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1 Introduction

The design and investigation of "smart" photosensitive and field-responsive materials is a rapidly growing field in modern materials science. Among organic photosensitive materials, photoisomerizable azobenzene-based substances possess remarkable photochromic properties, providing a large variety of photoinduced phenomena, including photo-optical activity, photomechanical actuation, photoregulated wetting–dewetting effects, *etc.*¹⁻⁴ Liquid crystalline (LC) systems possessing photochromic azobenzene moieties are of special interest. Such

Photochromic LC–polymer composites containing azobenzene chromophores with thermally stable Z-isomers†

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

> systems may either be formed as mixtures of LCs with azobenzene derivatives, or an azobenzene moiety may be covalently bound in mesogens, thus forming photochromic materials.¹⁻¹⁶ The combination of LC order with photochromism provides the possibility of obtaining unique materials that are highly sensitive to light action, which induces reversible E-Z isomerization and significant 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 the azobenzene groups and formation of bent Z-isomers.^{1–16} The low anisometry of the Z-form induces a phase transition from an ordered to a less ordered mesophase, or even complete disordering (isotropization) of the sample. As a result of light action, significant and reversible changes in the optical properties, such as birefringence, dichroism and diffraction efficiency (for photosensitive diffractive gratings), occur.¹²

> Numerous research groups have focused much attention on the design of new chiral photochromic dopants, including those containing azobenzene groups capable of E-Z photoisomerization followed by changes in the helical twisting



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Table 1 Components of the polymerizable photochromic LC mixture



power.²⁻²⁶ Due to the fact that such changes are usually associated with the decrease in the anisometry of azobenzene, the introduction of these substances into nematic matrices allows the possibility of the creation of cholesteric LC materials with phototunable selective light reflection band positions.

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 photochromic or fluorescent LC mixtures in a highly porous matrix of PE. The highly anisotropic oriented structure of the porous PE– LC molecules, together with the fact that functional dopant molecules are well-aligned along the stretching direction of the PE films, provides the possibility of creating flexible, birefringent, dichroic, and fluorescent materials. Addition of photochromic moieties, such as diarylethenes, spiropyranes, and especially azobenzenes allowed us to obtain photosensitive and photomechanical-mobile films based on PE.²⁷⁻³²

In our previous paper,²⁹ we demonstrated the possibility of photomanipulation of the dichroism and birefringence of LC– PE composites, owing to E-Z isomerization of the azobenzene dopant, embedded in the pores of PE together with the LC mixture. UV light irradiation leads to conversion of the *E*-form of the azobenzene moiety, which has a rigid rod-like shape, to the bent *Z*-isomer, disrupting the LC order. Despite significant photoinduced changes in the dichroism and birefringence, the obtained photochromic LC composites have noticeable drawbacks associated with the thermal reversibility of the E-Zisomerization process, which results in fast recovery of the initial birefringence and, thus, causes the photo-optically recorded images to be rapidly erased.

Another important disadvantage of the LC composites described previously^{27,29,30} is the interdiffusion inside the

porous PE films of low molar mass components from the irradiated zone to the non-irradiated zones and *vice versa*, which also leads to instability and fast erasing of the photorecorded images.

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

For the nematic matrix, we selected the mixture of cyclohexane derivatives **MLC6816** (Merck) due to their high transparency in the UV range,³³ diminishing light absorbance and increasing the depth of light penetration through the photochromic LC samples. Moreover, this mixture has a refractive index similar to that of PE, which reduces light scattering in the LC-PE composites, as was shown by us previously.³⁰

Monomer **MDATL** contains two methyl substituents on one of the benzene rings of the azobenzene fragment (in positions *ortho* to the azo group), providing high thermostability of the photoinduced *Z*-form, and a chiral terminal group that induces formation of the cholesteric phase, which is of special interest due to the possibility of helix pitch tuning and selective light reflection on UV irradiation.

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

The first part of the paper describes the photo-optical properties of the planar-oriented polymer-stabilized cholesteric

mixture in glass cells and focuses on studying the photoinduced changes in the helix pitch values and the position of the selective light reflection band. The second part is devoted to the study of PE-based composites and isothermal photoinduced phase transitions, leading to decreases in the birefringence and dichroism.

2 Experimental

Materials

All substrates and reagents for the synthesis of monomer **MDATL** were purchased from either 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 Scheme 1. The 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 dilute sulfuric acid. The 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**. A methacrylate moiety was introduced to the side-chain of the molecule by treating phenol **4** with an excess of potassium methacrylate in DMSO to obtain azo-phenol **5**. Acid **8**, with a chiral side chain, was prepared in two steps starting from 4-

formylbenzoic acid, **6**. In the first step, 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 a carboxylic group by the action of potassium permanganate in pyridine. In the final step of the synthesis, acid **8** and azo-phenol **5** were reacted *via* DCC-coupling to yield monomer **MDATL**. A detailed description of the synthesis is presented in the ESI.[†] Phase transitions of monomer: N* 36–37 °C I (LC phase at room temperature; crystallization does not take place).

LC composite film preparation

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

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



Scheme 1 Synthesis of monomer MDATL.

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

Phase behaviour and selective light reflection study

The polarizing optical microscopy investigations were performed using a LOMO P-112 polarizing microscope equipped with a Mettler TA-400 heating stage. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC-7 thermal analyzer (at a scanning rate of 10 K min⁻¹).

For the selective light reflection study, absorbance spectra were recorded using a Unicam UV-500 UV-vis spectrophotometer.

Photo-optical investigations

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

Non-polarized absorbance spectra were measured using a 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 TIDAS photodiode array UV-visible spectrometer (J & M) equipped with a rotating polarizer (Glan–Taylor prism controlled by a computer).

3 Results and discussion

Photo-optical properties of the polymer-stabilized cholesteric mixture in glass cells

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

Thermal polymerization of the mixture in glass cells was carried out in order to obtain planar anchoring (see Experimental section for details), affording stable planar-oriented films with selective light reflection in the orange–red spectral range (Fig. 2). The polymerization process leads to a shift of the



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



Fig. 2 Shift of the selective light reflection peak during UV irradiation (365 nm, \sim 2 mW cm⁻²) of the planar-oriented polymer-stabilized mixture in a glass cell. Spectra were recorded every 20 s during irradiation. The dashed line shows the selective light reflection peak after 20 min of UV irradiation.

selective light reflection peak to shorter wavelength ($\lambda_{max} \sim 610$ nm, Fig. 1). Most probably, formation of a polymer network induces shrinking during the course of polymerization, implying a decrease in the period of the helical supramolecular structure.

Irradiation of the cells by UV light (365 nm) leads to E-Z isomerization of the 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 a long wavelength spectral range (near-IR) occurs (Fig. 2). It is important to stress that the photoinduced *Z*-form of the chiral-photochromic units is relatively stable at room temperature in the dark, *i.e.* thermal back conversion into the *E*-form and helix twisting occurs rather slowly (Fig. 4). Moreover, our investigation of the thermal *Z*-*E* relaxation revealed rather unusual phenomena: instead of a gradual shift of the selective light reflection peak back to the short wavelength spectral region, we observed the appearance and growth of the short wavelength peak during annealing of the samples at 30 °C (Fig. 4 and S1†). At the same time, a



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



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

decrease in the intensity of the long wavelength peak 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, action of visible blue light (436 nm) on the UV-irradiated cells induces a fast gradual shift of the selective light reflection band back towards its initial position (Fig. S2†). Fig. 5 shows the kinetic curves of the photoinduced spectral shift of the selective light reflection peak,



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

demonstrating that the rate of the photoinduced changes is fast, even at moderate light intensities ($\sim 2 \text{ mW cm}^{-2}$).

Photo-optical properties of the LC-PE composite

The second type of LC composite 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, stable, flexible, and highly birefringent films were obtained. The LC composite films display noticeable linear dichroism in the visible spectral range (Fig. 6): the absorbance of light polarized along the stretching direction of the films is higher than that of light polarized along the perpendicular direction. Fig. 6b shows polar diagrams of the polarized absorbance at 480 nm that corresponds to the $n-\pi^*$ electronic transition range of azobenzene chromophores (absorbance at $\lambda < 400$ nm is too high to be adequately measured). These results indicate a significant degree of cooperative uniaxial orientation of chromophores and mesogens that could be explained by complete untwisting of the cholesteric helix due to the intrinsic anisometry of the porous PE structure (Fig. 7). We observed a similar phenomenon in PEbased composites in cholesteric LC mixtures with helix pitch,



Fig. 6 (a) Polarized absorbance spectra of LC-PE composite film before and after UV irradiation (40 min). (b) Corresponding polar plots of polarized absorbance before, after UV irradiation and after subsequent visible light action (436 nm, 40 min).

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









Fig. 8 Changes in the dichroism of the PE composite film: (a) under UV and visible light irradiation; (b) under polarized visible light irradiation (457 nm laser, \sim 0.5 W cm⁻²); laser polarization was parallel and perpendicular to the LC director of the PE composite film.

Fig. 9 Polarizing optical microscopy photos of the LC–PE composite film after 20 min of UV irradiation through the mask (a), after 14 days at room temperature (b), and after 15 min of visible light irradiation (436 nm) (c). The bar corresponds to 100 μ m. The temperature of the sample is *ca.* 22 °C.

corresponding to selective light reflection in the visible or IR spectral ranges.²⁷

UV irradiation of the composite films significantly decreases the 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 likely associated with the photoinduced isothermal phase transition from the nematic to the isotropic phase of the LC material embedded in the porous PE structure (Fig. 7). This effect is explained by formation of the bent Z-isomer of the azobenzene chromophore (Fig. 3 and 7) and disruption of the mesophase order. It is noteworthy that we did not observe the same isothermal phase transition in the glass cells described in the previous section, even after 3 hours of UV irradiation. Most probably, the porous structure of PE plays a crucial role, and not only induces untwisting of the cholesteric helix but also partially decreases the degree of mesophase order. Unfortunately, in the case of the LC composites based on our porous oriented PE films, direct observation of the phase transition is a rather complicated task due to the intrinsic birefringence of oriented stretched PE films. The birefringence value of PE films is relatively low (~ 0.003),³¹ but in films with thickness of the order of tens of micrometers, the optical retardation value provided by PE is quite significant, which makes an exact determination of the phase transition almost impossible.

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

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

4 Conclusions

In conclusion, two novel types of photochromic azobenzenecontaining LC composites were prepared and their photooptical properties were studied. Irradiation with UV and visible light allows one to realize colour phototuning of selective light reflection for the first type of composite, whereas, for the PEbased composite, photovariation of dichroism and birefringence was demonstrated. It was also shown that the presence of two methyl substituents on the azobenzene core significantly improves the thermal stability of the photoinduced *Z*-form, which opens up new opportunities for the use of such materials in optics and photonics.

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References

- 1 Smart Light Responsive Materials: Azobenzene-Containing Polymers and Liquid Crystals, ed. Y. Zhao and T. Ikeda, John Wiley & Sons, 2009.
- 2 Intelligent Stimuli Responsive Materials: from Well-defined Nanostructures to Applications, ed. Q. Li, John Wiley & Sons, Hoboken, New Jersey, 2013.
- 3 T.-H. Lin, Y. Li, C.-T. Wang, H.-C. Jau, C.-W. Chen, C.-C. Li, H. K. Bisoyi, T. J. Bunning and Q. Li, *Adv. Mater.*, 2013, 25, 5050.
- 4 Q. Li, Y. Li, J. Ma, D.-K. Yang, T. J. White and T. J. Bunning, *Adv. Mater.*, 2011, 23, 5069.
- 5 Y. Wang, A. Urbas and Q. Li, J. Am. Chem. Soc., 2012, 134, 3342.
- 6 J. Ma, Y. Li, T. White, A. Urbas and Q. Li, *Chem. Commun.*, 2010, **46**, 3463.
- 7 M. Mathews, R. S. Zola, D. Yang and Q. Li, *J. Mater. Chem.*, 2011, **21**, 2098.
- 8 V. Shibaev, A. Bobrovsky and N. Boiko, *Prog. Polym. Sci.*, 2003, 28, 729.
- 9 H. Yu and T. Ikeda, Adv. Mater., 2011, 23, 2149.
- 10 R. Hori, D. Furukawa, K. Yamamoto and S. Kutsumizu, *Chem.-Eur. J.*, 2012, **18**, 7346.
- 11 D. Tanaka, H. Ishiguro, Y. Shimizu and K. Uchida, *J. Mater. Chem.*, 2012, **22**, 25065.
- 12 J. Tomczyk, A. Sobolewska, Z. T. Nagy, D. Guillon, B. Donnio and J. Stumpe, *J. Mater. Chem. C*, 2013, 1, 924.
- 13 A. Sobolewska, J. Zawada, S. Bartkiewicz and Z. Galewski, J. Phys. Chem. C, 2013, 117, 10051.
- 14 A. Marini, B. Zupancic, V. Domenici, B. Mennucci, B. Zalar and C. A. Veracini, *ChemPhysChem*, 2012, **13**, 3958.
- 15 T. Garcia, L. Larios-Lopez, R. J. Rodriguez-Gonzalez, J. R. Torres-Lubian and D. Navarro-Rodriguez, *ChemPhysChem*, 2012, 13, 3937.
- 16 M.-J. Gim, S.-T. Hur, K.-W. Park, M. Lee, S.-W. Choi and H. Takezoe, *Chem. Commun.*, 2012, **48**, 9968.
- 17 Y. Li, M. Wang, T. J. White, T. J. Bunning and Q. Li, *Angew. Chem., Int. Ed.*, 2013, **52**, 8925.
- 18 Y. Li, M. Wang, A. Urbas and Q. Li, *J. Mater. Chem. C*, 2013, 1, 3917.

- 19 S. J. Aßhoff, S. Iamsaard, A. Bosco, J. J. L. M. Cornelissen, B. L. Feringa and N. Katsonis, *Chem. Commun.*, 2013, 49, 4256.
- 20 R. Thomas, Y. Yoshida, T. Akasaka and N. Tamaoki, *Chem.– Eur. J.*, 2012, **18**, 12337.
- 21 G. Wang, M. Zhang, T. Zhang, J. Guan and H. Yang, *RSC Adv.*, 2012, **2**, 487.
- 22 I. Gvozdovskyy, O. Yaroshchuk, M. Serbina and R. Yamaguchi, *Opt. Express*, 2012, **20**, 3499.
- 23 N. Katsonis, E. Lacaze and A. Ferrarini, *J. Mater. Chem.*, 2012, 22, 7088.
- 24 Y. Wang and Q. Li, Adv. Mater., 2012, 24, 1926.
- 25 A. Y. Bobrovsky, N. I. Boiko and V. P. Shibaev, *Liq. Cryst.*, 1998, **25**, 393.
- 26 A. Y. Bobrovsky, N. I. Boiko and V. P. Shibaev, *Mol. Cryst. Liq. Cryst.*, 2001, **363**, 35.
- 27 A. Bobrovsky, V. Shibaev, G. Elyashevitch, A. Shimkin and V. Shirinyan, *Liq. Cryst.*, 2007, **34**, 791.
- 28 A. Bobrovsky, V. Shibaev and G. Elyashevitch, *J. Mater. Chem.*, 2008, **18**, 691.
- A. Bobrovsky, V. Shibaev, G. Elyashevitch, E. Rosova,
 A. Shimkin, V. Shirinyan, A. Bubnov, M. Kaspar,
 V. Hamplova and M. Glogarova, *Liq. Cryst.*, 2008, 35, 533.

- 30 A. Bobrovsky, V. Shibaev, G. Elyashevich, E. Rosova,
 A. Shimkin, V. Shirinyan and K.-L. Cheng, *Polym. Adv. Technol.*, 2010, 21, 100.
- 31 E. Pozhidaev, A. Bobrovsky, V. Shibaev, G. Elyashevich and M. Minchenko, *Liq. Cryst.*, 2010, 37, 517.
- 32 A. Ryabchun, A. Bobrovsky, J. Stumpe and V. Shibaev, Macromol. Rapid Commun., 2012, 33, 991.
- 33 G. Chilaya, A. Chanishvili, G. Petriashvili, R. Barberi, M. P. de Santo and M. A. Matranga, *Mater. Sci. Appl.*, 2011, 2, 116.
- 34 A. Priimagi, A. Shimamura, M. Kondo, T. Hiraoka, S. Kubo, J.-I. Mamiya, M. Kinoshita, T. Ikeda and A. Shishido, ACS Macro Lett., 2012, 1, 96.
- 35 V. G. Chigrinov, V. M. Kozenkov and H.-S. Kwok, *Photoalignment of Liquid Crystalline Materials*, Wiley-SID Series in Display Technology, 2008.
- 36 A. Bobrovsky, A. Ryabchun and V. Shibaev, *J. Photochem. Photobiol.*, *A*, 2011, **218**, 137.
- 37 G. K. El'yashevich, A. G. Kozlov and E. Y. Rozova, J. Polym. Sci., Part A: Polym. Chem., 1998, 40, 956.
- 38 A. Bobrovsky and V. Shibaev, Polymer, 2006, 47, 4310.
- 39 Y. Wu, J. Mamiya, A. Kanazawa, T. Shiono, T. Ikeda and Q. Zhang, *Macromolecules*, 1999, 32, 8829.