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Thermo-, chiro- and photo-optical properties of cholesteric azobenzene-containing copolymer in thin films

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Abstract

Thin films (100–350 nm) of liquid crystalline copolymer containing the photoactive azobenzene and the chiral cholesterol groups were prepared by spin-coating technique and their optical and chiro-optical properties were investigated. In thick films (several microns), copolymer is characterized by the following phase transitions: g 27 SmA 83–85 N* 127–128 I, whereas spin-coated thin films are optically isotropic. Nevertheless, the films possess a noticeable circular dichroism with a maxima corresponding to the absorbance of the non-chiral azobenzene fragments. This phenomenon is evidence for the existence helical supramolecular structure elements in the polymer films. Annealing of the films at temperatures, higher glass transition leads to disappearance of circular dichroism and formation of the strong out-of-plane order with orientation of side groups of copolymer perpendicular to substrate. The annealed films are characterized by the high order degree comparable with that of SmA phase. The same effect was observed under visible light irradiation (436 nm). Action of UV light (365 nm) results in *E*–*Z* isomerization of azobenzene groups and significant drop in circular dichroism values (almost to zero) in the fresh films, and disruption of the out-of-plane order in the annealed films. Such complicated chiro-optical and ordering behaviour of the copolymer films opens new opportunities for creation active switchable optical devices.

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Keywords: Liquid crystalline copolymer; Cholesteric phase; Smectic phase; Azobenzene groups; *E*–*Z* isomerization; Out-of-plane order

1. Introduction

The modern state-of-art in an area of nanotechnology, optical information processing deals mostly with very thin layers, films of organic or inorganic materials. A large number of research groups are focusing their attention on the preparation and detailed study of the thin layers, films, coatings, etc. prepared by different techniques. Among these techniques one of the most prominent method is the spin-coating. This method has found a wide application in the microelectronics, optics, display technology and other fields. In this connection, a special interest from both fundamental and practical points of view presents a study of influence of the surface and phase boundaries on optical, thermal and other characteristics of thin polymer films. For example, in some papers [1–3] was found that in the case of very thin films (about ∼100 nm and thinner), their glass transition temperature, structure and molecular mobility markedly depend on the thickness of polymer film. In the recent work [4], chiro-optical properties of chiral polyfluorene derivative were studied and it was shown that the degree of circular polarization in the light absorption depends strongly on the thickness of the film. Authors found the exceptionally high dissymmetry ratios originating on a nanoscopic level and related to the long-range correlation in the polymer chain orientation induced by annealing the film in its liquid crystalline phase.

In our last paper [5], we described very interesting tendency to spontaneous out-of-plane order formation in two azobenzene-containing side-chain liquid crystalline polymers. Both thermal annealing and visible light action result in the cooperative orientation phenomena and lead to the alignment of side groups in the direction perpendicular to a substrate.

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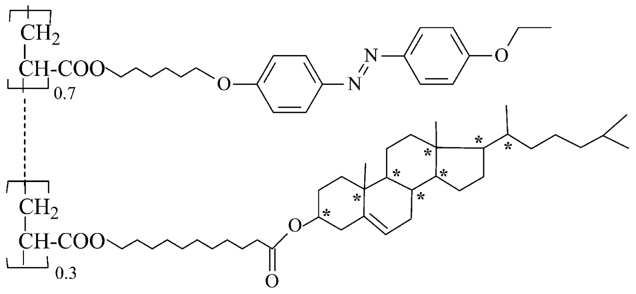
In present paper, we focused our attention on the study of chiro-optical properties of cholesterol-containing copolymer with the following structure and phase transitions.



g 27 SmA 83-85 N* 127-128 I

Copolymer contains two different mesogenic side groups—azobenzene and cholesterol. As well-known, azobenzene groups are capable of undergoing reversible *E*–*Z* isomerization under a light action [6,7]. This feature makes such type of polymer systems very interesting from the photo-optical point of view. On the other hand, the cholesterol fragments have several optically active centers and a relatively high helical twisting power in liquid crystalline media, i.e. ability to induce helical supramolecular structure [8–10]. The combination of two different monomer units in the same polymer chain stimulates the chiral nematic and smectic phases formation. Structural parameters of these phases could be controlled by the light irradiation due to an existence of the azobenzene fragments.

The main idea of this work is focused on the investigations of the optical properties of thin films of the combined copolymer. A special attention will be paid to revealing the influences of different factors, such as the film thickness, annealing on the structure and optical characteristics of the thin films. This knowledge will give a new opportunity for the understanding ordering tendencies in the thin polymer liquid crystalline or amorphous films under the heat and light external actions.

2. Experimental

Ethoxyazobenzene and cholesterol-containing monomers were synthesized according to the procedures described in [11,12], respectively. The copolymer was synthesized by radical polymerization of monomers in benzene solution at 65 °C; AIBN was used as an initiating agent. The synthesized polymer was purified by the repeated precipitation with methanol and dried in vacuum.

The average molecular mass of polymer was determined by gel permeation chromatography (GPC). GPC analyses were carried out with a KNAUER instrument equipped with an KNAUER HPLC 64 column. Measurements were made by using a UV detector, THF as solvent (1 ml/min, 40 °C), and a calibration plot constructed with polystyrene standards. The polymer obtained had the following molar mass characteristics: $M_n = 8200$, $M_w/M_n = 1.3$.

The phase transitions in the polymer were studied by differential scanning calorimetry (DSC) with a Perkin Elmer DSC-7 thermal analyzer (a scanning rate of 10 K/min). The polarizing microscope investigations were performed using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarizing microscope.

Thin films for photo-optical experiments were obtained by spin-coating technique using solutions of different concentration in chloroform. For drying, the spin-coated films were kept at room temperature during 1 day. Thickness of the films was measured using DEKTAK profilemeter.

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

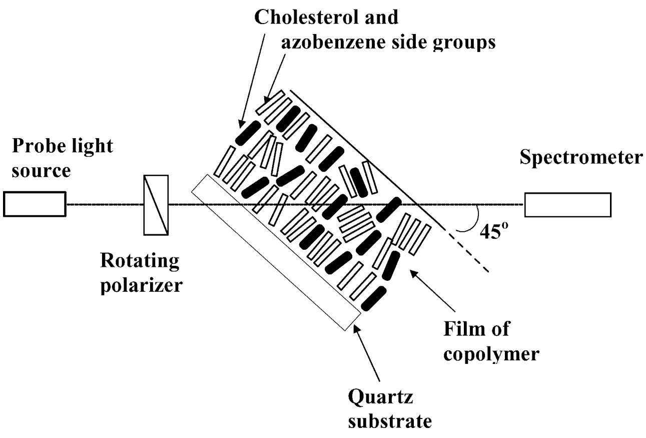
The orientational order was studied using polarized UV–vis spectroscopy, because the transition moment of the *E*-isomer of azobenzene moiety is directed along the long axis of this group. For this purpose, the angular dependence of the absorbance was measured using a photodiode array UV–vis spectrometer (J&M) with a step-width of 10°.

The values of dichroism were calculated from the spectra using the following equation:

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

where $A_{\parallel}$ is the absorbance at the preferred direction; $A_{\perp}$ the absorbance perpendicular to this direction.

To study the out-of-plane photo-orientation phenomena, we measured the angular distribution of the polarized ab-



Scheme 1. Experimental setup for out-of-plane order formation. (The backbone of copolymer is omitted for simplicity.)

sorbance spectra at an angle equal of about 45° to film normal (Scheme 1).

3. Results and discussion

3.1. Optical and chiro-optical properties of spin-coated films of the copolymer

First of all, let us consider the spectral properties of the spin-coated films of copolymer. As is seen from Fig. 1, copolymer films are characterised by strong absorbance with maximum at 352 nm corresponding to the π–π^* electronic transition and small “shoulder” at $\lambda > 420$ nm corresponding to the n–π^* transition. At $\lambda < 280$ nm, an absorbance corresponding to aromatic Φ–Φ^* electronic transition is observed.

It is important to stress that the fresh films of the copolymer are optically transparent in other spectral regions (visible and near IR), i.e. they do not show any light scattering and are preserved isotropic.

The annealing of the films at temperatures higher then glass transition temperature leads to a dramatic decrease in the absorbance corresponding to the π–π^* electronic transition (Fig. 1). The polarized absorbance spectra measured at 45° to the normal of the film show a strong out-of-plane order formation (Fig. 2b). This type of orientation is stable at temperatures below the clearing transition, but starts to decrease under heating above 100 °C and drops to 0 above T_{cl} (Fig. 2c). Even at temperatures corresponding to the chiral nematic phase (above 83–85 °C), the out-of-plane order remains still very high. Probably, the helical structure formation does not occur in thin films, whereas in thick films (10–20 μm) a good helical order displaying selective light reflection at these temperatures takes place [18].

Circular dichroism (CD) spectra reveal some specific features for freshly prepared spin-coated films. Two peaks of the opposite sign for films with thickness higher ca. 100 nm were observed (Fig. 3). The positive peak has maximum at 393 nm whereas a very strong negative peak is located at 345 nm. A decrease in the films thickness results in a disappearance of positive peak, whereas negative peak shifts to the longer wavelengths.

Note that the appearance of both CD peaks does not relate to an intrinsic molecular chirality of the cholesterol fragments. The examination of copolymer solutions in dichloroethane showed zero CD values at higher wavelength 250 nm (Fig. 3). On other hand, appearance of circular dichroism does not associated with selective light reflection, because the thin spin-coated films of the copolymer cannot form

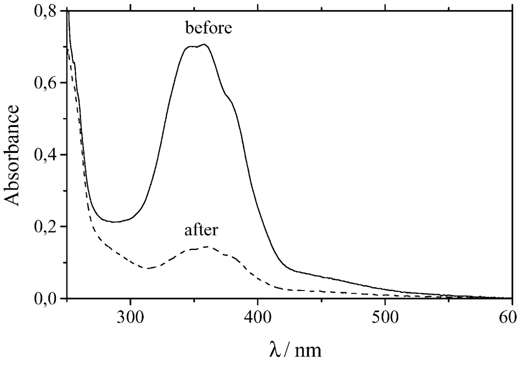


Fig. 1. Absorbance spectra for one film before and after annealing during 30 min at 70 °C.

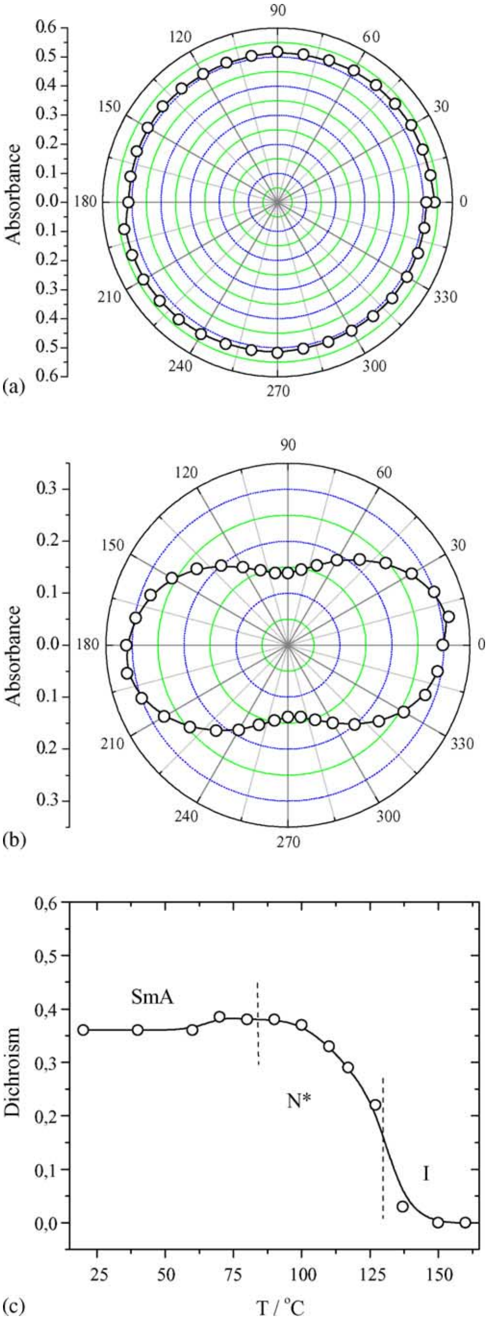


Fig. 2. Polar plots demonstrating absorbance of polarized light (a) before and (b) after annealing, respectively (for $\lambda = 330$ nm). (c) Temperature dependence of out-of-plane dichroism. Measurements were made at 45° to film normal.

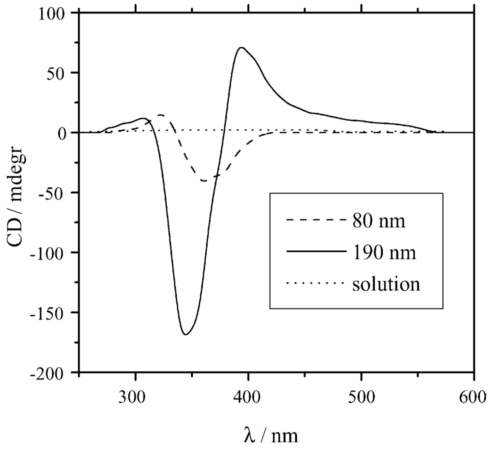


Fig. 3. CD spectra for two films with different thickness and for solution in dichloroethane.

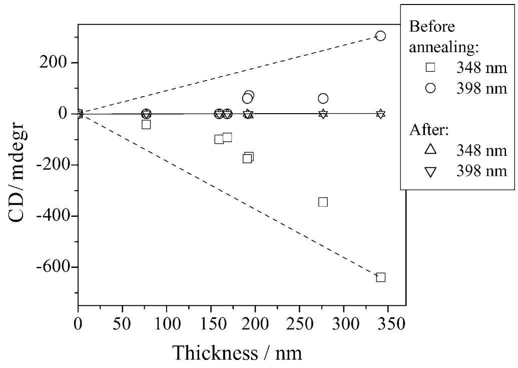
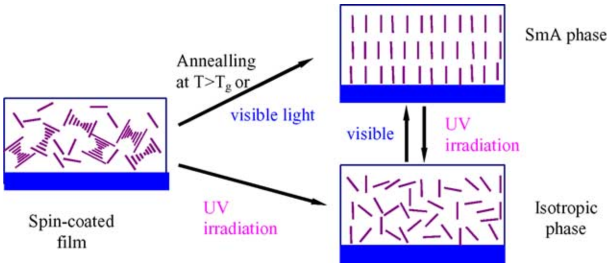


Fig. 4. Dependence of CD values at two wavelengths on the thickness of films. Dashed lines are shown for demonstration of CD dependencies non-linearity. After annealing, CD value drops almost to zero.

planar texture with the highly developed helical structure. The selective light reflection was observed for this copolymer earlier in thick (about 20 μm) planarly oriented films and has maximum at longer wavelength strongly depending on the temperature of sample [18].

In our opinion, an appearance of the strong circular dichroism is connected with formation of the elements of the helical supramolecular structure in films just after spin-coating as schematically represented in Scheme 2. The induction of similar circular dichroism in the cholesteric media was demonstrated many times and theoretically described in the literature earlier [13–17]: an addition of the achiral guest molecules into the cholesteric matrix leads to the appearance of the so-called induced circular dichroism with maxima coinciding with the absorbance peak of the additive.

But in our case, the spin-coated films of the copolymer are isotropic and, moreover, the thick (10–20 μm) annealed films at the room temperature produce well-developed SmA phase possessing strongly scattered texture [5,18]. The spin-coating technique, as was discussed above, in our case leads to the formation of the isotropic films. But according to the CD data, we can conclude that instead the SmA formation some elements or fluctuation of the helical supramolecular structure are realized in the films (Scheme 2). Of course, the formation of more complicated helical supramolecular structures, for example, such as blue phases (especially BPIII) [19–24], or others, cannot be completely excluded.



Scheme 2. Schematic representation of possible side-group organization in thin copolymer films.

Values of CD at both maxima are extremely dependent on the film thickness. It is noteworthy that these dependencies are strongly nonlinear (Fig. 4). Probably, a tendency to the helical supramolecular structure formation are nonlinearly determined by film thickness, because of significant influence of surface boundaries. This influence leads to suppression of the helix formation in the films whose thickness is low and comparable with the helical pitch. The same fact can explain the shift of CD maxima to the longer wavelengths for the thinner films (Fig. 3).

The annealing of the films results in a fast drop of absorbance (Fig. 1) and CD values (Fig. 4). After annealing, the circular dichroism of all films is vanished. This effect is explained by a strong out-of-plane orientation comparable with the homeotropic orientation of the SmA phase (Fig. 2b) which completely disrupts the helical structure (Scheme 1). As clearly seen from Fig. 5, the rate of ordering process is strongly determined by the temperature of the films and their thickness. The higher rates of the process are observed at the higher temperatures and for the thinner films. The increase in temperature increases the rate of the thermal motion of the side groups. The influence of thickness decreasing on the rate of this process most probably is associated with the increased influence of the surfaces and interfacial regions [1–3,25,26]. The experimental and theoretical consideration of cholesteric liquid crystals showed that in some cases the strong tendency to the homeotropic orientation at the free surface is occurred [25,26]. In the thinner films, this tendency easily spreads through whole film leading to the full homeotropic orientation.

3.2. *Effect of UV and visible light irradiation on optical and chiro-optical properties of the copolymer films*

UV irradiation of the copolymer films leads to the spectral changes inherent to the *E*–*Z* isomerization of azobenzene fragments of such type (Fig. 6) [6,19,27]. Hence, the details of this phenomenon are beyond the scope of this publica-

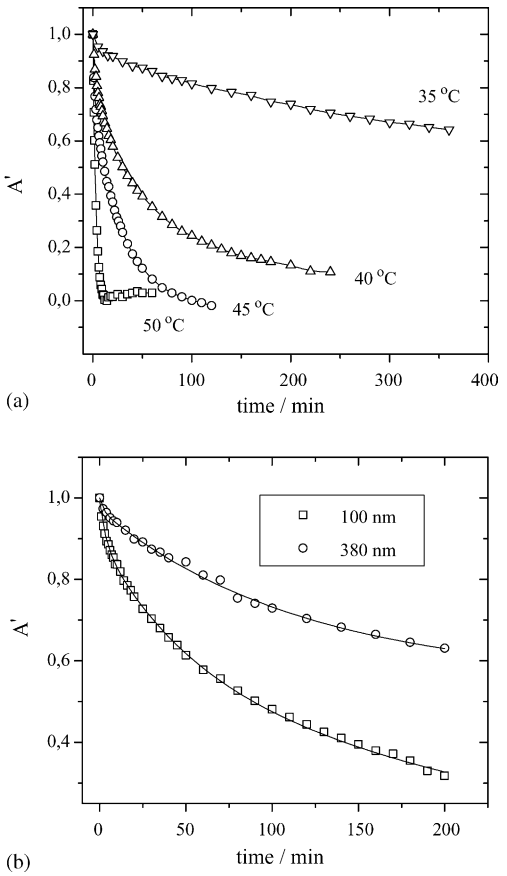


Fig. 5. Kinetics of relative absorbance changes during annealing: (a) at different temperatures (film thickness is ca. 100 nm); (b) for films of different thickness at 40 °C. $A' = (A_\infty - A_t) \times (A_\infty - A_0)^{-1}$, where A_0, A_t and A_∞ are the absorbance at 352 nm at the time $t = 0$, current time t, and $t \to \infty$, respectively.

tion but we would like to mention that this process is either thermally reversible or reversible under the action of visible light. The back thermal isomerization is relatively slow at room temperature: back conversion to *E*-isomer needs several hours.

The CD values are strongly decreasing during light action (Fig. 7). It is important to note that the rate of the circular dichroism decrease is significantly higher then for the absorbance (Fig. 8). The decrease in the CD values is most probably associated with disruption of the helical order elements during the *Z*-isomer formation. It is well-known that the azobenzene fragments in the *Z*-form have a very low anisometry and strongly destroy the liquid crystalline order [27–31]. According to the kinetic curves presented in Fig. 8, a very small concentration of forming *Z*-isomer is needed for isothermal transition to the fully isotropic state of polymer films (Scheme 2).

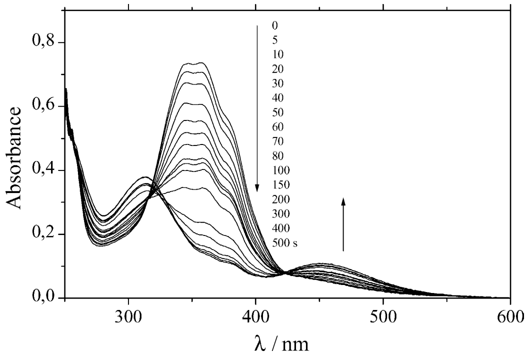


Fig. 6. Changes of absorbance spectra of copolymer film during UV irradiation (365 nm); room temperature, thickness of film is about 250 nm.

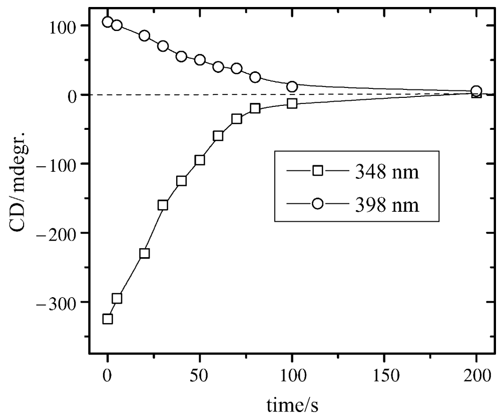


Fig. 7. Changes of CD values at two wavelengths during UV irradiation (365 nm); room temperature, thickness of film is about 250 nm.

The subsequent visible light irradiation leads to only the partial recovery of CD and absorbance. This is associated with competing process of the out-of-plane order formation [5]. The prolonged visible light action results in the out-of-plane order with the same degree of ordering like in the case of the thermal treatment. As was discussed in our previous paper [5], this phenomenon is associated with selective excitation of azobenzene chromophores directed along electric vector of the light, in other words, in direction, perpendicular to a film normal. This activates photo-orientation of chromophores along incident light propagation direction.

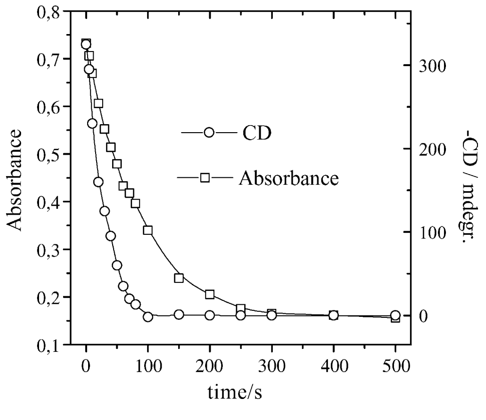


Fig. 8. Comparison of kinetics of absorbance and absolute circular dichroism changes (at wavelength corresponding to π–π^* electronic transition) during UV irradiation (365 nm).

4. Conclusions

In conclusion, we have demonstrated a complicated optical and photo-optical behaviour of the thin copolymer films prepared by spin-coating technique. Several competing factors, such as ordering tendency, surfaces and phase boundaries, *E*–*Z* and *Z*–*E* isomerizations, strongly determine a very interesting phenomena in thin films of the chiral liquid crystalline copolymer (Scheme 1). For the first time, formation of some elements of helical structure formation in freshly prepared films of smectogenic copolymer has been observed. The thermal treatment of the films converts such structure to layered smectic phase with orientation of layers along the film plane. The same effect is observed under visible light action. UV light leads to disruption of the helical or the out-of-plane order in fresh or annealed films, respectively.

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