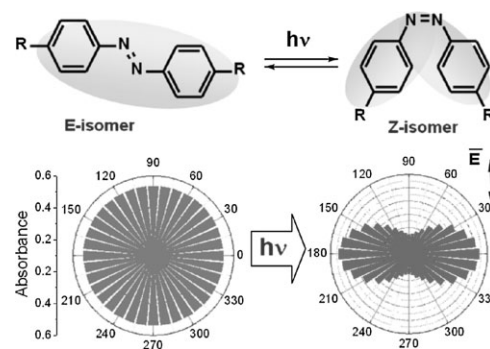


Effect of Molecular Structure and Thermal Treatment on Photo-optical Properties of Photochromic Azobenzene-containing Polymer Films

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Three novel photochromic azobenzene-containing comb-shaped polyacrylates are synthesized and their phase behavior and photo-optical properties are studied. The influence of the side photochromic group structure, thermal treatment, and light irradiation on aggregation of azobenzene chromophores in thin spin-coated films of the polymers is investigated in detail. Special attention is paid to studying the photo-orientation processes in polymers films induced by polarized blue light (473 nm). The relationship between the photochromic group architecture, phase behavior, thermal treatment of films, and kinetics of chromophore photo-orientation is established and discussed. It is found that the position of the N=N bond in chromophores plays an important role in the kinetics of the process, but does not affect the maximum value of dichroism.



Introduction

Liquid crystalline (LC) or amorphous polymers containing azobenzene side groups are very promising and unique materials for optical data recording and optoelectronics.^[1–4] Polarized light action induces photo-orientation of

azobenzene groups in films of such polymers. In most cases, these groups are oriented perpendicularly to the polarization plane of the incident light.^[5–16] The origin of this phenomenon is explained by the process of selective excitation and E-Z-E isomerization cycles of the chromophores oriented predominately along the polarization plane. After many cycles of excitation-relaxation and isomerization accompanied by a rotational diffusion, the assembly of chromophores becomes oriented in the direction perpendicular to the polarization plane. This process has cooperative character and non-photochromic rod-like mesogenic fragments of the azobenzene-containing copolymers also adopt this orientation.

Despite the large number of publications devoted to the study of photo-orientation phenomena,^[5–16] the relationship between the molecular structure and photo-orientation kinetics, as well as the values of photoinduced

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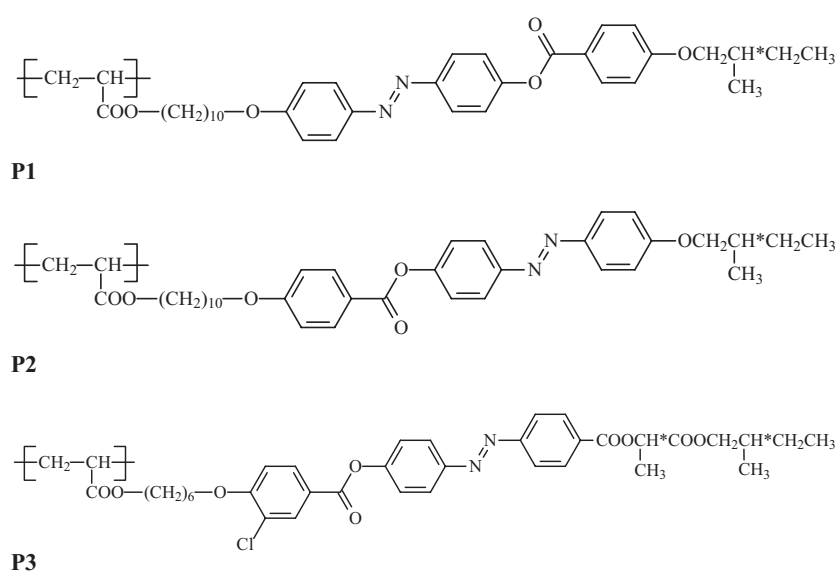
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dichroism, is still not completely clear. Another important topic for future research in this field is related to the investigation of the effect of the thermal treatment of samples on the kinetics of photo-orientation.

In this paper, we have synthesized and studied a novel series of azobenzene-containing LC and amorphous side chain polymers with the structures shown in Scheme 1.

Polymers **P1** and **P2** have a different position of the N=N double bond in the three benzene ring mesogenic group but the other structural elements of the side groups are completely the same. The photochromic aromatic fragment of **P3** is similar to that of **P2**, but contains the chlorine substituent. In addition, the chiral terminal fragment of this polyacrylate contains two optically active carbon atoms. In the present paper we do not consider the impact of chirality on the photo-optical behavior of these polymers; this topic is the subject of future investigations. For polymer **P1**, some results of studies of the chiro-optical properties have been published recently.^[17] Investigations of the influence of the chirality on the optical properties are particularly interesting from the point of view of basic research as well as for potential applications as photo-optical switchable smart materials.

The main objective of the present paper is a comparative study of the phase behavior and photo-optical properties of these three photochromic side chain polymers with different chemical structures of their chromophores. Special attention will be paid to the investigation of photo-orientation phenomena occurring in polymer films under the action of a polarized light.



Scheme 1. Structures of the series of azobenzene-containing LC and amorphous side chain polymers synthesized.

Experimental Part

Synthesis

Monomer Synthesis

The synthesis of monomers **M1** and **M2** has been published in previous papers.^[17,18] Monomer **M3** was synthesized according to the procedure presented in Figure 1.

Preparation of acid **3**

4-(acryloyloxyhexyloxy)-3-chlorobenzoic acid **3** was prepared from 3-chloro-4-hydroxyacetophenone using a similar method to that described elsewhere.^[16,17]

¹H NMR (CDCl₃): δ = 8.12 (s, 1H, ortho to -Cl), 7.98 (dd, 1H, para to -Cl), 6.95 (d, 1H, meta to -Cl), 6.10 (dd, 1H, =CH-), 5.81 and 6.40 (d + d, 2H, CH₂=), 4.18 (t, 2H, COOCH₂), 4.10 (t, 2H, CH₂OAr), 1.40–1.90 (m, 8H, CH₂).

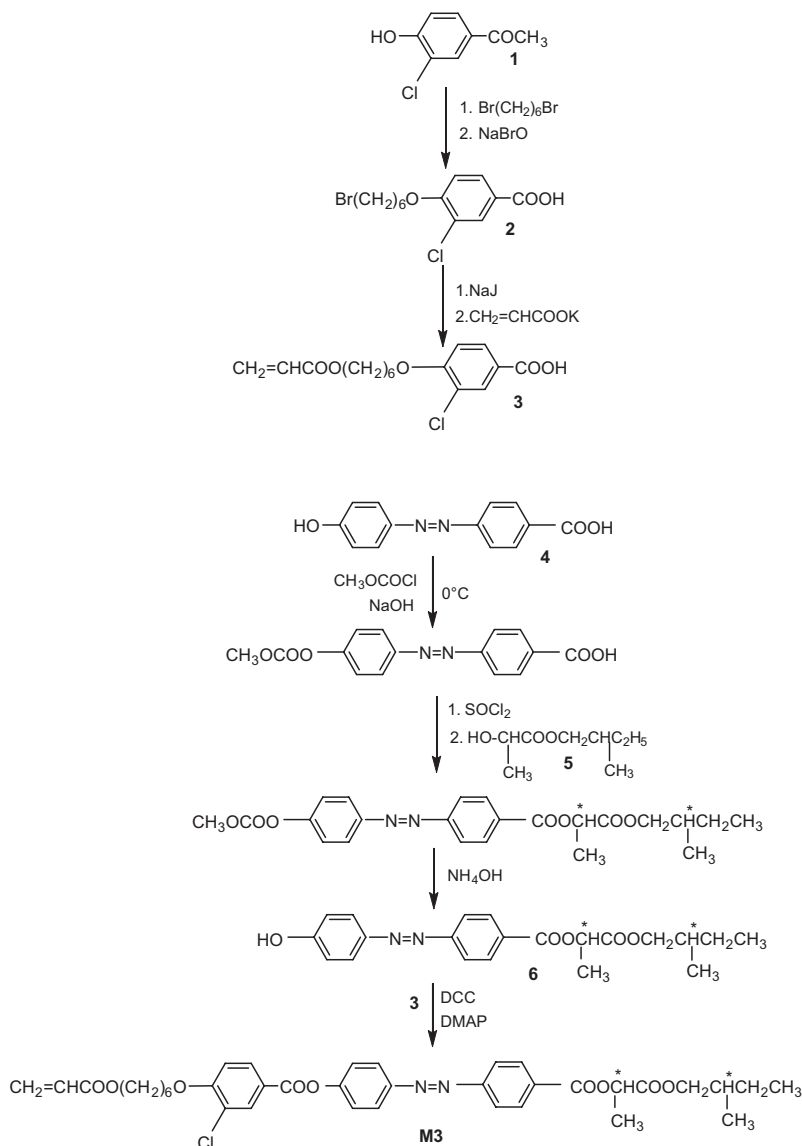
Preparation of Mesogenic Phenol **6**

Acid **4** was protected by methyl chloroformate and transferred into the acyl chloride using thionyl chloride. Thionyl chloride was evaporated in vacuo and the crude acyl chloride was reacted with 2-methylbutyllactate in pyridine/dichloromethane solution for 24 h under reflux. (S)-2-methylbutyl-(S)-lactate **5** was prepared according to a method described elsewhere.^[19] The reaction mixture was poured into water, extracted using diethylether, washed with dilute hydrochloric acid and evaporated. The product was stirred in a mixture of tetrahydrofuran and ammonia at room temperature. The reaction was monitored by TLC on silica gel. After completing the reaction, the obtained solution was poured into water and extracted using diethylether several times. The solvent was evaporated and crude mesogenic phenol **6** was crystallized from toluene.

¹H NMR (CDCl₃): δ = 8.17 (d, 2H, ortho to -COO), 7.75–7.85 (dd, 4H, ortho to -N=N-), 6.90 (d, 2H, ortho to -OH), 5.36 (q, 1H, *CHOCO), 4.03 (m, 2H, CH₂O), 1.68 (d, 3H, CH₃C*OCO), 1.70 (m, 1H, CH₂C*H), 1.20 and 1.40 (m, 2H, CH₂C*), 0.90 (m, 6H, CH₃).

Preparation of Monomer **M3**

The final product **M3** was obtained by condensation of acid **3** and mesogenic phenol **6** in dichloromethane/tetrahydrofuran solution in the presence of dicyclohexylcarbodiimide as a condensation agent and dimethylaminopyridine as a catalyst. The details are described elsewhere.^[17] The crude product was purified by column chromatography under daylight protection. Silica gel (0.063–0.100 mm, Merck) was used as a stationary phase using a mixture (99.8:0.2) of dichloromethane and acetone as the eluent. The product was crystallized twice from methanol. The structure of the final product was confirmed by ¹H NMR (300 MHz, Varian). The chemical purity of materials was checked using high pressure liquid chromatography (HPLC)



■ Figure 1. General procedure for synthesis of **M3** monomer.

using a silica gel column (Biosphere Si 100–5 μm , 4×250 , Watrex) with a mixture of 99.9% of toluene and 0.1% of methanol as an eluent and detection of the eluting products with a UV-Vis detector ($\lambda = 290 \text{ nm}$). The chemical purity was found to be better than 99% under these conditions.

^1H NMR (CDCl_3): $\delta = 8.27$ (m, 3H, ortho to $-\text{COOC}^*$, ortho to $-\text{Cl}$), 8.10 (d, 1H, para to $-\text{Cl}$), 8.05 (dd, 4H, ortho to $-\text{N}=\text{N}-$), 7.41 (d, 2H, ortho to $-\text{OCO}$), 7.02 (d, 1H, meta to $-\text{Cl}$), 6.10 (dd, 1H, $=\text{CH}-$), 5.80 and 6.40 (d + d, 2H, $\text{CH}_2=$), 5.36 (q, 3H, $^*\text{CHOCO}$), 4.20 (t, 2H, COOCH_2), 4.11 (t, 2H, CH_2OAr), 4.03 (m, 2H, $\text{C}^*\text{CH}_2\text{O}$), 1.68 (d, 3H, CH_3C^*), 1.20–1.90 (m, 11H, CH_2CH), 0.90 (m, 6H, CH_3).

Polymerization

Photochromic polymers were prepared by the radical polymerization of the corresponding acrylic monomers in benzene solution in the presence of 2 wt.-% (to monomer) AIBN. After 3 d storage at 65°C , the solvent was evaporated and the solid product was washed several

times using boiling ethanol. The yield of polymerization was about 60–70%. Such a relatively low yield is explained by the competing radical transfer reaction promoted by azobenzene fragments. During the polymer synthesis, a lot of low molar mass products (dimers, short oligomers) are formed. Molecular masses (\overline{M}_w) and polydispersity of polymers ($\overline{M}_w/\overline{M}_n$) as determined by GPC chromatography using the instrument “Knauer” are listed below:

P1: $\overline{M}_w \approx 15\,000$, $\overline{M}_w/\overline{M}_n \approx 1.7$;

P2: $\overline{M}_w \approx 12\,400$, $\overline{M}_w/\overline{M}_n \approx 1.5$;

P3: $\overline{M}_w \approx 9\,900$, $\overline{M}_w/\overline{M}_n \approx 1.6$.

The values of molar masses correspond to a degree of polymerization of about 15–20. Such a low degree of polymerization is explained by the high chain transfer constant to the $\text{N}=\text{N}$ double bond of photochromic monomers. This effect is associated with the formation of a stable hydrazyl radical.^[20,21]

Phase Behavior and Selective Light Reflection

The phase transition temperatures of the monomers and polymers were detected by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-7 thermal analyzer (a scanning rate of $10 \text{ K} \cdot \text{min}^{-1}$).

The polarizing optical microscope investigations were performed using a LOMO P-112 polarizing microscope equipped with a Mettler TA-400 heating stage.

Small-angle X-ray diffraction (XRD) studies were performed using a Bruker Nanostar system ($\text{CuK}\alpha$ radiation, Vantec 2000 area detector, MRI TCPU H heating stage). The wide-angle diffraction was performed on a Bruker GADDS system ($\text{CuK}\alpha$ radiation, HiStar area detector, MRI TCPU H heating stage). In both systems, the temperature stability was 0.1 K .

Samples were prepared in thin-walled glass capillaries with 1.5 mm diameter for the Nanostar or as droplets on a heated surface for GADDS.

For a selective light reflection study, films of polyacrylates were prepared between two glass plates coated with polyvinyl alcohol and rubbed in one direction in order to achieve a good planar alignment. The thickness of the films was pre-determined by $20 \mu\text{m}$ Teflon spacers. Before investigation, the films were annealed over 30 min at a temperature 10°C below the clearing point, followed by a slow cooling down ($1^\circ\text{C} \cdot \text{min}^{-1}$). Transmittance spectra were recorded on a Hitachi U3400 UV-Vis-NIR spectrophotometer.

Photo-optical Investigations

Thin films of the polymers for photo-optical experiments were obtained by a spin-coating technique using solutions of different concentration in chloroform. In order to completely remove any traces

of chloroform, the spin-coated films were kept at room temperature for 1 d. The thickness of the films was estimated using the AFM method (Ntegra, NT-MDT, Russia) and was in range 100 – 500 nm.

Photochemical investigations were performed using an optical set-up equipped with a DRSh-250 ultra-high pressure mercury lamp and a KLM-473/h-150 diode laser (473 nm, $\sim 2 \text{ W} \cdot \text{cm}^{-2}$). To prevent heating of the samples due to the IR irradiation of the mercury lamp, a water filter was introduced in the optical scheme. To ensure a plane-parallel light beam, a quartz lens was applied. Using the filters, a light with the wavelengths 365 and 436 nm was selected. The intensity of the light was measured with a LaserMate-Q (Coherent) intensity meter.

Spectral measurements were performed using a Unicam UV-500 UV-Vis spectrophotometer.

The linearly polarized spectra of the film samples were studied with a TIDAS spectrometer (J&M) equipped with a rotating polarizer (Glan-Taylor prism controlled by a computer program).

The dichroism values, D , of the polymer films were calculated from the spectra using the Equation (1):

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

where A_{\parallel} and A_{\perp} are the absorbance parallel and perpendicular to the preferred azobenzene chromophore orientation direction, respectively.

In order to study the out-of plane photo-orientation phenomena, the angular distribution of the polarized absorbance spectra was measured at an angle of about 45° with respect to the film normal.

Results and Discussion

Phase Behavior and Optical Properties of Planarly Oriented Polymer Films

According to the polarizing optical microscopy observations and DSC studies polymers **P1** and **P2** form LC phases

Table 1. Phase transition temperatures of monomers (**M1-M3**) and respective polymers (**P1-P3**) (in $^\circ\text{C}$) and their transition enthalpies (in parentheses, $\text{J} \cdot \text{g}^{-1}$) measured on cooling ($10^\circ\text{C} \cdot \text{min}^{-1}$).

| Monomer/Polymer | Phase Transitions |
|-----------------|---|
| M1 | Cr 61 (51.0) SmC* 87 (1.6) N* 152 (2.1) I |
| P1 | Cr 127 (5.1) N* 194 (1.8) I |
| M2 | Cr 91 (73.0) SmC* 110 (0.1) TGB _A 112 (0.01) N* 153 (1.6) I |
| P2 | Cr 118 (5.8) SmC* 145 (- ^a) SmA* 154 (0.6) N* 194 (2.3) I |
| M3 | Cr 17 (2.3) SmC* 22 (0.01) TGB _A 57 (0.1) I |
| P3 | Amorphous polymer, $T_g = 26^\circ\text{C}$ |

^a) Enthalpy of phase transition was not detected by DSC - temperature of the phase transition has been detected by polarizing optical microscopy.

with high isotropization temperatures, whereas polymer **P3** is amorphous. This indicates that the introduction of the voluminous chlorine substituent in the aromatic core and increasing the length of the chiral chain (**P3**) completely

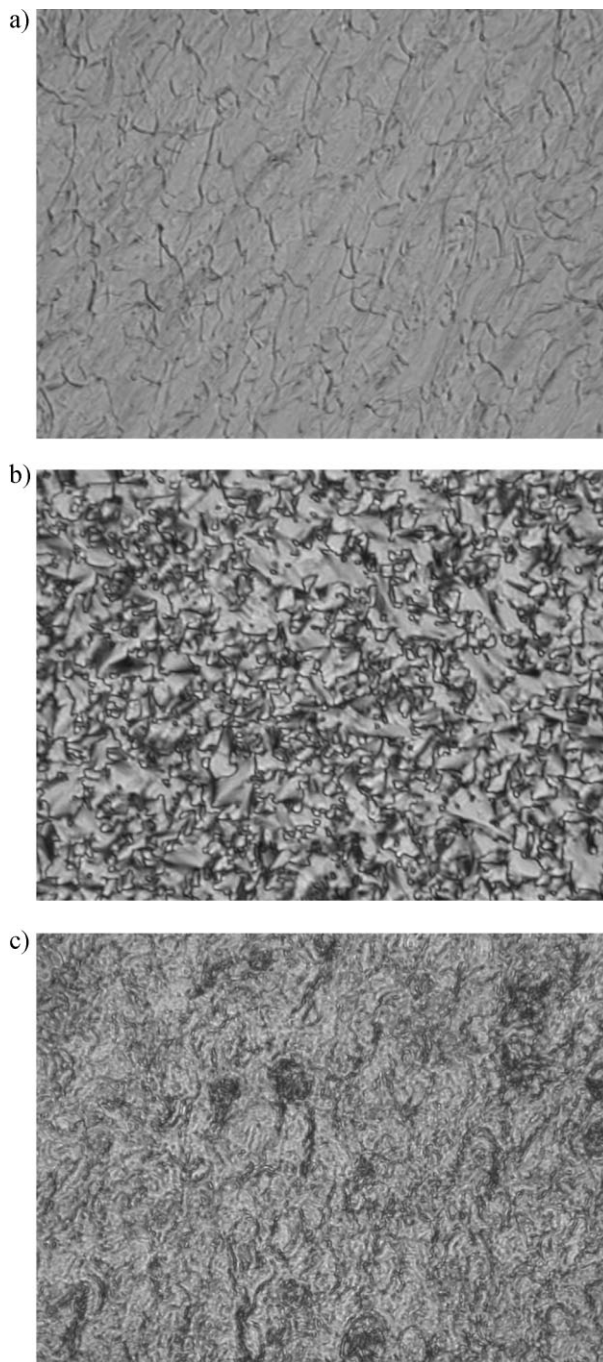


Figure 2. Microphotographs of the textures obtained by polarizing optical microscopy for polymer **P2** (in $12 \mu\text{m}$ thick cell with uniaxially rubbed polyimide coating) showing the oily-streaks texture in the N* phase at 180°C (a), focal conics texture in the SmC* phase at 140°C (b) and non-typical texture of crystalline phase at 90°C (c). Width of the photos is about $300 \mu\text{m}$.

prevent mesophase formation. At low temperatures, both polymers **P1** and **P2** form crystalline phases. Phase transition temperatures and their enthalpies for polymers **P1-P3**, as well as for related monomers **M1-M3**, are shown in Table 1.

For homopolymer **P2**, Figure 2(a)-2(c) show microphotographs of textures in different phases. Focal conic texture in Figure 2(b) allowed us to identify this phase as the SmA* or the SmC*.

According to X-ray investigations, polymers **P1** and **P2** have a crystalline structure at room temperature, characterized by many sharp reflexes at both small and wide scattering angles. The crystalline phases transform to the cholesteric phase in the case of **P1** (at 127 °C) and to the SmC* phase in the case of **P2** (at 118 °C). It was found that interlayer distance in the SmA* phase slightly decreased under heating (Figure 3) and became close to the length of the side group (34–36 Å as estimated using modelling by

Hyperchem software). In the temperature range of the SmC* phase, an increase in the interlayer distance on cooling occurs that might be explained by stretching of the spacers of the side groups.^[22] The width of the small-angle X-ray scattering peak is almost independent on temperature within the whole range of the smectic phases, but extreme growth is seen on heating above 160 °C in the N* phase (Figure 3). This indicates that the layer order fluctuations still exist in the cholesteric phase, but are gradually suppressed under a temperature increase.

Both LC polymers (**P1** and **P2**) display a selective light reflection in the near IR spectral range (see Figure 4). The values of the selective light reflection wavelengths are almost equal for both polymers within a high temperature range of 175–185 °C. Cooling the samples induces helix un-twisting (a shift of selective light reflection to the long wavelength spectral range) that can be associated with the growth of smectic order fluctuations or elements.

Thus, changing the N=N bond position in the side group located closer to the chiral centre leads to a decrease of

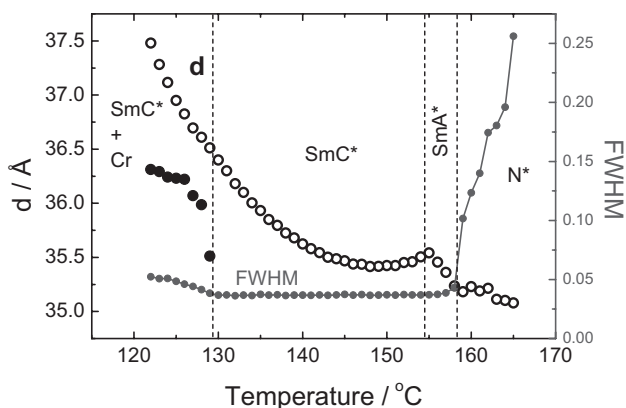


Figure 3. Temperature dependence of interlayer distance (d) and peak half width (FWHM) for polymer **P2**. Phases are indicated.

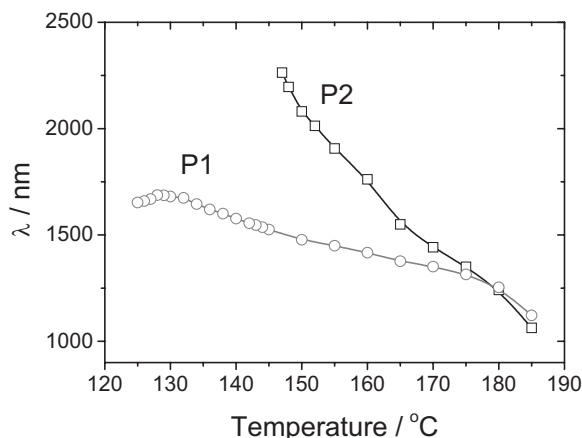


Figure 4. Temperature dependencies of selective light reflection wavelength in the cholesteric phase for planarly-oriented films of **P1** and **P2** polymers.

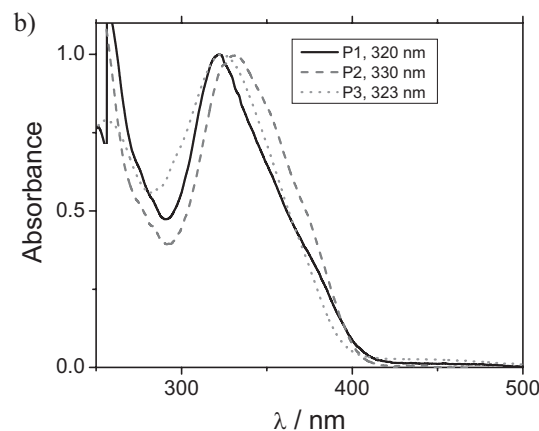
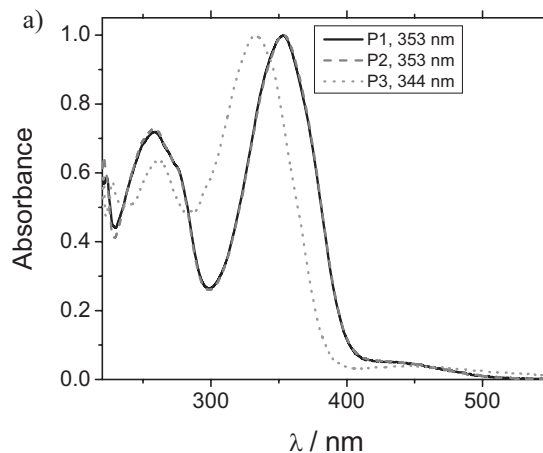


Figure 5. Normalized absorbance spectra of indicated polymers in dichloroethane solution (a) and freshly prepared films (b). The maxima correspond to π - π^* electronic transitions.

the interval of the cholesteric phase existence and an increase in the average pitch of the helix. The temperature dependence of helix untwisting under cooling is much sharper in the case of **P2**. This fact is probably associated with different structures of phases lying below the cholesteric phase: for **P2**, the smectic phase is formed, whereas for **P1** a transition to the crystalline phase takes place.

Absorbance Spectra and Alignment Phenomena in Thin Spin-coated Films of Polymers

Let us first compare the absorbance spectra of solutions and thin amorphous films of polymers obtained by spin-coating. The spin-coating method prevents LC or crystalline phase formation due to very fast solvent evaporation. As a result, isotropic transparent films of all three polymers with thicknesses within the range of 100 – 200 nm were obtained.

As can be clearly seen in Figure 5(a), the absorbance spectra of the solutions of polymers **P1** and **P2** completely coincide, whereas the maximum of the π - π^* electronic transition of the azobenzene chromophore in **P3** is shifted by ca. 10 nm to a shorter wavelength. This shift is probably associated with the difference in nature of the

para-substituent terminal groups linking the azobenzene chromophores with the chiral chain. In the case of **P2** and **P1**, this linkage is an electron donor ester group, whereas for **P3** an ether group has been used. The peak at about 250 nm is related to the π - π^* and n - π^* electronic transitions of phenylbenzoate chromophores. The phenylbenzoate fragment has aromatic C–C and ester C=O groups. The n - π^* transition involving unpaired C=O coincides with the π - π^* transition.

For spin-coated amorphous films of all the polymers, the absorbance peaks are shifted to shorter wavelengths,

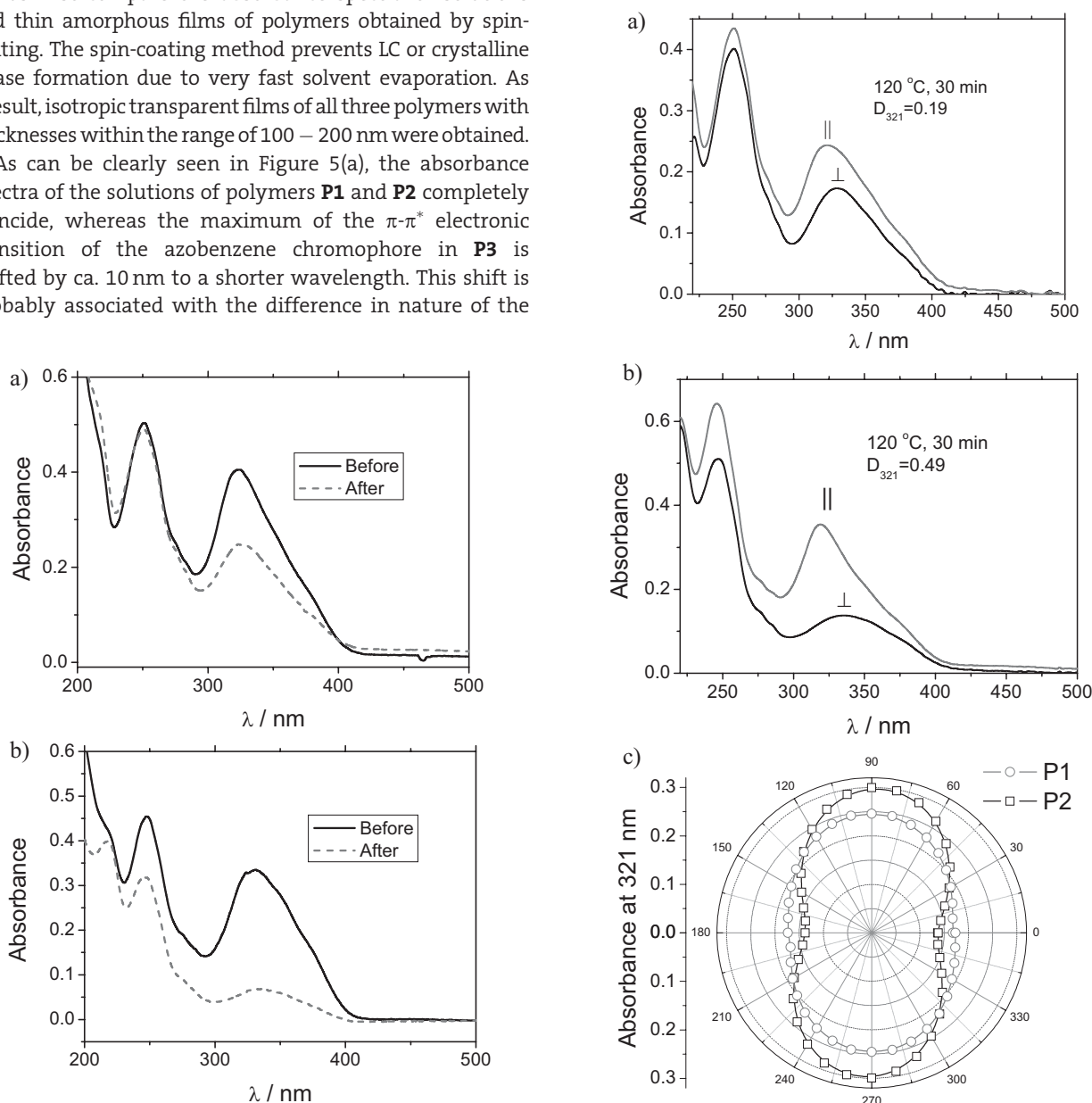


Figure 6. Absorbance spectra of homopolymer **P1** (a) and **P2** (b) before and after annealing (120 °C, 30 min). Thicknesses of the films are 350 ± 15 nm (**P1**) and 300 ± 20 nm (**P2**).

Figure 7. Polarized absorbance spectra measured at 45° with respect to the film normal for annealed films of **P1** (a) and **P2** (b), and corresponding polar plots of both polymers (c).

which can be explained by the formation of H-aggregates consisting of parallel stacks of the azobenzene chromophores (see Figure 5(b)).^[23–25] The shift is more pronounced for **P1**, which indicates the higher degree of aggregation in this polymer (Figure 5(b)).

The annealing of LC polymers leads to a decrease of the absorbance peak (Figure 6) corresponding to the π - π^* electronic transition of azobenzene chromophores. This decrease indicates further aggregation and homeotropic (out-of-plane) alignment of chromophores in a direction along the normal to the film plane. It should be pointed out that the annealing does not change the absorbance peak at ~ 250 nm for the films of **P1** (Figure 6(a)), whereas a significant decrease in absorbance at this wavelength was found for **P2** (Figure 6(b)). The appearance of homeotropic orientation, especially for **P2**, has been confirmed by polarized spectroscopy measurements of the film oriented at 45° towards the direction of the spectrometer beam axis (Figure 7(c)). It is noteworthy that the degree of alignment is higher for polymer **P2**. It can also be clearly seen from the polar plots in Figure 7(c). Such a difference may be associated with the difference in phase behavior of these polymers. At annealing temperature (120°C), polymer **P1**

forms a crystalline phase, whereas **P2** exhibits a smectic phase, which favors homeotropic alignment.^[26–28]

E-Z Photoisomerization Process in Spin-coated Polymer Films

UV-irradiation results in considerable spectral changes in the amorphous films of the studied polymers. As an example, Figure 8(a) shows the absorbance spectra during the irradiation of **P2** film as a function of time. Such spectral changes are induced by E-Z isomerization of the azobenzene chromophores. On the other hand, absorbance of the annealed films is only slightly influenced by UV irradiation (Figure 8(b)). The origin of such differences can be explained using two reasons, namely, a homeotropic alignment of chromophores (low probability of photon absorption) and a decrease in Z-isomer concentration in the annealed films, where the isomerization process is strongly suppressed due to the ordered polymer matrix having a small free volume.

Figure 9(a) and 9(b) show the comparison of isomerization kinetics for the two indicated LC polymers before and after annealing. In both cases, annealing strongly suppresses absorbance changes. For polymer **P2** this difference

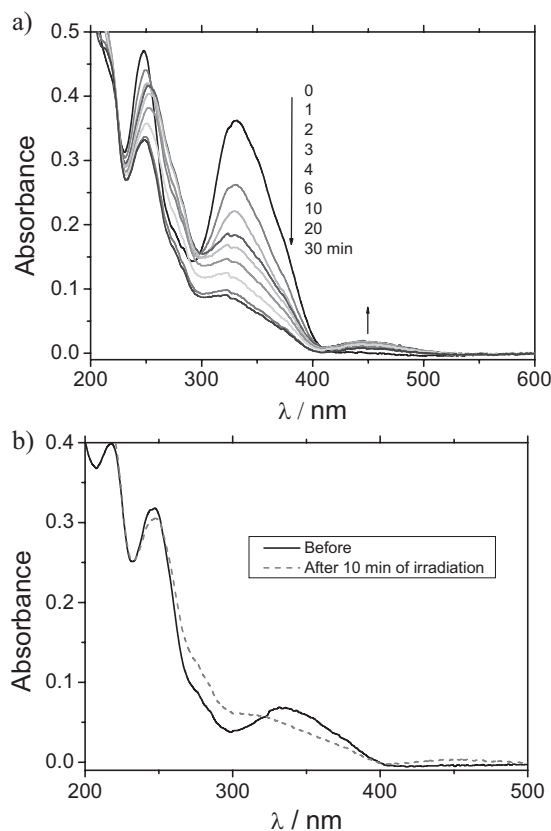


Figure 8. Spectral changes of the fresh (a) and annealed (b) film of **P2** under UV irradiation (365 nm, $2.0\text{ mW} \cdot \text{cm}^{-2}$).

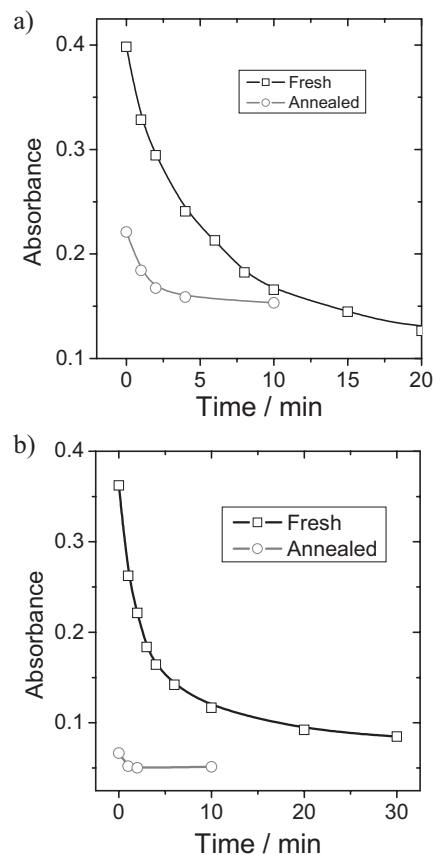


Figure 9. Kinetics of spectral changes under UV irradiation (365 nm). Fresh and annealed films of **P1** (a) and **P2** (b) under the light intensity of $0.9\text{ mW} \cdot \text{cm}^{-2}$ and $2.0\text{ mW} \cdot \text{cm}^{-2}$, respectively.

in kinetics is more evident, which reflects the higher degree of homeotropic alignment in the annealed films.

The annealing of amorphous polymer **P3** has no influence on the isomerization kinetics as it does not lead to any noticeable free volume changes.

Photo-orientation Phenomena in Spin-coated Polymer Films

As can be clearly seen from the polarized absorbance spectra in Figure 10(a) and 10(b), irradiation with blue polarized light from a 473 nm laser induces a strong difference in the polarized absorbance components due to alignment of the azobenzene chromophores (see also polar diagrams in Figure 11). Their orientation becomes perpendicular to the plane of the polarized light. In the case of LC polymers, the degree of photoinduced orientation is higher for fresh films, whereas an annealing before irradiation decreases the photo-orientation degree.

Changes in the polarized absorbance components of amorphous films during irradiation are accompanied by a significant decrease in average, non-polarized absorbance

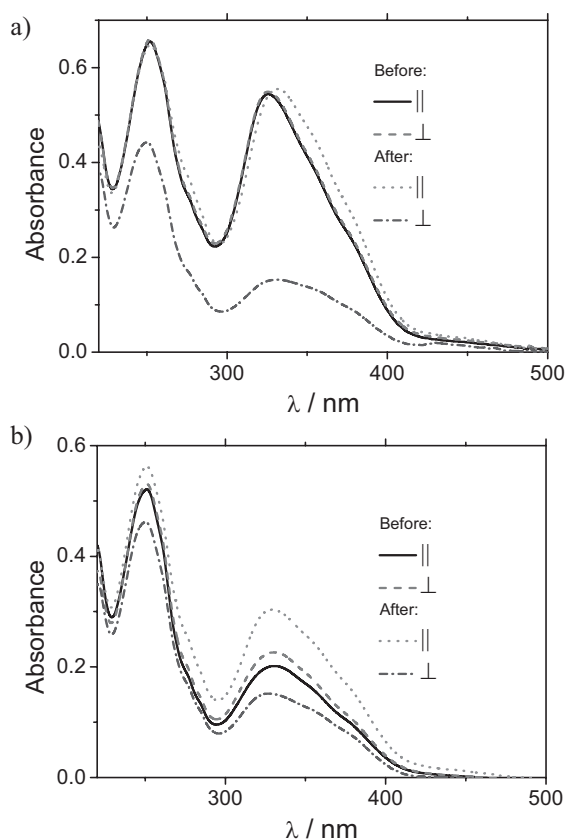


Figure 10. Polarized absorbance spectra of **P1** film before and after irradiation with blue polarized light (473 nm, 20 min). Film thickness is 490 ± 20 nm; measurements were performed before (a) and after annealing (b) at 120°C over ≈ 2 h.

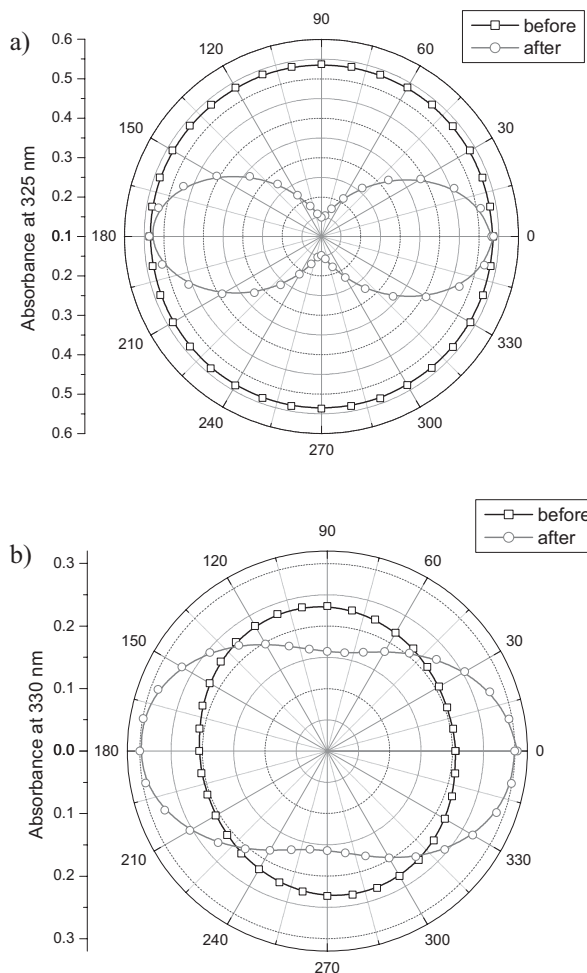


Figure 11. Polar plot of polarized absorbance of **P1** films before and after irradiation with polarized blue light over 20 min: (a) fresh film; (b) after annealing at 120°C over ≈ 2 h.

(Figure 12). This effect is explained by the partial photo-induced homeotropic orientation of chromophores. The same phenomenon has already been observed by us^[27,28] and also by the other authors^[10] for a number of azobenzene-containing polymers. For the annealed film of **P1** this effect is less pronounced (Figure 12(b)) because this film has already exhibited a high degree of homeotropic alignment before irradiation, as discussed above. Conversely, in annealed **P2** films, the non-polarized absorbance increases under irradiation, which indicates partial disruption of the homeotropic orientation (Figure 12(c)). The annealed film of this polymer exhibits a higher degree of the homeotropic out-of-plane orientation compared to **P1** (see discussion above and Figure 7(c)).

The decrease in average absorbance (Figure 12(d)) indicating photoinduced out-of-plane order has been found also for amorphous polymer **P3**.

Figure 13 shows the comparative kinetic curves of dichroism growth for all three polymers before and after

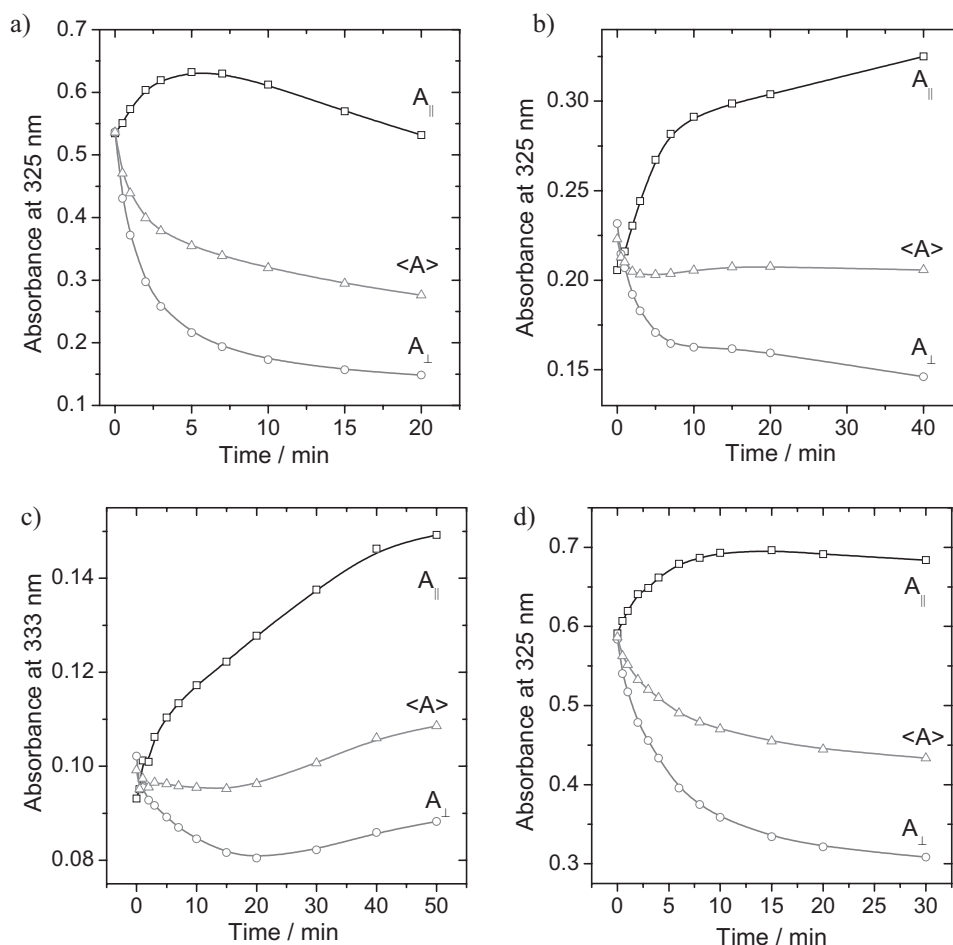


Figure 12. Kinetics of polarized (A_{\parallel} , A_{\perp}) and average non-polarized absorbance ($\langle A \rangle$) changes during irradiation (473 nm) of: **P1** films before (a) and after annealing (b) at 120 °C over ≈ 2 h; (c) annealed film of **P2**; (d) **P3** film.

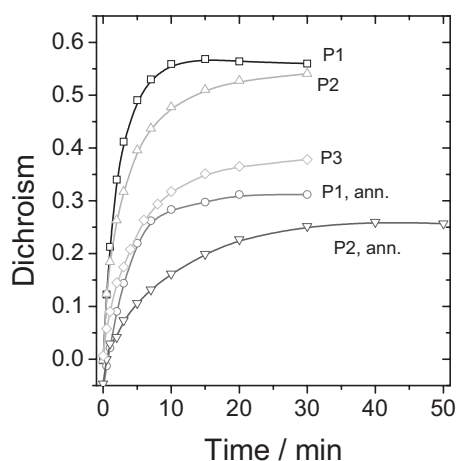
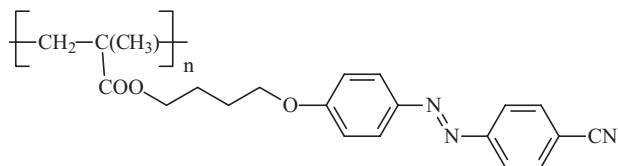


Figure 13. Comparison of dichroism growth kinetics under irradiation with polarized blue light of laser (473 nm) for three polymers before and after annealing.

annealing. The highest values of dichroism and the rate of photo-orientation were observed for amorphous films of mesomorphic polymers **P1** and **P2**. The potential ability to form the LC ordering pre-determines the uniaxial orientation induced by a polarized light. However, the annealing and LC phase formation prevents the photo-orientation process. As is shown above, LC order occurring in the films suppresses E-Z isomerization and the rotational mobility of chromophores, which are necessary for photo-orientation.

Let us compare the kinetics of photo-orientation and the values of dichroism to those studied for the nematic polymer **PAzo4M**,^[29,30] which possesses the cyano-substituent instead of a chiral chain and shorter spacer (Scheme 2).

For amorphous films of the polymer **PAzo4M**, the rate of the photo-orientation process is comparable to that of **P1**, but the value of dichroism is slightly lower (≈ 0.4). The most exciting difference was found for the evolution of photo-induced orientation during the annealing of irradiated



■ Scheme 2. Nematic polymer **PAzo4M**.

films. The annealing of **PAzo4M** increases the dichroism value up to 0.73, due to the well-known gain effect^[11] associated with LC order formation. In contrast, the annealing of oriented **P1** and **P2** films has a completely different effect because of the complete loss of orientation. Such an extreme difference in thermal behavior can probably be explained by the type and symmetry of polymer mesophases. The nematic phase possessing uniaxial symmetry is preferable for the gain effect improving the orientation, whereas the formation under annealing of the helical structures of chiral mesophases leads to breaking of uniaxial symmetry provided by polarized light action.

Careful examination of kinetic curves in Figure 13 for both LC polymers (**P1** and **P2**) shows that the rate of photo-orientation is higher for **P1** for both fresh and annealed films. In other words, the position of the N=N bond in chromophores plays an important role in the kinetics of the process, but does not influence the maximum value of dichroism much.

The rate of photo-orientation and values of dichroism of amorphous polymer **P3** come between the values for amorphous and annealed films of LC polymers. Annealing of this polymer film does not change the kinetics of dichroism growth. Polymer **P3** is amorphous, but nevertheless demonstrates a higher value of dichroism in comparison with other azobenzene-containing amorphous polymers studied before ($D \approx 0.1 - 0.2$).^[31–33] The possible explanation for such a difference may be the following. **P3** consists of a long rigid mesogenic core that may play a crucial role in higher values of dichroism and their stability. We have checked the time stability of photoinduced orientation in all the polymers and did not find a decrease in dichroism values at room temperature at least for one month.

Conclusion

The phase behavior and photo-optical properties of three chiral photochromic azobenzene-containing polymers were comparatively studied. It has been shown that the ability of the LC phase formation has a strong influence on spectral features, aggregation, the kinetics of photoisomerization and photo-orientation. For LC polymers, an annealing of films in the LC state results in strong

aggregation of chromophores and the formation of out-of-plane (homeotropic) orientation. Analysis of dichroism growth kinetics during polarized light action revealed a strong influence of the mesomorphic properties on the rate and maximal value of dichroism, i.e., the photo-orientation process is more pronounced for LC polymers. On the other hand, an annealing suppressed to some extent the photo-orientation process.

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