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Comparative study of holographic recording in cholesteric and nematic azo-containing side-chain polymers

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For the first time a comparative study of holographic recording in planarly oriented films of nematic and cholesteric azobenzene-containing polymers was performed. The influence of temperature and light intensity on the values of diffraction efficiencies of holographic gratings was investigated. The kinetics of grating relaxation at different temperatures was studied. It was shown that the helical supramolecular structure of cholesteric copolymer causes a significant decrease of the diffraction efficiency in comparison with the one observed for the nematic state of the homopolymer.

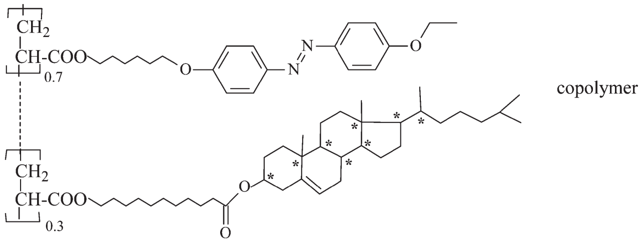
1. Introduction

The introduction of photosensitive azobenzene groups into the polymeric matrix provides a broad range of approaches for the design of materials for optical data recording and storage [1–32]. Azobenzene-containing main-chain and side-chain types of polymers [3, 4, 18–29] are of particular interest for the holographic recording because of their large information storage capacity and other advantages.

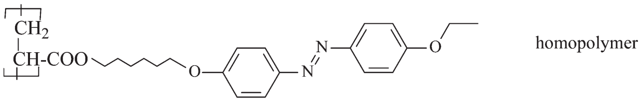
A considerable number of papers concerned with holographic recording in azobenzene-containing polymers have been published, but only a few of them have discussed so far the specific role of the liquid crystalline state with respect to the holographic recording process [28–31] and this is particularly true for cholesteric polymers [31]. To our knowledge a comparative study on holographic recording performed in different liquid crystalline states for similar polymers has not yet been performed.

It is well-known that the cholesteric phase has unique optical properties; the most important of which are the huge optical rotation and the selective light reflection [33, 34]. The influence of the helical supramolecular structure of the cholesteric phase on various features of the formation of holographic gratings is still unclear. The exploitation of the optical peculiarities for holographic image storage could be very interesting from an application point of view.

This paper presents the first comparative investigation of holographic recording on films of cholesteric and nematic polyacrylates containing azobenzene side groups:



g 27 SmA 83–85 N* 127–128 I



g 28 SmA 96–98 N 130–134 I

The copolymer containing cholesterol fragments forms a SmA phase and chiral nematic (cholesteric) phase due to the presence of chiral cholesterol fragments. The azobenzene-containing homopolymer displays a SmA phase and a nematic phase in a temperature range close to the one where the copolymer displays its liquid crystalline phases. Our previous studies showed that the planar cholesteric texture obtained at high temperature (in the chiral nematic phase) can be frozen-in for the copolymer by the fast quenching of the sample down to room temperature [32].

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The main purpose of the investigations reported in the following was to compare the formation of the grating within the liquid crystalline phases of the co- and homopolymer. A specific issue is to analyse the role of the cholesteric helical supramolecular structure on the recording behaviour as well as the dependence of the kinetics of hologram recording process and the magnitude of the diffraction efficiency on the temperature and the intensity of the incident light.

2. Results and discussion

At first we will consider the peculiarities of holographic recording for the homopolymer and copolymer at high temperatures, corresponding to the temperature range of the nematic or the chiral nematic phases, respectively. As can be clearly seen from figure 1, the irradiation of the homo- and copolymer using the holographic set up leads to a fast increase in diffraction efficiency. Most probably, the grating formation in such polymers is caused by the photo-orientation of azobenzene fragments into a direction perpendicular to electric field vector of light as described previously [2–5].

Polarized light is absorbed by azobenzene groups with a transition moment lying along the electric field vector direction. The azobenzene fragments oriented perpendicular to the polarization plane remain almost inactive. The great number of *E–Z* and *Z–E* photoisomerization cycles to which the azobenzene fragments are subjected during irradiation induces a cooperative orientation of azobenzene and other mesogenic fragments perpendicular to the polarization direction. Such a reorientation results in refractive index changes in areas irradiated with high light intensity and, as a consequence, the formation of a diffraction grating takes place. Schemes 1 and 2 demonstrate, in simplified form, mechanisms of grating formation in rubbed polyimide-coated cells of cholesteric and nematic polymers, respectively.

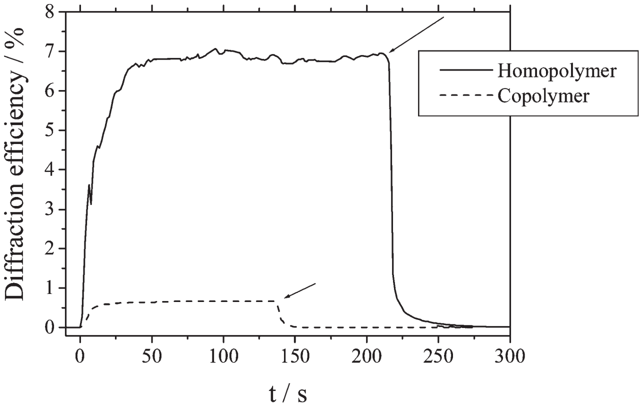


Figure 1. Time evolution of diffraction efficiency for homo- and copolymer films. Light power was 215 μW; sample temperature 110°C. The arrows show the laser beam switching off.

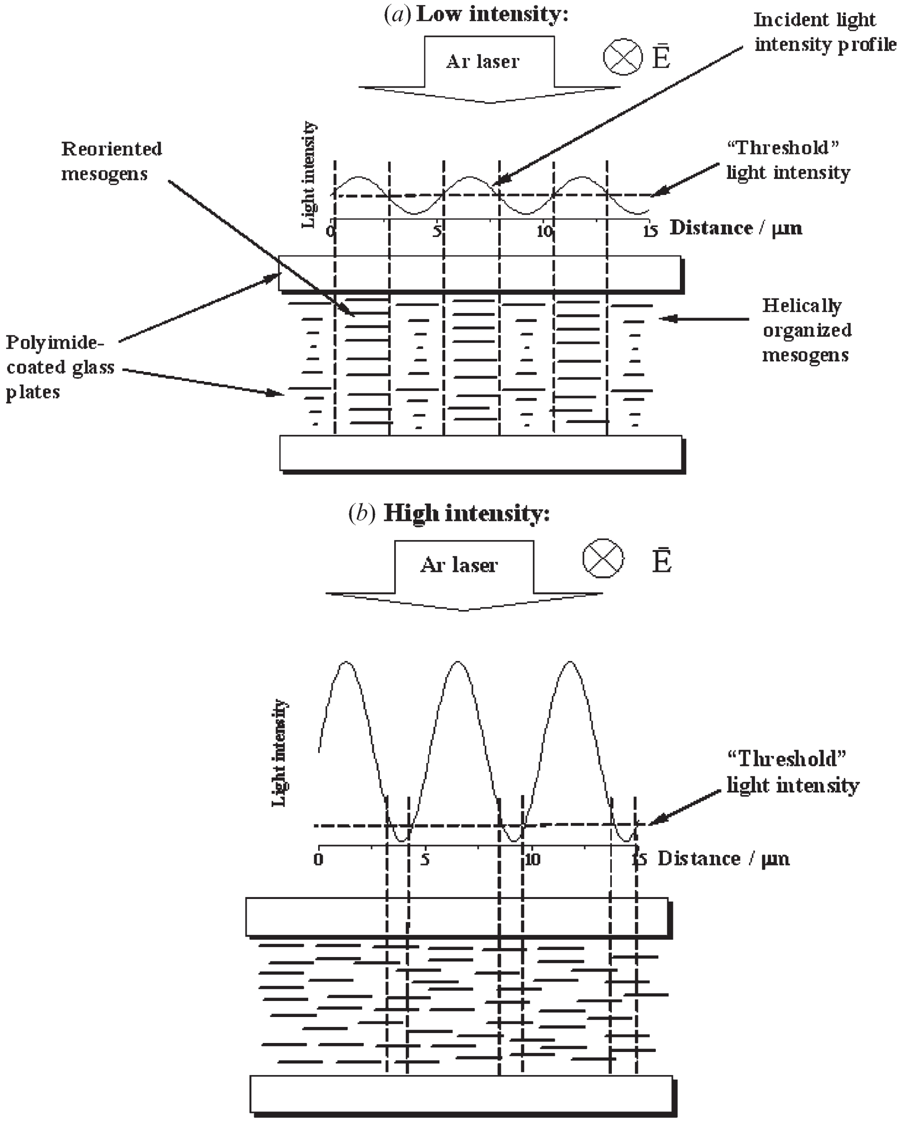
As seen from figure 1, the magnitude of the diffraction efficiency is about one order of magnitude higher for the homopolymer as compared to the one for the copolymer. This fact reflects a significant influence of the helical supramolecular organization within the cholesteric copolymer on the light-induced optical modulations. The presence of the helical structure seems to prevent the reorientation of azobenzene moieties induced by polarized light to a significant extent. After switching off the recording laser beams, the diffraction efficiency rapidly drops down to zero. Figure 2 shows microphotos of the texture of the copolymer before and after holographic recording followed by switching the recording beam off. Initially the copolymer film forms a planar texture with typical cholesteric disclination lines (oily strikes) (figure 2a). After irradiation and switching off the laser the texture transforms to a non-oriented scattering state (figure 2b).

We have studied the influence of some parameters, i.e. the light intensity and the temperature, on the kinetics of the holographic grating formation and the diffraction efficiency. Figure 3 presents the dependence of the saturation value of the diffraction efficiency on the light intensity. It was unexpectedly found that the highest diffraction efficiency resulted for relatively low intensity of the recording light.

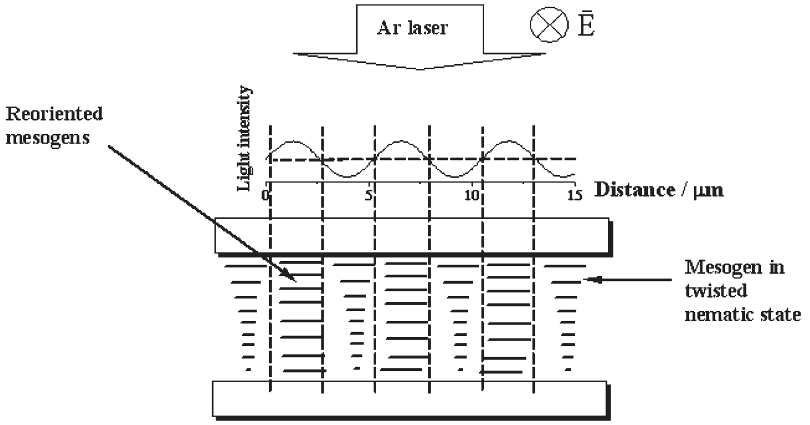
A possible explanation is presented schematically in scheme 1. The assumption is that certain threshold intensity is needed for significant optical modulations to take place. So for low recording intensities, no photo-orientation will be induced in these parts of the intensity grating corresponding to the "dark" regions (see minimum of intensity profile in scheme 1). Yet as the total writing intensity is increased, a reorientation process also takes place in these dark regions causing the contrast to decrease.

The diffraction efficiency is also strongly dependent on the temperature of the samples. An increase in the diffraction efficiency was observed for the homo- and copolymer for increasing temperature (figure 4). The rate of thermal back relaxation is also greater at higher temperatures (figure 5). It is obvious that the cholesteric copolymer is characterized by a particularly high rate of the thermal relaxation. This can probably be traced back to the strong tendency of the mesogenic groups towards a helical structure formation.

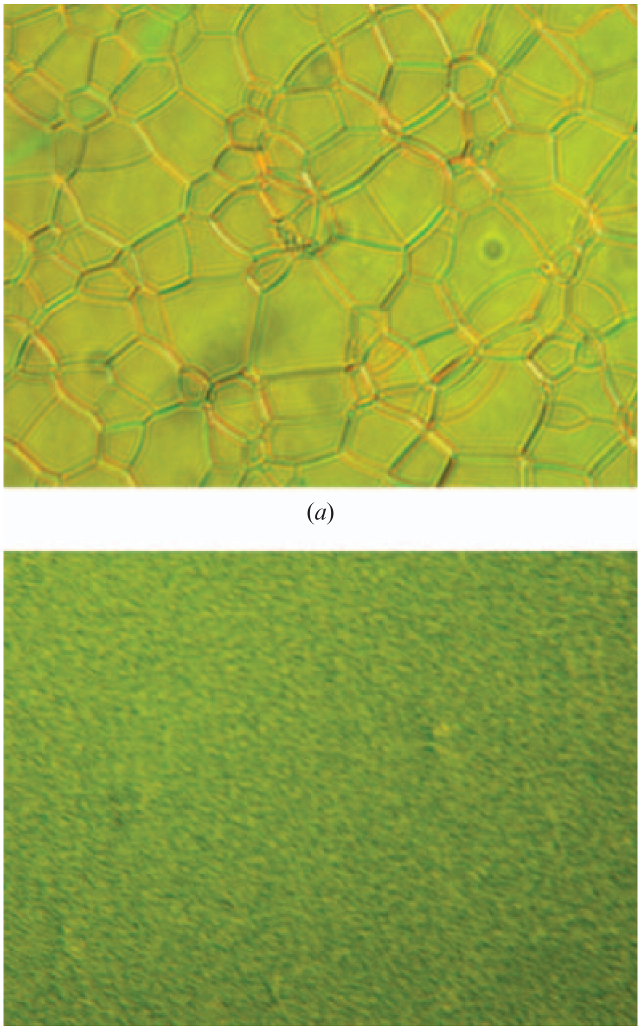
Solid films of both polymers were prepared from nematic and chiral nematic phase by cooling them rapidly down to room temperature. In both cases the



Scheme 1. Simplified representation of possible mechanism of azobenzene and cholesterol group cooperative reorientation induced in cholesteric copolymer film by light of low (a) and high intensity (b).



Scheme 2. Simplified representation of possible mechanism of azobenzene group cooperative reorientation induced in nematic homopolymer film by light of low intensity.


(*a*)

(*b*)

Figure 2. Microphotos of textures for copolymer film: (a) planar texture before irradiation; (b) focal conics texture after holographic recording and erasing during heating at 120°C. Recording and erasing were performed at 120°C followed by fast cooling to room temperature.

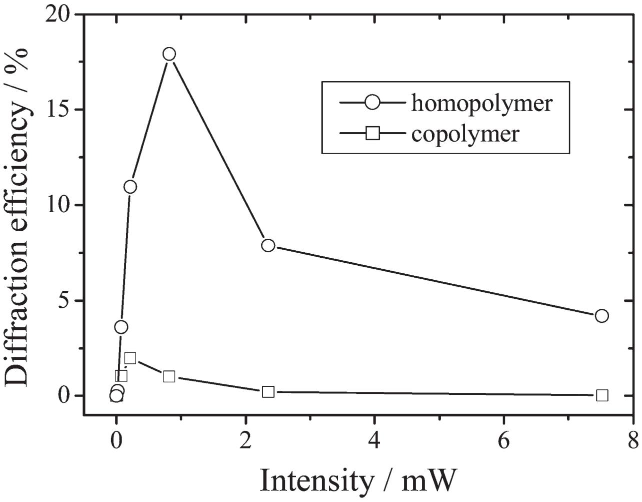


Figure 3. Dependence of the maximal value of the diffraction efficiency after steady state achieving on light power. Sample temperature 120°C.

"frozen" nematic and cholesteric structures were found to be rather stable for long times and a transition towards the equilibrium SmA phase was not observed at all [32]. Unfortunately, the investigations on the kinetics of grating formation and on the diffraction efficiency in such non-equilibrium films did not show a good reproducibility but rather a strong sensitivity with respect to the sample preparation procedure and other factors. In our future works we will have to try to find more appropriate techniques for the film quenching procedures. In any case we observe very high diffraction efficiency for such quenched films as obvious from figure 6. Figure 7 shows micrographs of holographic gratings recorded on such supercooled films of the copolymer and homopolymer in their nematic and cholesteric phase, respectively. The superposition of photo-optically induced gratings and the textures characteristic for the nematic and cholesteric phases including some defects are clearly seen in the photos. Holographic grating recorded on supercooled samples are very stable at least for several months.

Holographic recording performed at the room temperature on the supercooled cholesteric films resulted in significant spectral changes in a wavelength range corresponding to the selective light reflection range (figure 8). The most noticeable changes are

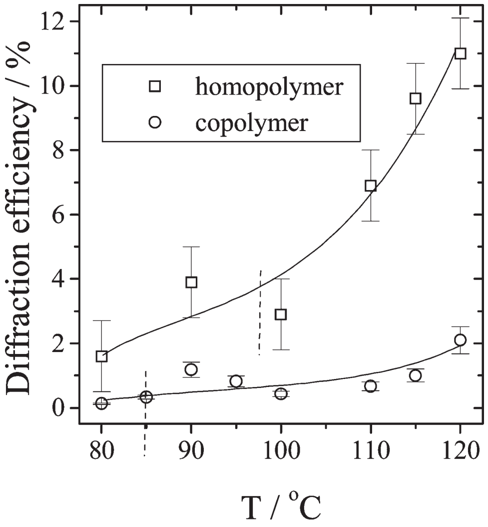


Figure 4. Dependence of the maximal value of the diffraction efficiency on the temperature. Incident Ar laser beams power was 215 µW. Solid lines are guides for the eye only; dashed lines indicate SmA–N (N*) transition temperatures.

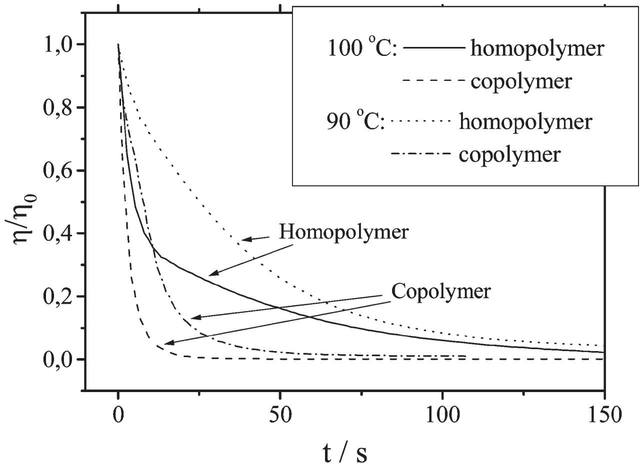


Figure 5. Kinetics of the thermal relaxation of the normalized diffraction efficiency value for homopolymer and copolymer at two temperatures; η_0 is the maximal value of diffraction efficiency after saturation.

observed in the spectral shape for the left-handed circularly polarized light. Such effects are probably associated with an essential deformation of the helical supramolecular structure during the interaction with the polarized light and the resulting reorientational motions of the azobenzene fragments.

An irradiation with one laser beam (homogeneous light intensity along surface) at room temperature has similar spectral effects. In both cases the light does not lead to a complete disruption of the helical order. Only a partial uniaxial deformation in the direction perpendicular to the helix axis takes place.

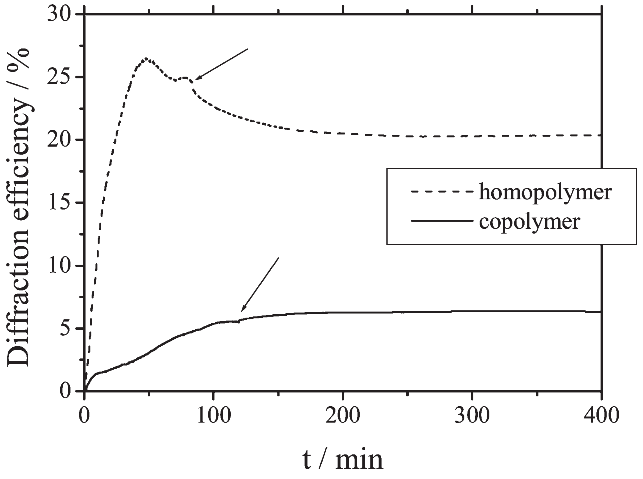
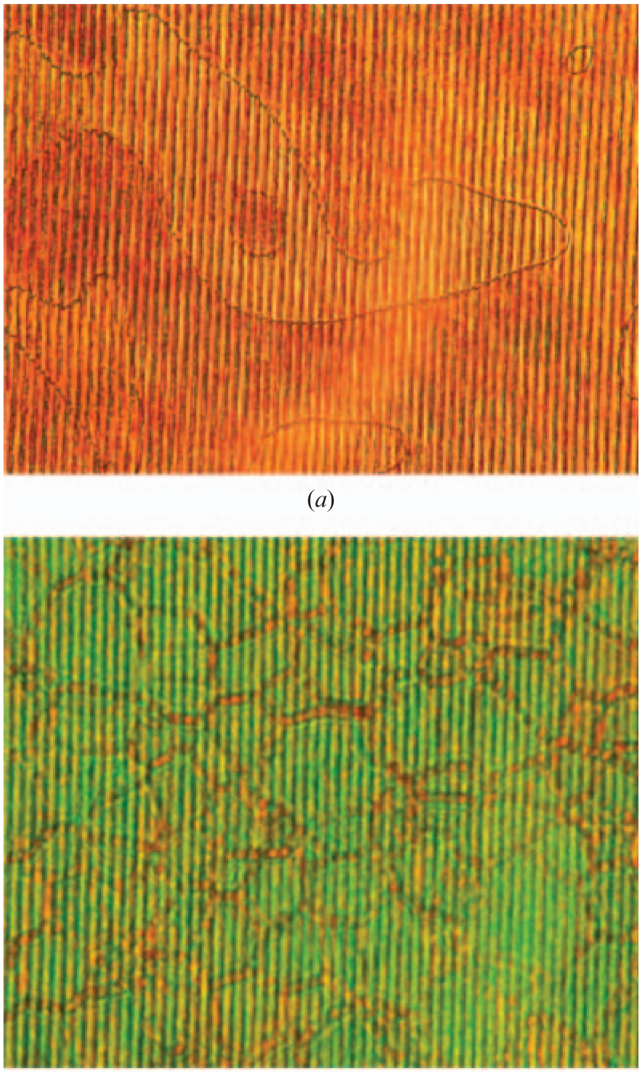


Figure 6. Changes of the diffraction efficiency during recording and thermal relaxation for copolymer film supercooled from 120°C to the room temperature. The light power is 2.35 mW; arrows indicate the moment of switching irradiation off.


(*a*)

(*b*)

Figure 7. Microphotos of holographic gratings recorded in (a) homopolymer and (b) copolymer films. Holographic recording was performed at room temperature; before irradiation the films were annealed at 120°C followed by fast cooling to the room temperature. Grating period is about 5 µm.

3. Conclusion

In conclusion, we have performed for the first time a comparative study of holographic recording in films of cholesteric and nematic polymers having the same azobenzene side groups. It was demonstrated that the helical supramolecular structure prevents to a significant extent the photo-orientation of the azobenzene groups. The result is a strong decrease of the diffraction efficiency in the cholesteric as compared to the nematic phase. At the same time the helical structure essentially increases the thermal back-relaxation process: the

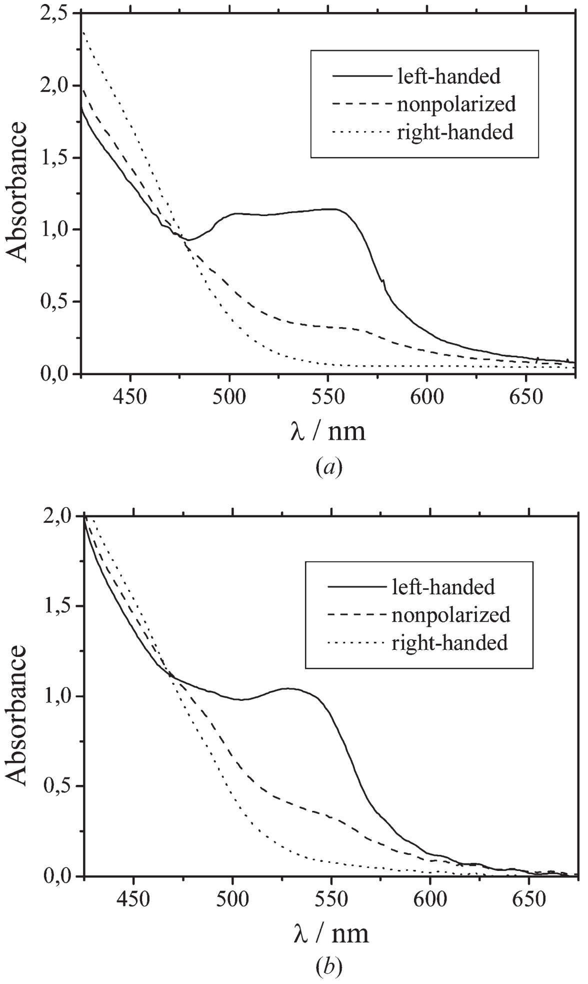


Figure 8. Non-polarized and circularly polarized absorbance spectra of the copolymer film supercooled from 120°C to the room temperature before irradiation (a) and after the holographic grating recording (b) (2.35 mW, 200 min).

cholesteric copolymer is characterized by the high rate of diffraction efficiency drop as compared with the homopolymer. Our investigations furthermore revealed the strong influences of the temperature and the light intensity on the kinetics of grating formation and on the saturation value of the diffraction efficiency.

4. Experimental

Procedures from the literature were used to synthesize 4-ethoxyazobenzene [35] and cholesterol-containing [36] monomers. The homopolymer and the copolymer were synthesized by radical polymerization of monomers in benzene solutions 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 average molecular weights of the polymers were determined by gel permeation chromatography (GPC). The GPC analyses was carried out with a Knauer instrument equipped with a Knauer HPLC 64 column using an UV detector, THF was used as solvent (1 ml min^{-1}, 40°C), and the data were calibrated with respect to polystyrene standards. The polymers obtained have the following molar weights: homopolymer: M_n=8000, M_w/M_n=1.4; copolymer: M_n=8200, M_w/M_n=1.3.

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

Holographic recording experiments were performed with a special set up described in detail previously [28]. An argon ion laser operating at 488 nm (single mode, single frequency) was used as light source. Gratings were obtained by the interference of two planar s-polarized waves in a Mach Zehnder interferometer. The grating period amounted to about 5.1 µm (schemes 1–2).

A helium-neon laser operating at 632.8 nm with polarization parallel to the writing beans was used to read out the induced optical modulation. The intensity diffracted into the first order was measured by a photodiode and normalized to the intensity of the incident read-out beam to obtain the diffraction efficiency, η.

Holographic gratings were recorded by illuminating the polymers in 7 µm thick cells with polyimide-coated rubbed surfaces. The direction of rubbing of the two surfaces in the cells was perpendicular to each other. Before recording, a planar texture for cholesteric and nematic polymers was obtained by annealing the samples at temperatures corresponding to the range of existence of the nematic or the chiral nematic phase (120°C).

Circularly polarized light absorbance spectra were recorded using a special set up [32] equipped with a Xe lamp (1000 W, Müller Elektronik Optik), two monochromators (SpectraPro 300 I, Acton Research, Polytec), controlled by a NCL single-channel spectroscopy detection system (Roper Scientific GmbH, Germany).

Acknowledgments

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