Functionally Integrated Liquid Crystalline Photochromic Triple Block Copolymer With Locally Light- and Thermal-Controllable Sub-Blocks

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ABSTRACT: Photoorientation and reorientation processes induced by illumination of the samples with oppositely directed polarized light and by the thermal treatment were studied for the films of triblock copolymer $pAzo_{10}$ -b-pPhM₈₀-bpAzo10 consisting of a nematic phenyl benzoate central subblock (PhM, DP = 80) with two terminal smectic azobenzene sub-blocks (Azo, DP = 10). For amorphized films of triblock copolymer, illumination with polarized light ($\lambda = 546$ nm) is shown to be by orientation of only Azo-containing groups, but upon following annealing of the film, PhM groups are adjusted to the orientation of Azo fragments. It was found, that the subsequent illumination of the block copolymer sample with oppositely directed polarized light changes the orientation of azobenzene groups, while the orientation of phenyl benzoate groups is remained unchanged. Thus, the cyclic illumination of

INTRODUCTION Ongoing interest of both academic and applied scientists is focused on the problems of synthesis and characterization of diverse block copolymers which comprise hybrid functionally integrated systems whose macromolecules are composed of differing blocks which can often exhibit quite different properties.¹⁻⁴

Seemingly, one of the reasons behind the keen interest to block copolymers is related to their unique ability to produce microsegregated systems provided by phase separation due to thermodynamic incompatibility of different macromolecular sub-blocks. This behavior of block copolymers is responsible for their ability for self-organization and self-assembly, and for the development of a broad array of periodic and ordered micro- and nanostructures (lamellas, micelles, cylinders, etc.). Their dimensions and morphology are controlled by the chemical nature, length, and mutual arrangement of the constituent sub-blocks.

Presently, most publications are devoted to synthesis and characterization of linear block copolymers.^{3,4} Branched polymers, including side-chain or comb-shaped polymers, are credited as exceptionally convenient objects for the synthesis

the triblock copolymer samples by the linear polarized light and subsequent thermal treatment make it possible to control and fix orientation of azobenzene and phenyl benzoate groups located in different sub-blocks in the desired and independent manner. The comparison of these results with the data on random $p(Azo_7-ran-PhM_{30})$ copolymer of the similar composition revealed, that in the random copolymer, both Azo and PhM mesogenic groups are involved in the orientational cooperative process regardless of films process treatment. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part B: Polym. Phys. **2016**, *54*, 1602–1611

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of liquid-crystalline (LC) block copolymers. The above block copolymers are able to produce an anisotropic LC phase via self-organization of their side groups. These side groups are so-called mesogenic fragments which are similar to the molecules of low-molecular-mass liquid crystals and which are able to produce certain types of mesophases—nematic, smectic, or cholesteric.^{5–8} The number of publications on this particular subject is constantly increasing and most publications address the problems related to design of so-called stimuli-sensitive comb-shaped block copolymers containing photo- and/or electrosensitive groups which can be easily tuned under the external action. This approach offers new advantages for the development of innovative photo-, electro-, and thermo-tunable materials.^{9–11}

Among photochromic LC polymers and LC block copolymers, of special interest is the family of azobenzene-containing macromolecular systems which contain azobenzene groups in their main chain or side branchings of comb-shaped macromolecules. The use of azobenzene chromophores as photosensitive fragments is dictated by several reasons.

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Firstly, azobenzene groups in the *trans*-form (E-isomers) and their derivatives have a rodlike structure and can readily produce diverse types of mesophases.

At the same time, as follows from Figure 1(a), under illumination with UV or visible light anisometric rodlike E-isomer experiences isomerization and concomitant formation of the bent Z-isomer; as a result, the LC phase breaks down. This process is known to be reversible. Hence, illumination with light of different wavelengths or thermal treatment can induce the E-Z-E isomerization via changes in the structural reorganization of polymers.

Secondly, under the action of polarized light on azobenzenecontaining side-chain polymers, their azobenzene fragments located along the polarization plane of the incident beam absorb light and undergo *trans-cis* (E-Z) isomerization. Chromophores aligned perpendicular to vector E of light wave do not experience any light absorbance. As a result of numerous repeated cycles of the *trans-cis-trans* (E-Z-E) isomerization and rotational diffusion of chromophores, azobenzene, and adjacent non-photochromic groups of polymers appear to be involved in their cooperative orientation. Hence, local photoinduced birefringence ($\Delta n > 0$) and dichroism (D > 0) arise [Fig. 1(b)]. Therefore, the above orientational processes can be used for optical data and image recording.^{12,13}

The mechanism of photoorientational processes in diverse azobenzene-containing polymers and copolymers was discussed in detail in numerous publications.^{12–18} The problems related to the synthesis and characterization of photochromic LC comb-shaped block copolymers are reduced to the preparation of diblock copolymers composed of LC and amorphous sub-blocks.

According to our present knowledge, only several articles were devoted to photosensitive comb-shaped block copolymers composed of two LC sub-blocks.^{19–21}

example, diblock copolymers containing For nonphotosensitive biphenyl and photochromic azobenzene mesogenic groups located in different sub-blocks were studied.¹⁹ The authors showed that, upon illumination of the copolymer films by a linearly polarized light, azobenzene groups experience their orientation. Photoinduced orientation of azobenzene groups leads to the orientation of nonphotosensitive biphenyl fragments located in the second subblock or, in other words, orientation proceeds via a cooperative scenario, and this behavior is typical of the formerly studied azobenzene-containing random LC copolymers.¹⁵ Taking into account the fact that diblock copolymers under study experience microphase separation, the above behavior can be explained by the effect of azobenzene-containing subblocks on nonphotochromic sub-blocks at the intermaterial dividing surfaces between the sub-blocks. In Ref. 20, diblock copolymers composed of LC sub-blocks which do not produce self-separated microphase structures were synthesized. However, upon illumination with UV light, these block copolymers experience photoinduced microphase separation



FIGURE 1 Schemes illustrating *E-Z-E* isomerization of azobenzene groups in side-chain photochromic polymers. Red cylinders designate photosensitive azobenzene groups and green cylinders are non-photosensitive mesogen groups (a). Schematic representation of the development of photoinduced anisotropy (Δn and *D*) in azobenzene-containing copolymer films. E is the electric vector of the light wave, n is the director (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

due to «geometric incompatibility» between the Z-isomer of azobenzene groups and the LC phase formed by the subblocks containing non-photosensitive side mesogenic groups.

In Ref. 21, the interplay between effects of mechanical stretching, photoisomerization, and thermal annealing was examined for diblock copolymer bearing biphenyl and photochromic azobenzene mesogenic groups and photosensitive homopolymer. It was shown, that the stretching-induced orientation of the homopolymer on the surface of a supporting poly(vinyl alcohol) film exerts no influence on the azobenzene groups photoinduced reorientation, the direction of which is determined by the polarization of the light. At the same time, the diblock copolymer displays a strong orientation memory effect, that is, regardless of the condition used (photoinduced reorientation or thermal annealing in the liquid crystalline phase), only the initial stretching-induced orientation in the same manner of both azobenzene and biphenyl mesogens can be recovered.

Considering these few examples, it should be emphasized, that the reversibility of photoinduced orientation and reorientation process of photochromic groups in fully LC block copolymers and the possibility to control of local optical properties of individual sub-blocks by illumination in such block copolymers still remains an open questions.

According to these considerations, in this work, we focused our attention to finding conditions under which it is possible to control and fix different orientations of side mesogenic

groups located in the sub-blocks with different chemical nature.

Recently, we proposed a new method for the synthesis of more complex photosensitive LC triblock ABA copolymers composed only of LC sub-blocks and studied their structural features and photochemical properties [Fig. 2(a)].²²

This work presents the results of our studies on photooptical and photoinduced orientational processes taking place in photochromic films based on symmetrical fully LC triblock copolymer which is composed of sub-blocks of the nematic polymer (B) located at the center of the macromolecule and terminal photochromic sub-blocks (A) containing azobenzene side groups (Fig. 2). To gain a deeper insight into the mechanism of photoinduced orientational processes in the above block copolymer, we studied the films based on random photochromic copolymer containing the same components of similar nature and the films based on the photochromic homopolymer [Fig. 2(b)].

Problems related to the character and mechanism of mutual influence of LC sub-blocks on the illumination-induced structural rearrangements of irradiated photochromic fully LC block copolymers are of special interest because these systems can be used in diverse display and photonic devices. Illumination of functionally integrated photochromic block copolymers offers substantial advantages for the development of innovative phototunable materials with locally (at the level of individual sub-blocks) controlled optical characteristics and morphology.

EXPERIMENTAL

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Three photosensitive polymers were chosen in the present study: triblock copolymer, random copolymer and homopolymer (Fig. 2). Homopolymer pAzo₂₀ is able to form only smectic A phase (SmA), random copolymer p(Azo₇-*ran*-PhM₃₀) produce only nematic mesophase (N), whereas block copolymer pAzo₁₀-*b*-pPhM₈₀-*b*-pAzo₁₀ is characterized by the microphase-separated structure where Azo groups are ordered within smectic layers in microphases (cylindrical or spherical form) which are incorporated into the PhM₈₀ nematic matrix.²² Molecular weights and phase behavior of polymers as well as microphase-separated structure of triblock copolymer is represented in more detail in Supporting Information Figure S1 and Table S1.

For photooptical experiments, thin polymer films were prepared by spin-coating from the THF solutions of different concentrations. To remove completely any traces of THF, the spin-coated films were allowed to stay at room temperature for 1 day. Film thickness was about 400 nm for homopolymers and 1.5 μ m for copolymers. These values of film thickness allow to obtain samples with approximately equal absorbance of azobenzene groups independently of polymer composition. Film thickness was measured on a profilometer.

Photochemical studies were performed using an optical setup equipped with a DRSh-250 ultrahigh pressure mercury

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FIGURE 2 Schemes illustrating structure of photochromic triblock copolymer, random copolymer, and photochomic homopolymer (a). Chemical formulas of triblock copolymer, random copolymer, and photochromic homopolymer (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

lamp. Light wavelength was 546 nm (interference filter). To prevent heating of the samples induced by the IR irradiation of the lamp, a water filter was used. Light intensity was measured on 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 collected on a TIDAS spectrometer (J&M) equipped with a rotating polarizer (a computercontrolled Glan-Taylor prism).

Dichroism, *D*, of the polymer films was calculated from the spectra through the following equation:

$$D = \frac{A_{\perp} - A_{\parallel}}{A_{\perp} + A_{\parallel}} \tag{1}$$

where A_{\parallel} and A_{\perp} stand for optical absorbance at 422 or 260 nm upon illumination with a linearly polarized light along the directions parallel and perpendicular to the exciting light polarization direction (546 nm), respectively.

RESULTS AND DISCUSSION

Photoorientational and Photoreorientational Phenomena in Amorphized Polymer Films

As far as all photochromic polymers under investigations are characterized by the different types of mesophase, the values of glass and isotropization temperature, usually their photooptical and photoorientational properties are being studied on the amorphized samples obtained by spin-coating method. Using this method the thin films with thickness 0.4–1.5 μ m were prepared from the THF solutions followed by THF removing. Spectra of the freshly prepared amorphized films of all polymers are presented in Supporting Information Figure S2.

Illumination of the amorphized polymer films with the linearly polarized light leads to the photoorientation of azobenzene groups and their alignment perpendicular to the light polarization plane [similar to photoorientation of azobenzene fragments in Fig. 1(a)].

Let us consider in more detail the kinetics of changes in normalized optical densities $A^*_{||}$ and A^*_{\perp} at the wavelength corresponding to the absorbance of azobenzene groups ($\lambda = 422$ nm) upon illumination with the linearly polarized light defined as

$$A_{\perp(||)}^* = A_{\perp(||)} / A_{\text{initial}}$$
⁽²⁾

and average absorbance A_{av}^* defined as

$$A_{\rm av}^* = (A_{\perp}^* + A_{\parallel}^*)/2 \tag{3}$$

where A_{\parallel}^* and A_{\perp}^* stand for optical densities of the film measured along parallel and normal directions of the probe beam polarization, respectively (relative to the exciting beam polarization plane).

For all polymers, as the component $A_{||}^*$ decreases, the component $A_{||}^*$ increases by the same absolute value (Fig. 3).

For homopolymer pAzo₂₀, random copolymer p(Azo₇-*ran*-PhM₃₀), and block copolymer pAzo₁₀-*b*-pPhM₈₀-*b*-pAzo₁₀, a somewhat disproportional decrease in component $A_{||}^*$ as compared with component A_{\perp}^* is likely to be related to the formation of *cis*-isomers of azobenzene groups upon illumination.

Therefore, upon illumination of the films based on $pAzo_{20}$, $pAzo_{10}$ -*b*- $pPhM_{80}$ -*b*- $pAzo_{10}$ and $p(Azo_7$ -*ran*- $PhM_{30})$ polymers with the linearly polarized light, chromophores change their orientation only in the plane of the sample. From the measured optical density, photoinduced dichroism of azobenzene groups of the polymers under study is calculated according to eq (1).

Random copolymer $p(Azo_7-ran-PhM_{30})$ shows the maximum dichroism which is equal to 0.57, and the illumination time is about 5 h. For homopolymer $pAzo_{20}$ and block copolymer $pAzo_{10}-b-pPhM_{80}-b-pAzo_{10}$, photoinduced dichroism is the same and this value is nearly three times lower than that of the films based on the random copolymer but its "induction period" is shorter (Table 1). As was mentioned above, block copolymer $pAzo_{10}-b-pPhM_{80}-pAzo_{10}$ shows a wellpronounced microsegregation, and this observation can be invoked to explain similar values of photoinduced dichroism for block copolymer and homopolymer samples.



FIGURE 3 Kinetics of changes in polarized $(A_{\parallel}^*, A_{\perp}^*)$ and average nonpolarized absorbance (A_{av}^*) upon illumination of polymer films with the linearly polarized light ($\lambda = 546$ nm, I = 1.5 mW/cm²): pAzo₂₀ (a), pAzo₁₀-*b*-pPhM₈₀-*b*-pAzo₁₀ (b), and p(Azo₇-*ran*-PhM₃₀) (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Variations in optical density at the wavelength corresponding to the absorbance of phenyl benzoate groups ($\lambda = 260$ nm) with varying orientation of the scanning beam polarization show that, in the random copolymer p(Azo₇-ran-PhM₃₀), orientation of azobenzene and phenyl benzoate groups proceeds simultaneously [Fig. 4(a)]. This cooperative process is also typical of the earlier studied random azobenzene-containing copolymers.¹⁵



Polymer	Photoorientation		Photoreorientation		
	D _{Azo}	D _{PhM}	D _{Azo}	D_{PhM}	
pAzo ₂₀	0.22	0	-0.22	0	
p(Azo ₇ - <i>ran</i> -PhM ₃₀)	0.57	0.55	-0.15	-0.17	
pAzo ₁₀ - <i>b</i> -pPhM ₈₀ - <i>b</i> -pAzo ₁₀	0.23	0.05	-0.21	-0.05	

TABLE 1 Maximum Values of Photoinduced Dichroism of Azobenzene (D_{Azo}) and Phenyl Benzoate (D_{PhM}) Groups Upon Photoorientation and Photoreorientation of Azobenzene-Containing Polymer Films

The reverse scenario is observed for the film based on block copolymer $pAzo_{10}$ -*b*-pPhM₈₀-*b*-pAzo₁₀ when photoorientation of azobenzene groups is accompanied by a nearly zero dichroism [Fig. 4(b)] at the wavelength corresponding to the absorbance of phenyl benzoate groups (low dichroism of the samples in the UV region is primarily provided by the low absorbance of azobenzene groups within the above spectral interval, Supporting Information Fig. S3).

Therefore, microsegregation in the sample based on triblock copolymer $pAzo_{10}$ -*b*-pPhM₈₀-*b*-pAzo₁₀ due to the block distribution of units along the chain prevents interaction between the sub-blocks with different chemical nature. In other words, in the amorphized film of this copolymer, no cooperative photoorientation occurs.

To gain a deeper insight into the mechanism of reorientational processes taking place in the polymer films under study, the samples were pre-illuminated by a linearly polarized light; then, the samples were illuminated by the light with the polarization axis rotated by 90° with respect to that in the first irradiation cycle.

As follows from Figure 5(a), upon illumination of homopolymer $pAzo_{20}$ films, changes in the direction of the polarization plane of the exciting light initially lead to a fast erasing of dichroism induced at the first stage; then, orientation of azobenzene groups is reversed to the perpendicular direction. Similar behavior is observed for block copolymer $pAzo_{10}-b$ $pPhM_{80}-b$ - $pAzo_{10}$ [Fig. 5(b)].

Comparing Figure 5(a,b), one can conclude that the rates of dichroism erasure and subsequent orientation of azobenzene groups are nearly the same for both polymers. Let us mention that, for $pAzo_{20}$ and $pAzo_{10}$ -*b*- $pPhM_{80}$ -*b*- $pAzo_{10}$, photo-induced dichroism appears to be the same upon photoorientation and photoreorientation (Table 1).

For both polymers, changes in orientation of azobenzene groups can be performed in the cyclic manner without any loss in the efficiency of this process (Fig. 6). Therefore, the behavior of azobenzene groups of the block copolymer $pAzo_{10}$ -*b*-pPhM₈₀-*b*-pAzo₁₀ and homopolymer $pAzo_{20}$ in the course of photoreorientation appears to be virtually the same. This fact implies that photoorientational processes in azobenzene-containing sub-blocks proceed via the same mechanism as in the individual macromolecules of homopolymer pAzo₂₀. Mesogenic sub-blocks PhM₈₀ exert no effect on

photoinduced processes taking place in azobenzene fragments of the block copolymer macromolecules. As follows from Table 1 and Supporting Information Figure S3, nonphotosensitive phenyl benzoate groups in the films of triblock copolymer $pAzo_{10}$ -*b*-pPhM₈₀-*b*-pAzo₁₀ remain disordered upon photoorientation and photoreorientation processes. This independent behavior of photochromic sub-blocks offers fascinating benefits for local phototuning of their optical characteristics whereas the initial matrix (long macromolecular fragments containing nematogenic phenyl benzoate groups) preserves its initial properties.



FIGURE 4 Polar plots of the polarized absorbance of azobenzene and phenyl benzoate groups for $p(Azo_7-ran-PhM_{30})$ (a) and $pAzo_{10}-b$ -pPhM₈₀-b-pAzo₁₀ (b) polymer films (λ = 546 nm, I = 1.5 mW/cm²). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 5 Kinetics of changes in dichroism of azobenzene groups upon photoorientation and photoreorientation under the action of polarized light ($\lambda = 546 \text{ nm}$, $I = 1.5 \text{ mW/cm}^2$) for the films of pAzo₂₀ (a), pAzo₁₀-*b*-pPhM₈₀-*b*-pAzo₁₀ (b), and p(Azo₇-*ran*-PhM₃₀) (c). The negative sign of dichroism indicates that the orientation direction of chromophores is perpendicular to that achieved at the first irradiation cycle. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]

For the films of the random copolymer $p(Azo_7-ran-PhM_{30})$, the situation is different. In this case, when orientation of the exciting light polarization plane is changed from parallel to perpendicular, photoinduced dichroism is erased [Fig. 5(c)], as was observed for homopolymer $pAzo_{20}$ [Fig. 5(a)]. However, upon further illumination with the linearly polar-

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ized light, a lower dichroism is induced; in this case, optical density of the sample decreases at the normal beam incidence. This behavior indirectly indicates the development of a homeotropic orientation of the side groups in the sample.

The measurements of optical density of the film upon the inclined beam incidence of the spectrometer make it possible to identify the homeotropic orientation of chromophores.¹⁶ These measurements proved (Supporting Information Fig. S4) the development of the homeotropic orientation of azobenzene groups in the course of photoreorientation.

Therefore, photoreorientation in the film of the random copolymer $p(Azo_7$ -*ran*-PhM₃₀) is accompanied by the cooperative effect and by the development of the homeotropic orientation of the side groups which prevent high photoinduced dichroism.

Effect of Annealing Temperature on Photoinduced Dichroism

As was shown in our earlier publications and in the publications by other authors, heating of azobenzene-containing photooriented films of homopolymers and copolymers is often accompanied by so-called "gain-effect".²³⁻²⁷ This effect is related to the oriented growth of the LC phase in the photooriented sample; as a result, ordering of mesogenic groups is enhanced, and dichroism of the sample increases. To study the effect of temperature on dichroism of the copolymers under study, we selected the temperature interval for annealing from room temperature (when all polymers exist in the glassy state) up to the melting temperature of the LC phases of the polymer films. To achieve the equilibrium state, the samples were annealed at each temperature for 30 min; then, the samples were quickly cooled down to 0°C and spectroscopic measurements were conducted. Due to the development of homeotropic orientation in homopolymer



FIGURE 6 Changes in dichroism of azobenzene groups upon cyclic irradiation of $pAzo_{20}$ and $pAzo_{10}$ -*b*- $pPhM_{80}$ -*b*- $pAzo_{10}$ films by the linear polarized light with different directions of their polarization ($\lambda = 546$ nm, I = 1.5 mW/cm²). [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]



FIGURE 7 Changes in dichroism of the photooriented copolymer film $p(Azo_7-ran-PhM_{30})$ upon annealing at various temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

 $pAzo_{20}$ films upon annealing above glass transition temperature, the temperature dependence of induced dichroism was not studied.

As follows from Figure 7, upon annealing of the photooriented sample of the random copolymer $p(Azo_7-ran-PhM_{30})$, dichroism only slightly increases. At the same time, growth of dichroism of the groups with different chemical nature— D_{Azo} and D_{PhM} is clearly observed, that testifies the cooperative mechanism of orientation.

Upon annealing of the illuminated films of the block copolymer $pAzo_{10}$ -*b*-pPhM₈₀-*b*-pAzo₁₀, dichroism increases with increasing annealing temperature [Fig. 8(a)].

However, maximum dichroism of azobenzene groups is somewhat higher than that of phenyl benzoate groups. The difference in dichroism of azobenzene and phenyl benzoate groups is also observed upon annealing of the photoreoriented film of the block copolymer pAzo₁₀-*b*-pPhM₈₀-*b*-pAzo₁₀ [Fig. 8(b)]. In both cases, maximum dichroism of phenyl benzoate units (D_{PhM}) is nearly equal to 0.60; for azobenzene groups, $D_{Azo} = 0.75$. Let us also mention that, for photooriented and photoreoriented films, the dependences of dichroism D_{PhM} and D_{Azo} on the annealing temperature appear to be nearly the same.

The above results concerning the effect of the annealing temperature on photoorientational behavior of block copolymer make it possible to propose the mechanisms of the underlying processes and to present a structural phase model explaining their orientational behavior upon annealing of polymer films.

Block copolymer pAzo₁₀-*b*-pPhM₈₀-*b*-pAzo₁₀ is characterized by the microphase separated structure when azobenzene groups produce locally separated microphases in the continuous nematic matrix composed of phenyl benzoate groups (Supporting Information Fig. S1). Upon annealing of the photooriented film of the block copolymer pAzo₁₀-*b*-pPhM₈₀-*b*-pAzo₁₀ above its glass transition temperature, azobenzene-containing fragments that produce microphases serve as "commanding surfaces",²⁸ which control orientation of phenyl benzoate groups through intermaterial dividing surface of microphases formed by azobenzene and phenyl benzoate fragments. A somewhat higher dichroism of azobenzene groups is provided by a higher ordering of the formed smectic mesophase as compared with the nematic phase of phenyl benzoate units.

Let us mention that, due to the presence of microphaseseparated structure in the block copolymer pAzo₁₀-*b*-pPhM₈₀-*b*pAzo₁₀ films, two phenomena can be observed independently: the cooperative effect between phenyl benzoate and azobenzene groups and the cooperative effect between similar groups (azobenzene or phenyl benzoate groups). This is related to the fact that interaction between different groups (the groups with different chemical nature) takes place only at the intermaterial dividing surfaces between microphases.

Specific Features of Photoreorientation in the LC Films Based on Triple Block Copolymer pAzo₁₀-*b*-pPhM₈₀-*b*-pAzo₁₀

Let us consider structural features of photoreorientation under the action of the linearly polarized light for the photooriented films of block copolymer pAzo₁₀-*b*-pPhM₈₀-*b*-pAzo₁₀



FIGURE 8 Changes in dichroism of block copolymer $pAzo_{10}$ -*b*- $pPhM_{80}$ -*b*- $pAzo_{10}$ films upon annealing at various temperatures after photoorientation (a) and photoreorientation (b). The negative sign of dichroism indicates that the direction of orientation of chromophores is perpendicular to the direction at the first irradiation cycle. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 2 Dichroism Values for	or Block Copolymer (pAzo ₁₀ -b-pPhM ₈₀ -b-pAzo ₁₀	Films Under Different External Actions
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		External Action		
Stage	Sample Prehistory	Result	D_{PhM}	D_{Azo}
1	Amorphized film	LPL ^a illumination	0.05	0.23
		Photoorientation		
2	Photooriented film	Annealing ($T = 50$ °C)	0.22	0.23
		Cooperative effect		
3	Photooriented film	Annealing ($T = 120$ °C)	0.57	0.71
		Gain and cooperative effect		
4	Photooriented and annealed ($T = 50$ °C) film	LPL illumination	0.18	-0.13
		Photoreorientation		
5	Photooriented and annealed ($T = 120$ °C) film	LPL illumination	0.49	0.02
		Photoreorientation		

^aLinearly polarized light.

after their annealing at temperatures corresponding to the gain effect or to its absence.

Upon illumination of the block copolymer film after photoorientation and annealing at 50°C (Table 2, Stage 2, no gain effect, only the cooperative effect between phenyl benzoate and azobenzene groups), initial orientation of azobenzene groups is changed by 90° (Table 2, Stage 4, negative sign of dichroism). However, the resultant photoinduced dichroism is two times lower as compared with the corresponding values for the illuminated amorphized film. In this case, dichroism of phenyl benzoate groups remains virtually unchanged.

Quite different behavior is observed for the photooriented films after annealing at 120°C when the cooperative effect between phenyl benzoate and azobenzene groups and the gain-effect occur (Table 2, Stage 3). In this case, as a result of the repeated illumination with a linearly polarized light, dichroism of azobenzene groups decreases down to a nearly zero level and, upon further illumination, no marked changes take place (Table 2, Stage 5). Variations in dichroism of phenyl benzoate groups are negligible as compared with the annealed film.

Therefore, in the annealed films and in the amorphized films, no cooperative effect between azobenzene and phenyl benzoate groups upon photoreorientation takes place or, in other words, upon the illumination with a linearly polarized light, only azobenzene groups change their orientation.

The results illustrating orientational processes taking place in the block copolymer films under the action of polarized light and temperature can be summarized as follows.

Illumination of the freshly prepared amorphized block copolymer $pAzo_{10}-b-pPhM_{80}-b-pAzo_{10}$ film (Fig. 9, I) leads to photoorientation of only azobenzene groups whereas phenyl benzoate groups remain disordered (Fig. 9, II). However, upon subsequent annealing of the photooriented block copolymer $pAzo_{10}-b-pPhM_{80}-b-pAzo_{10}$ film, phenyl benzoate units are adjusted to the orientation of azobenzene groups due to the

cooperative effect (Fig. 9, IV), which can be accompanied by the gain effect at certain temperatures (above 60 °C, Fig. 9, III).

At the same time, feasibility of photoreorientation of azobenzene groups is shown to depend on the annealing temperature. When the photooriented film is annealed at a temperature of 50 °C when only the cooperative effect between phenyl benzoate and azobenzene groups is observed (Fig. 9, IV), the possibility of photoreorientation of azobenzene groups is preserved even though the resultant dichroism is lower ($D_{Azo} = -0.13$, Fig. 9, VI). On the other hand, annealing at 120°C leads to the occurrence of both cooperative and gain effects (Fig. 9, III) but further photoreorientation of azobenzene groups is hindered (Fig. 9, V). Illumination only leads to disordering of azobenzene groups and dichroism of azobenzene groups decreases from 0.71 to 0.02.

Comparing these results with the data shown in Figure 8, one can conclude that, at temperatures above 50 °C, certain mobility of azobenzene groups is activated and this evidence suggests that the glass transition temperature of azobenzene subblocks is about 50-60 °C. Hence, the observed phenomena can be explained as follows. When the photooriented film is annealed at temperatures below 50 °C, only devitrification of phenyl benzoate sub-blocks takes place ($T_{\rm g} \sim 30$ °C), nematic LC phase is formed, and only cooperative effect is observed whereas azobenzene sub-blocks still exist in the amorphized state. Annealing at temperatures above 50 °C leads to devitrification of both sub-blocks, formation of the corresponding LC phases, and development of the cooperative effect and gain effect. Formation of a sufficiently ordered smectic mesophase A by azobenzene sub-blocks in the film annealed at temperatures above 50 °C can serve as the reason prohibiting the development of photoreorientational processes.

The expected glass transition temperature of sub-blocks appears to be somewhat lower than the glass transition temperature of azobenzene-containing homopolymer $pAzo_{20}$ ($T_g = 75$ °C). Nevertheless, on the one hand, within the





FIGURE 9 Schematic representation of photoreorientation processes in the films of block copolymer pAzo₁₀-*b*-pPhM₈₀-*b*-pAzo₁₀ after annealing at different temperatures. The fragment illustrating structural rearrangements induced by photoreorientation and annealing in the sample is presented. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

oligomeric interval, glass transition temperature is known to depend markedly on the degree of polymerization.²⁹

On the other hand, the temperature of transitions of subblocks in the block copolymers can be appreciably different from that of individual homopolymers.^{30,31} Let us mention that the DSC measurements are unable to trace the glass transition temperature of azobenzene-containing sub-blocks.

Therefore, in block copolymer $pAzo_{10}$ -*b*-pPhM₈₀-*b*-pAzo₁₀, thermal annealing and illumination with the linearly polarized light makes it possible to control and fix different orientations of side groups located in the sub-blocks with different chemical nature.

CONCLUSIONS

Specific features of photoorientational processes were studied for the films based on azobenzene-containing side-chain fully liquid crystalline triblock copolymer composed of a nematic phenyl benzoate central sub-block (PhM, DP = 80) with two terminal azobenzene sub-blocks (Azo, DP = 10). In comparison with the triblock copolymer the photooptical and photoorientational behavior of random copolymer $p(Azo_7-ran-PhM_{30})$ and azobenzene-containing homopolymer $pAzo_{20}$ was examined in detail. For amorphized films of triblock copolymer $pAzo_{10}$ -*b*-pPhM₈₀-*b*-pAzo₁₀, illumination with polarized light is shown to be accompanied by the orientation of only azobenzene-containing sub-blocks, whereas phenyl benzoate groups remain disordered. At the same time, under illumination of the amorphized films of random copolymer, both photochromic and nonphotochromic fragments are involved in the cooperative orientational process.

Upon annealing of photooriented films, dichroism (*D*) increases ("gain-effect") for all copolymers and this effect (the temperature dependence of dichroism growth) is most pronounced for triblock copolymer, where dichroism achieves its maximum level and becomes equal to D = 0.6 and D = 0.75

for sub-blocks of PhM and Azo, respectively. In other words, upon annealing of the oriented triblock copolymer film, PhM groups are "adjusted" to the orientation of Azo fragments.

Special attention is focused on the consideration of photoreorientational processes in block copolymer. It was found, that behavior of azobenzene groups of both block copolymer and homopolymer amorphized films in the course of photoorientation and photoreorientation appears to be the same. However, the values of annealing temperature of preoriented block copolymer films play a certain role in the photoreorientational processes. If the annealing temperature of such film was above glass transition temperature of azobenzene sub-blocks, the further photoreorientation of azobenzene groups is hindered and the illumination only leads to their disordering and order parameter (i.e., dichroism) decreases. When the preliminary photooriented triblock copolymer film was annealed at a temperature below glass transition point of azobenzene subblocks, the initial orientation of azobenzene groups is changed by 90° under polarized light illumination of the sample with oppositely directed polarized light, while the initial orientation of phenyl benzoate groups is remained unchanged.

Thus, the cyclic illumination of the triblock copolymer sample by the linear polarized light and subsequent thermal treatment offer efficient tool for the controlled orientation of azobenzene and phenyl benzoate groups in desirable directions. This efficient approach can be applied for development of mesogen group orientation direction modulation at nanometer scale in the block copolymer film. The new symmetrical fully LC photochromic triblock copolymers are the first example of block copolymers, in which each subblock is characterized by own specific properties inherent to LC phases and can be photo- and thermo-controlled individually on the nanometer scale. Controlled tuning of local optical properties of individual sub-blocks by illumination and/or thermal treatment make it possible to offer the above photosensitive LC triblock copolymers as promising photo- and thermo-tunable materials for photonics, display technology, and holography.

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