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Photorecording in the "Isotropic Smectic Phase" of Dyed Side Chain Polymers

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SUMMARY: The "isotropic smectic" phase of chiral side chain polymers combines layered liquid crystalline ordering with macroscopic transparency and low light scattering without any pretreatment, thus providing considerable advantages for photo-optical applications. Photoinduced birefringence in that mesophase of dye containing copolymers has been investigated.

A novel LCPT (Light Controlled Phase Transition) photorecording technique has been developed. The light intensity required for the method is as low as 0.3 mW/cm², and both writing and reading of the image can be performed by nonpolarized light.

Introduction

During the last decade, a prominent interest has grown to the photoinduced structural reorganization in liquid-crystalline (LC) polymers containing dichroic dye moieties capable to isomerization under the light illumination, and in the first line among those dyes - the azobenzene chromophores. Such polymers are promising media for numerous applications, particularly in reversible, optical, high density data recording and data storage[1-7)].

The mechanism of the photo-optical recording is based on the cooperative structural transformation in the entire polymer mesophase induced by reorientation of small proportion of dichroic dye sub-units under light illuminaton. The latter sub-units can be incorporated into the polymer structure either physically (polymers doped with low molar mass dichroic dyes) or chemically (copolymers combining mesogenic and dichroic monomer moieties). Thus, illumination of such photosensitive polymers by polarized light results in photoinduced birefringence, Δn_{ind}, which can be kept for a long time at ambient conditions but easily erased by heating above the clearing point or by illuminaton with non-polarized UV light.

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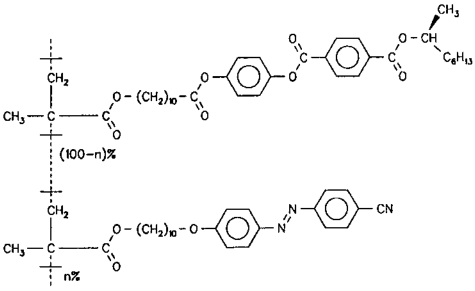
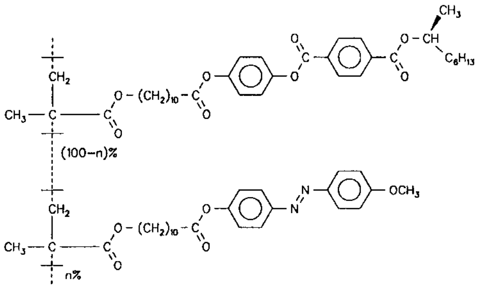
The LC polymers, as compared with amorphous polymers, have however such a disadvantage, that the spontaneously formed polydomain samples scatter light strongly at domain boundaries. Hence, for photorecording applications a uniform monodomain film should be created first. The process usually requires coating of cell surfaces with orienting polyimide layers, special treatment of those (rubbing), application of an electric field, annealing of the film at certain temperature, etc. Moreover, the monodomain polymer film prepared in such a way possesses already some birefringence which should be overcome during the photorecording process, thus increasing the required light intensity[8)].

Since 1991, we have reported an anomalous phase condition of several chiral side chain homo- and copolymers[9,10)]. The "isotropic smectic" phase of the polymers (**IsoSm*** phase) possesses layered ordering and a helical supramolecular twist but shows no birefringence of visible light. An amorphous, short pitch TGB-like structure has been suggested later for the phase[11)]. Polymers in the mesophase above appear as transparent non-scattering films without any pretreatment, thus providing considerable advantages for photo-optical applications. To investigate the possibilities of photorecording in the "isotropic smectic" phase, two series of chiral copolymers containing azobenzene dye moieties had been synthesized, and the photoinduced structural transformations were studied.



SKn series, n = 5, 8, 16, and 25



KWn series, n = 7, 19, 30, and 40

Experimental

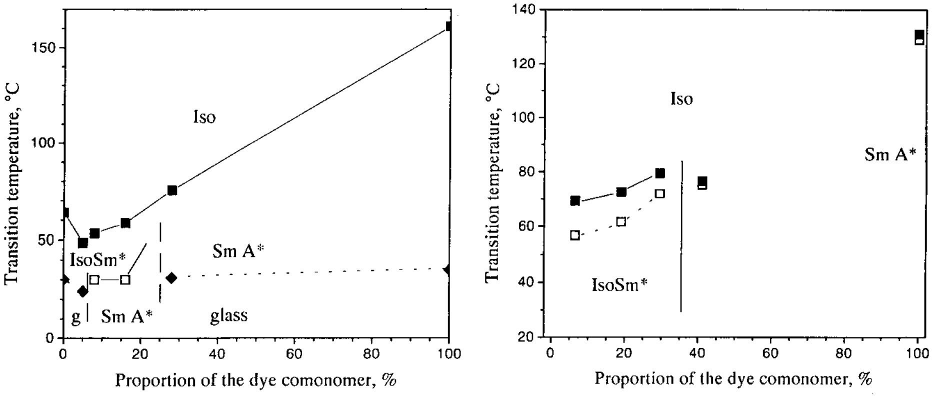
The two series of dye-containing chiral copolymers were studied in the present work, SKn series and KWn series. Both series have the same chiral matrix comonomer providing formation of the **IsoSm*** phase but differ slightly in the chemical stucture of chromophore moieties. Synthesis of the SKn copolymers has been described earlier[12)], while the KWn copolymers were synthesized using the same procedure but another dichroic comonomer[13)].

Thin polymer films were prepared in several different ways. Thus, 6 to 25 μm thick films were obtained by pressing a piece of a dyed LC polymer (SK5, SK8, SK16) at ~ 80°C between two glass (or quartz) plates, using appropriate teflon spacers. Also standard 10 μm LC cells but without any orienting layers at inner surfaces (EHC, Japan) were filled with the polymer melt at the same temperature. Finally, a 3 μm thick film of KW40 was cast from 2% cyclohexanone solution onto a glass substrate.

Results and Discussion

As seen from the phase diagrams of the copolymer systems (Fig. 1), introduction of 28 per cent dichroic side chains destroys completely the IsoSm* for SK copolymers (Fig. 1a), while the copolymers of the KW series still form that phase at 30% of chromophore units at least. We should note here that phase behaviour of KW40 copolymer is not clear yet and requires further investigations. The copolymer forms in bulk a proper smectic phase below 76°C, but structural parameters of that phase, e.g. layer thickness, seem to depend on previous history of the sample, including its exposure to light. On the other hand, thin films of the copolymer, both 0.1 μm thick spin-coated and 3 μm thick cast films, appear transparent and have in virgin state a negligible birefringence only, thus suggesting formation of the IsoSm* phase at those conditions[14,15)]. The fact that p-methoxyazobenzene moieties can be incorporated much better into the IsoSm* phase than p-cyanoazobenzene ones should be related not to any steric hindrance (since shape and dimensions of both dye groups are quite similar) but to higher polarity of the cyano-derivative.

Absorption spectra are known to be more or less similar for the most of azobenzene dyes. Fig. 2 presents the particular spectra of KW40 copolymer solution with the band in near UV range (350 nm for our case, band B at Fig. 2) correspondig to π-π* electronic transition in the *trans*-isomer only, while the band C at 450 nm corresponds mostly to the n-π* transition in the *cis*-isomer, though the same transition in the *trans*-isomer can also give a small contribution[15)]. The band A at 240 nm relates to the absorption of aromatic mesogenic cores. Thus, the isomerization process of the chromophores can be traced easily by change in relative intensity of the B and C bands.



SK series

KW series

Fig. 1: Phase diagrams for the copolymer systems SKn and KWn in heating (■) and cooling (□).

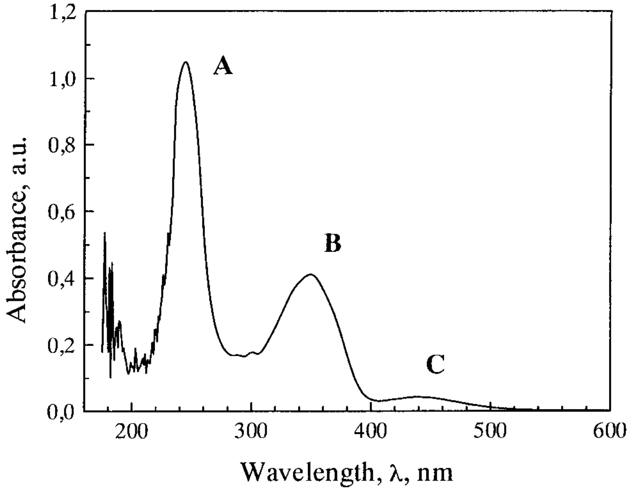
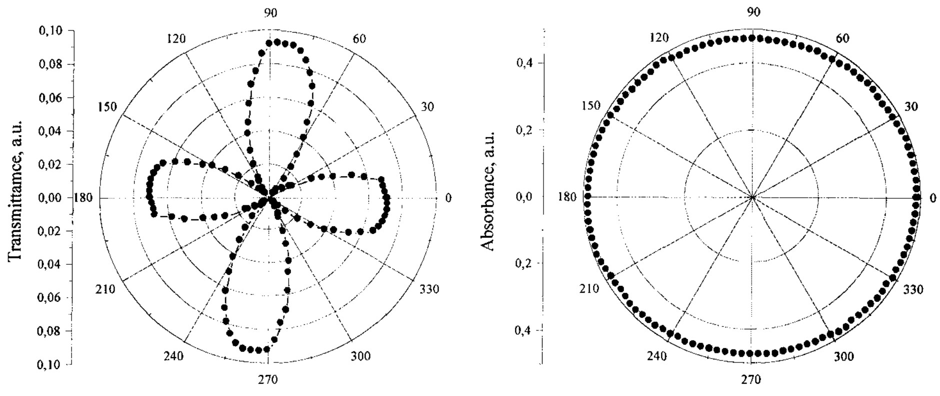


Fig. 2: Characteristic absorption spectra (KW40, 35 mg/L solution in chloroform).

Passing to the photo-optical recording features of the materials discussed, we should note first that azobenzene moieties in the SKn and KWn copolymers show an extraordinarily long lifetime of *cis*-isomers in both solutions and films, as compared with other reported low molar mass dyes, polymers and thin LB films[16, 17)]. For SK8, when the *cis*-isomer is excited once by UV irradiation, a 24 h annealing in darkness results in 20% increase of the B-band absorption only, while a 10 s illumination with yellow-green light within 450-550 nm forcing the backward isomerization, restores the absorption band completely. And for KW40 copolymer, the spontaneous *cis-trans* relaxation is even twice slower[14, 15)].

Illumination of the copolymer films by polarized light induces birefringence in originally optically isotropic polymer films of both series, thus opening the way for photorecording applications. However, the Δn_{ind}, value and stability of written images over time depend strongly on the photorecording conditions. Thus, illumination of a 10 μm thick film of SK8 with polarized white light (10 mW/cm^2) results in a pronounced birefringence which disappears however completely within 1 min. For a virgin 3 μm thick cast film of KW40 and using an Ar-ion laser at λ = 514 nm, only the light intensity ~250 W/cm^2 during 2 s was sufficient for a photo-optical recording of a stable holographic grating. We should underline however, that illumination at the absorption band C (blue-green light) promotes the *cis*-to-*trans* isomerization of the azobenzene groups. The photosensitivity of the films can be therefore drastically enhanced by increasing the concentration of *cis* isomers: when the same film was exposed first to UV light of a Xe lamp (~65 mW/cm^2 within the range 300-400 nm, 5 min), the grating was then successfully written with a 100 times lower energy – 5 W/cm^2 during 1 s [13)].

One more possibility to increase stability of the photorecorded images is an "imprinting": when a polymer film is irradiated during its cooling, the orientation of side groups can be frozen in glass. Thus, a 23 μm thick film of SK5 pressed between two glasses was irradiated with polarized white light of an incandescent lamp (~9 mW/cm^2 within the range 350-2000 nm) during its cooling from 60 to 25°C at 2.5 K/min (18 min total). The photorecorded birefringent spot is being kept already 18 months at ambient temperature without any deterioration. Fig. 3a illustrates the birefringence in such a film; for 5 times higher recording intensity, the Δn_{ind} value has been estimated as 0.003[18)]. Much higher values, Δn_{ind} ~0.06, have been reported for a similar film of copolymer KW40[14)].



a) b)

Fig. 3: Light transmission of the photorecorded birefringent spot in a SK5 film between crossed polarizers (a) and absorption of polarized light by same the film (b), both versus sample rotation angle. Film thickness 23 μm, wavelength λ = 600 nm.

As seen from Fig. 3b, dichroism of the birefringent SK5 film is vanishingly low. The birefringence in the dichroic IsoSm* copolymers may be created not only by reorientation of the azobenzene chromophores themselves under illumination but due to a cooperative structural transformations in the whole mesophase induced by that reorientation. This conclusion has been confirmed also by experiments on photorecording of holographic gratings in KW40 films15). A grating, once recorded, is conserved much longer than the lifetime of *cis*-isomers (several days at room temp.). Further, an additional illumination with visible light, sufficient to convert all the *cis*-isomers to the *trans*-form (2mW/cm^2 within the range 450-650 nm during 0.5 h) suppresses the capability of the film to photorecording of new images but does not erase the previous records.

The most interesting is nevertheless the capability of the copolymers SK8 and SK16 to quite novel technique of photorecording, namely LCPT – Light Controlled Phase Transition12). As seen from Fig. 1a, the two copolymers reveal in cooling the phase transition IsoSm* - Sm A*. The transition accompanied with the formation of white, scattering and birefringent polydomain Sm A texture, occurs however only when the cooling is slow enough (2.5 K/min or less), otherwise the transparent, optically isotropic, and nonscattering IsoSm* texture is frozen in glass. Moreover, the transition can be hindered (or prevented) even in slow cooling by light illumination of low intensity, either with nonpolarized white light or selectively by blue-green light. For the latter case, the light intensity required is as low as 0.3 mW/cm^2 within the wavelength range 400-500 nm.

The hindering of the phase transition from the IsoSm* phase to Sm A phase by light irradiation could be explained by the following considerations, which are discussed in more detail elswere[12)] and agree well with the results above on photoinduced birefringence in the IsoSm* phase. The light illumination (either by white light or within the 400-500 nm wavelength range) changes the proportion of *cis*- and *trans*-conformers of the azo dye moieties. Excess of the *trans*-conformer could prevent the phase transition from IsoSm*phase to Sm A phase due to steric factors or because of difference in induced chirality. We have shown earlier a higher chirality of the *trans*-conformer of low molar mass chiral azo dye, as compared with the *cis*-conformer[19)]. Hence, higher virtual chirality in configuration of chromophore dopant units can be induced by local field of chiral matrix, so they can better adjust to the IsoSm* phase even at low temperatures.

Using the observed effect, we have developed a new photorecording technique, namely the LCPT (Light Controlled Phase Transition) recording. To record an image, a polymer sample is simply pressed between two glasses on the surface of a heating stage at 70°C. Then the negative mask is put above, a standard incandescent lamp switched on, and the heater switched off. After the sample is cooled down to room temperature (0.5 h), the illumination can be stopped and the image has been recorded as a scattering white texture of Sm A phase on the transparent background of the IsoSm* phase. An example of LCPT-recorded image with the name of first author is presented in Fig. 4.

Fig. 4: An image recorded in SK8 film with the LCPT technique.

Conclusions

Two new series of chiral photochromic side chain LC copolymethacrylates have been synthesized containing chiral mesogenic fragments and photochromic diazo moieties. The copolymers can form at certain conditions the "isotropic smectic" phase which possesses low range LC ordering of Sm A type and helical superstructure but shows neither birefringence nor light scattering. Birefringence can be induced in the IsoSm* phase of copolymer films by light irradiation, and film sensitivity to the recording can be drastically increased by preliminary UV illumination.

The copolymers SK8 and SK16 can show the phase transition from the IsoSm* phase to a proper Sm A phase, which transition can be prevented by light illumination. Using that capability, a new approach to photorecording in photochromic polymers (LCPT recording) has been suggested. The first photo images have been recorded.

Acknowledgements

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