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Effect of Molecular Structure on Chiro-Optical and Photo-Optical Properties of Smart Liquid Crystalline Polyacrylates

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Supporting Information

ABSTRACT: Comparative study of chiro- and photo-optical properties of three novel chiral photochromic liquid crystalline azobenzene-containing comb-shaped polyacrylates was performed. The synthesized polymers contain the same polyacrylate backbones and uniform spacer size (10 methylene units), but have different structure of azobenzene-containing mesogenic groups with different chiral tail. The polymers are characterized by crystalline, SmA*, SmC*, and N* phases formation depending on chemical structure of the variable fragments. Presence of the lateral chlorine substituent in the mesogen fragment leads to an extreme decrease of isotropization temperature and causes a disappearance of cholesteric mesophase. Circular dichroism (CD) spectra demonstrate formation of helical order elements even in the amorphousized spin-coated polymer films. Possibility of manipulation of CD values and degree of the helical



order by light and annealing was established and studied. UV-irradiation of all polymers induces E-Z isomerization of azobenzene groups and thus disrupting the LC-order. Besides, irradiation of films by polarized light leads to photoorientation process due to cycles of E-Z-E isomerization. As a result, appearance of significant linear dichroism dependent on the relative position of azobenzene moiety in aromatic core was evidenced.

INTRODUCTION

Azobenzene-containing polymer systems are very promising materials from both academical and practical points. Their application in photonics and optoelectronics is very promising owing to their high photosensitivity combined with strong fatigue resistance.¹ They are very interesting because position of absorbance band and photooptical features are predetermined not only by the molecular chromophore structure (presence of different substituents)¹⁻³ but also by the supramolecular structure, for example, by self-assembled liquid crystalline (LC) media forming nematic, smectic and cholesteric phases.⁴ Moreover, E-Z isomerization of azobenzene groups results in changes of their molecular shape and polarity, which usually causes significant structural transformations having impact on phase transitions,⁵⁻⁷ wettability and surface tension modification,⁸⁻¹⁰ and even photoactuation phenomena.¹¹⁻¹⁵

In most cases the action of polarized light on azobenzenecontaining systems induces photoorientation of chromophores perpendicular to the polarization plane of excitation light that can be used for of LC-director reorientation,¹⁶ induction of birefringence and dichroism,¹ preparation of "command surfaces",¹⁷ etc.

In recent years remarkable attention is focused on the study of photoswitchable chiral self-organized systems (i.e., possessing the liquid crystalline behavior see, e.g., refs 18 and 19) or photoinduced chirality induction.^{20–31} For example, chirooptical properties and photoinduced changes in supramolecular organization under light action were studied for a number of chiral-photochromic azobenzene-containing LC polymers having different structure of chiral terminal group. $^{\rm 23}$

Let us point out that similar investigations of photo-chirooptical properties of LC polymers were performed by us earlier.^{29–33} We have also demonstrated a complicated photoand thermoinduced behavior of the azobenzene-containing cholesteric copolymers and found elements of chiral organization even in amorphousized films of cholesteric polymers prepared by spin-coating technique. The E-Z isomerization induced by the UV-irradiation reversibly disrupts the helical superstructure, whereas an annealing of the films leads to more pronounced helical structure formation.^{30,33} In the case of smectogenic copolymers, homeotropic alignment of chromophores and mesogens (with the molecular axis normal to the film plane) is observed.^{31,33}

However, despite a large number of papers devoted to the azobenzene-containing LC systems, there are still a number of questions related to the structure-properties relationship regarding the chiro-optical behavior, mechanism of photoorientation phenomena, etc. Moreover, up to now it is almost impossible to predict the polymorphism type for LC polymer just considering only their chemical structure.

Taking into account the above-mentioned problems in the present paper we continued the study of chiral-photochromic

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LC polymers focusing on their phase behavior, chiro-optical properties, and effect of photoinduced E-Z isomerization on mesomorphism, supramolecular chirality, and photoorientation processes. We have synthesized three polymers (P1, P2, P3) having the same polyacrylate backbone and spacer consisting of 10 methylene units.



Scheme 1. General Procedure for Synthesis of Monomer M3

These polymers have the same azobenzene-containing chromophore fragments, but different relative position of -N=N- and -COO- linkers in respect of the spacer and the chiral terminal group. In polymer P1 -N=N- group is located closer to the spacer, whereas in polymers P2 and P3 azobenzene chromophores are placed near the chiral fragment. Methylbutyl chiral chain was used in polymers P1 and P2 while the lactate based moiety was used in P3 to induce stronger chirality. In addition, polymer P3 has lateral chlorine substituent in ortho position to the spacer. The presence of the lateral substituent and lactate based chiral part allows one to expect the decrease of phase transition temperatures similarly as observed earlier.^{34–36} Also changes in rotational mobility of the side groups in the comb-shaped liquid crystalline polymers can be expected.

In this work we have focused our attention on the study of chiro- and photooptical properties, as well as photoorientation processes in thin spin-coated films of synthesized polymers in order to elucidate an influence of the chromophore chemical structures, polymorphism and film thermal prehistory on their photooptical behavior.



Table 1. Phase Transition Temperatures of Monomers (M1, M2, M3), Respective Polymers (P1, P2, P3) (in °C) and Their Transition Enthalpies (in Parentheses, J/g) Measured on Cooling (10 K/min)

monomer/polymer	phase transitions
M1	Cr 61 (51.0) SmC* 87 (1.6) N* 152 (2.1) I
M2	Cr 91 (73.0) SmC* 110 (0.1) TGBA* 112 (0.01) N* 153 (1.6) I
M3	Cr –23 (1.2) TGBA* 62 (0.4) N* 79 (0.8) I
P1	Cr 127 (5.1) N* 194 (1.8) I
P2	Cr 118 (5.8) SmC* 145 (a) SmA* 154 (0.6) N* 194 (2.3) I
P3	g 15 SmA 70–80 (a) I
^a Enthalpy of phase transition was not detected by DSC; temperature of the phase transition has been determined by polarizing optical microscopy.	

EXPERIMENTAL PART

Synthesis. Synthesis of monomers M1 and M2 was published in our previous papers.^{30,33} Monomer M3 was synthesized according to the procedure presented in Scheme 1.

Preparation of 4-(Acryloyloxydecyloxy)-3-chlorobenzoic acid (3). 3-Chloro-4-hydroxyacetophenone (1) (0.1M; 17.0 g) obtained from ochlorophenol by Friedel–Crafts acylation and subsequent hydrolysis was alkylated by 0.3 M (90 g) of 1,10-dibromodecane in a solution of 6 g of potassium hydroxide in water/dioxane mixture (1:1). The solution was then refluxed for 10 days. After that 500 mL of water was added to the reaction mixture and the mixture was evaporated to half volume to remove dioxane. The cold residue was extracted twice by *n*hexane to remove unreacted dibromodecane.

Acid (2) was obtained by oxidation reaction using NaBrO in dioxane solution at 0 $^{\circ}$ C by usual method. The crude product was crystallized from ethanol, dried and converted into iodide by boiling in sodium iodide/acetone mixture for 6 h. The reaction mixture was poured into water, cooled and separated by suction. Finally, the product was dried in vacuo at 60 $^{\circ}$ C. The yield was 20 g (45%).

Dry potassium acrylate (0.1 M) was dissolved in hot dimethyl sulfoxide and, after cooling down, 19 g of 4-(iododecyloxy)-3-chlorobenzoic acid was added and the mixture was stirred for several days at room temperature. Then the reaction mixture was poured into water, the precipitate was filtered off by suction and washed with dilute hydrochloric acid and water. Crude acid (3) was finally crystallized from acetone and undesirable byproduct (4) was discharged by column chromatography on silica gel. Total yield was 6.5 g (15%).

¹*H* NMR of **3** (300 MHz, CDCl₃). 8.12 s (1H, ortho to -Cl); 7.98 dd (1H, para to -Cl); 6.95 d (1H, meta to -Cl); 6.12 dd (1H, =CH-); 5.81 and 6.40 d + d (2H, CH₂=); 4.18 t (2H, COOCH₂); 4.08 t (2H, CH₂OAr); 1.40–1.90 m (16H, CH₂).

Preparation of Mesogenic Phenol 5. The mesogenic chiral phenol 5 was prepared from (S)-amyllactate using a similar method described elsewhere.³⁷

¹*H* NMR of **5** (300 MHz, CDCl₃). 8.17 d (2H, ortho to -COO); 7.80 dd (4H, ortho to -N=N-); 6.90 d (2H, ortho to -OH); 5.32 q (1H, C*H); 4.18 t (2H, COOCH₂); 1.68 d (3H, CH₃C*); 1.20–1.60 m (6H, CH₂); 0.90 m (3H,CH₃).

Preparation of Monomer **M3**. Final product **M3** was obtained by condensation of acid **3** and mesogenic phenol **5** in dichloromethane/ tetrahydrofuran solution in presence of dicyclohexylcarbodiimide as a condensation agent and dimethylaminopyridine as a catalyst. The crude product was purified by column chromatography under day light elimination. 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 an eluent. Product was crystallized twice from methanol. Structure of final product was confirmed by ¹H NMR (300 MHz, Varian). The chemical purity of materials was checked by high pressure liquid chromatography (HPLC) 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 by a UV–vis detector (λ = 290 nm). The chemical purity was found better than 99% under these conditions.

¹*H* NMR of **M3** (300 MHz, CDCl₃). 8.27 m (3H, ortho to -COOC*, ortho to -Cl); 8.10 d (1H, para to -Cl); 8.00 dd (4H, ortho to -N=N-); 7.41 d (2H, ortho to -OCO); 7.00 d (1H, meta to -Cl); 6.10

dd (1H, =CH-); 5.80 and 6.40 d + d (2H, CH₂=); 5.35 q (1H, *CH); 4.15 m (6H, $2 \times COOCH_2$, CH₂OAr); 1.68d (3H, CH₃C*); 1.20–1.80 m (22H, CH₂); 0.9 t (3H, CH₃).

Polymerization. The polymers were synthesized by a radical polymerization of corresponding acrylic monomers (M1, M2, M3) in benzene solution in the presence of 2 wt % (with respect to monomer) of AIBN. After 3 day storage at 65 °C the solvent was evaporated and solid product was washed several times by boiling ethanol. Yield of polymerization was about 60-70%. Such relatively low yield is explained by competing radical transfer reaction promoted by azobenzene fragment. During polymer synthesis a number of low-molar-mass products (dimers and oligomers) are formed.

Molecular masses (M_w) and polydispersity of polymers (M_w/M_n) , determined by GPC chromatography using instrument "Knauer" had values in the following ranges: $M_w \sim 10000-15000$, $M_w/M_n \sim 1.5-1.7$. Obtained values of molar masses correspond to degree of polymerization of about 15–20. Such low degree of polymerization is explained by the high chain transfer constant to N=N double bond of photochromic monomers. This effect is associated with formation of a stable hydrazyl radical.^{38,39}

Phase Behavior and Selective Light Reflection. The phase transition temperatures of monomers (M1-M3) and polymers (P1-P3) were detected by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 thermal analyzer (scanning rate of 10 K/min).

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

For 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. Thickness of the films was fixed by 20 μ m Teflon spacers. Before investigation the films were annealed during 30 min at temperature 10 K below the clearing point followed by slow cooling down (1 K/min). 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 spin-coating technique using polymer solutions in chlorophorm ($c \sim 20 \text{ mg/mL}$). In order to completely remove any traces of chlorophorm the spin-coated films were kept at room temperature during one day. Thickness of the films was estimated from the UV–vis spectral data as 100–200 nm.

Photochemical investigations were performed using an optical set up equipped with a DRSh-350 ultrahigh pressure mercury lamp and MBL-N-457 diode laser (457 nm, CNI laser). To prevent heating of the samples due to the IR irradiation of the mercury lamp, a water filter was introduced in the optical setup. To ensure the plane-parallel light beam, a quartz lens was applied. Using the filters a light with the wavelengths 365 and 436 nm was selected. The intensities of light were equal to ~2.0 mW/cm² (365 nm), ~1.0 mW/cm² (436 nm) for lamp, and ~0.5 W/cm² for laser.

Spectral measurements were performed using Unicam UV-500 UV-vis spectrophotometer. CD spectra were measured by JASCO J-500C spectropolarimeter.

The studies of photoorientation process were performed using polarized UV/visible spectroscopy. For this purpose the angular dependence (with a step-width of 10°) of the polarized light absorbance was measured using a photodiode array UV/visible

spectrometer TIDAS (J&M) equipped with rotating polarizer (Glan-Taylor prism controlled by a computer).

RESULTS AND DISCUSSION

Phase Behavior and Optical Properties of Planarly Oriented Polymers Films. Mesomorphic properties of the monomers (M1-M3) and related polyacrylates (P1-P3) are shown in Table 1. Three synthesized polymers demonstrate very different phase behavior. Polymer P1 forms only the cholesteric phase and a low temperature crystalline phase, whereas structurally similar polymer P2 exhibits the cholesteric phase and two smectic phases (Table 1). Despite the different polymorphism, clearing temperatures for the both polymers are completely the same (~194 °C). Some details of mesophases structure are considered in our previous paper.³⁷

Cholesteric mesophase of the polymers P1 and P2 possesses the selective light reflection in near IR spectral region (Figure S1 in Supporting Information). Wavelength of the selective light reflection maximum λ_{max} extremely increases under cooling (Figure 1), which is associated with helix unwinding due to increase of smectic order fluctuations under temperature decrease.



Figure 1. Temperature dependencies of selective light reflection wavelength for the polymers and corresponding monomers (M1, M2).

For corresponding monomers (M1 and M2) we have analyzed properties of the selective light reflection and found that they have a similar spectral position of the selective light reflection bands but curves of the temperature dependencies are strongly shifted to the shorter wavelengths (see Figure 1) due to the lower phase transitions temperatures.³⁷ This result allows one to conclude that helical twisting power of chiral fragment is the same for monomer and corresponding polymer, i.e. polymer backbone has no influence on pitch of cholesteric helix but strongly increases the phase transition temperatures. The shift in the phase transition temperatures between polymers and their monomers is about 60 K. For our knowledge, in spite of a large number of papers concerning cholesteric side-chain polymers (see, for review, refs 40 and 41), this is the first direct experimental evidence comparing the selective light reflection properties of homopolymers with corresponding monomers.

Polarizing optical microscopy (Figure 2) and DSC data have revealed that polymer P3 forms only a smectic mesophase. On cooling polymer P3 sample from isotropic melt well-defined "batonettes" are formed typical for smectic phases.⁴² The clearing temperature of this polymer is more than 100 °C lower than that for polymers P1 and P2. Such significant disruption of mesophase thermostability is caused by the presence of chlorine atom laterally substituted on aromatic mesogenic



Figure 2. Polarizing optical microscopy photo of focal conic texture of polymer P3 after annealing at 63 °C for several days. Scale bar corresponds to 100 μ m.

core in polymer P3 (see the models of the polymers side-chain in Figure S2, Supporting Information).

Considering the phase behavior of synthesized polymers, one may conclude that the structure of the mesogenic fragment, namely, the relative position of -N=N- and -COO- linkers and, in particular, the introduction of lateral chlorine substituent plays a crucial role in polymorphism and mesophase thermostability. For the polymer P2 position, the -N=Nbond closer to the chiral terminal group favors smectic phase formation. Introduction of lateral chlorine substituent to the mesogenic group of polymer P3 prevents cholesteric phase formation and strongly decreases its clearing temperature.

Thermo-Optical Properties of Spin-Coated Polymers Films. Absorbance spectra of three polymers were studied on thin amorphousized films prepared by spin-coating technique. As seen in Figure 3 the normalized absorbance spectra are quite



Figure 3. Normalized absorbance spectra of the amorphousized polymer films obtained by spin-coating. Wavelengths of maximum of $\pi - \pi^*$ electronic transition are shown.

similar for all polymers due to similarity of azobenzenecontaining chromophore structures. The absorbance bands at 320-330 nm correspond to $\pi - \pi^*$ electronic transition of azobenzene group. Peaks at ~250 nm are the superposition of $\Phi - \Phi^*$ electronic transition of aromatic cores of azobenzene moieties and $\pi - \pi^*$, $n - \pi^*$ electronic transitions of phenylbenzoate chromophores in the aromatic mesogenic cores of all polymers. Note that latter peak for polymer P3 has lower intensity than for polymers P1 and P2 probably due to the presence of the chlorine substituent bringing about decrease of



Figure 4. Changes of absorbance spectra of the polymers P1 (a), P2 (b), and P3 (c) films under annealing for 30 min at 130 °C (polymers P1, P2) and 70 °C (polymer P3). (d) Polar plot of polarized absorbance measured at 45° to films normal (see Figure S3 in Supporting Information for experimental details).



Figure 5. (a) CD spectra of amorphousized polymers films. (b) CD spectra of P3 film before and after annealing at 70 $^{\circ}$ C for 30 min followed by fast cooling to room temperature.

extinction coefficients of $\pi - \pi^*$, $n - \pi^*$ electronic transitions of the phenylbenzoate chromophores.⁴³

A slight difference in absorbance of polymers **P1** and **P2** having completely the same chromophores can be explained by different degree of aggregation which becomes much stronger after annealing these polymers as demonstrated in Figure 4. Absorbance spectra of diluted solutions of polymers **P1** and **P2** completely coincide (see Figure S3 in Supporting Information).

Annealing of spin-coated films at temperatures above the glass transition⁴⁹ decreases absorbance corresponding to $\pi-\pi^*$ electronic transition of azobenzene group (Figure 4a–c). This effect is related to homeotropic (out-of-plane) orientation of chromophores due to annealing and smectic or crystalline phase formation. Such chromophore alignment was proved by measurements of the polarized absorbance spectra at angle of 45° to film normal (see Figure S4, Supporting Information, for experimental details).

As was shown earlier homeotropic alignment in spin-coated films under annealing is caused by a tendency to normal orientation of mesogens at the air–LC interface and additionally provoked by growth of the smectic (layered) mesophase starting from the surface to films bulk.^{44,45}

It is noteworthy that degree of homeotropic orientation is maximal for polymer **P2** forming smectic mesophase with high transition temperature to the cholesteric phase on heating (Figure 4d, Table 1). Low degree of out-of-plane orientation in smectic polymer **P3** probably can be explained by a lower order parameter of mesogen fragments due to the effect of the lateral substituent.

Summarizing the spectral properties of the polymers one can conclude that phase behavior and thermal treatment of polymer films play a crucial role for optical properties of polymer films reflected in the shape of UV—vis absorbance spectra.

Chiro-Optical Properties of Spin-Coated Polymer Films. Although the just-prepared amorphousized spin-coated films of polymers have no birefringence and do not exhibit light scattering, circular dichroism (CD) spectra show noticeable peaks in the spectral range corresponding to $\pi - \pi^*$ and $n - \pi^*$



Figure 6. Temperature dependences of absolute CD values for annealed films of polymers P1 (a), P2 (b), and P3 (c).



Figure 7. Changes of CD spectra of amorphousized films of polymers P1 (a), P2 (b), and P3 (c) under UV-light (365 nm, 10 min) and subsequent visible light irradiation (436 nm, 20 min).

electronic transitions of azobenzene chromophores (Figure 5). It is noteworthy, that all three polymers in good solvents do not exhibit the Cotton effect and CD signals in the spectral range above 210 nm. Thus, CD peaks obtained for spin-coated films are definitely related to the supramolecular chirality and reflects an appearance of elements of cholesteric order of chromophores even in amorphousized spin-coated films. Presence of elements of cholesteric order in its turn leads to asymmetrical exciton coupling of azobenzene chromophores.⁴⁶

The highest CD values, of both positive and negative signs, are found for polymer P3, whereas for polymers P1 and P2 the CD signal is weaker (Figure 5a). Such difference could be

explained by absence of ordered crystalline phases in polymer **P3** due to the presence of the lateral substituent which increases mobility of side groups providing easier possibility to form chiral superstructures. An annealing of polymer **P3** films, as well as polymers **P1** and **P2** strongly decreases CD values, which is related to the formation of nonhelical phases, crystalline or SmA* structures (Figure 5b). Nevertheless, it is important to stress that coexistence of at least two phases takes place in the annealed films (crystalline and N* for polymer **P1**, crystalline and SmC* for **P2**, and, probably N* and SmA* for **P3**). This assumption comes up because CD values do not become zero even after long annealing time (Figures 5b,6).

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Figure 8. (a) Polarized absorbance spectra before and after 220 s of polarized light irradiation (457 nm, $\sim 0.5 \text{ W/cm}^2$) of amorphousized film of the polymer P1. Spectra were measured for direction of polarized light along and perpendicular to preferred chromophores orientation. (b) Polar diagram of polarized absorbance before and after 220 s of irradiation.

Figure 6 shows temperature dependencies of maximal values of CD (Figure 6a–c) for the studied polymers. Polymers P1 and P3 demonstrate an increase of CD values under heating followed by decrease at approaching to the isotropic phase (Figure 6a,c). For polymer P2 temperature dependence of CD value is more complicated (Figure 6b). In all the cases increase of CD maximum could be related to elements of cholesteric order formation of helically twisted mesophases, N* for polymer P1, and SmC*, and N* for polymer P2. Surprisingly, the same feature is found for polymer P3 exhibiting only the SmA* phase. Probably, some elements of helical order are formed at temperatures between ~55 and 75 °C which cannot be detected by conventional polarizing optical microscopy method (Figure 2).

The complicated character of the temperature dependencies of CD values for polymers **P1** and **P2** can be explained by nonlinear relation between induced CD values and helix pitch as was shown earlier experimentally and theoretically for cholesteric low-molar-mass and polymer systems.^{47,48}

UV irradiation leads to E-Z isomerization of chromophores (see absorbance spectra changes in Supporting Information, Figure S5). This process is accompanied by a significant decrease in CD values for all polymers (Figure 7), which is explained by bent-shaped form of Z-isomer disrupting elements of helical order. For polymer **P2** the CD peak almost disappears (Figure 7b), whereas for polymer **P3** the CD values even change their sign in some wavelength regions (Figure 7c).

Subsequent visible light irradiation changes the ratio between E and Z isomers and increases the concentration of the E-form, inducing partial recovery of CD values (Figure 7).

Thus, the amorphousized spin-coated films of the synthesized polymers are characterized by the Cotton effect with high values of induced CD values, which can be manipulated by the thermal treatment and UV and visible light irradiation. The observed peculiarities allow one to conclude that CD spectroscopy is a powerful tool for detection the chiral supramolecular structure in such polymer systems providing the possibility to detect even traces of helical superstructure and two phase coexistence.

Photoorientation Processes in Spin-Coated Polymers Films. Irradiation of the studied polymers with polarized light of blue laser (457 nm) induces photoorientation process and appearance of a large linear dichroism in spin-coated polymer films (Figures 8 and 9). Polarized light absorbance is much



Figure 9. Kinetic curves of dichroism growth during polarized light irradiation of polymers P1, P2, and P3 (laser 457 nm, ~0.5 W/cm²).

higher for the polarization direction along chromophore orientation (perpendicular to the polarization plane of the excitation laser light). This process is caused by cycles of E-Z-E isomerization, rotational chromophores diffusion eventually leading to their alignment in direction perpendicular to the polarization plane of the excitation light.^{1,17}

Analyzing the polarized absorbance spectra the dichroism values, D, of the polymers films were calculated from the spectra by use of eq 1.

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

where A_{\parallel} is the absorbance of light polarized along the preferred chromophore orientation direction and A_{\perp} is the absorbance perpendicular to this direction.

Comparison of kinetics of dichroism growth revealed that process rate and values of maximal achievable dichroism are much higher for polymer P1 (Figure 9). For polymer P2 having the same chromophore but a different position of the -N=N- bond in the aromatic core, the dichroism growth occurs more slowly and its values is about twice lower than that for polymer P1. Such an extreme difference could be explained only by variation in the position of the -N=N- bond in the position of the -N=N- bond in the photochromic fragment.

The scheme in Figure 10 illustrates a possible reason in the difference of the photoorientation process efficiency. As mentioned above photoorientation takes place due to the cycles of E-Z-E isomerization and therefore the shape of the Z-isomer plays a key role in this process. As clearly seen in

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Figure 10. Comparison of polymers P1, P2, and P3 side-chain idealized models (in *Z*-form). Length and "width" of side groups as well as anisometry ratio is also depicted.

Figure 10, anisometry of Z-form of side group in polymer P1 is lower than that of polymers P2 and P3. The spacers consisting of methylene units have higher flexibility in comparison with the mesogenic core, but connection to the polymer backbone significantly diminishes their mobility. Thus, Z-isomeric side groups in polymer P1 having lower anisometry have stronger influence on their polymer environment providing more free volume for the rotational diffusion after back Z-E isomerization and resulting in more effective reorientation in comparison with polymers P2 and P3.

Introduction of lateral substituent results in further decrease of rate of dichroism growth (polymer P3) due to disruption of photoinduced orientational order by decrease of the chromophores anisometry (in *E*-form).

Annealing at temperatures higher than the glass transition temperature of all polymers leads to a complete dichroism disappearance due to homeotropic alignment and formation of polydomain structures of ordered phases as discussed in previous sections.

It is noteworthy that induction of dichroism is accompanied by the appearance of photoinduced birefringence, which can be used for the photopatterning (Figure 11). The recorded image is stable during at least several months at room temperature.

CONCLUSIONS

The study of phase behavior, chiro-optical properties, and photoorientation processes in three novel chiral-photochromic



Figure 11. Polarizing optical microphoto showing spin-coated film of the polymer P1 irradiated through the mask during 10 s (457 nm); scale bar corresponds to 100 μ m.

liquid-crystalline azobenzene-containing side-chain polyacrylates was performed. Considering the obtained experimental results several important findings can be formulated. (i) Presence of the lateral chlorine substituent in mesogen fragment of the side group leads to an extreme decrease of LC-transition temperatures and complete disappearance of cholesteric mesophase. (ii) Even the amorphousized spincoated polymer films possess the noticeable values of circular dichroism (in the spectral range corresponding to the azobenzene chromophores absorbance) caused by a formation of helical order elements. (iii) The possibilities of manipulation of CD values and degree of helical order by light action or thermal treatment were demonstrated. (iv) It was shown that irradiation of polymer films by polarized light causes photoorientation process accompanied by an appearance of significant linear dichroism.

It should be pointed out that the observed photo-optical phenomena are of considerable interest for possible application of chiral-photochromic polyacrylates in photonics and optoelectronics. In particular, the synthesized polymers could be used as photoactive media for optical data storage with the possibility of nondestructive data reading. Optical recording could be realized by photoinduced local change of birefringence (in the case of polarized light action, see Figure 10) or optical activity modulation (by UV-light action). In the both cases, reading of recorded information could be performed by light with wavelength outside the azobenzene chromophores absorbance band ensuring the absence of erasing during reading.

ASSOCIATED CONTENT

Supporting Information

Figures showing transmittance and absorbance spectra of polymers and molecular models of polymers side chains. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

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REFERENCES

(1) Zhao, Y.; Ikeda, T. Smart Light-responsive Materials: Azobenzenecontaining Polymers and Liquid Crystals; Wiley & Sons: Hoboken, NJ, 2009.

(2) Duer, H.; Bouas-Laurent, H. Photochromism. Molecules and System: Elsevier: Amsterdam, 1990.

(3) Bandara, H. M. D.; Burdette, S. C. Chem. Soc. Rev. 2012, 41, 1809-1825.

- (4) Zebger, I.; Rutloh, M.; Hoffmann, U.; Stumpe, J.; Siesler, H. W.; Hvilsted, S. *Macromolecules* **2003**, *36*, 9373–9382.
- (5) Zupancic, B.; Diez-Berart, S.; Finotello, D.; Lavrentovich, O. D.; Zalar, B. *Phys. Rev. Lett.* **2012**, *108*, 257801.

(6) Dolganov, P. V.; Demikhov, E. I.; Dolganov, V. K.; Bolotin, B. M.; Krohn, K. *Eur. Phys. J. E* **2003**, *12*, 593–597.

(7) Prasad, S. K. Mol. Cryst. Liq. Cryst. 2009, 509, 317-327.

(8) Tylkowski, B.; Peris, S.; Giamberini, M.; Garcia-Valls, R.; Reina, J. A.; Ronda, J. C. *Langmuir* **2010**, *26*, 14821–14829.

(9) Pei, X.; Fernandes, A.; Mathy, B.; Laloyaux, X.; Nysten, B.; Riant,

(10) Kessler, D.; Jochum, F. D.; Choi, J.; Char, K.; Theato, P. ACS

- (10) Ressler, D.; Jochuni, F. D.; Choi, J.; Char, K.; Theato, P. ACS Appl. Mater. Interfaces **2011**, *3*, 124–128.
- (11) Shimamura, A.; Priimagi, A.; Mamiya, J.; Ikeda, T.; Yu, Y.; Barrett, C. J.; Shishido, A. *ACS Appl. Mater. Interfaces* **2011**, *3*, 4190–4196.
- (12) Lee, K. M.; Wang, D. H.; Koerner, H.; Vaia, R. A.; Tan, L.-S.; White, T. J. Angew. Chem., Int. Ed. 2012, 51, 1–6.

(13) Lee, K. M.; White, T. J. Macromolecules 2012, 45, 7163–7170.
(14) Lee, K. M.; Tabiryan, N. V.; Bunning, T. J.; White, T. J. J. Mater. Chem. 2012, 22, 691–698.

(15) Ryabchun, A.; Bobrovsky, A.; Stumpe, J.; Shibaev, V. Macromol. Rapid Commun. 2012, 33, 991–997.

(16) Fischer, T.; Läsker, L.; Stumpe, J. J. Photochem. Photobiol. A: Chem. **1994**, 80, 453–459.

(17) Chigrinov, V.; Kozenkov, V.; Kwok, H.-S. Photoalignment of liquid crystals materials: Physics and application; Wiley-SID series; Wiley: New York, 2008.

- (18) Kašpar, M.; Bubnov, A. M.; Hamplová, V.; Pirkl, S.; Glogarová, M. *Liq. Cryst.* **2004**, *31*, 821–830.
- (19) Novotná, V.; Hamplová, V.; Bubnov, A. M.; Kašpar, M.; Glogarová, M.; Kapernaum, N.; Bezner, S.; Giesselmann, F. J. *Mater. Chem.* **2009**, *19*, 3992–3997.
- (20) Cipparrone, G.; Pagliusi, P.; Provenzano, C.; Shibaev, V. P. *Macromolecules* **2008**, *41*, 5992–5996.

(21) Shibaev, V.; Bobrovsky, A.; Boiko, N. Prog. Polym. Sci. 2003, 28, 729–836.

- (22) Ruiz, U.; Pagliusi, P.; Provenzano, C.; Shibaev, V. P.; Cipparrone, G. Adv. Funct. Mater. 2012, 22, 2964–2970.
- (23) del Barrio, J.; Tejedor, R. M.; Oriol, L. Eur. Polym. J. 2012, 48, 384–390.
- (24) Vera, F.; Serrano, J. L.; De Santo, M. P.; Barberi, R.; Ros, M. B.; Sierra, T. J. *Mater. Chem.* **2012**, *22*, 18025–18032.
- (25) Tejedor, R. M.; Serrano, J.-L.; Oriol, L. Eur. Polym. J. 2009, 45, 2564–2571.
- (26) Sogawa, H.; Shiotsuki, M.; Matsuoka, H.; Sanda, F. Macromolecules 2011, 44, 3338-3345.
- (27) Goto, H.; Ohta, R. Macromol. Chem. Phys. 2010, 211, 2071–2080.
- (28) del Barrio, J.; Tejedor, R. M.; Chinelatto, L. S.; Sanchez, C.; Pinol, M.; Oriol, L. J. *Mater. Chem.* **2009**, *19*, 4922–4930.
- (29) Bobrovsky, A.; Shibaev, V. Polymer 2006, 47, 4310-4317.

(30) Bobrovsky, A.; Shibaev, V. J. Photochem. Photobiol., A: Chemistry 2005, 172, 140–145.

- (31) Bobrovsky, A.; Boiko, N.; Shibaev, V.; Stumpe, J. J. Photochem. Photobiol., A: Chemistry **2004**, 163, 347–358.
- (32) Bobrovsky, A.; Shibaev, V.; Hamplova, V.; Kaspar, M.; Glogarova, M. Monatsh. Chem. 2009, 140, 789–799.
- (33) Bobrovsky, A.; Shibaev, V.; Hamplová, V.; Kašpar, M.; Glogarová, M. Colloid Polym. Sci. 2010, 288, 1375–1384.
- (34) Bubnov, A.; Hamplová, V.; Kašpar, M.; Glogarová, M.; Vaněk, P. Ferroelectrics **2000**, 243, 27–35.
- (35) Kašpar, M.; Hamplová, V.; Pakhomov, S. A.; Stibor, I.; Sverenyák, H.; Bubnov, A. M.; Glogarová, M.; Vaněk, P. *Liq. Cryst.* **1997**, 22, 557–561.

(36) Kašpar, M.; Bilková, P.; Bubnov, A.; Hamplová, V.; Novotná, V.; Glogarová, M.; Knižek, K.; Pociecha, D. *Liq. Cryst.* **2008**, *35*, 641–651.

- (37) Bobrovsky, A.; Shibaev, V.; Bubnov, A.; Hamplova, V.; Kaspar,
 M.; Pociecha, D.; Glogarova, M. Macromol. Chem. Phys. 2011, 212, 342–352.
- (38) Nuyken, O.; Weidner, R. Adv. Polym. Sci. 1986, 73/74, 145-199.
- (39) Hallensleben, M. L.; Weichart, B. Polym. Bull. 1989, 22, 553-556.
- (40) Plate, N.; Shibaev, V. Comb-Shaped Polymers and Liquid Crystals. Plenum Press: New York and London, 1987.
- (41) Boiko, N.; Shibaev, V. Int. J. Polym. Mater. 2000, 45, 533–583.
 (42) Handbook of liquid crystals; Demus, D., Gray, G. W., Goodby, J. W., Eds.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 1998.
- (43) Forbes, W. F.; Sheratte, M. B. *Can. J. Chem.* **1955**, 33, 1829–
- (13) Fores, W. F., Shenare, W. D. ew. J. Color, 1935, 55, 1629 1839.
- (44) Lau, Y. G. J.; Richardson, R. M.; Dalgliesh, R. M.; Zimmermann, H. *Liq. Cryst.* **2007**, *34*, 333–341.
- (45) Lau, Y. G. J.; Klein, S.; Newton, C. J. P.; Richardson, R. M. Liq. Cryst. 2007, 34, 421–429.
- (46) Davydov, A. S. *Theory of molecular excitons*; McGraw-Hill: New York, 1962.
- (47) Iizuka, E.; Chen, G. C. Mol. Cryst. Liq. Cryst. 1984, 111, 237-254.
- (48) Sisido, M.; Narisawa, H.; Kishi, R.; Watanabe, J. *Macromolecules* **1993**, *26*, 1424–1428.

(49) The annealing temperature was selected in order, on one hand, to provide low enough viscosity of polymer films allowing the formation of ordered phases but, on the other hand, to warrant the stability of films and avoid the dewetting.