

Journal of Materials Chemistry C

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Photochromic LC-polymer composites containing azobenzene chromophores with thermally stable *Z*-isomer.

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Novel types of photochromic liquid crystalline (LC) polymer-based composites containing azobenzene chiral-photochromic moieties were elaborated. For this purpose a new chiral azobenzene-containing methacrylic monomer was synthesized. In one of the benzene rings of the azobenzene chromophore there are methyl substituents in both *ortho* positions to the azo-group. This substitution increases extremely thermal stability of its photoinduced *Z*-form. The first type of the novel photosensitive composites presents a glass-cell filled with cholesteric polymer-stabilized layers produced by thermal polymerization of a mixture containing synthesized chiral photochromic azobenzene monomer, nematic mixture of cyclohexane derivatives, mesogenic diacrylate and thermal initiator. UV-irradiation of such samples leads to *E-Z* isomerization of the photochromic groups of azobenzene monomer units accompanied by a shift of selective light reflection peak to a long wavelength spectral region. This process is thermally and photochemically reversible; the kinetics of selective light reflection shift was studied. The second type of the novel LC composites was obtained by the introduction of the same cholesteric photochromic mixture into porous stretched polyethylene (PE) films. Due to the highly anisotropic porous structure of PE an uniaxially aligned nematic phase inside the pores was obtained. UV and visible light irradiation provides the possibility of the dichroism and birefringence photocontrol in the obtained LC composite films. The possibility of photooptical image recording on the prepared composite was demonstrated. It is noteworthy that the images recorded by the novel type composites have extremely high thermal stability in comparison with those based on the other azobenzene derivatives (weeks).

1 Introduction

Design and investigation of “smart” photosensitive and field-responsive materials is a rapidly growing field of the modern material science. Among organic photosensitive materials photoisomerizable azobenzene-based substances possess remarkable photochromic properties providing a large variety of photoinduced phenomena including photooptical activity, photomechanical actuation, photoregulated wetting-dewetting effects, etc.¹⁻⁴ Of a special interest there are liquid crystalline (LC) systems possessing azobenzene photochromic moiety. Such systems may be formed either as mixtures of LCs with azobenzene derivatives or an azobenzene moiety may be covalently bound in mesogens thus forming photochromic materials.¹⁻¹⁶ Combination of LC order with photochromism gives the possibility to get unique materials highly sensitive to light action that induces reversible *E-Z* isomerization and strong structural changes in these systems.

One of the interesting and promising phenomena observed in such systems is so-called photoinduced isothermal phase transition resulting from *E-Z* photoisomerization of azobenzene groups and formation of bent-shaped *Z*-isomers.¹⁻¹⁶ Low anisometry of *Z*-form induces phase transition from ordered to less ordered mesophase or even complete disordering (isotropization) of the sample. As a result of a light action significant and reversible changes of optical properties, as birefringence, dichroism and diffraction efficiency (for photosensitive diffractive gratings) occur.¹²

A great attention of numerous research groups has been focused on design of new chiral photochromic dopants including those containing azobenzene grouping capable to *E-Z* photoisomerization followed by the change of helical twisting power.²⁻²⁶ Due to the fact that such changes are usually associated with the decrease of anisometry of azobenzene, the introduction of these substances into nematic matrices opens the possibility for the creation of cholesteric LC-materials with a phototunable position of selective light reflection band.

In our previous papers we described new types of photochromic and fluorescent materials based on stretched aligned porous polyethylene (PE) films.²⁷⁻³² Our approach for the creation of these LC composites is based on embedding in highly porous matrix of PE photochromic or fluorescent LC-mixtures. Owing to the highly anisotropic oriented structure of porous PE LC-molecules together with functional dopants molecules are well-aligned along stretching direction of PE films

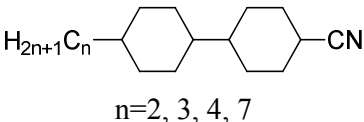
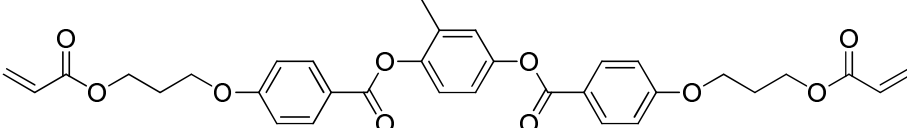
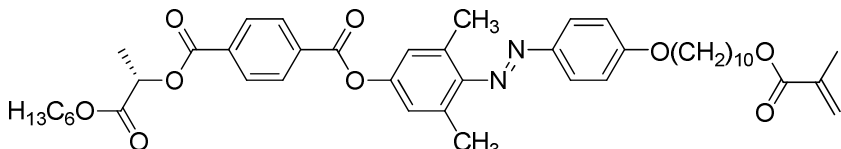
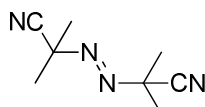
providing the possibility to create flexible birefringent, dichroic, fluorescent materials. Addition of photochromic moieties, such as diarylethenes, spiropyranes, and, especially, azobenzenes allowed us to obtain photosensitive and photomechanical-mobility films based on PE.²⁷⁻³²

In our previous paper²⁹ we have demonstrated the possibility of photomanipulation of dichroism and birefringence in LC PE composite owing to *E-Z* isomerization of azobenzene dopant embedded together with LC-mixture in pores of PE. UV-light irradiation leads to conversion of *E*-form of azobenzene moieties with rigid rod-like shape to bent-shaped *Z*-isomer disrupting LC-order. Despite to extreme photoinduced changes in dichroism and birefringence the obtained photochromic LC-composites have noticeable drawback associated with thermal reversibility of the *E-Z* isomerization process that results in fast recovery of initial birefringence and, thus, the photooptically recorded images are rapidly erased.

Another important disadvantage of LC-composite described previously^{27, 29, 30} is the interdiffusion of low molar mass components inside the porous PE films from the irradiated zone to the non-irradiated ones and *vice versa*, that also leads to instability and fast erasing of the photorecorded images.

In the present paper successful ways for the overcoming of the above-mentioned drawbacks are presented. In the first place, we have synthesized a new chiral azobenzene-containing compound exhibiting extremely thermally stable *Z*-form (monomer **MDATL**). In the second place, we have introduced in LC-mixture polymerizable diacrylate **RM257**. Copolymerization of **RM257** with monomer **MDATL** allows one to create polymer network stabilizing the LC-composite and preventing component diffusion. The components of the prepared photochromic mixture are listed in Table 1.

Table 1. Components of the polymerizable photochromic LC-mixture.

Name	Chemical structure	Content / wt%
Nematic mixture MLC6816 (Merck)		55.0
Nematic diacrylate RM257		4.2
Azobenzene-containing monomer MDATL		39.2
Thermo-initiator AIBN		1.6

As a nematic matrix we have selected a mixture of cyclohexane derivatives **MLC6816** (Merck) due to their high transparency in UV-range³³ diminishing light absorbance and increasing light penetration depth through the photochromic LC samples. Moreover, this mixture has refractive index similar to PE that reduces light scattering of LC PE composites as was shown by us before.³⁰

Monomer **MDATL** containing two methyl substituents in one of the benzene rings of the azobenzene fragment (in *ortho* positions to azo-group) providing high thermostability of the photoinduced *Z*-form and a chiral terminal group inducing formation of cholesteric phase which is of special interest from the point of view of the possibility of the helix pitch tuning and, as a consequence, of the selective light reflection wavelength by UV-irradiation.

In order to avoid the competing photoinduced isomerization processes during polymerization we have used thermoinitiator **AIBN** instead of other widely used photoinitiators.^{9,34}

The first part of the paper describes the photooptical properties of planar oriented polymer-stabilized cholesteric mixture in glass cells and focused on the study of photoinduced changes of the helix pitch values and the position of selective light reflection band. The second part is devoted to the study of PE-based composites and

isothermal photoinduced phase transition leading to the birefringence and dichroism decreasing.

2 Experimental

Materials

All substrates and reagents for the synthesis of monomer MDATL were purchased either from Sigma-Aldrich or Acros Organics. The nematic mixture **MLC6816** and diacrylate **RM257** (Merck), as well as initiator **AIBN** (Aldrich) were used as received.

Synthesis of monomer MDATL

MDATL monomer was synthesized according to the synthetic route shown in the Scheme 1. Synthesis of the photosensitive part of the monomer started from *p*-acetamidophenol (**1**), which was alkylated with 1,10-dibromodecane and subsequently, the *N*-acetyl group was cleft by acid hydrolysis in diluted sulfuric acid. Thus obtained hydrogensulfate **3** was diazotized in acetic acid and reacted with 3,5-dimethylphenol following the standard azo-coupling procedure to yield azocompound **4**. Methacrylate moiety was introduced to the side-chain of the molecule by treating the phenol **4** with an excess of potassium methacrylate in DMSO to obtain azo-phenol **5**. Acid **8** with the chiral side chain was prepared in two steps starting from 4-formylbenzoic acid **6**. In the first step, the acid **6** was esterified with (*S*)-hexyl lactate using a mild method (DCC-coupling) to avoid racemization. In the second step, the formyl group of ester **7** was oxidized to the carboxylic group by the action of potassium permanganate in pyridine. In the final step of the synthesis, the acid **8** and azo-phenol **5** were reacted in the DCC-coupling to yield monomer **MDATL**. Detailed description of synthesis is presented in Supporting Information. Phase transitions of monomer: N* 36-37 °C I (LC phase at room temperature; crystallization does not take place).

LC-composite films preparation

The first type of composite films was prepared by thermal polymerization of the mixture (see Table 1) at 60 °C in a glass cells with a 10 μm gap, whereas the second type was based on the porous PE films with thickness ~14 μm.

In the case of glass cells for the preparation of uniaxially aligned LC layers a photoalignment method was applied.^{35, 36} For this purpose glass substrates spin-coated with poly[1-[4-(3-carboxy-4-hydroxy-phenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt (**PAzo**) (Aldrich) solution in chloroform (2 mg/mL) were used.³⁶ Before the cell preparation the substrates were irradiated with polarized polychromatic light of mercury lamp (DRSh-350, 20 min, ~ 15 mW/cm²). Thickness of **PAzo** layers was ca. 4 nm to ensure their low absorbance. Cells were filled with polymerizable mixture at room temperature followed by annealing at 60 °C during 3 days (in order to ensure completeness of polymerization).

The second type of LC-composite was prepared using stretched porous PE as a polymer matrix. Microporous films of PE were obtained from commercially available PE of low density ($M_w \sim 1.4 \times 10^5$, $M_w/M_n \sim 6-8$, $T_m \sim 132$ °C) as described previously.³⁷ During the extrusion and stretching processes polymer films are deformed and oriented that stimulates a formation of a porous structure with pore sizes of about 50–500 nm. Pores size distributions were measured by the filtration porometry method described elsewhere.³⁷

Phase behaviour and selective light reflection study.

The polarizing optical microscope investigations were performed using LOMO P-112 polarizing microscope equipped with Mettler TA-400 heating stage. Differential scanning calorimetry (DSC) was performed by Perkin Elmer DSC-7 thermal analyzer (a scanning rate of 10 K/min)

For selective light reflection study absorbance spectra were recorded by Unicam UV-500 UV-Vis spectrophotometer.

Photooptical investigations

Photochemical investigations were performed using an optical setup equipped with a DRSh-350 ultra-high pressure mercury lamp and MBL-N-457 diode laser (457 nm, CNI Laser). To prevent the heating of the samples due to the IR radiation of the mercury lamp, a water filter was introduced in the optical scheme. To assure the plane-parallel light beam, a quartz lens was applied. Using the filters a light of Hg lamp with the wavelengths 365 nm and 436 nm were selected. The intensity of light was measured by LaserMate-Q (Coherent) intensity meter.

Non-polarized absorbance spectra were measured using Unicam UV-500 UV-Vis spectrophotometer. For polarized UV/visible spectroscopy the angular dependence (with a step-width of 10°) of the polarized light absorbance was measured using a photodiode array UV/visible spectrometer TIDAS (J&M) equipped with rotating polarizer (Glan–Taylor prism controlled by a computer).

3 Results and discussion

Photooptical properties of polymer-stabilized cholesteric mixture in glass cells

First of all let us consider the photooptical properties of planarly-oriented polymer-stabilized cholesteric mixture in glass cells. The prepared photochromic mixture does not show any phase separation and forms cholesteric mesophase at room temperature; clearing temperature for the mixture (without AIBN) is 63-65 °C. The mixture possesses selective light reflection in visible spectral range with maximum at ~ 650 nm (Fig. 1). Using these data the helical twisting power of new chiral-photochromic monomer **MDATL** is calculated and it is equal to ca. 6 μm^{-1} .

Thermal polymerization of the mixture in glass cells carried out in order to obtain planar anchoring (see Experimental for details) affords stable planarly-oriented films with selective light reflection in orange-red spectral range (Fig. 2). Polymerization process leads to the shift of selective light reflection peak to the shorter wavelengths ($\lambda_{\text{max}} \sim 610$ nm, Fig. 1). Most probably, a polymer network formation induces its shrinking in the course of polymerization implying a decrease of the period of helical supramolecular structure.

Irradiation of the cells by UV-light (365 nm) leads to *E-Z* isomerization of chiral azobenzene chromophores which decreases their anisometry (Fig. 3) and, consequently, also their helical twisting power ($\beta_E \gg \beta_Z$). As a result, a fast shift of the selective light reflection peak to long-wavelength spectral range (near-IR) occurs (Fig. 2). It is important to stress that the photoinduced *Z*-form of chiral-photochromic units is relatively stable at room temperature in the dark, i.e. thermal back conversion into *E*-form and helix twisting occurs rather slowly (Fig. 4). Moreover, our investigation of thermal *Z-E* relaxation has revealed rather unusual phenomena: instead of the gradual shift of the selective light reflection peak back to the short-wavelength spectral region we have found an appearance and growth of the short-wavelength peak during annealing of samples at 30 °C (Fig. 4, S1). At the same time,

a decrease of the long-wavelength peak intensity is observed. The origin of this unexpected phenomenon is still unclear, but, most likely, it is associated with the “memory effect” provided by the polymer network.

On the other hand, an action of visible blue light (436 nm) on UV-irradiated cells induces a fast back gradual shift of selective light reflection band towards to the initial position (Fig. S2). Fig. 5 shows the kinetic curves of photoinduced spectral shift of the selective light reflection peak demonstrating high rate of photoinduced changes even at moderate light intensities ($\sim 2 \text{ mW/cm}^2$).

Photooptical properties of LC PE composite.

The second type of LC-composites was obtained by thermal polymerization of the above-mentioned mixture (Table 1) inside pores of the stretched PE films (see Experimental part for the details). Using this approach the stable flexible, highly birefringent films were obtained. LC-composite films display noticeable linear dichroism in visible spectral range (Fig. 6): absorbance of the light polarized along stretching direction of the films is higher than of that polarized along the perpendicular direction. Fig. 6b shows polar diagrams of polarized absorbance at 480 nm that corresponds to $n-\pi^*$ electronic transition range of azobenzene chromophores (absorbance at $\lambda < 400 \text{ nm}$ is too high to be adequately measured). These results indicate significant degree of cooperative uniaxial orientation of chromophores and mesogens that could be explained by complete cholesteric helix untwisting due to the intrinsic anisometry of the porous PE structure (Fig. 7). The similar phenomenon was observed by us for PE-based composites with cholesteric LC-mixtures with helix pitch corresponding to selective light reflection in visible or IR spectral ranges.²⁷ UV-irradiation of the composite films strongly decreases birefringence and dichroism values (Fig. 6). As seen from Fig. 8a the dichroism values drop almost to zero, whereas subsequent visible light action partially recovers the initial state. This effect is most probably associated with the photoinduced isothermal phase transition from nematic to isotropic phase of LC-material embedded in porous PE structure (Fig. 7). This effect is explained by a formation of bent-shaped Z-isomer of azobenzene chromophores (Figs. 3, 7) and disruption of mesophase order. It is noteworthy, that we did not find the same isothermal phase transition in glass cells described in the previous section even after UV-irradiation in duration of 3 hours. Most probably, the porous structure of PE plays crucial role and does not only induce the untwisting the

cholesteric helix but also partially decreases the degree of mesophase order. Unfortunately, in the case of LC composites based on our porous oriented PE films a direct observation of the phase transition is rather complicated task due to the intrinsic birefringence of oriented stretched PE films. The values of PE films birefringence is relatively low (~ 0.003),³¹ but in the films with thickness of the order of tens micrometers the optical retardation values provided by PE is quite significant, that makes almost impossible an exact determination of the phase transition.

Photoinduced isothermal phase transition could be used for recording of images: irradiation of the films through the mask allows one to obtain high contrast in birefringence easily visible in polarizing optical microscope (Fig. 9). It is noteworthy, that in contrast with photochromic LC PE composites described before^{27, 29, 30} the recorded images are very stable in time. Due to the slow back *Z-E* isomerization and diminished molecular diffusion ensured by polymer network the recorded images are stable for weeks (Fig. 9b). Nevertheless, a visible light action could be used for fast erasing of recorded images (Fig. 9c).

Irradiation of LC-composites films with polarized light also induces changes in dichroism (Fig. 8b). When the polarization direction coincides with LC alignment axis a strong decrease in dichroism has been found. This effect is related to photoorientation phenomena, i.e. to the photoinduced rotational diffusion of chromophores in direction perpendicular to electric field vector of the polarized light. The occurrence of the similar phenomenon is confirmed experimentally in previous publications for other azobenzene-containing systems.^{1, 35, 36} In the case of polarization of laser light perpendicular to LC-alignment axis decrease in dichroism is much smaller and could be related to alignment of chromophores along laser beam (photoinduced homeotropic alignment).^{38, 39}

4 Conclusions

In conclusion, two novel types of photochromic azobenzene-containing LC-composites were prepared and their photooptical properties were studied. UV and visible light irradiation allows one to realize colour phototuning of selective light reflection for the composites of the first type, whereas for PE-based composites photovariation of dichroism and birefringence was demonstrated. It was also shown that the presence of two methyl substituents in azobenzene core strongly improves

thermal stability of photoinduced Z-form that opens new opportunities for the using of such materials in optics and photonics.

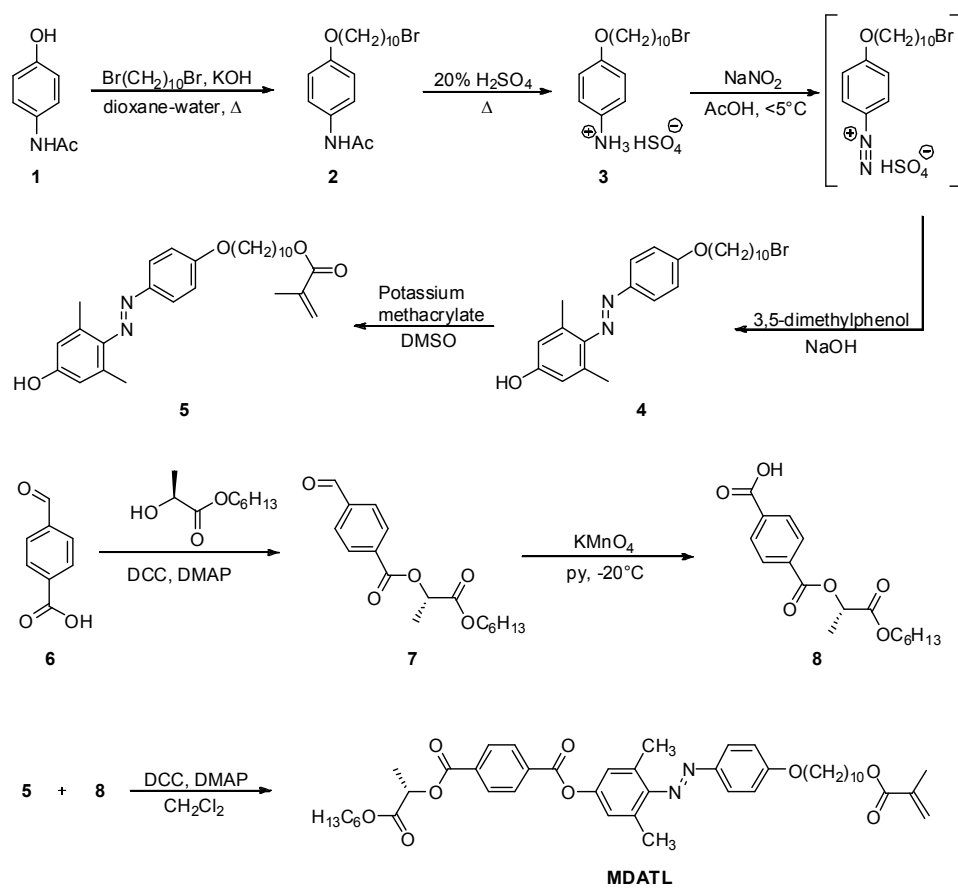
Acknowledgements

This research was supported by the Russian Foundation of Fundamental Research (12-03-00553-a, 13-03-00648, 13-03-12071, 13-03-12456 and 13-03-00219) and Czech Science Foundation (projects No. P204/11/0723 and 13-14133S) and specific university research (MSMT No 20/2013).

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Scheme 1 Synthesis of monomer MDATL.

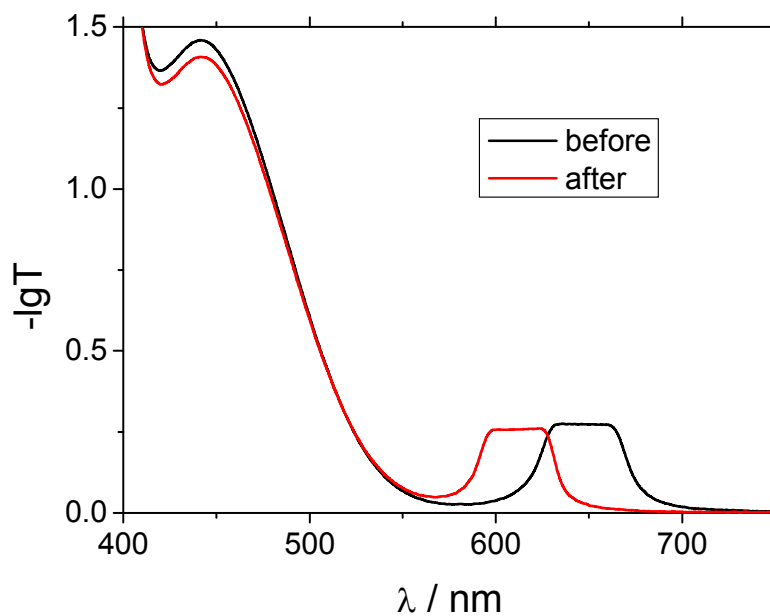


Fig. 1 Absorbance spectra of the mixture in planarly-aligned glass cell before and after thermal polymerization (3 days at 60 °C).

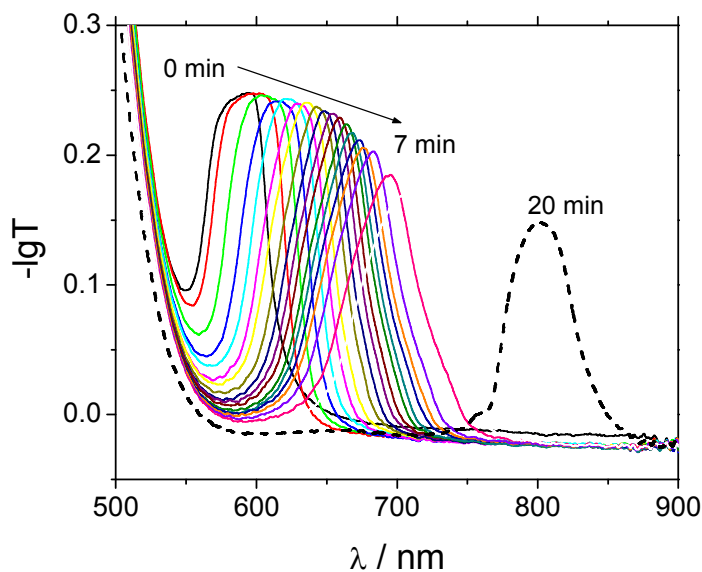


Fig. 2 Shift of selective light reflection peak during UV irradiation (365 nm, $\sim 2 \text{ mW/cm}^2$) of planarly-oriented **polymer-stabilized mixture in glass cell**. Spectra were recorded each 20 s of irradiation. Dashed line shows selective light reflection peak after 20 min of UV irradiation.

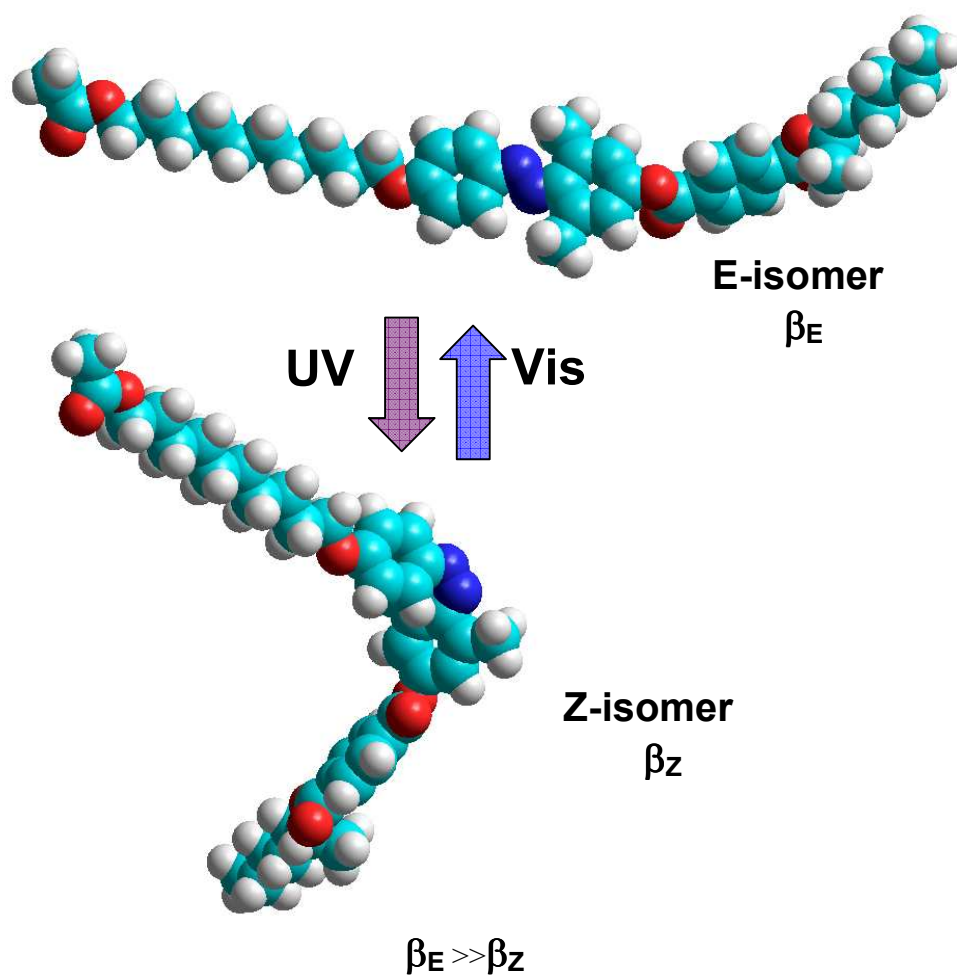


Fig. 3 Molecular model of MDATL side chains showing the decrease in their anisotropy due to *E-Z* photoisomerization.

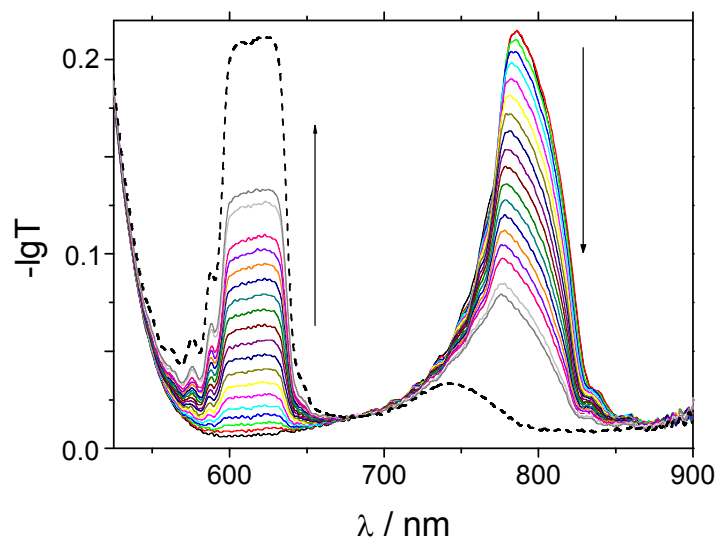


Fig. 4 Changes of absorbance spectra of UV-irradiated mixture film (in glass cell) during thermal *Z-E* isomerization at 30 °C. Spectra were recorded each 20 min of relaxation.

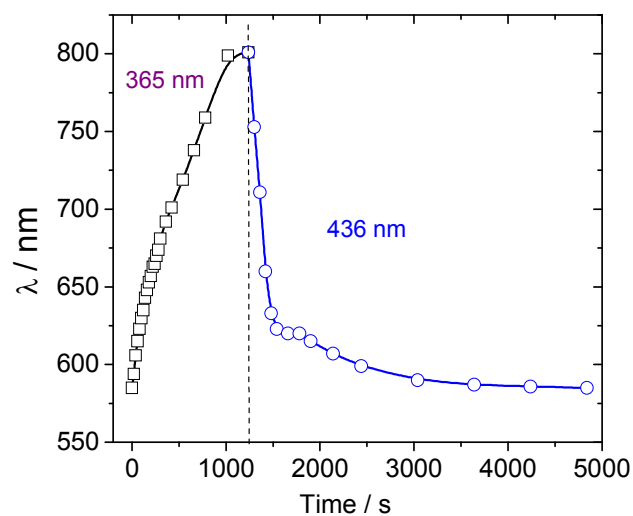
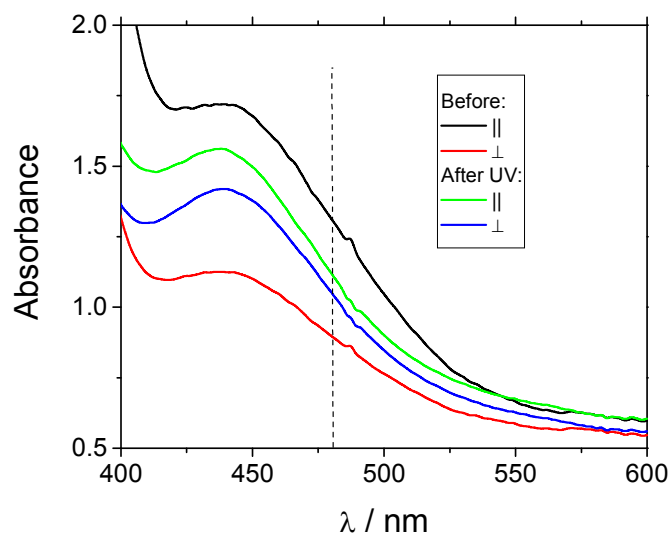
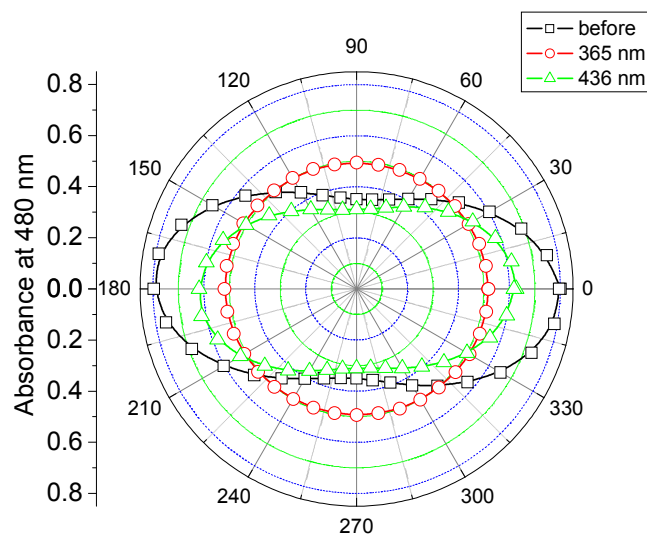


Fig. 5 Kinetics of the selective light reflection peak shift during UV and visible light irradiation of **polymer-stabilized mixture**.



a



b

Fig. 6 (a) Polarized absorbance spectra of LC PE composite film before, after UV irradiation (40 min) and after subsequent visible light action (40 min). (b) Corresponding polar plots of polarized absorbance.

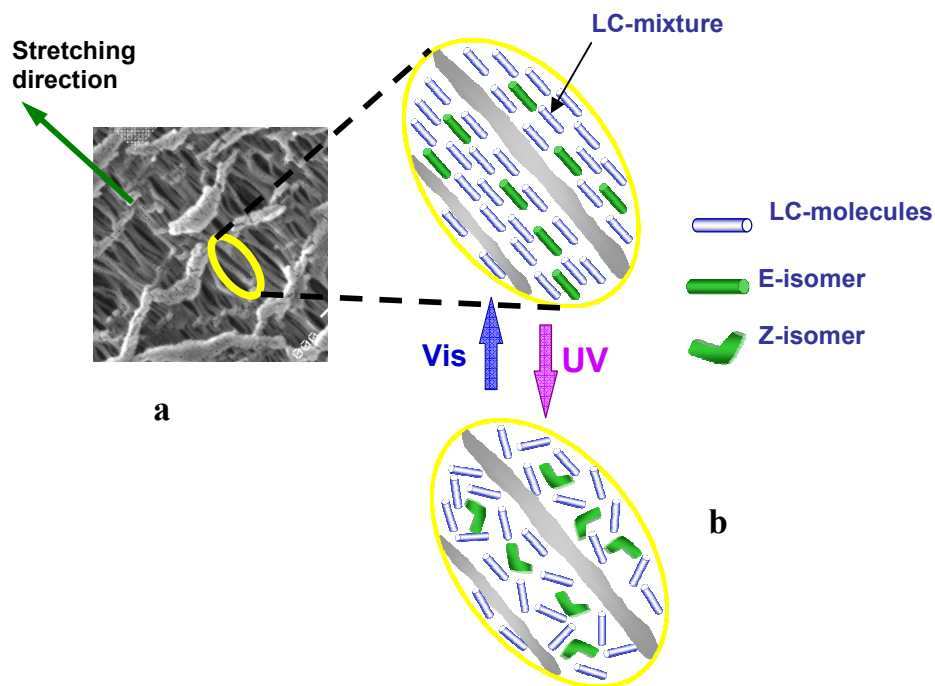
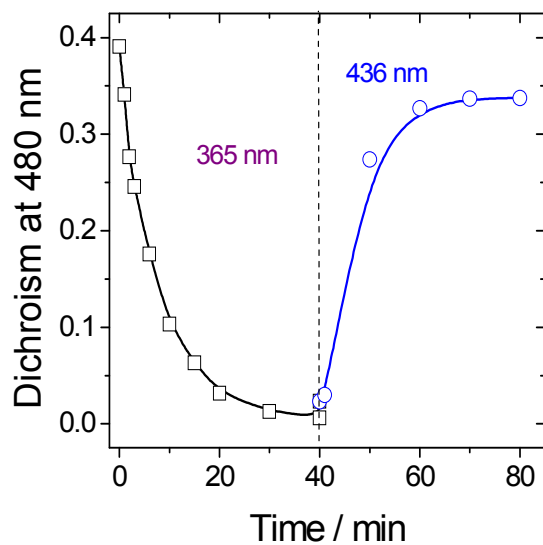
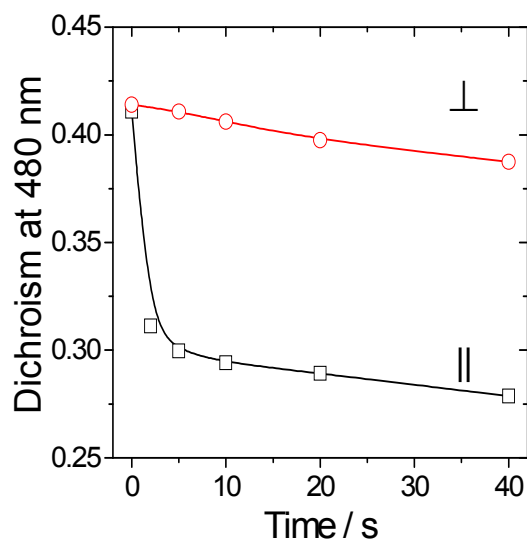


Fig. 7 SEM microphotograph showing microporous structure of porous PE film (a) and schematic representation of LC-molecules orientation along PE film stretching direction and photoinduced phase transition initiated by E–Z isomerization of azobenzene fragments (b).



a



b

Fig. 8 (a) Changes of dichroism of **PE composite** film under UV and visible light irradiation; (b) under polarized visible light irradiation (laser 457 nm, ~ 0.5 W/cm²); laser polarization was parallel and perpendicular to the LC director of PE composite film.

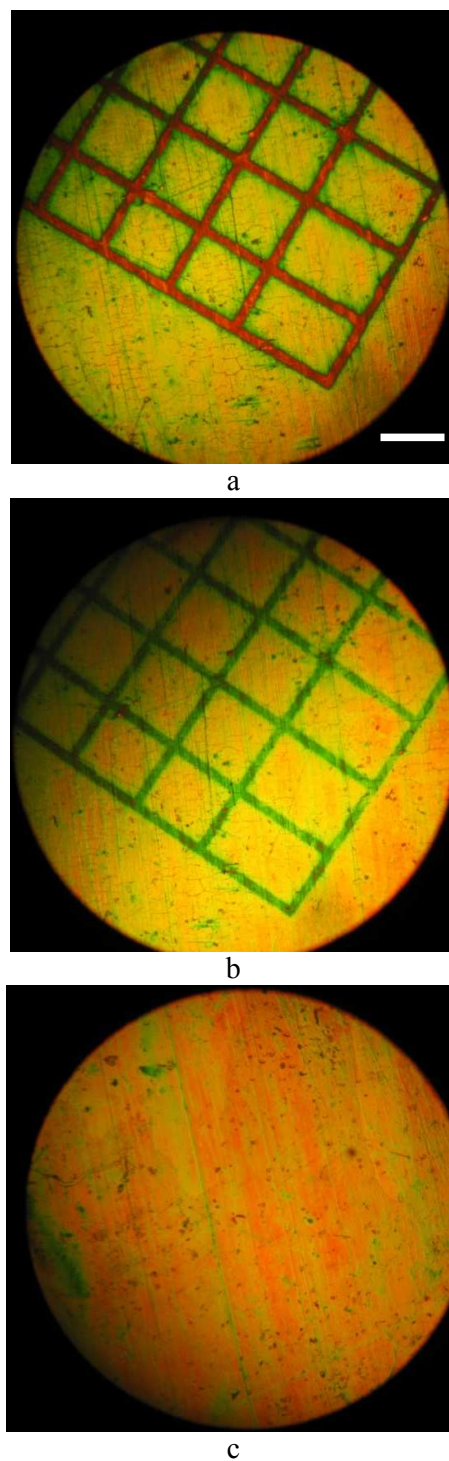


Fig. 9 Polarizing optical microscopy photo of LC PE composite film after 20 min of UV irradiation through the mask (a), after 14 days at room temperature (c), and after 15 min of visible light irradiation (436 nm). Bar corresponds to 100 μm . Temperature of the sample is ca. 22 $^{\circ}\text{C}$.