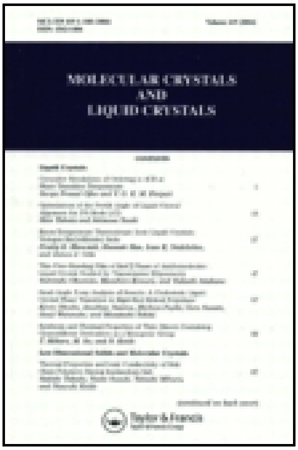

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Chiral Smaectic Side-Chain Copolymers - 3. Copolymers Containing a Diazo Chromophore

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Chiral Smaectic Side-Chain Copolymers - 3. Copolymers containing a diazo chromophore

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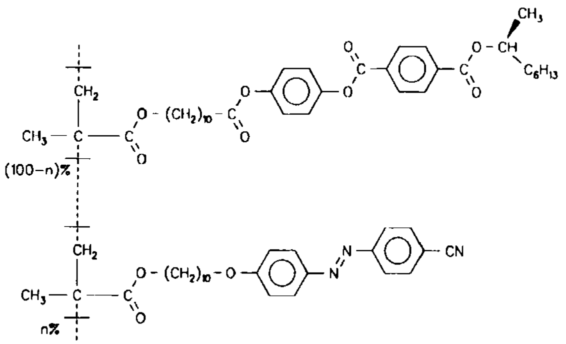
A new series of photochromic copolymethacrylates has been synthesized. Some of those form the „isotropic smectic phase“ and are therefore promising for optoelectronic and data recording applications. Phase transitions and structure of the copolymers have been measured, optical properties have been studied.

INTRODUCTION

In the previous papers of the series [1,2] we have reported the "isotropic smectic phase" of a methacrylic homopolymer which contains phenyl benzoate side chains substituted by 2-(*S*)-octyl chiral radical, and the same phase of several related copolymers as well. The observed mesophase of the reported materials possesses a layer structure according to DSC, X-ray and broad line PMR data but shows no birefringence of visible light. A TGB-like amorphous smectic structure with extremely short helical pitch (~200 nm) has been suggested later for the mesophase [3].

The "isotropic smectic phase" combines high transparency and low scattering without any preorientation of the sample, typical for amorphous polymers, with the local smectic ordering and twisted helical structure of the TGB phase. That might be an advantage for applications in optoelectronics and photorecording. In course of our search for enhanced photosencitive materials we have synthesized a series of dye doped copolymers SKn,



where n = 5, 8, 16, and 28, is concentration of the dichroic azobenzene side chains (mol. %). Here we report phase behaviour, structure and optical properties of the copolymers.

EXPERIMENTAL

Synthesis of the copolymer SK8 has been already reported [4]. All other copolymers were synthesized according to the same scheme by radical polymerization in toluene solution using AIBN as initiator. The composition of the copolymers has been assumed to be equal to that one of the monomer mixtures due to almost identical chemical structure of the comonomers.

DSC curves were taken with a Perkin-Elmer DSC-2C calorimeter at various heating/cooling rates from 1.25 to 20 K/min. The temperatures of phase transitions reported below are the values reduced to zero heating/cooling rates. Microscopic textures were observed under a Leitz microscope supplied with a Mettler FP-82 heating stage and a videorecording system. X-ray scattering curves were measured from 2 mm capillary samples by a modified STOE STADI 2 diffractometer using CuK$_\alpha$ radiation and a PSD linear position scanning detector.

Absorption spectra of the copolymers were studied using a Hitachi U3400 spectrophotometer. Cirular dichroism curves were taken with a JASCO 500C spectropolarimeter.

RESULTS AND DISCUSSION

Phase transitions of the copolymers, as detected by DSC measurements and supported by X-ray data and microscopic observations, are summarized in Fig. 1 and in Table 1. The SK5 copolymer with the smallest content of azobenzene dye side chains forms only the "isotropic smectic" TGB-like mesophase similar to the chiral homopolymer SK0 (named P8*M in our previous publication [1]).

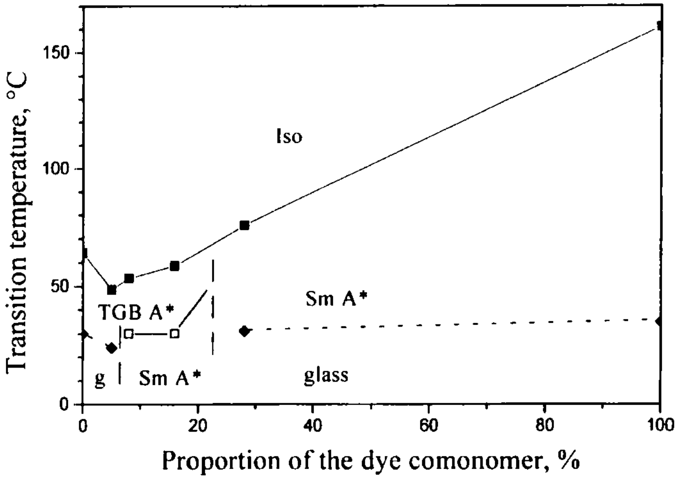


Fig. 1. Phase diagram of the copolymer system SKn (in slow cooling)

TABLE 1. Phase transitions of the copolymers SKn

Copolymer	Phase transitions, °C
SK5	glass $\xleftrightarrow{24}$ TGB A* $\underset{48.5}{\overset{57.4}{\rightleftarrows}}$ Iso
SK8	$\begin{tikzcd} \text{Sm A* glass} \arrow[r, leftrightarrow] & \text{Sm A*} \arrow[rr, "62"] & & \text{Iso} \\ \text{TGB A* glass} \arrow[rr, leftrightarrow, "\text{(fast)}"] & & \text{TGB A*} \arrow[ul, "\text{(slow)}\ 29.9"] \arrow[ur, leftrightarrow, "53.3"'] & \end{tikzcd}$
SK16	$\begin{tikzcd} \text{Sm A* glass} \arrow[r, leftrightarrow] & \text{Sm A*} \arrow[rr, "63"] & & \text{Iso} \\ \text{TGB A* glass} \arrow[rr, leftrightarrow, "\text{(fast)}"] & & \text{TGB A*} \arrow[ul, "\text{(slow)}\ 29.0"] \arrow[ur, leftrightarrow, "58.5"'] & \end{tikzcd}$
SK28	glass $\xleftrightarrow{28}$ Sm A* $\underset{75.7}{\overset{85.7}{\rightleftarrows}}$ Iso

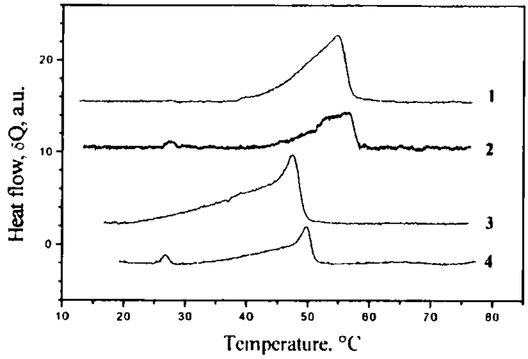


Fig. 2. DSC curves from the copolymers, in cooling: *1* - SK16, at 5 K/min; *2* - SK16, at 1.25 K/min, *3* - SK8, at 10 K/min, *4* - SK8, at 5 K/min

Fig. 3. Optical texture of the copolymer SK8 in the Sm A* phase at room temperature.

The mesophase appears as a transparent coloured (red-orange) plastic and shows no birefringence within the wavelength range of visible light. On the other hand, the SK28 copolymer with the highest proportion of dye moieties forms the Sm A* phase similar to the azodye homopolymer SK100 (named CABO-10-OM in our previous publication [5]).

Of the most interest is however the ambiguous phase behaviour of the copolymers SK8 and SK16. When cooled from the isotropic liquid melt, they form first the (monotropic) highly twisted TGB-like phase similar to SK5, but the further phase behaviour depends on the cooling rate. When the cooling is being performed fast (10 K/min and faster), the TGB structure is frozen in glass. Starting from a critical cooling rate (5 K/min for SK8 and 2.5 K/min for SK16), the TGB A* - Sm A* phase transition occurs, and it is the Sm A* structure that is frozen in glass in that case (Fig. 2). When heated back from either glass, the texture and phase state of the copolymers remains undisturbed until the clearing point (Table 1). So the two copolymers can appear at any

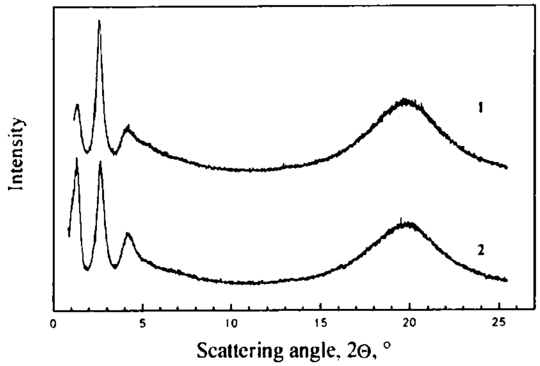


Fig. 4. X-ray curves from the copolymer SK16 at 25°C: 1 - in the TGB phase; 2 - in the Sm A* phase

TABLE 2. Positions of the X-ray peaks for the copolymers at room temp.

Copolymer	Mesophase	d_0, Å	d_1, Å	d_2, Å	D, Å
SK5	TGB A*	~ 67	33.2	21.2	4.50
SK8	TGB A*	~ 67	34.0	21.1	4.49
	Sm A*	~ 65	32.5	21.3	4.47
SK16	TGB A*	~ 67	34.6	21.5	4.48
	Sm A*	~ 66	33.8	21.0	4.46
SK28	Sm A*	-	34.8	20.8	4.49

temperature below the clearing point either as a transparent isotropic texture, or as a high-scattering, birefringent confocal texture (Fig. 3).

Fig. 4 shows typical X-ray curves from the both copolymer mesophases for the particular case of the copolymer SK16, and Table 2 summarizes the positions of X-ray peaks for the copolymers in different mesophases. Data of the Fig. 4 indicate a layered smectic structure for both mesophases of the copolymers (small angle range), and the disordered distribution of the mesogenic side chains within the layers as well (a broad wide angle peak). The three small angle peaks correspond to a single lattice with a period of d_0 ~ 67 Å for the TGB A* phase, whereas the Sm A* phase is characterised by a somewhat shorter layer thickness (d_0 ~ 65 Å for SK8). Changes in the interlayer distance upon the copolymer composition are presented in Fig. 5, and Fig. 6 shows the position of the small angle peak of maximum intensity, d_1, and that one of the wide angle peak, D, for SK8, versus temperature. The orthogonal smectic structure of both mesophases has been confirmed by almost constant d_1 values

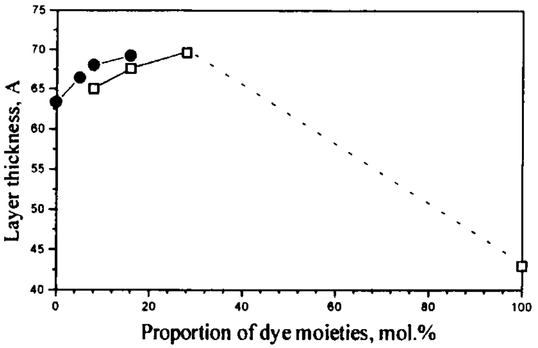


Fig. 5. Layer thickness of the copolymers SKn in the TGB A* phase (solid circles) and in the Sm A* phase (open squares) versus the copolymer composition

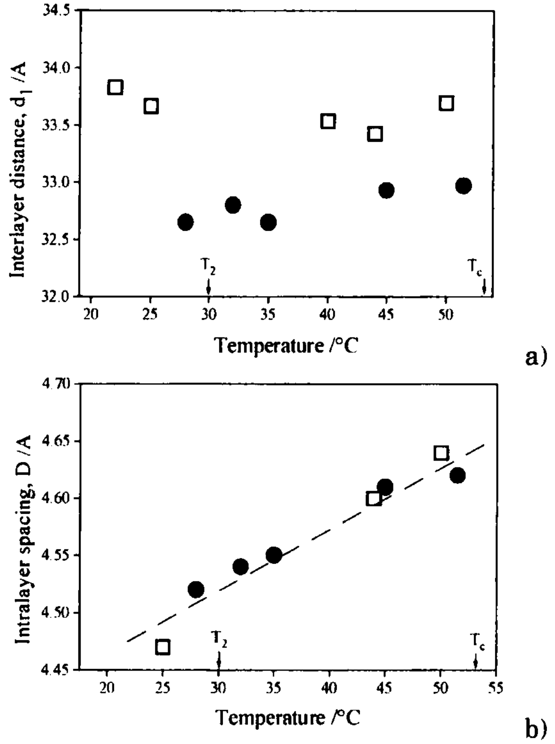


Fig. 6. The positions of small angle peak of maximum intensity, d_1, (a) and of the wide angle peak, D, (b) for SK8, in the TGB A* phase (open squares) and in the Sm A* phase (closed circles), both versus temperature

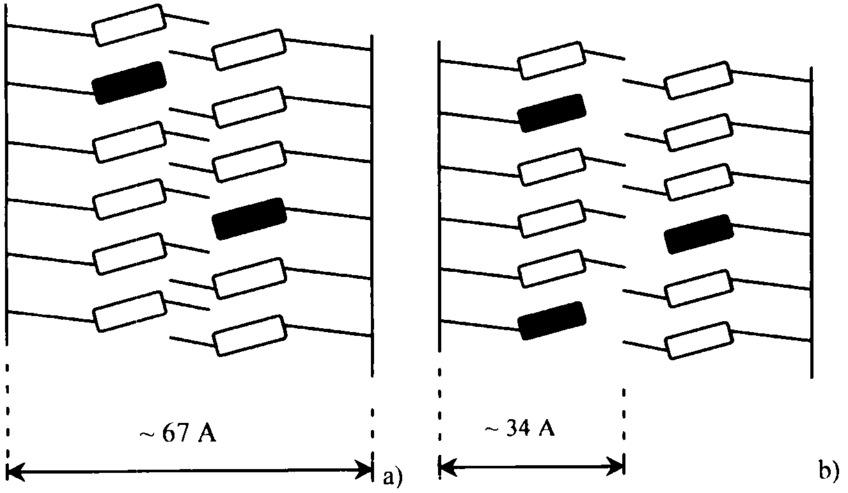


Fig. 7. Proposed local packing of mesogenic groups in smectic layers

of all the copolymers over temperature, and also by the fact that the copolymers show no ferroelectric switching within the whole temperature range of the mesophases.

The thickness of smectic layers for the copolymers SK5 and SK16 is between the single and double length of the chiral phenyl benzoate side chain, $l \sim 40$ Å, but it should not be influenced much by the shorter azobenzene mesogenic chains, $l \sim 30$ Å, due to the small concentration of the latter. The only reasonable structure of the mesophase layer should include mutual penetration of the chiral terminal groups of the side chains (Fig. 7a), similar to the layer packing suggested for the homopolymer SK0 [1].

The X-ray curves from the copolymer SK28 at various temperatures (Fig. 8) indicate however the coexistence of two different packings of the mesogenic side chains: the structure of Fig. 7a with $d \sim 69$ Å, and a simple monolayer packing with $d \sim 36$ Å (Fig. 7b) similar to the homopolymer SK100 [5]. The d_1 peak is rather wide at room temperature, probably due to the superposition of the second order reflex from the former lattice and the first one of the latter lattice. At higher temperatures it becomes narrow; the peak at $\theta \sim 4.0°$ corresponding to the third order reflection from the Sm A_d lattice ($d_2 \sim 21$ Å), disappears, and the peak at $\theta \sim 5.0°$ corresponding to the second order reflection from the monolayer Sm A lattice ($d_3 \sim 17$ Å), grows, thus indicating shift of the equilibrium to the monolayer structure.

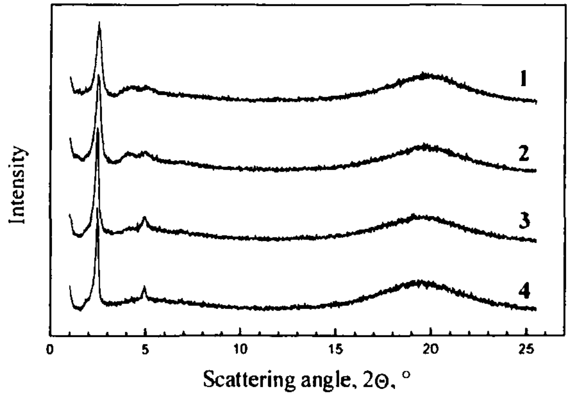


Fig. 8. X-ray curves from the copolymer SK28 in the Sm A* phase. 1 - at 20°C; 2 - at 35°C; 3 - at 50°C; and 4 - at 57°C

As seen from the Fig. 5, the layer thickness of either mesophase grows with the increasing proportion of azobenzene dye moieties; whereas for the copolymers SK8 and SK 16, the layer spacing in the Sm A* phase is somewhat shorter than in the TGB A* phase. This indicates a more dense packing of the smectic layers, i.e. deeper overlap of the chiral terminal fragments within the Sm A* phase, as compared with the TGB A* phase of the same polymer. That would explain also the increased intensity of the d_0 peak, in relation to the d_1 peak, at the TGB A* - Sm A* transition (Fig. 4). For both mesophases, the total layer thickness of ~ 69 Å seems to be the maximum possible value for the structure of Fig. 7a: after reaching that critical dimension, the TGB A* phase ceases to exist at all (copolymer SK28), and the Sm A* phase changes for the monolayer structure (SK28 at higher temperatures and the homopolymer SK100 [5]).

In contrast, the packing of the mesogenic side chains within a smectic layer seems not to be affected by the TGB A* - Sm A* phase transition (Fig. 6b): the D values for the both mesophases follow the same straight line with increasing temperature.

Fig. 9a shows the absorption spectra of SK28 in solution. The absorption is caused by azobenzene dye moieties and should not change qualitatively for other copolymers: the greenish blue 450 nm absorption band correspond to the absorption of the *cis* isomer, and the near UV 360 nm absorption band corresponds to the absorption of *trans* isomer. Absorption spectra of the copolymer films are presented in Fig. 9b. We shoud note here, that J.Wendorff and M.Eich [6] have reported similar curves for nonchiral copolyacrylate containing the same p-cyano-azobenzene chromophore groups.

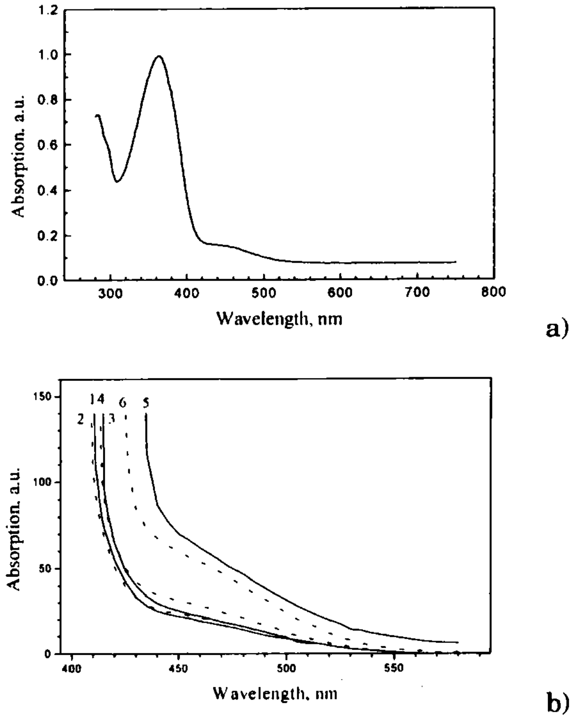


Fig. 9. Absorption spectra of the copolymers: a) SK28, chloroform solution; b) copolymer films: *1* - SK8, TGB A* phase at 28°C; *2* - SK8, Iso phase at 60°C; *3* - SK16, TGB A* phase at 28°C; *4* - SK16, Iso phase at 70°C; *5* - SK28, Sm A* phase at 28°C; 6 - SK28, Iso phase at 80°C.

The data of Fig. 9b (curve 5) show prominent contribution of scattering from the Sm A* texture of SK28 copolymer, as compared with TGB A* phase of other polymers and with the isotropic melt of all copolymers. On the other hand, there is almost no difference in absorption between those two latter phases.

The helical superstructure of the TGB A* mesophase is confirmed by the CD spectra (Fig. 10). The TGB A* phase shows ten times higher specific rotation than the Sm A* phase, where the circular dichroism is caused by molecular rotation only but not because of the helical superstructure. The effect is most pronounced close to the absorption band ot the dye, λ_{max} = 470 nm.

The inversion of the rotation sign has been observed at λ_0 = 380 nm. So we can evaluate the helical pitch of the TGB A* phase for SK8 as $\lambda_0/n \sim 250$ nm,

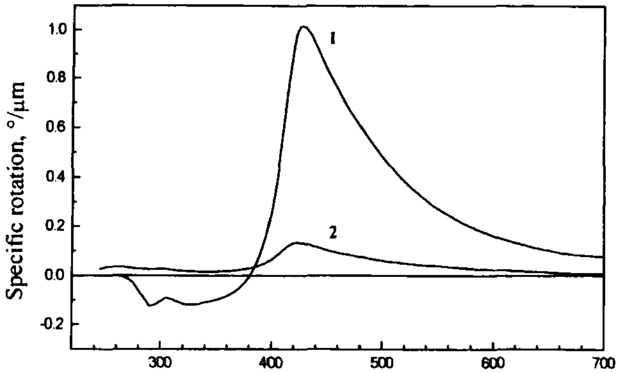


Fig. 10. CD spectra from the 6 μm thick copolymer films at room temperature: *1* - SK8, TGB A* phase; *2* - SK16, Sm A* phase

that agrees with the helical pitch estimations for TGB A* phase of other homo- and copolymers ~ 200-280 nm [3, 7]. The molecular rotation and the rotation due to helical superstructure seem to have the same sign at the yellow-red wavelength range ($\lambda > \lambda_0$), but they are acting in the opposite directions at violet-blue part of the spectra ($\lambda < \lambda_0$), and this should cause a small maximum (towards positive values) at 310 nm related to the second absorption band of the dye.

The azobenzene dye fragments of the copolymers reveal the reversible *cis-trans* isomerization under illumination by UV light (*trans* to *cis*) or by visible light (*cis* to *trans*). Two mechanisms of photorecording are possible in the copolymers. The first one, i.e. the standard photooptical recording [8], occurs due to creation of the photoinduced birefringence in copolymer films, especially within the higly transparent, optically isotropic TGB A* phase. A separate paper will be devoted to the optical properties of the copolymer films illuminated by polarized light, particularly during the cooling from isotropic liquid melt to room temperature.

Second, the light illumination during the cooling, also with nonpolarized white light or selectively at the wavelength range of the absorption band, 400 - 500 nm, can prevent the TGB A* - Sm A* transition in the copolymers SK8 and SK16. This effect and the related new principle of photorecording in chiral LC polymers are discussed elsewhere [4].

CONCLUSIONS

A new series of chiral photochromic side chain LC copolymethacrylates has been synthesized containing chiral mesogenic fragments and of photochromic diazo moieties.

The copolymers form smectic phases of two types: a proper smectic phase, Sm A*, and an "isotropic smectic" phase, TGB A*. The copolymers SK8 and SK16 can form both mesophases, and any of those can be frozen in glass depending on cooling conditions. Structure of the mesophases has been studied and packing scheme of the mesogenic side chains in smectic layers has been suggested.

Absorption spectra of the "isotropic smectic" copolymer films have been studied, and circular dichroism measured. Interrelated influence of temperature and light illumination on the phase state of the copolymer has been investigated.

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