Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Photo-optical properties and photo-orientation phenomena in an immiscible blend of cholesteric copolymer with azobenzene-containing polymer

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To cite this Article Bobrovsky, Alexey and Shibaev, Valery(2007) 'Photo-optical properties and photo-orientation phenomena in an immiscible blend of cholesteric copolymer with azobenzene-containing polymer', Liquid Crystals, 34: 4, 411 — 419

To link to this Article: DOI: 10.1080/02678290601176518

URL: http://dx.doi.org/10.1080/02678290601176518

Liquid Crystals, Vol. 34, No. 4, April 2007, 411–419

Photo-optical properties and photo-orientation phenomena in an immiscible blend of cholesteric copolymer with azobenzene-containing polymer

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(*Received 4 July 2006; in final form 11 November 2006; accepted 14 November 2006*)

Novel side chain liquid crystalline polymer blends containing immiscible non-chiral and cholesteric polymers were prepared. A non-chiral polymer was used containing azobenzene side groups capable of *E*–*Z* photoisomerization. Phase behaviour and miscibility properties of the blends were studied. Thin films of the blends were prepared by spin-coating; it was shown that just after preparation these films are optically isotropic and homogeneous. Photo- and chiro-optical properties of the films as well as photo-orientation phenomena induced by the action of polarized light were investigated. It was found that the photo-optical behavior of these films is rather complicated and considerably different from the properties of both individual components. This difference is associated with the strong influence of blend morphology on the photo-optical properties.

1. Introduction

Investigation of immiscible polymer blends provides the remarkable possibility of combining the properties of two different polymers in one material [1–11]. Immiscible multiphase polymer blends are of considerable interest from fundamental and applied standpoints. In the quoted studies, principal attention was devoted to the rheological and mechanical properties of such systems, whose morphology was studied by scanning electron microscopy, AFM, etc.

The attention of researchers has in general primarily been focused on the study of compositions of either amorphous or semicrystalline polymers; fewer studies have been devoted to blends of LC polymers [7–11], and almost none to immiscible compositions of cholesteric polymers. The cholesteric mesophase is known to possess unique optical properties which are determined by a periodic helical structure [12, 13]. The key feature of such systems is the development of selective light reflection in a fixed spectral region dictated by the helix pitch. The preparation of compatible (miscible) and incompatible (immiscible) blends of cholesteric polymers offers new unique advantages for the controllable modification of the optical properties of such materials.

The first interesting results dealing with the study of miscibility and optical properties of blends of two cholesteric copolymers was presented by Boiko *et al.* [14]. It was shown that the two high molecular mass copolymers ($\bar{M}_w > 10^4$) containing different amounts of chiral cholesteric side groups appear to be immiscible at temperatures above ~66°C, i.e. these copolymers are immiscible at the high temperatures at which a cholesteric phase and an isotropic melt are formed. At temperatures below ~66°C, a single phase blend shows only one selective light reflection maximum, whereas the phase separation leads to the appearance of the two selective light reflection maxima corresponding to the individual components. In this case, the phenomenon seems to be particularly interesting, as it clearly illustrates that the analysis of the selective light reflection spectra allows one to investigate the processes of phase separation in cholesteric polymers blends.

Our recent work [15] can be considered as a pioneering publication on the study of the photo-optical properties of photosensitive immiscible blend composed of two cholesteric copolymers containing different types of chiral side groups, one of which contained photoactive azobenzene groups. Planarly oriented films based on this blend show two distinct peaks of selective light reflection: one peak was seen in the visible spectral region whereas the other was observed in the near-IR. Under the action of light, the IR peak is shifted to higher wavelengths whereas the second peak remained almost unchanged. The specific features of the kinetics of the photo-optical processes taking place in such a system were studied.

This paper presents new results on the study of an immiscible blend containing the non-chiral azobenzene-based homopolymer PEtAzo and the cholesteric copolymer ACh30:

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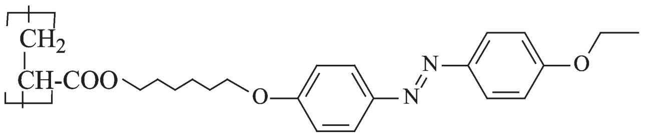
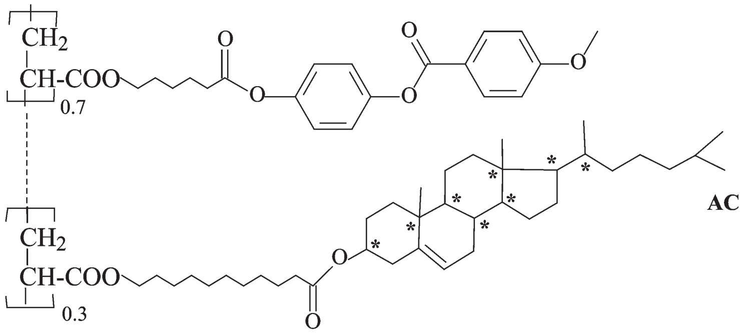
Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290601176518



PEtAzo



ACh30

The photo-optical and photo-orientation processes of the nematogenic homopolymer PEtAzo were reported in detail previously [16, 17]. This polymer has the following phase transitions: g 28 SmA 96–98 N 130–134 I. Copolymer ACh30 forms only a chiral nematic (cholesteric) phase with the following transitions: g 26 N* 119–120 I.

It was shown that visible light irradiation or annealing of thin films of homopolymer PEtAzo obtained by spin-coating results in homeotropic orientation of the side groups. This tendency arises from the influence of glass–polymer and polymer–air phase boundaries. In our opinion, such effect can be diminished in a blend with an other polymer due to the formation of a two-phase dispersed system with large interface area.

The present paper deals with the study of the photo-optical properties of this blend in thin spin-coated films, in relation to the wavelength and polarization of incident light. Special attention was paid to the comparison of these photo- and chiro-optical properties of the blend with the same properties of the initial polymer components.

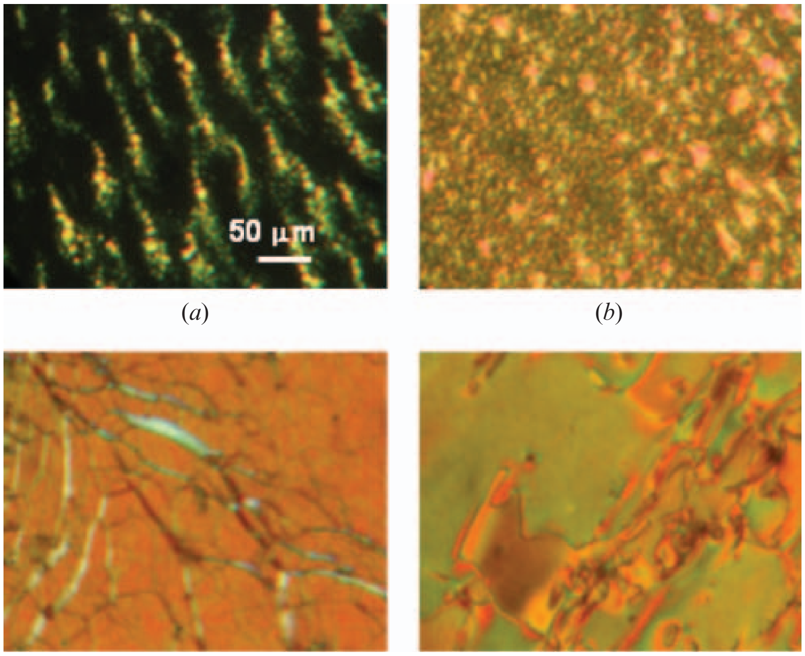
2. Experimental

4-Ethoxyoazobenzene, cholesterol-containing copolymer and 4-phenyl 4-methoxybenzoate monomers were synthesized according to literature procedures [18, 19]. The homo- and co-polymer were synthesized by radical polymerization of monomers in benzene solution at 65°C; AIBN was used as an initiating agent. The synthesized polymers were purified by repeated precipitation with methanol and dried in vacuum.

The relative molecular mass of the polymers was determined by gel permeation chromatography (GPC), using a GPC-2 Waters instrument equipped with an LC-100 column oven and a Data Modul-370 data station. Measurements were made using a UV detector, THF as solvent (1 ml min^{-1}, 40°C), and a calibration plot constructed with polystyrene standards. The polymers obtained have the following molar mass characteristics: PEtAzo, $M_n = 8\,000$, $M_w/M_n = 1.4$; ACh30, $M_n = 12\,000$, $M_w/M_n = 2.0$. Blends were prepared by dissolving the components in chloroform followed by solvent evaporation at 60°C. Then the blends were dried in vacuum at 130–140°C for two hours. Thin films of the blends for photo-optical experiments were obtained by spin-coating using chloroform solutions of different concentrations. For drying the spin-coated films were kept at room temperature for one day. Film thickness was varied in the range 100–200 nm as estimated from the UV-Vis spectral data.

The phase transition temperatures of the polymers and the blends were studied by differential scanning calorimetry (DSC) with a Perkin-Elmer DSC-7 thermal analyser, scanning rate 10 K min^{-1}. Polarizing microscope investigations were performed using a Mettler TA-400 thermal analyser and a LOMO P-112 polarizing microscope.

Photochemical properties were studied using an instrument equipped with a DRSh-250 ultra high pressure mercury lamp. Light of wavelengths 365 and 436 nm was selected using interference filters. To prevent heating of the samples by IR irradiation from the lamp, a water filter was used. A quartz lens was used to obtain a plane-parallel light beam. Polarized light was obtained by using Glan–Taylor polarizer; its intensity was 1.0 mW cm^{-2} (365 nm) and 0.5 mW cm^{-2} (436 nm), as measured by a LaserMate-Q (Coherent) intensity meter. Spectral measurements were performed using a Unicam UV-500 spectrophotometer and a JASCO J-500C spectropolarimeter.



(*a*) (*b*)

(*c*) (*d*)

Figure 1. Photomicrographs of the blend (50:50 wt%) textures obtained by cooling the sample from the isotropic melt and held at various temperatures: (*a*) 128°C, (*b*) 110°C; (*c*) the planar texture of copolymer ACh30 at 110°C, (*d*) the marbled texture of homopolymer PEtAzo at 120°C.

The orientational order was studied with polarized UV-Vis spectroscopy, because the transition moment of the *E*-isomer of the azobenzene moiety is directed along the long axis of this group. For this purpose the angular dependence of the polarized light absorbance was measured using a photodiode array UV-Vis spectrometer (J&M) with a step-width of 10°. The dichroism and spectral order parameter values were calculated from the spectra using the equations:

$$D=(A_{\parallel}-A_{\perp})/(A_{\parallel}+A_{\perp}) \tag{1}$$

$$S=(A_{\parallel}-A_{\perp})/(A_{\parallel}+2A_{\perp}) \tag{2}$$

where D is the dichroism, S is the order parameter, $A_{\parallel}$ is the absorbance in the preferred direction, $A_{\perp}$ is the absorbance perpendicular to this direction.

3. Results and discussion

3.1. *Miscibility and phase behaviour of the blends; optical properties of planarly oriented films*

Structural, optical microscopy investigations of the blend showed that the two components are completely miscible at temperatures corresponding to the isotropic state (i.e. above *c*. 137°C). Below this temperature small birefringent droplets formed, with coalescence under further cooling, figure 1 (*a*). At a temperature of about 115°C the isotropic regions disappeared and a non-typical highly birefringent texture was formed, figure 1 (*b*); this texture changed only slightly under further cooling. It is important to note that even a very long annealing and multiple mechanical deformation do not lead to the formation of well defined textures. In contrast, the individual components of the blend, homo- and co-polymer, form very well defined planar cholesteric textures, such as figure 1 (*c*), and marbled nematic textures, figure 1 (*d*), respectively. These results testify to the presence of phase separation in the blend of polymers, because in the case of miscibility we might expect the formation of a cholesteric phase with planar texture.

Figure 2 gives a phase diagram for blends of the different compositions. In the isotropic melt complete miscibility is observed, whereas LC phase formation induces phase separation. Planarly oriented films of the blend containing 25 wt% of PEtAzo demonstrate a broad selective light reflection peak (figure 3), whose position is shifted to longer wavelength in comparison with copolymer ACh30. This effect can be associated with partial (but very poor) mixing of the components. At temperatures below the transition to the smectic phase, and for blends containing higher proportions of PEtAzo, no selective light reflection was observed, due to strong light scattering.

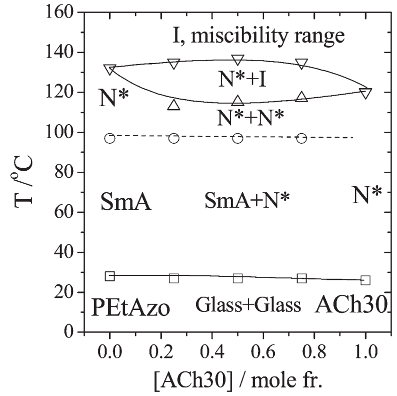


Figure 2. Phase diagram for blends PEtAzo+ACh30. Phase transitions temperatures were obtained by polarizing optical microscopy, glass transition temperature were measured by DSC.

Spin-coating technique allows one to prepare thin films (100–200 nm) with no any optical evidence of phase separation. Optical microscopy showed the absence of any birefringence or light scattering. But after annealing at temperatures higher than the glass transition, light scattering and small birefringent domains were found in the blend films. These effects, associated with phase separation of the initially homogeneous spin-coated films, were accompanied by liquid crystal phase formation.

3.2. *Optical and chiro-optical properties of thin spin-coated films of the blend*

For optical and photo-optical investigations the blend containing 50 wt% of each component was selected. Just after preparation, the spin-coated films have spectral features that are very typical for systems containing azobenzene chromophores: a strong absorbance peak corresponding to a π–π* electronic transition with maximum at 345 nm, and a small absorbance 'shoulder' at *c.* 450 nm corresponding to an n–π* electronic transition, figure 4 (*a*).

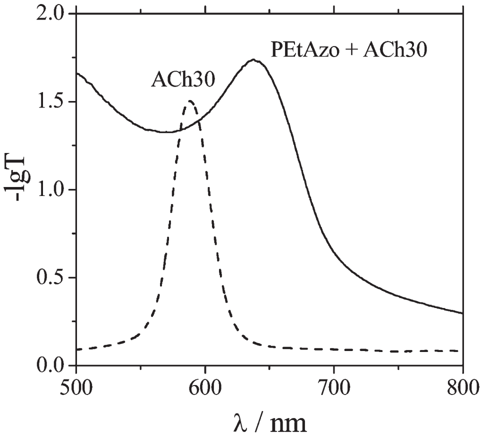
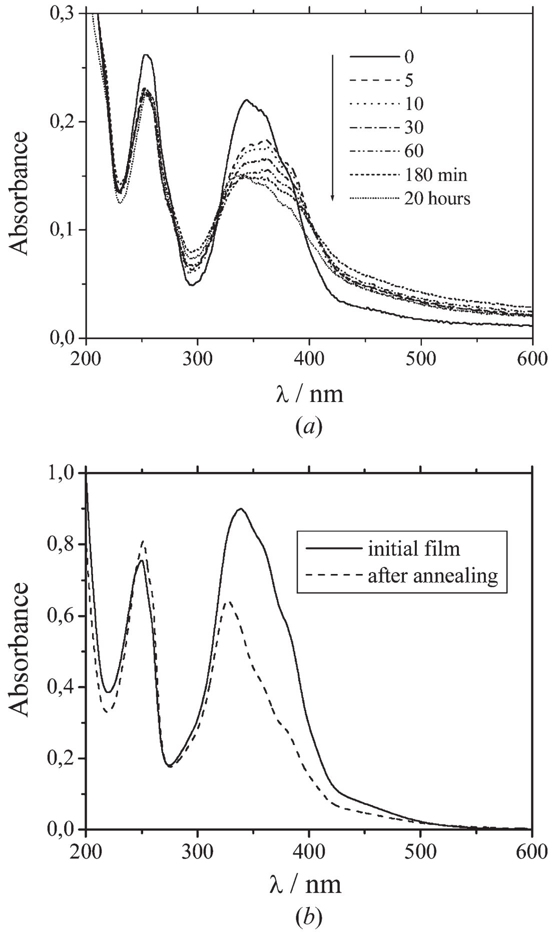


Figure 3. Transmittance logarithm spectra for mixture containing 25 wt% PEtAzo and for copolymer ACh30. Left-handed circularly polarized light; 100°C.

Films obtained by such methods are optically isotropic and no phase separation was observed by optical microscopy. Annealing of the films leads to spectral changes: a decrease and shift of maximum of the π–π* transition to longer wavelengths (by about 10 nm), and the appearance of a small absorbance in the visible spectral region. These spectral changes are attributed to the possible aggregation of azobenzene chromophores [20, 21], as well as to phase separation and formation of small liquid crystalline domains displaying light scattering. Polarizing optical microscopy of annealed films revealed the appearance of a small birefringence during annealing.



(*a*)

(*b*)

Figure 4. Absorbance spectra for spin-coated films of (*a*) blend and (*b*) homopolymer PEtAzo during annealing at 70°C. Annealing time for the blend is shown in the figure; annealing time for PEtAzo was 30 min.

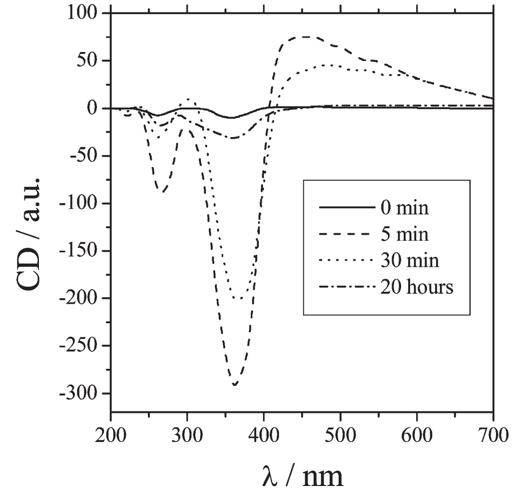
The phenomena observed in the blend films under annealing are completely different from the properties of spin-coated films of homopolymer PEtAzo [16]. Annealing of the homopolymer films leads to a stronger decrease in absorbance, associated with the formation of out-of-plane order or homeotropic orientation of azobenzene chromophores [17] (figure 4 (*b*)). This reorientation phenomenon was confirmed by polarized spectral measurements at 45° to the film plane. The driving force of this reorientation is probably associated with the influence of the polymer–air phase boundary at which mesogens have a tendency to homeotropic alignment [17, 22]. In the case of the blend, however, this reorientation is almost completely suppressed due to the presence of the cholesteric copolymer with a tendency to helical structure formation. In addition, annealing of homopolymer films leads to a more pronounced blue shift of the absorbance maximum, which is related to aggregation phenomena with the formation of H-aggregates of azobenzene chromophores.

Circular dichroism (CD) spectra reveal some specific features for the freshly prepared spin-coated films. Two peaks of negative sign for films with thickness greater than *c.* 100 nm were observed, figure 5 (*a*). The small peak has its maximum at 265 nm; the large peak is located at 365 nm.

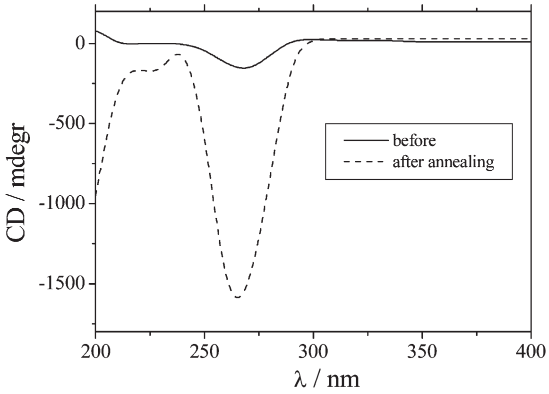
Note that the appearance of both CD peaks is unrelated to an intrinsic molecular chirality of the cholesterol fragments. The examination of copolymer as well as homopolymer solutions in dichloroethane showed zero CD values at wavelengths higher than 250 nm. On the other hand, the appearance of circular dichroism is not associated with the selective light reflection because the thin spin-coated films of the blend cannot form a planar texture with the highly developed helical structure. Selective light reflection is observed for the copolymer ACh30 and blend in thick (about 20 μm) planarly oriented films and has a maximum at a longer wavelength (figure 3 [13]).

In our opinion the appearance of strong circular dichroism may be explained by the formation of elements of a helical supramolecular structure in films just after spin-coating [23]. The induction of a similar circular dichroism in cholesteric media has been demonstrated many times and theoretically described in the literature [24–28]. The incorporation of achiral guest molecules into a cholesteric matrix leads to the appearance of so-called induced circular dichroism, with maxima coinciding with the absorbance peak of the additive.

CD spectra of the copolymer ACh30 has one negative peak with a maximum at 265 nm, corresponding to the spectral region of phenylbenzoate chromophore absorbance. Therefore, CD spectra of the blend consist of the superposition of two induced CD peaks corresponding to phenylbenzoate and azobenzene chromophores.



(*a*)



(*b*)

Figure 5. Changes in CD spectra of (*a*) the blend during annealing, and (*b*) copolymer ACh30 before and after 15 h of annealing (*ab*) 70°C.

An annealing of the blend films results in significant increase of both CD maxima and appearance positive peak at $\lambda\sim$450–470 nm at first minutes of the process, figure 6. Nevertheless, further annealing leads to back decrease in the circular dichroism. Initial increase in CD is explained by improvement of helical supramolecular structure of the film, but during subsequent annealing a phase separation takes place leading to formation of small separated domains of copolymer ACh30 and homopolymer PEtAzo in films. As a result of such prolonged thermal treatment concentration of azobenzene chromophores in cholesteric subphase of copolymer ACh30 is strongly decreased followed by decreasing in CD values.

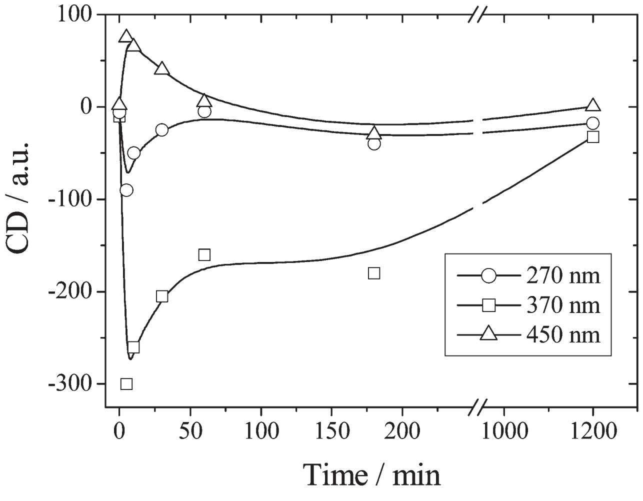
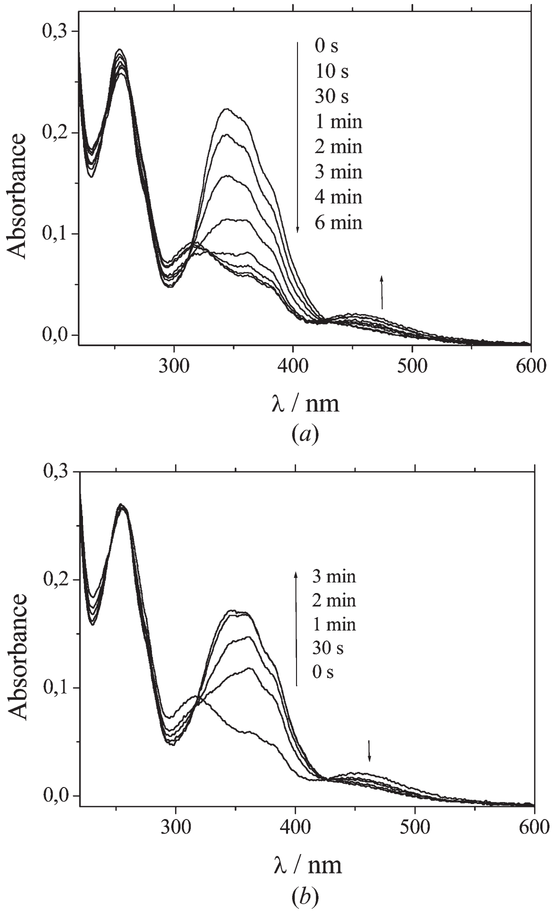


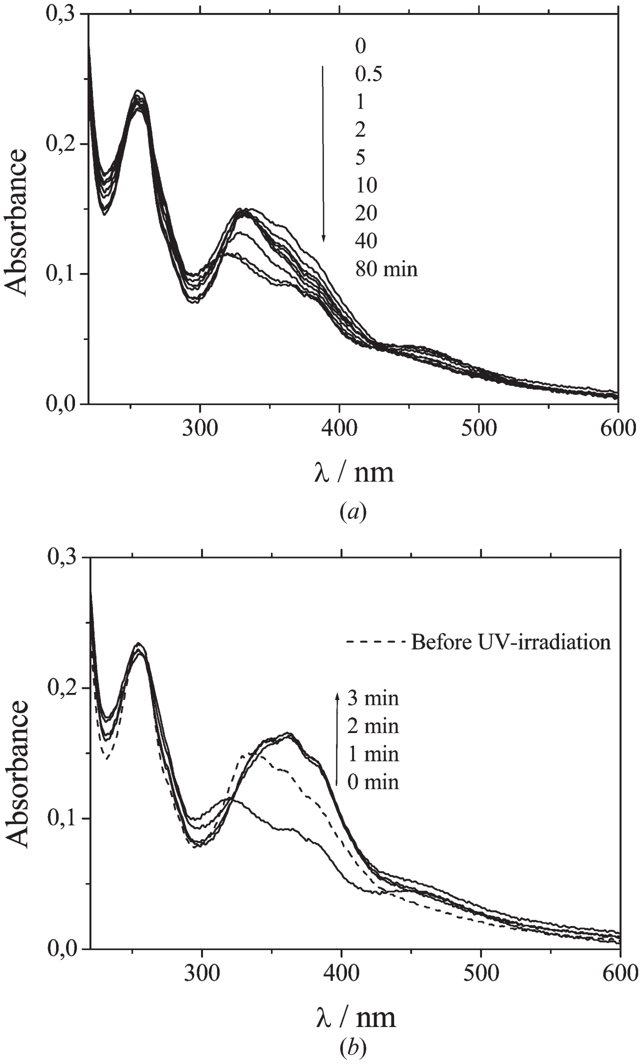
Figure 6. Changes in CD values at different wavelengths during annealing of the blend films at 70°C.



(a)

(b)

Figure 7. Changes in absorbance spectra of the blend film during (a) UV irradiation (365 nm) and (b) subsequent visible light irradiation (436 nm).



(a)

(b)

Figure 8. Absorbance spectra of the annealed spin-coated film under (a) UV irradiation (365 nm), and (b) subsequent visible light irradiation (436 nm). The film was annealed at 70°C for 30 min.

3.3. *Photo-optical properties of the blend under non-polarized light action*

UV irradiation of fresh spin-coated films of the blend results in a significant drop in absorbance for the π–π* electronic transition peak, and an increase for the n–π* transition, figure 7 (*a*). Such spectral changes clearly indicate *E-Z* isomerization of azobenzene groups [21, 22, 29]. Subsequent visible light irradiation restores the absorbance peak almost to its initial shape, figure 7 (*b*).

For annealed films the character of the spectral changes is almost the same (figure 8) but the rate of the process and amplitude of absorbance decrease are significantly lower. Liquid crystalline order formed in films during annealing strongly suppresses the isomerization process [20, 21]. It is interesting that the position of the π–π^* absorbance peak after subsequent visible light action is shifted to higher wavelengths, figure 8 (*b*), in comparison with the spectrum before UV irradiation, figure 8 (*b*), dashed line; that is an indication of the disruption of LC order under UV irradiation and in complete recovery under light-induced *Z*–*E* back-isomerization.

UV irradiation of fresh, non-annealed blend films results in the complete disappearance of circular dichroism, whereas the situation is more complicated for annealed films, as shown in figure 9. In this case, the peak at 270 nm corresponding to phenylbenzoate fragments is insensitive to the action of light. Thermal and photo-optical effects therefore provide the possibility for controlling the chiro-optical properties of blend films.

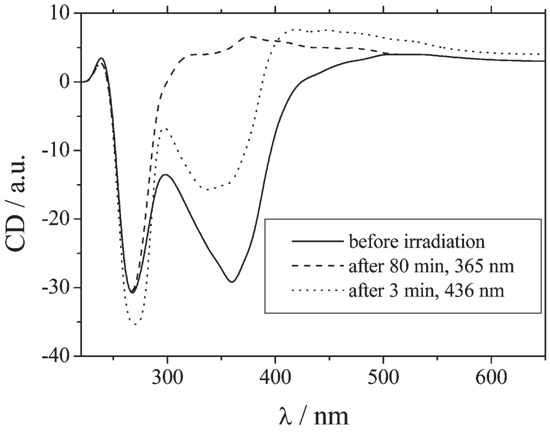


Figure 9. Changes in CD spectra of the annealed blend film before, after UV- and visible light irradiation.

3.4. *Photo-orientation phenomena of the blend under polarized light action*

Let us consider the photo-orientation processes in the blend films occurring under the action of polarized UV or visible light. Polarized UV light (365 nm) induces the fast photoselection and orientation of azobenzene side groups in a direction perpendicular to the plane of the electric field vector of light, see figures 10 and 11. After *c.* 10 min of irradiation the photoinduced dichroism reaches a maximum; continuous irradiation then results in its decrease (figure 11). Such behaviour is associated with a large concentration of the *Z*-isomer forming in the film under UV irradiation. The low anisometry of this isomer destroys the orientational order of the side group arrangement. The maximal value of dichroism is about 1.5 times lower than for the homopolymer PEtAzo [17]. It should be noted that the dichroism value is very small at wavelength corresponding to absorbance by the phenylbenzoate side groups of copolymer ACh30. From previous studies it is well known that in copolymers containing mesogenic and azobenzene side groups the photo-orientation process is referred to as cooperative, and the values of photoinduced dichroism are comparable [17]. In our case partial phase separation probably takes place during spin-coating, even in non-annealed blend films. Despite the optical isotropy and homogeneity, microphase separation takes place under these conditions. This process is accompanied by the formation of small domains, which cannot be observed in the polarizing microscope. The absence of observable light scattering in the fresh spin-coated films indicates that the size of these domains is smaller than the wavelength of visible light.

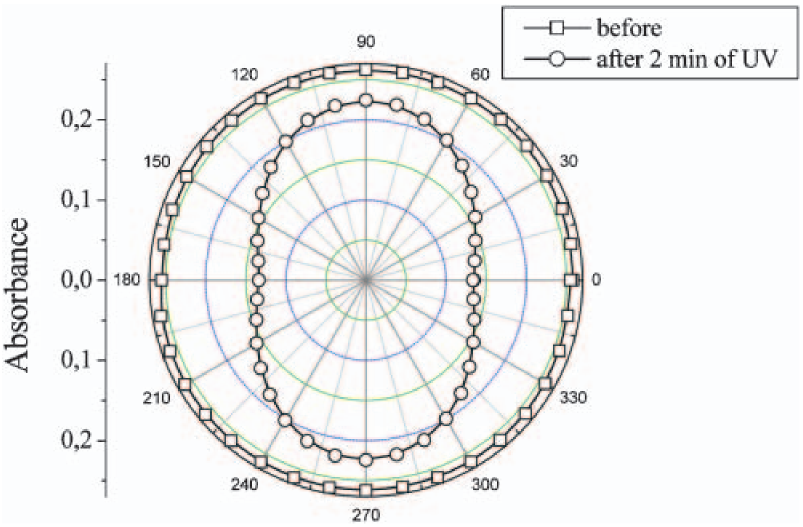


Figure 10. Polar plots of absorbance at 350 nm measured before and after 2 min of polarized UV irradiation (365 nm).

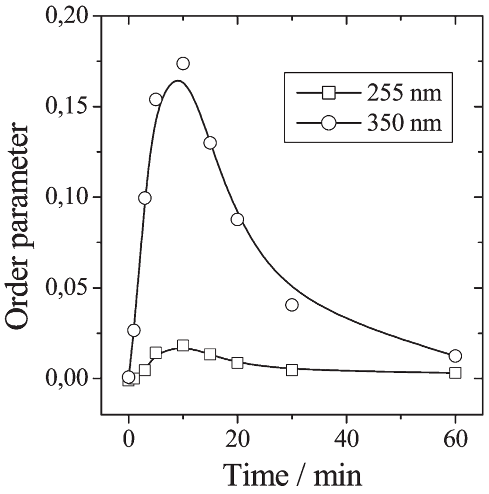


Figure 11. Changes in order parameter measured at two wavelengths during polarized UV irradiation (365 nm) of the blend film.

Irradiation using polarized visible light results in higher dichroism values, see figures 12 and 13. Another feature is the absence of a decrease in dichroism under long irradiation time as observed for the pure azobenzene-containing homopolymer [17]. The dichroism value is comparable to that of homopolymer PEtAzo films, but rate of the process is significantly lower [17].

Annealing of the blend films and phase separation strongly affect the photoinduced orientation: values of photoinduced dichroism in such films are *c.* 6 times lower (figure 14). Nevertheless, we found no indication of photo-orientation processes for annealed films of homopolymer under the same conditions; this is explained by the homeotropic orientation and strong

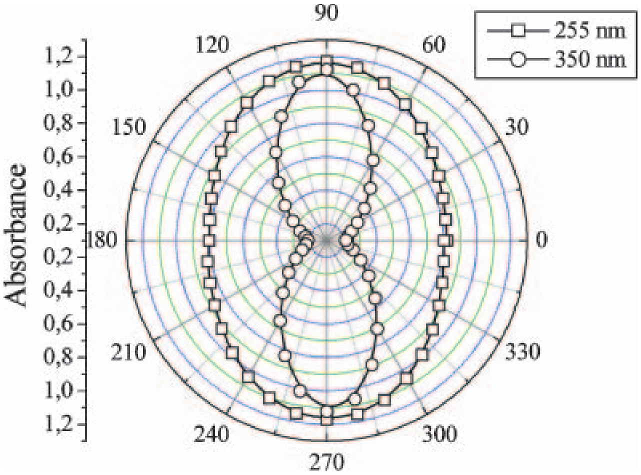


Figure 12. Polar plots of absorbance at 255 and 350 nm measured after 600 min of polarized visible light (436 nm) irradiation.

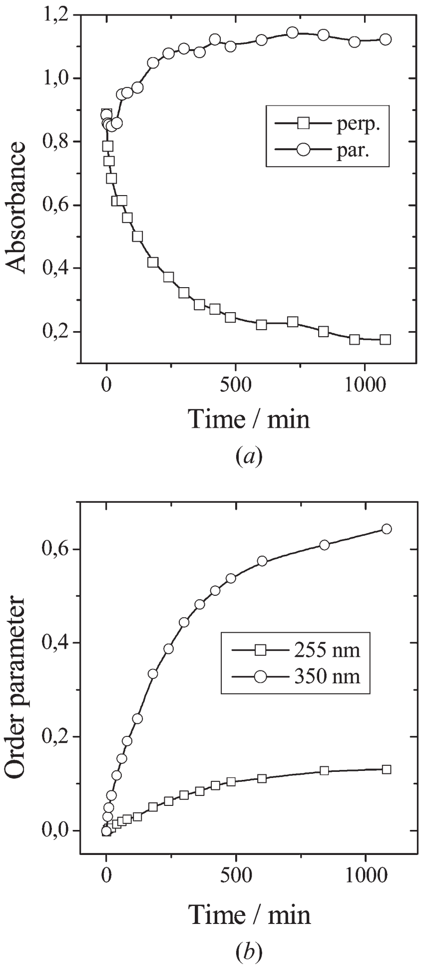


Figure 13. Kinetics of changes in (*a*) polarized absorbance at 350 nm, and (*b*) spectral order parameter at two wavelengths during polarized visible light irradiation (436 nm).

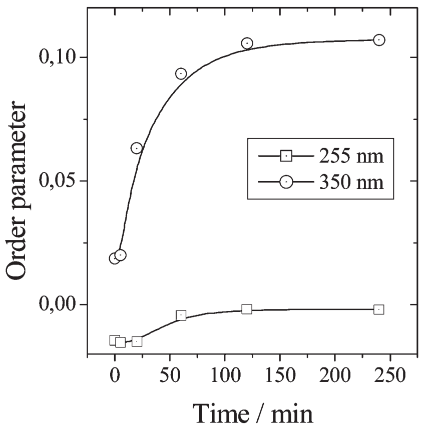


Figure 14. Changes in order parameter during polarized visible light irradiation of a blend film annealed for 24 h at 70°C. Before visible light action, the film was irradiated by non-polarized UV light (365 nm) for 30 min.

ordering of the side groups in PEtAzo homopolymer films [17].

In conclusion, the photo- and chiro-optical properties of a novel blend of two liquid crystalline polyacrylates were studied. It was shown, that phase separation leads to significant changes in the photo-optical properties of thin films of blend obtained by spin-coating. These photo-optical effects seem to be strongly affected by the complicated morphology of the films, which have high interface boundary areas. In future work we will study relatively thick (10–20 μm) planarly oriented films of blends of this type.

Ackowledgements

This research was supported by the Russian Foundation of Fundamental Research (05-03-33193) and Federal Scientific Technical Program (Agreement MN-476/05-MSU in the framework of Contract No 02.434.11.2025). A.B. gratefully acknowledges the Russian Science Support Foundation, and the research fellowships provided by the Alexander von Humboldt Foundation and INTAS (Ref. No. 03-55-956).

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