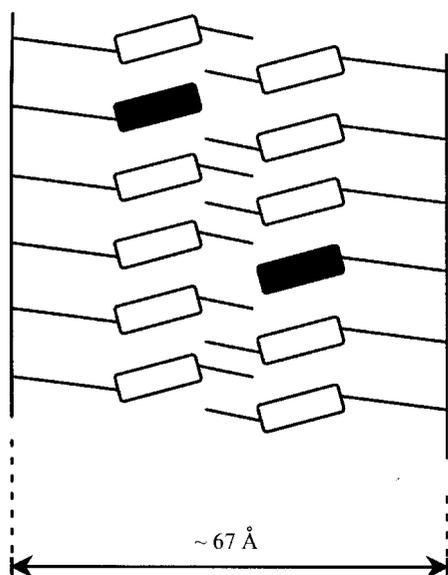


Figure 6. Proposed local packing of mesogenic groups in the smectic layers.

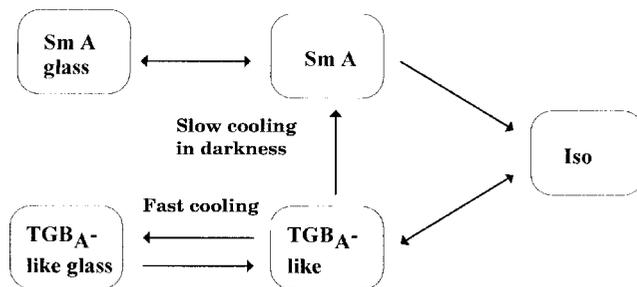


Figure 7. Proposed scheme of phase transitions for the copolymer SK8.

3.2. Optical properties and photosensitivity of the copolymer SK8

The copolymer SK8 contains a small percentage of azobenzene dye moieties which are capable of photo-induced *cis-trans*-isomerization. The absorption spectra of the polymer in solution [figure 8(a)] show two

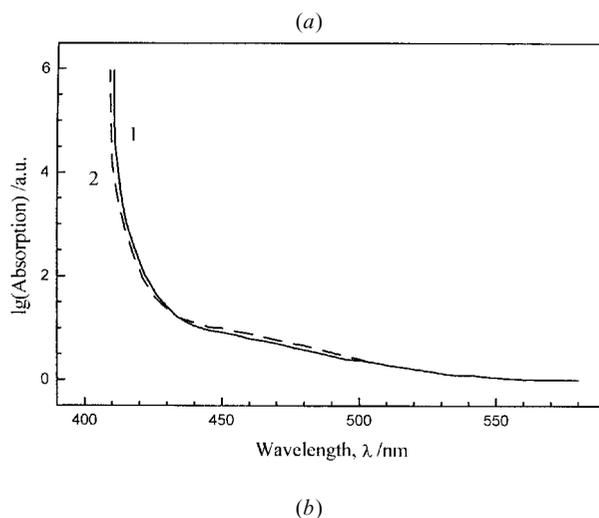
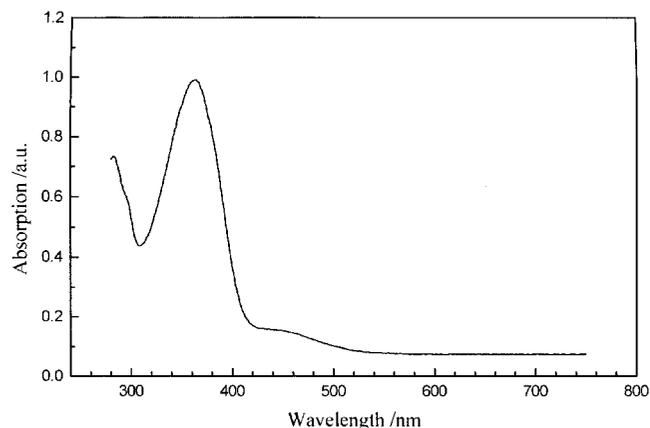


Figure 8. Absorption spectra of the copolymer SK8: (a) toluene solution; (b) $6 \mu\text{m}$ thick film in the TGB_A -like phase at 28°C (1) and in the isotropic liquid phase at 60°C (2).

absorption bands within the wavelength range of visible light, namely at 360 and 450 nm, which should correspond to the *trans*- and *cis*-isomers, respectively [5]. The spectra of the thin polymer film [figure 8(b)] show practically no difference in absorption between the 'isotropic smectic phase' at room temperature and the proper isotropic liquid phase above the clearing point. It should be noted that Wendorff and Eich [19] reported similar absorption curves for an acrylate LC copolymer having the same chromophoric side groups but a shorter spacer.

The helically twisted TGB_A -like phase should possess circular dichroism. Indeed, the CD spectrum of the copolymer film (figure 9) shows prominent rotation of the polarization plane with the maximum value of the

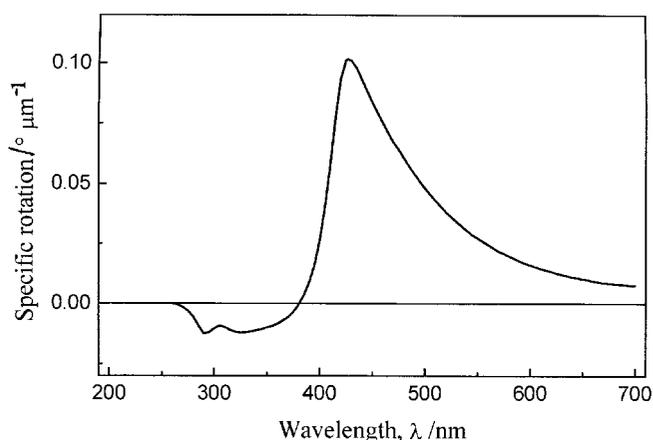


Figure 9. CD spectrum of a 6 μm thick film of the copolymer SK8 at room temperature in the TGB_A -like phase.

rotating power above $0.1^\circ \mu\text{m}^{-1}$ at the dye absorption band $\lambda_{\text{max}} \sim 430 \text{ nm}$. This is less than the values reported for the cholesteric (N^*) phase of LC polymers, but much higher than the optical rotation induced by molecular chirality in centrosymmetric LC phases [20]. From the sign inversion point in the spectrum, $\lambda_0 \sim 380 \text{ nm}$, the helical pitch can be estimated as $p = \lambda_0/n \sim 250 \text{ nm}$, that is close to the values evaluated for the 'isotropic smectic phase' of other homo- and co-polymers within the range 200–280 nm [21, 22].

We have found that illumination of the polymer film during slow cooling hinders the phase transition from the TGB_A -like phase to the SmA^* phase. Figure 10 presents a sketch of various photosensitivity tests carried out. The phase transition can be prevented either by unfiltered white light of total intensity 11 mW cm^{-2} within the wavelength range 200–2000 nm (b) or selectively by illumination at an intensity up to 0.3 mW cm^{-2} within the 400–500 nm wavelength range (c), while excitation at the other absorption band (within the 300–400 nm wavelength range) does not disturb the phase transition at 30°C (a). If the irradiating light is polarized (d), the orientation of chromophores takes place. As a result, the irradiated polymer film remains completely transparent and does not scatter light, but shows prominent birefringence. Such a film itself polarizes the propagating light.

Figure 11 presents the absorption of polarized light by a polymer film prepared in this way [figure 10(d)] versus the polarization angle (the film has been first cooled at 2 K min^{-1} under irradiation by polarized light). Two measurements have been made: close to the second

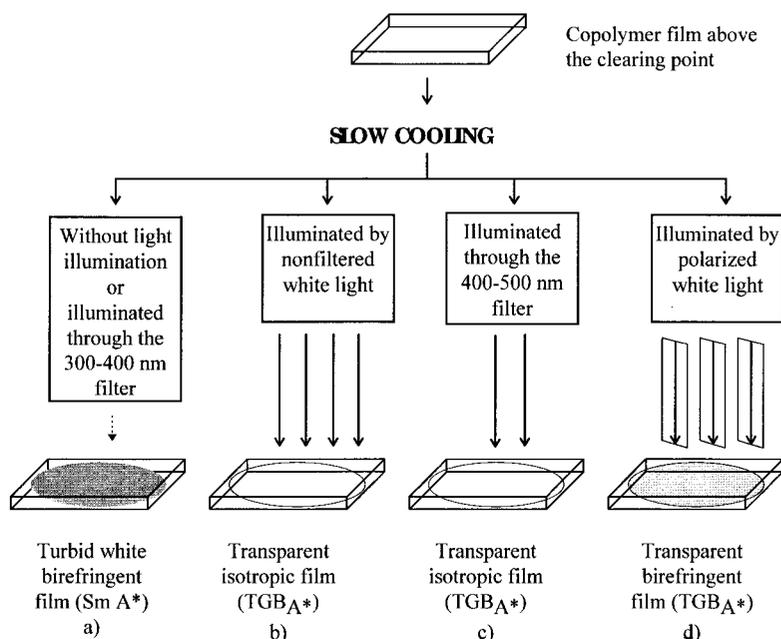


Figure 10. Sketch of the structural transformations during cooling and irradiation by light.

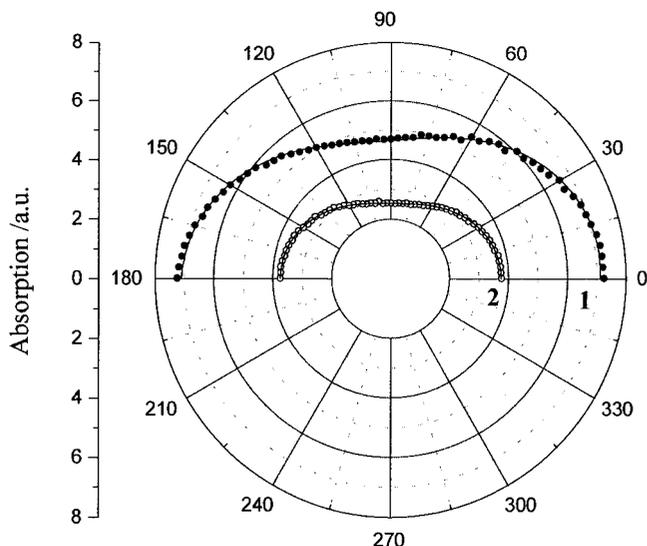


Figure 11. Absorption of the polymer film [figure 10(d)] versus the polarization angle at 460 nm (1) and 500 nm (2)—experimental points and fitting curves.

absorption band at $\lambda = 460$ nm and out of that band, at $\lambda = 500$ nm. As seen from the figure, the linear dichroism is much better developed in the vicinity of the absorption band, as observed for the circular dichroism (figure 9). The data of figure 11 were fitted as

$$A = A_{\parallel} \cos^2(\theta - \theta_0) + A_{\perp} \sin^2(\theta - \theta_0)$$

where A is the total absorption, A_{\parallel} and A_{\perp} are the light absorption components in the plane of maximal absorption and normal to that plane, and θ is the polarization angle. The order parameter of the chromophore groups was estimated as

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}$$

The S values calculated for both wavelengths are almost the same: $S_{500} \sim 0.14$ and $S_{460} \sim 0.15$. Such small S values also confirm a TGB-like amorphous state for the irradiated film, but not an oriented monodomain SmA structure.

The hindering of the phase transition from the TGB_A-like phase to SmA* by light irradiation could be explained by the following considerations. The light illumination (either by white light or within the 400–500 nm wavelength range) changes the proportion of *cis*- and *trans*-isomers of the azo dye moieties. Excess of an isomer (probably the *trans*-isomer) could prevent the phase transition from TGB_A-like phase to SmA* phase due to steric factors or because of a difference in induced chirality. We have shown earlier a higher chirality of the *trans*-isomer of a low molar mass chiral azo dye, as compared with the *cis*-isomer [23]. On the

other hand, Dinescu and Lemieux reported recently the higher chirality of the *cis*-isomer of a chiral thioindigo dye used as a dopant [24]. Absence of the effect when illuminating within the wavelength range 300–400 nm can be explained either by preferable formation of the *cis*-isomer, or by the small intensity of the irradiating light within that wavelength range and/or by the absorption of the light only within a thin surface layer (less than 1 μm), since the extinction of the dye at that band is much higher.

An alternative explanation of the effect observed would involve a shift of the phase transition point towards lower temperatures, as reported for the N–I transition in a photosensitive polyacrylate with azobenzene side groups [10], so that the glass is being formed first.

Whatever the explanation, the observed effect can be used for photorecording purposes. Figure 12 shows the simplest photorecording set-up. The polymer sample is simply pressed between two glass plates on the surface of a heating stage at 70°C. Then the negative mask is put above, the standard incandescent lamp switched on, and the heater switched off. After the sample has cooled to room temperature (0.5 h), the illumination is stopped and the image has been recorded.

According to the above mentioned scheme of phase transitions (figure 7), the SmA* phase is formed in the shadow under the mask. It scatters the incident light strongly and appears white. At the same time, the proper smectic phase is not formed in the illuminated parts of the cell and the TGB_A-like phase is being frozen in the glass. In other words, the written image is realized as a result of the strong light scattering by the smectic A phase against the background of the transparent glassy 'isotropic smectic' phase. An example of the photorecorded image with the name of the first author of this paper is presented in figure 13. The written image shows good stability: to date, it has kept for 9 months at room temperature with no visible changes.

We should underline here some advantages of the suggested photorecording principle.

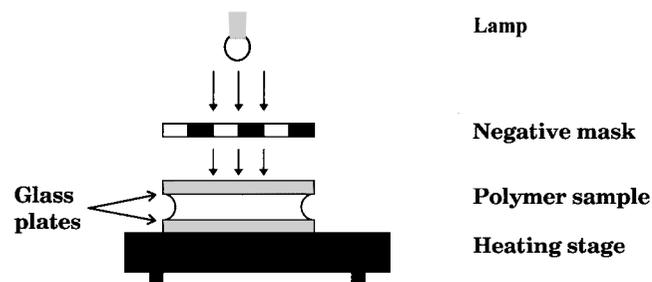


Figure 12. Sketch of the photorecording set-up.

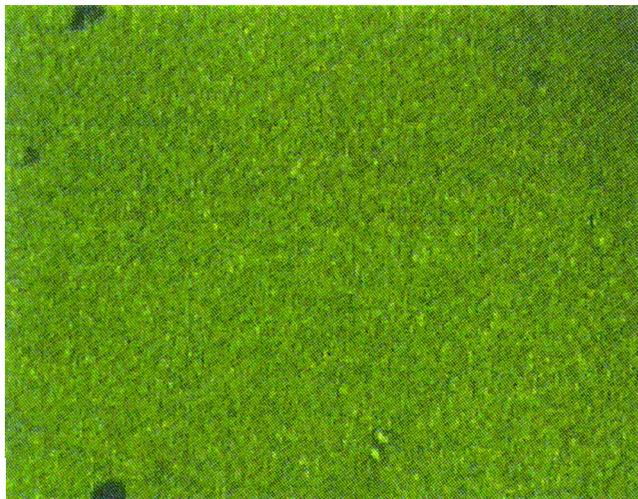


Figure 3. Optical texture of SK8 at room temperature in the SmA* phase.

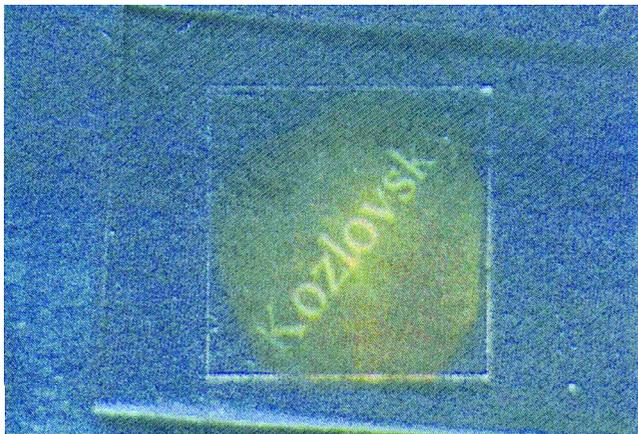


Figure 13. Photoimage recorded in a SK8 sample.

- (1) The recording can be done with non-polarized white light of low intensity up to 0.3 mW cm^{-2} (no laser or UV lamp needed).
- (2) The recorded image can be easily read out with non-polarized light.
- (3) No film prealignment (electric field, polyimide orienting layer, surface rubbing, etc.) is required.

This article had already been prepared for publication when we observed the same photosensitive phase behaviour and photorecording capability for the copolymer SK16 with twice the proportion of the dye component [25]. A detailed photo-optical study on this LC chiral photochromic polymer system is now in progress and will be published elsewhere.

4. Conclusions

A new chiral photochromic side group LC copoly-methacrylate has been synthesized containing 92 mol %

of chiral mesogenic fragments and 8 mol % of photochromic side groups. The copolymer forms two smectic phases: a proper smectic phase, SmA*, and an 'isotropic smectic' phase, or a TGB_A-like amorphous phase; either of these can be frozen in a glass depending on cooling conditions. The structure of the mesophases has been studied and a packing scheme of the mesogenic side chains in the smectic layers has been suggested.

The optical properties of the 'isotropic smectic' copolymer films have been studied, the linear and circular dichroism have been measured, and the order parameter of the dichroic dye moieties has been evaluated. The inter-related effects of temperature and light illumination on the phase state of the copolymer have been investigated.

A new approach to photorecording in photochromic LC polymers has been suggested based on hindering the phase transition from the TGB_A-like phase to the SmA* phase in chiral copolymers by light illumination. A set-up for such photorecording has been assembled and the first photo images have been recorded.

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References

- [1] MCARDLE, C. B. (editor), 1982, *Applied Photochromic Polymer Systems* (London: Blackie).
- [2] ANDERLE, K., and WENDORFF, J., 1994, *Mol. Cryst. liq. Cryst.*, **243**, 51.
- [3] SHIBAEV, V. P., 1994, *Mol. Cryst. liq. Cryst.*, **243**, 201.
- [4] IVANOV, S. A., YAKOVLEV, I., KOSTROMIN, S., SHIBAEV, V., LASKER, L., STUMPE, J., and KREISIG, D., 1991, *Makromol. Chem., Rapid Commun.*, **12**, 709.
- [5] SHIBAEV, V. P., KOSTROMIN, S. A., and IVANOV, S. A., 1996, in *Polymers as Electrooptical and Photooptical Active Media* (edited by V. P. Shibaev) (Berlin: Springer), pp. 37–110.
- [6] HAASE, W., and BORMUTH, F. J., 1989, in *Polymers in Information Storage Technology*, edited by K. L. Mittal (New York: Plenum Press), pp. 51–64.
- [7] STUMPE, J., LASKER, L., FISCHER, TH., KOSTROMIN, S., IVANOV, S., SHIBAEV, V., and RUHMANN, R., 1994, *Mol. Cryst. liq. Cryst.*, **253**, 1.
- [8] NATHANSON, A., ROCHON, P., GOSSELIN, J., and XIE, S., 1992, *Macromolecules*, **25**, 2268.
- [9] ICHIMURA, K., 1996, *Supramol. Sci.*, **3**, 67.
- [10] SCREROWSKY, G., BEER, A., and COLES, H. J., 1991, *Liq. Cryst.*, **10**, 809.

- [11] BATA, L., FODOR-CSORBA, K., SZABON, J., KOZLOVSKY, M. V., and HOLLY, S., 1991, *Ferroelectrics*, **122**, 149.
- [12] DEMIKHOV, E., and KOZLOVSKY, M. V., 1995, *Liq. Cryst.*, **18**, 911.
- [13] KOSTROMIN, S. G., STAKHANOV, A. I., and SHIBAEV, V. P., 1996, *Polym. Sci. Ser. A*, **38**, 1030.
- [14] FAN, Z. X., and HAASE, W., 1991, *J. chem. Phys.*, **95**, 6066.
- [15] GOODBY, J. W., SLANEY, A. J., BOOTH, C. J., NISHIYAMA, I., VUIJK, J. D., STYRING, P., and TOYNE, J., 1994, *Mol. Cryst. liq. Cryst.*, **243**, 231.
- [16] TSUKRUK, V. V., SHILOV, V. V., LOKHONIA, O. A., and LIPATOV, YU. S., 1987, *Sov. Phys. Crystallogr.*, **32**, 88.
- [17] TSUKRUK, V. V., KOZLOVSKY, M. V., SHILOV, V. V., and SHIBAEV, V. P., 1988, *Sov. Phys. Crystallogr.*, **33**, 423.
- [18] GOODBY, J. W., DUNMUR, D. A., and COLLINGS, P. J., 1995, *Liq. Cryst.*, **19**, 703.
- [19] WENDORFF, J. H., and EICH, M., 1989, *Mol. Cryst. liq. Cryst.*, **169**, 133.
- [20] DONALD, A. M., and WINDLE, A. H., 1992, *Liquid Crystalline Polymers* (Cambridge: Cambridge University Press), p. 146.
- [21] KOZLOVSKY, M. V., FODOR-CSORBA, K., BATA, L., and SHIBAEV, V. P., 1992, *Eur. Polym. J.*, **28**, 901.
- [22] KOZLOVSKY, M. V., and DEMIKHOV, E., 1996, *Mol. Cryst. liq. Cryst.*, **282**, 11.
- [23] BLINOV, L. M., KOZLOVSKY, M. V., NAKAYAMA, K., OZAKI, M., and YOSHINO, K., 1996, *Jpn. J. appl. Phys.*, **35**, 5405.
- [24] DINESCU, L., and LEMIEUX, R. P., 1997, in Abstracts 6th International Conference on Ferroelectric Liquid Crystals, Brest, France, July 20–24, 1997, 175.
- [25] KOZLOVSKY, M. V., SHIBAEV, V. P., STAKHANOV, A. I., WEYRAUCH, T., HAASE, W., and BLINOV, L. M., 1997, in Abstracts for: VIIth International Topical Meeting on Optics of Liquid Crystals, September 8–12, 1997, Heppenheim, Germany, 59.