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Liquid Crystals

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Photo-optical properties of polymer composites based on stretched porous polyethylene filled with photoactive cholesteric liquid crystal

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A new type of polymer–liquid crystal composite with photovisible dichroism and birefringence is described. Porous stretched polyethylene films were used as polymer matrices. To induce a cholesteric phase in a commercial nematic host, a chiral photochromic dopant based on sorbide and cinnamic acid capable of E–Z isomerization under UV irradiation was used. A merocyanine-type substance was selected as a dichroic dye. Introduction of a dye-doped cholesteric mixture with a helical pitch higher than ~300 nm to polymer film led to an almost complete transition from a cholesteric to an oriented nematic phase, as well as to an increase in birefringence and the appearance of dichroism. Decrease of the helical pitch by increasing in the chiral dopant concentration in the liquid crystal–polymer composite results in a reduction of the dichroism values. UV irradiation of polymer composite leading to an isomerization of the chiral dopant and helix untwisting induces a noticeable gradual growth of dichroism and birefringence. These new composites can be considered as promising materials for optical applications.

1. Introduction

Polymer-dispersed liquid crystals (PDLCs) are composite materials formed by micron-sized droplets of liquid crystal embedded in a solid polymer matrix [1–7]. In recent years they have attracted much attention from researchers for their applications as light shutters, switchable windows, displays and other electro-optical devices. Such interest in PDLCs is associated with the possibility of combining the high mechanical properties of polymer films with the unique optical and electro-optical properties of liquid crystals in the same material.

In recent papers we have described a composite material based on nematic liquid crystals doped with different dichroic or photochromic dyes embedded in highly porous stretched polyethylene films [8, 9]. The pore size in the polyethylene matrix was varied between 50 and 500 nm. We have discovered that a director of nematic liquid crystals embedded in the porous polymer films is oriented along a direction of the film stretching. Analysis of the polarized absorbance spectra of the dichroic dyes dissolved in liquid crystal allowed one to calculate the dichroism values. These values are

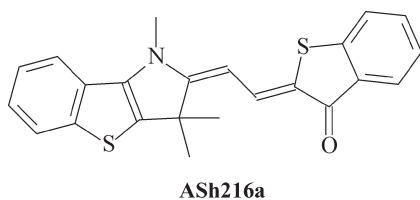
comparable with ones in glass cells coated with rubbed polyimide that indicates a high degree of liquid crystal orientation in the polyethylene films.

Investigation of the optical properties of cholesteric liquid crystals with helical pitch comparable with the pore size is a very interesting task, since it allows one to reveal the influence of the highly disperse structure of polyethylene films on the ability of the chiral nematic phase to form helical supramolecular structures.

On the other hand, the introduction of combined chiral photochromic fragments capable of photoisomerization into cholesteric or nematic matrix can be used for photoregulation and fine tuning of the helical pitch [10–18]. Under the irradiation of such composite films the helical twisting power of chiral photochromic dopant decreases, leading to reversible or irreversible shift of the selective light reflection wavelength. Preparation of polymer composite containing photoactive cholesteric liquid crystals may be used for the creation of a novel promising type of materials for optical data recording and optoelectronics.

In this study we describe the behaviour of a photo-sensitive cholesteric mixture introduced into highly porous stretched polyethylene films. We have used a merocyanine dye, **ASh216a** (see scheme 1), as dichroic

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Scheme 1. Chemical structure of **ASH216a**.

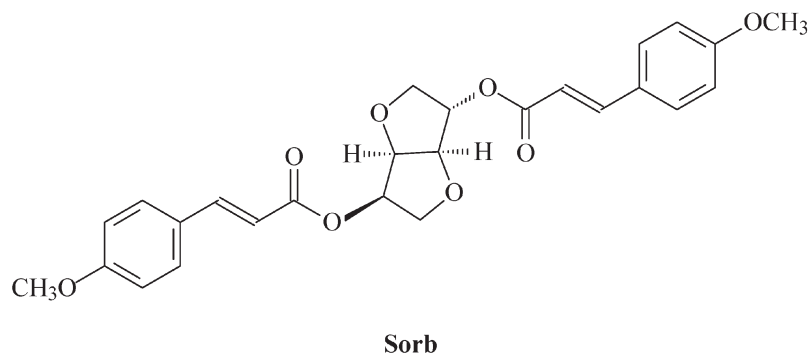
guest for spectral measurements and evaluation of the orientation degree of liquid crystal in composite. This dye is quite stable under our irradiation condition (313 nm).

As a chiral photochromic dopant, the previously described **Sorb** (scheme 2) [18] was used.

This right-handed chiral compound, **Sorb**, has a high twisting power (HTP) and can undergo E–Z isomerization under UV irradiation leading to a decrease in its HTP due to a reduction of the molecular anisometry (scheme 3) [18]. As a result, helix untwisting and a shift of the selective light reflection peak of the cholesteric phase takes place. (Under UV irradiation, two isomers (ZE and EZ) are formed due to the different stereochemical configurations of both carbons that contain hydroxyl groups in initial isosorbide. For simplicity, in scheme 3 only one of them is shown).

Several mixtures based on the commercially available nematic liquid crystal, ZLI 1695, with dichroic dye and chiral photochromic dopant were prepared (table 1). Mixture **I** contained 0.5 wt % of **ASH216a**, whereas mixtures **II** and **III** contained the same concentration of **ASH216a** and different concentrations of the dopant **Sorb** (10 and 20 wt %, respectively).

The main goal of this work was to study the influence of the helical structure of the cholesteric mesophase on the optical properties of liquid crystal (LC)–stretched porous polyethylene composites. Special attention was paid to investigation of the photo-optical changes in LC composites during E–Z isomerization of the chiral photochromic dopant, **Sorb**, induced by UV irradiation.

Scheme 2. Chemical structure of **Sorb**.

2. Experimental

2.1. Substances and polymer films

Microporous films of polyethylene were obtained from commercially available polyethylene of low density ($M_w=1.4 \times 10^5$, $M_w/M_n=6-8$, $T_m=132^\circ\text{C}$) as described previously [19]. During extrusion and stretching processes polymer films are deformed and was obtained a porous structure with pore sizes of about 50–500 nm. Pores size distributions were measured by the filtration porometry method described elsewhere [19].

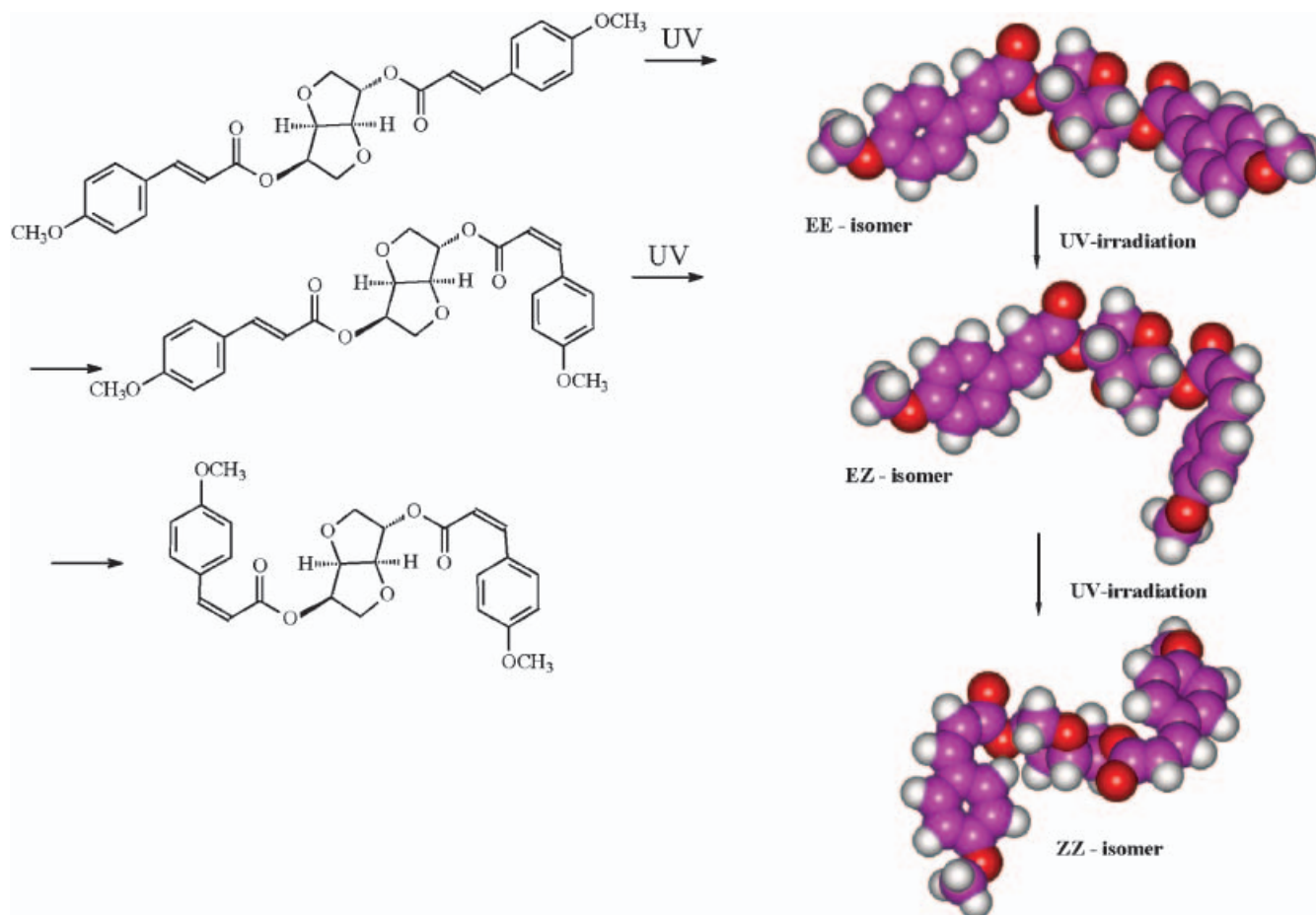
As nematic liquid crystal host, a commercial mixture of bicyclohexane derivatives was used (ZLI 1695, Merck).

The synthesis of chiral photochromic dopant **Sorb** [18] and merocyanine dye **ASH216a** [20] has been described elsewhere.

2.2. Mixture preparation and study of phase behaviour and optical properties of composite films

Liquid crystalline mixtures were prepared by dissolving of the components in chloroform followed by evaporation of the solvent and drying in vacuum. Polymer composites were prepared by coating of film with LC mixtures and subsequent removal of excess LC mixture using filter paper. The proportion of LC mixture in polyethylene composite obtained by weighing was about 55%.

Polarizing microscopy investigations were performed using LOMO P-112 polarizing microscope; the temperature of the samples was controlled by a Mettler FP-80 hot stage. The selective light reflection of the mixtures was studied with a diode array Tidas spectrometer (J&M) equipped with a Mettler FP-80 hot stage. The planar texture of cholesteric mixtures was obtained by the shear deformation of the samples, which were heated up to a temperature 5°C below N^*-I transition. Prior to the tests, the samples were annealed for 5 min at the appropriate temperatures.



Scheme 3. E-Z isomerization process taking place under UV irradiation of chiral photochromic dopant **Sorb**.

Table 1. Composition, clearing temperatures (T_{cl}), and maximum value of dichroism (D) in polyethylene film of nematic and cholesteric mixtures used for the composite preparation.

Mixture	Composition	$T_{cl}/^{\circ}\text{C}$	D
I	ZLI 1695+ ASh216a (0.5%)	70–71	0.57
II	ZLI 1695+ ASh216a (0.5%)+ Sorb (10%)	62–63	0.45
III	ZLI 1695+ ASh216a (0.5%)+ Sorb (20%)	50–51	0.20

2.3. Photo-optical investigations

Photochemical investigations were performed using a special optical set up equipped with a DRSh-250 ultra-high pressure mercury lamp. Using a filter, light with a wavelength of 313 nm was selected. To prevent heating of the samples due to the IR irradiation of the lamp, a water filter was used. To obtain the plane-parallel light beam, a quartz lens was applied. During the irradiation, the constant temperature of the test samples was maintained using a Mettler FP-80 heating unit. The intensities of the incident light were equal to

0.29 mW cm^{-2} , as measured by a LaserMate-Q intensity meter (Coherent).

The linearly polarized spectra of the film samples were studied with a TIDAS spectrometer (J&M) equipped with rotating polarizer (Glan-Taylor prism controlled by computer program).

3. Results and discussion

Figure 1 shows the UV-visible spectra and polar diagram of absorbance of the film of composite **I** at a wavelength corresponding to electronic transitions of

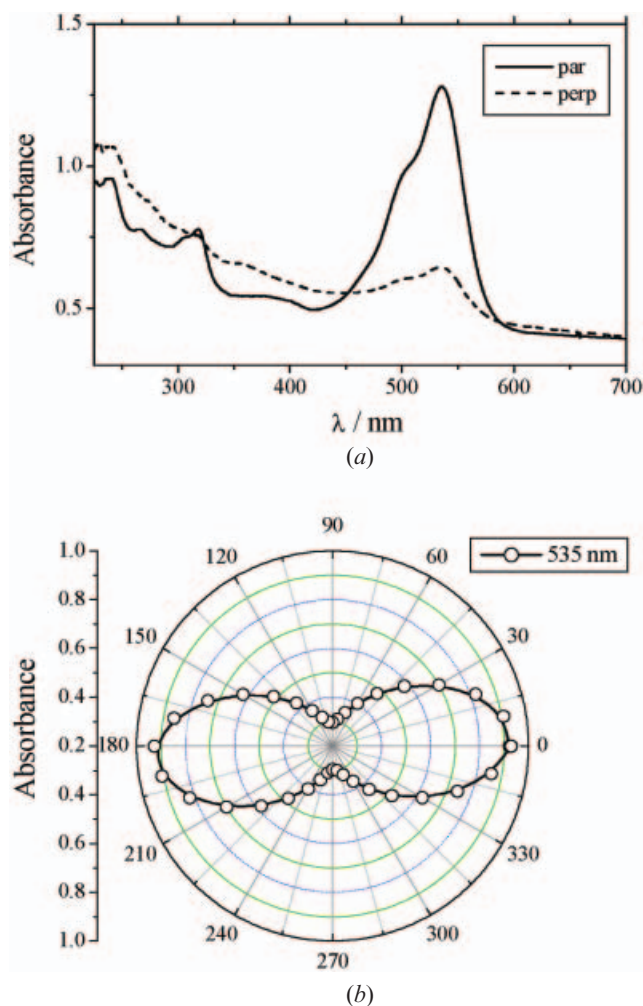


Figure 1. (a) Absorbance spectra and (b) corrected polar plot for composite based on mixture **I** at 25°C.

dye (535 nm). As can be clearly seen in figure 1, the film possesses a high dichroism that corresponds to the high orientation of molecules of liquid crystal and dye along the direction of polymer stretching.

Introduction of chiral photochromic dopant **Sorb** into the mixture and induction of the cholesteric phase leads to the noticeable decrease in values of dichroism (table 1, figures 2a, 3, 4). But, nevertheless, the composite films show measurable non-zero values of dichroism, even for the mixture with the very high concentration of chiral dopant. This effect is very unusual and can be explained by almost full or partial untwisting (in case of mixture with the high dopant concentration) of the cholesteric helix and transition to the uniaxially oriented nematic phase.

The dichroism of the composite films is strongly dependent on temperature and at temperature higher than the isotropization transition decreases almost to

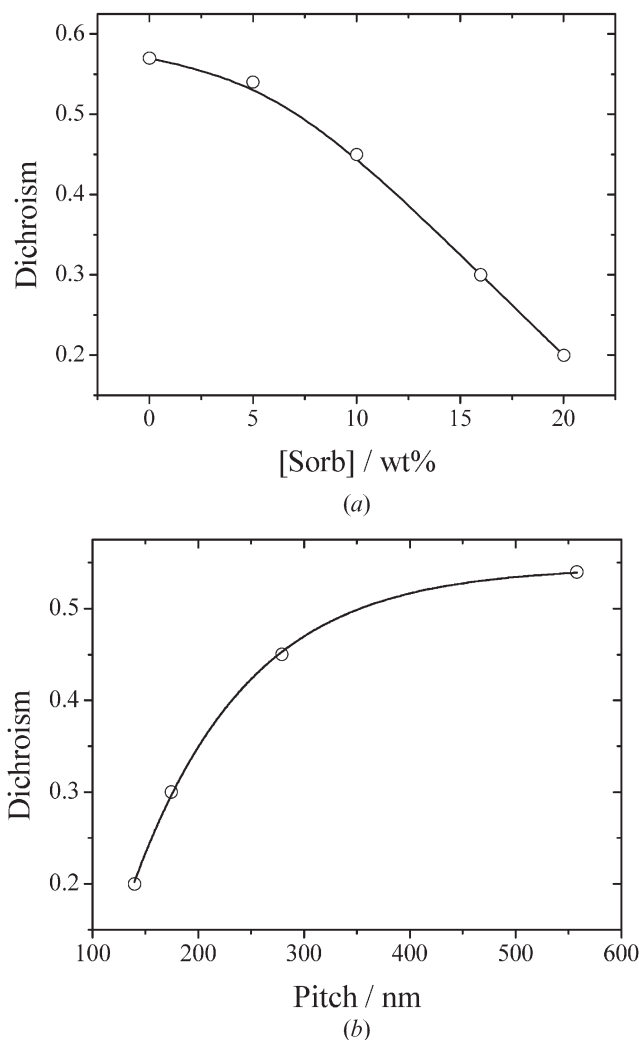


Figure 2. Dependence of dichroism of the composite films at 535 nm on (a) concentration of the chiral photochromic dopant **Sorb** and on (b) pitch of the cholesteric helix.

zero (figure 3). (The remaining value of about 0.05–0.1 is probably associated with the existence of dye molecules absorbed by the oriented surfaces of the polyethylene pores).

The strong absorbance in UV region (below 300 nm) makes it impossible to directly measure the selective light reflection spectra for mixtures with concentration of the chiral dopant higher than 10%, because selective light reflection maximum (λ_{\max}) for these samples is less than this wavelength. Hence, the helical twisting power, β , of this dopant in ZLI 1695 matrix was calculated via:

$$\beta = dP^{-1}/d[\text{Sorb}] = n(d\lambda_{\max}^{-1}/d[\text{Sorb}]), \quad (1)$$

where P is the pitch of the cholesteric helix, n is the average refractive index, and $[\text{Sorb}]$ is the concentration

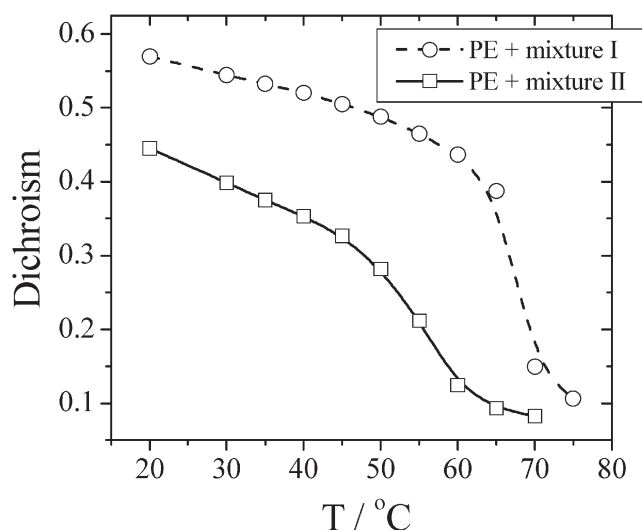


Figure 3. Temperature dependence of dichroism for the composite containing nematic mixture I and cholesteric mixture II.

of the chiral fragment (in our case the weight fraction values were used).

To calculate the HTP of the chiral dopant, several mixtures with different content of **Sorb** were prepared and the dependence of inverse wavelength of selective light reflection as a function of weight fraction of **Sorb** was determined. (Concentration of dopant was taken below 10 wt % in order to obtain the selective light reflection peak in the visible and near IR spectral ranges.) The value of β found from the slope of this linear dependence was equal to $35.8 \pm 0.7 \mu\text{m}^{-1}$.

Using the calculated β value the pitch of the helix for the mixtures with different content of **Sorb** was found. Figure 2b shows the dependence of dichroism on the value of helical pitch calculated from the selective light reflection maxima. A decrease of helical pitch to 300–400 nm results in a relatively sharp drop in dichroism. It is important to note that the size of the pores in polyethylene films lies in the range 50–500 nm [19]; in other words, values of pitch and pore size are close to each other.

Let us consider the influence of UV light irradiation and the isomerization of chiral dopant **Sorb** on the spectral properties of composite films. As can be seen clearly from figures 4–6, light action on the composites with the LC mixtures containing high amount of **Sorb** leads to an increase in the dichroism values by a factor of 2.5. This effect is associated with a partial untwisting of the cholesteric helix due to the E–Z isomerization followed by a complete helix untwisting and transition to the nematic state inside the small pores of composite. Eventually this processes leads to an orientation of the

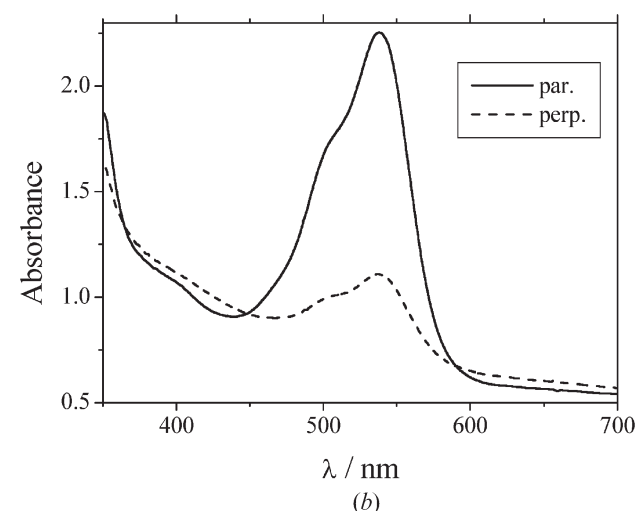
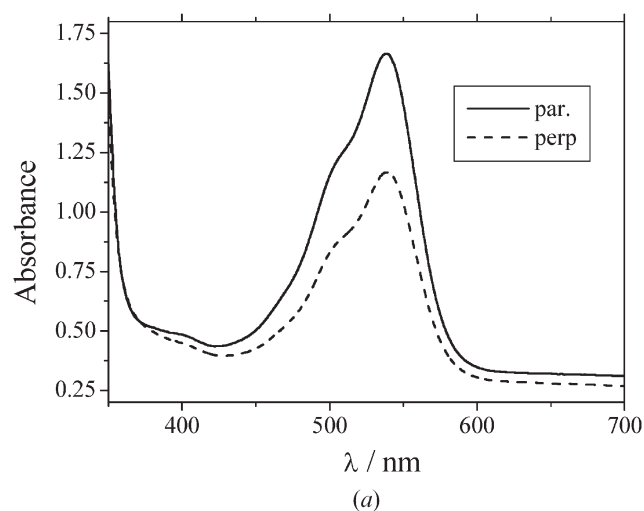


Figure 4. Absorbance spectra of composite with mixture III (a) before and (b) after UV irradiation for 540 min.

liquid crystal and dye molecules along the stretching direction.

UV irradiation also induces changes in the birefringence of the composite films. Figure 7 shows a microphotograph of the film after irradiation through the mask. Light action results in the changes in the optical retardation and colours of the films under observation between the crossed polarizers of the optical microscope.

It is noteworthy that retardation changes are clearly seen already after 5 min of irradiation. Using light with higher intensity should allow a decrease in irradiation time by the several orders of magnitude.

In summary, a novel type of polymer–liquid crystal composite based on porous stretched polyethylene films with photovisible dichroism and birefringence has been developed. Introduction of a dye-doped cholesteric mixture with helical pitch higher than ~ 300 nm into the

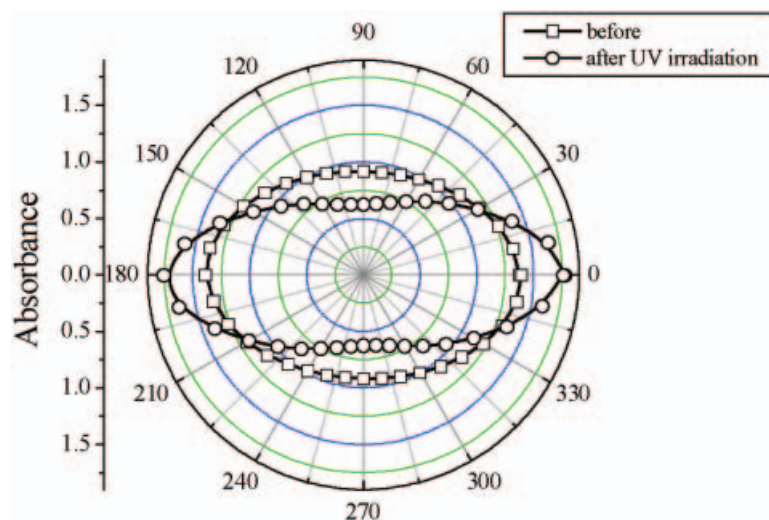


Figure 5. Polar plots of corrected absorbance at 535 nm of the composite with mixture **III** before and after 540 min of UV irradiation.

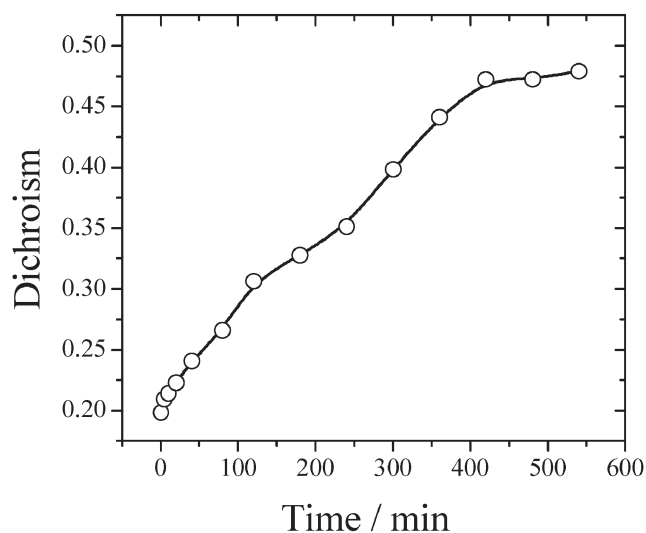


Figure 6. Kinetics of dichroism growth for the composite with mixture **III** at 535 nm during UV irradiation.

polyethylene films leads to almost complete transition from cholesteric to the oriented nematic phase, an increase in birefringence and the appearance of dichroism.

Decrease of the helical pitch by increasing in the chiral dopant concentration in the liquid crystal-polymer composite results in a reduction of the dichroism values. UV irradiation of polymer composite leading to an isomerization of the chiral dopant and helical untwisting induce a noticeable gradual growth of dichroism and birefringence. These new composites can be considered as the promising materials for the optical applications.

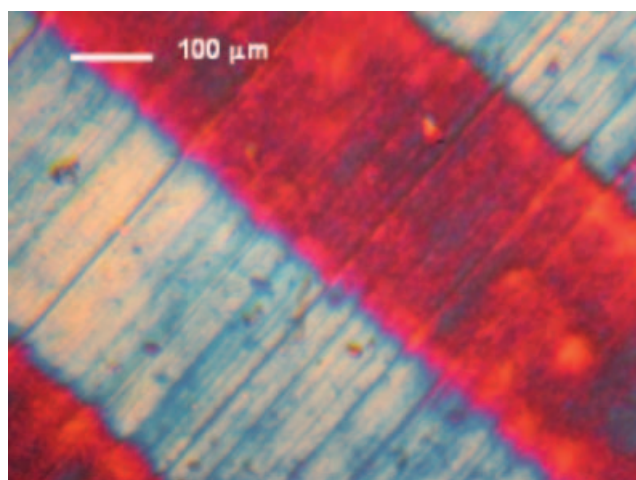


Figure 7. Polarizing microphotograph showing film of the composite **III** before and after irradiation (30 min, 313 nm) through the mask; bright regions correspond to the irradiated zones.

Acknowledgments

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