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Immiscible blend of cholesteric copolymers as a new type of material with photoregulated optical properties

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A blend containing two immiscible cholesteric comb-shaped polyacrylates was prepared. Upon light irradiation, one of the components is able to change the pitch of the cholesteric helix due to the isomerization of chiral photochromic side groups. The phase behavior and optical properties of the above blend were studied. Planarly oriented films based on the above blend show the two well-pronounced peaks of selective light reflection: one peak is seen in the visible spectral region whereas the other peak is observed in the near-IR region. Under the action of light, the long-wavelength peak is shifted to higher wavelengths whereas the second peak remains almost unchanged. The specific features of the kinetics of the photooptical processes taking place in this system were studied. The above immiscible blend is shown to be a new unique material for optical data recording and storage.

1. Introduction

Preparation and study of polymer blends present a challenging and well progressing aspect of the modern physical chemistry of polymers.[1–10] The keenest interest in this area is directed towards the development of new advanced materials as well as towards efficient modification of the known polymers. However, such systems are characterized by poor compatibility between the components, and the number of miscible (compatible) polymer blends is rather limited.[1,2]

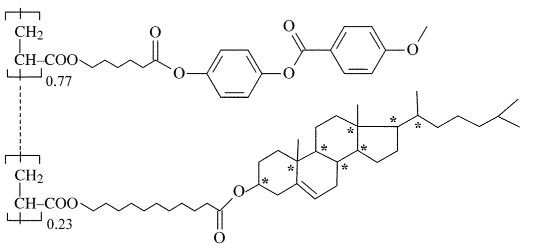
Nevertheless, as was shown in refs. 11–15, immiscible multiphase polymer blends are exceptionally interesting materials from the standpoint of fundamental scientific and applied aspects. In the above works, most of the attention was devoted to the rheological and mechanical properties of such systems, and the morphology of polymer compositions was studied by the methods of scanning electron microscopy, AFM, *etc.* Generally, the above works were primarily focused on studying the compositions of either amorphous or semicrystalline polymers; much fewer publications were devoted to the blends of LC polymers.[6–10] At present, almost no publications concerning the immiscible compositions of cholesteric polymers are available. At the same time, the cholesteric mesophase is known to possess unique optical properties which are related to a periodic helical structure,[16] and this aspect seems to present a challenging task for many researchers.[17] In this case, the key feature of such systems concerns the development of selective light reflection in a given spectral region which is specified 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.

Our recent work[18] presents a pioneering publication on studying the phase behavior and optical properties of the blends composed of the two cholesteric copolymers containing different amounts of chiral cholesterol-containing side groups. As was shown, high-molecular-mass copolymers ($\bar{M}_w > 10^4$) appear to be immiscible at temperatures above ~66 °C; in other words, the above copolymers are immiscible at high temperatures where a cholesteric phase and an isotropic melt exist. Let us describe one important feature of these compositions. At temperatures below ~66 °C, a single-phase blend shows a single selective light reflection maximum whereas phase separation leads to the appearance of two selective light reflection maxima which correspond to the individual components. In this case, the above phenomenon seems to be exceptionally interesting as this fact vividly illustrates that the analysis of the selective light reflection spectra allows one to investigate the processes of phase separation in the blends of cholesteric polymers.

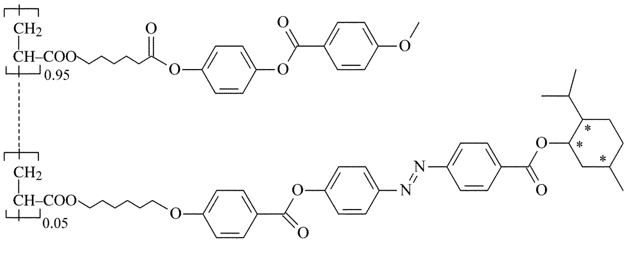
This publication presents a logical follow-up of the work started in ref. 18 and is focused on studying an immiscible blend of cholesteric copolymers based on copolymers **I** and **II** with different chiral side groups when the components are taken in equal parts (50 : 50 w/w). In this case, one of the components (copolymer **II** with azobenzene moieties) appears to be photosensitive.

This work presents the results on studying the compatibility and phase behavior of optical and photooptical properties of the as-prepared blend. As follows from the structural formulae, copolymer **I** contains nematogenic phenyl benzoate side groups and chiral cholesterol-containing units. Copolymer **II** is composed of the same nematogenic groups and contains chiral fragments with the double N=N bond. Upon light irradiation, light-induced *E*–*Z* photoisomerization around this bond might occur (Fig. 1). As was shown in refs. 19, 20 upon *E*–*Z* photoisomerization, such chiral fragments decrease their

Copolymer I:



Copolymer II:



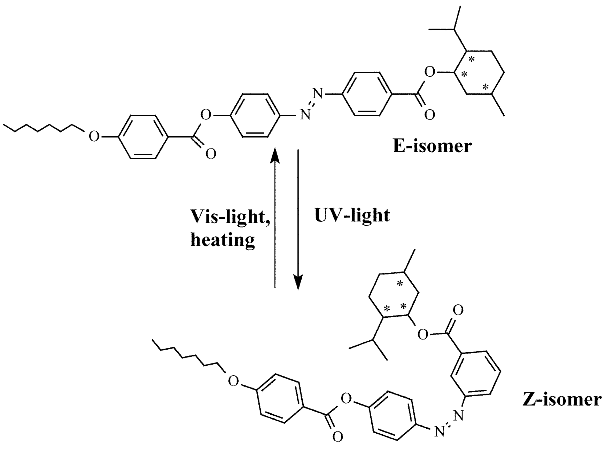


Fig. 1 Scheme of *E*–*Z* photoisomerization of chiral photosensitive azobenzene-containing side group of copolymer **II**.

anisometry. As a result, this leads a decrease in their helix twisting power expressed as

$$\beta = \mathrm{d}P^{-1}/\mathrm{d}X = \bar{n}(\mathrm{d}\lambda_{\max}{}^{-1}/\mathrm{d}X)_{X\,=\,0} \qquad (1)$$

where P is the pitch of the helix, $\bar{n}$ is the average refractive index, $\lambda_{\max}$ is the maximum of selective light reflection, and X is the concentration of the chiral fragments. As β decreases, according to eqn. (1) helix pitch increases, and untwisting of the cholesteric helix occurs. Therefore, the above bicomponent blend contains the cholesteric copolymer with a photocontrolled helix pitch.

Investigation of LC multicomponent photosensitive polymer systems constitutes a new and challenging scientific direction. This direction is related to the development of polyfunctional photochromic materials which may be modified *via* proper selection of the components. Characterization of the specific features of the photochemical transformations taking place in such systems has been successfully launched in refs. 17–24 and, presently, this problem has attracted great scientific and practical interest. This work presents a follow-up study in this direction.

2. Experimental

2.1. Synthesis and mixture preparation

Cholesteric copolymers were synthesized according to the procedures described in refs. 20 and 25. Relative molecular weights of the copolymers were determined by gel permeation chromatography (GPC) using a Knauer instrument equipped with a Waters column (8 × 300 mm). The measurements were made using a UV detector, THF as solvent (1 ml min^{-1}, 40 °C), a column of 10^3 Å and the calibration plot was constructed with polystyrene standards. The copolymers obtained have the following molar mass characteristics: copolymer **I**: M_n = 13000 and M_w/M_n = 2.6, copolymer **II**: M_n = 18000 and M_w/M_n = 2.8.

The blend was prepared by dissolving the copolymers in chloroform followed by solvent evaporation at 60 °C. The blend was then dried under vacuum at 120 °C for two hours.

2.2. Investigations of phase behaviour and optical properties

Phase transitions of the copolymers and blend were studied by differential scanning calorimetry (DSC) with a scanning rate of 10 °C min^{-1}.

The polarizing microscope investigations were performed using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarizing microscope.

Selective light reflection of copolymers and their blend films was studied with a Hitachi U-3400 UV–Vis–IR spectrometer equipped with a Mettler FP-80 hot stage. The ~20 μm thick samples were sandwiched between the two flat glass plates. The thickness of the test samples was preset by means of Teflon spacers. A planar texture was obtained by shear deformation of the samples (a small shift of the cover glass plate), which were heated to temperatures above the glass transition. Prior to tests, the test samples were annealed for 20–40 min.

2.3. Photooptical investigations

Photochemical properties were studied using a special optical instrument[22] equipped with a DRSh-250 ultra-high pressure mercury lamp. Light with wavelengths 365, >450 and ~550 nm was selected using cut-off filters. To prevent heating of the samples due to IR irradiation of the lamp, a water filter was used. To obtain a plane-parallel light beam, a quartz lens was used. During irradiation, the constant temperature of the test samples was maintained using a Mettler FP-80 heating unit. The intensity of light was equal to 1.9×10^{-8} einstein s^{-1} cm^{-2} (for light of 365 nm, as measured actinometrically[26]), the intensity of visible light ($\lambda_{ir} > 450$ nm and $\lambda_{ir} \sim 550$ nm) was equal ~8.0 mW cm^{-2} (for $\lambda_{ir} > 450$ nm) and ~0.7 mW cm^{-2} (for $\lambda_{ir} \sim 550$ nm).

Photochemical properties of blends were studied by illuminating the ~20 μm thick films. After irradiation transmittance spectra were recorded using a Hitachi U-3400 UV–Vis–IR spectrometer.

3. Results and discussion

3.1. Phase behaviour and optical properties of the cholesteric blend

Let us first consider the phase behavior and optical properties of the blend. In this case, a chiral nematic mesophase is developed over a wide temperature interval; the glass transition temperature of this mesophase is equal to about 25 °C, and the clearing temperature lies within a temperature interval of 115–125 °C. Let us emphasize that this blend is characterized by a complete immiscibility between the initial components. According to the data from optical polarizing microscopy and spectrophotometry, by increasing the temperature, one may observe the three following cases: co-existence of two cholesteric phases (i), co-existence of cholesteric and isotropic phases (at 115–125 °C) (ii) and, finally, co-existence of two isotropic phases (iii). Therefore, in the whole temperature interval below the temperatures of chemical decomposition of the components, these components are fully immiscible and the blend presents a typical two-phase system. Note that the phase separation is provided by the different structures of the chiral side groups of the copolymers whereas their nematogenic fragments are identical.

Let us discuss the effect of the above phenomena on the optical properties of the above blend. As follows from Figs. 2 and 3b, the planarly oriented films show the two selective light reflection peaks: the first peak is seen in the visible spectral region whereas the second peak is observed in the near-IR spectral region. As can be seen, the wavelength corresponding to the selective light reflection maximum is almost independent of temperature. Let us also mention that, in the case of the above blend, the intensity of the peaks is two times higher than that of the initial copolymers (*cf.* Figs. 3a and 3b). This fact is likely to be related to a higher defect level in the planar texture as developed in the two-phase blend due to a phase interface with large area. In this case, the wavelengths of selective light reflections peaks ($\lambda_{\max}$) are close to $\lambda_{\max}$ of the initial copolymers (Fig. 2). This trend suggests that the individual helical structure of each of the components is preserved, and both components are fully immiscible.

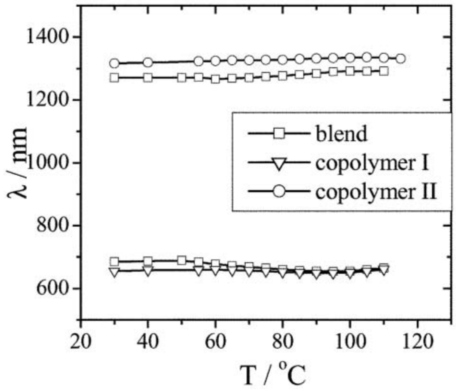


Fig. 2 Temperature dependences of the wavelengths of selective light reflection for blend and corresponding copolymers **I**, **II**.

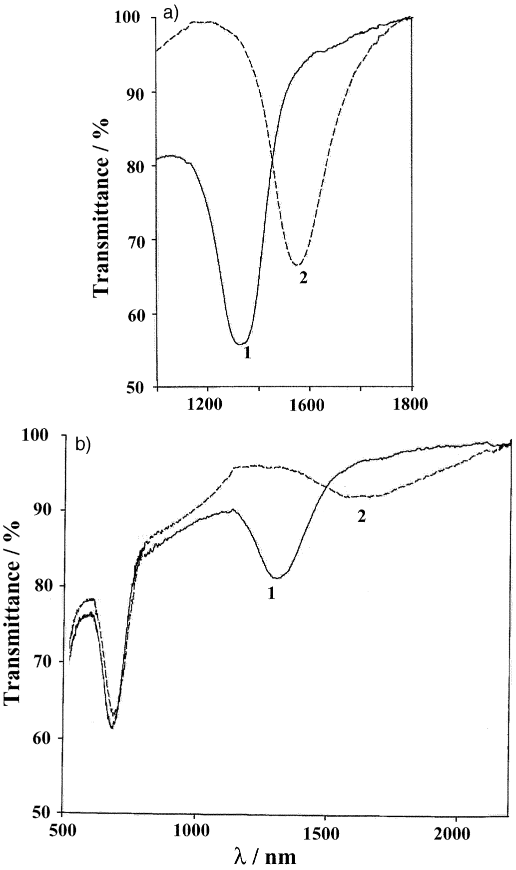


Fig. 3 Transmittance spectra of (a) plane-oriented films of copolymer **II** and (b) blend before (1) and after irradiation (2) by UV light (365 nm at 70 °C). Irradiation time: (a) 30 min, (b) 120 min; all spectra were recorded immediately after switching off light.

3.2. Photooptical properties of the cholesteric blend

Let us consider the photooptical properties of the blend. As follows from Figs. 3b, 4, and 5, upon UV and visible light irradiation, the plane oriented films show a gradual shift in the selective light reflection maximum to higher wavelengths. Note that, upon irradiation, the peak in the visible spectral region experiences no changes. Helix untwisting takes place only at temperatures higher by 20–30 °C than the glass transition temperature of the blend (in other words, at temperatures above 45 °C).

The sensitivity of the long-wavelength selective light reflection peak to the action of irradiation indicates that the phase with the corresponding selective light reflection peak in the near-IR spectral region contains copolymer **II** as its main component. Upon light irradiation, the *E*–*Z* photoisomerization of azobenzene photosensitive chiral side groups takes place (Fig. 1), and this process is accompanied by a concomitant decrease in anisometry and helix twisting power.[17–24]

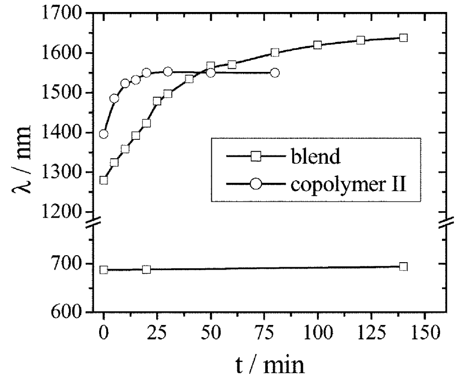


Fig. 4 Changes of the selective light reflection wavelength during UV irradiation (365 nm) of blend and copolymer **II** at 70 °C. The spectral measurements were made immediately after each cycle of irradiation.

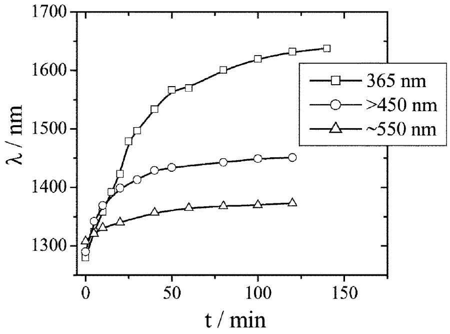


Fig. 5 Changes of the selective light reflection wavelength during irradiation with light of different wavelengths for the blend at 70 °C. The spectral measurements were made immediately after each cycle of irradiation.

The selective light reflection peak located in the visible spectral region remains unchanged.

Let us discuss some interesting features of untwisting the cholesteric helix in the system studied. First, for the blend, the rate of helix untwisting appears to be much lower as compared with the initial photosensitive copolymer **II** (Fig. 4). This behavior is likely to be related to the fact that, due to the existence of the two phases, the planar cholesteric texture of the blend is capable of a more pronounced light scattering. Therefore, the fraction of light required for the activation of photoisomerization appears to be somewhat lower.

Second, for the above blend, the shift in λ_{max} is found to be much higher (Fig. 4). Furthermore, for the irradiated blend, the half-width of the selective light reflection maximum is much higher than that of copolymer **II** (Fig. 3). The above phenomena may be related to the fact that, due to the two-phase character of the blend, a continuous size distribution of the regions with cholesteric phase is developed. Hence, in the case of the blend containing cholesteric small-sized "drops", one may hardly exclude the well-defined effect of phase boundaries on the helix pitch. This phenomenon may provide the development of the regions containing cholesteric phases with quite different values of helix pitch. However, to verify this hypothesis, a more detailed investigation of the morphology of the blend is necessary. In other words, the above phenomena may be explained by light scattering on the film of the blend. As a result, the rate of the photoinduced processes decreases, and the difference between the light intensities in the

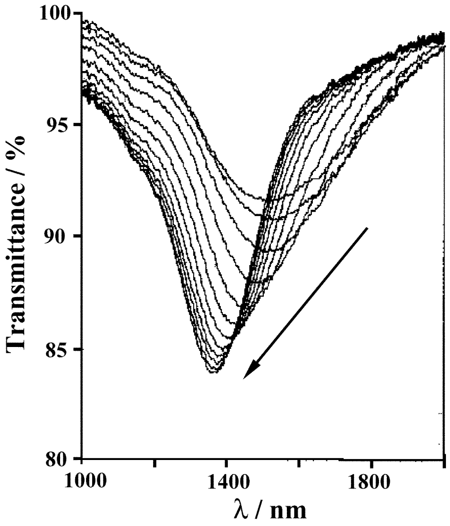


Fig. 6 Changes of transmittance spectra of plane-oriented films of the copolymer blend during annealing at 70 °C. Before measurements the sample was irradiated by UV light (365 nm). The arrow indicates the direction of spectral changes; spectra were recorded each 4 min during annealing.

different regions of the irradiated film is increased. The light intensity at the surface of the film facing the light source appears to be much higher than that of the opposite side. A marked gradient in the light irradiation doses leads to a well-pronounced widening of the selective light reflection peak due to different ratios between the formed *E*- and *Z*-isomers.

Upon irradiation with visible light, the selective light reflection maximum is also shifted (Fig. 5) but the range of this shift is much smaller as compared with that as induced by the UV irradiation. This fact suggests that, under the action of visible light, the *E*–*Z* photoisomerization takes place but, in this case, the concentration of the *Z*-isomeric azobenzene groups in the photostationary state is much lower.[27]

Photoisomerization and, hence, helix untwisting are supposed to be thermally reversible processes. As follows from Fig. 6, as a result of annealing, the selective light reflection peak comes back to its initial position. On the other hand, upon fast cooling of the blend to room temperature (glass transition), one may "freeze" the helical supramolecular structure and, thus, preserve this structure for a long period of time.

An important property of the reversible photosensitive systems concerns their so-called fatigue resistance which means their resistance in the repeated recording–erasing cycles. As follows from Fig. 7, the fatigue resistance of the system studied is quite high, and this fact allows one to rank this composition as a promising material for reversible optical data recording.

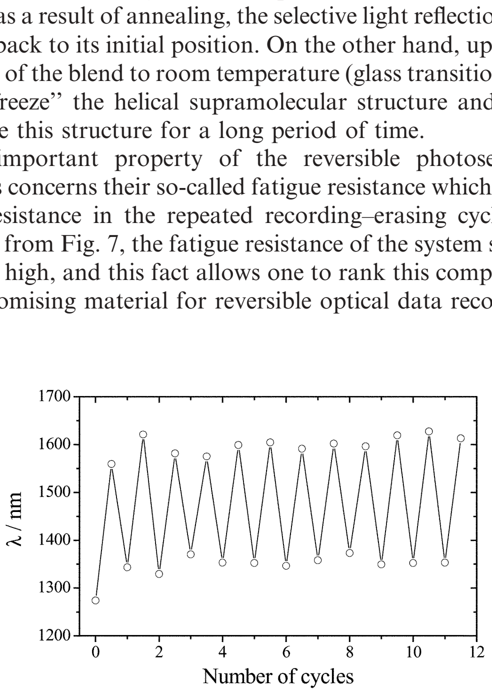


Fig. 7 Fatigue resistance properties of the blend film under the recording–erasing conditions. In each cycle a film of the blend was irradiated during 20 min by UV light at 70 °C, then was annealed during 40 min at the same temperature.

4. Conclusion

Hence, in this work, a new blend of cholesteric copolymers was prepared. This blend is characterized by unique optical properties: as compared with the cholesteric materials, the above blend shows two selective light reflection peaks, and the position of one of the above peaks may be changed under the action of light. Notwithstanding the fact that the above phenomenon may also be expected for multilayer structures based on cholesteric films of various polymers, the approach advanced in this work offers a much simpler solution for the preparation of the systems with the above optical and photooptical properties. Polymer blends of this type can be used as promising candidates for the preparation of new materials for storage of information, colour data recording, colour display technology, holography, colour projection systems and other applications.

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