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Photoinduced Orientational Ordering in the Series of Methacrylic Azopolymers

O. N. Nadtoka^{*a*}, O. V. Yaroshchuk^{*b*}, T. V. Bednaya^{*b*}, L. A. Ol'khovik^{*a*}, and V. G. Syromyatnikov^{*a*}

^a Shevchenko National University, Vladimirskaya ul. 64, Kyiv, 01033 Ukraine
 ^b Institute of Physics, National Academy of Sciences of Ukraine, pr. Nauki 46, Kyiv, 03680 Ukraine
 e-mail: nadtokaoksana@ukr.net
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Abstract—Polymethacrylates with side azo fragments containing various end substituents and spacers are synthesized and characterized. Spatial ordering of azo fragments in the series of the synthesized azo polymers under the action of polarized excitation light is studied by the methods of null ellipsometry and polarization spectroscopy. Two types of anisotropy development during photoirradiation are found. In homologs with strong acceptor substituents of azo fragments, biaxial orientational structure can be observed; as the radiation dose is increased, this structure is transformed into a uniaxial structure with a negative order parameter and with an axis parallel to the polarization vector of the excitation light. In this structure, the maximum degree of orientational order is achieved in polymers with high concentrations of azo fragments. In homologs with donor substituents of azo fragments, the initial stages of irradiation likewise lead to the development of biaxial orientation; later, this orientation is transformed into an isotropic distribution. The mode of anisotropy development is controlled by the lifetime of photoisomers of azo fragments.

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INTRODUCTION

Photochromic materials have attracted the attention of researchers as promising media for data recording, storage, and readout in both nonlinear optics and holography [1]. Among these materials, aromatic azo compounds hold a prominent place. The discovery of photochromic characteristics of these compounds, which earlier were primarily used as textile azo dyes, have aroused a new tide of their popularity.

Photochromic transformations in azo compounds are related to the photoinduced trans—cis isomerization of their molecules. During their photoinduced excitation, trans monomers are transformed into the cis form, while the principal absorption band ($\pi\pi^*$ band) demonstrates a marked hypsochromic shift with respect to the corresponding absorption band of trans isomers [2, 3].

Another remarkable property of many known azo compounds (primarily, derivatives of azo benzene) is concerned with their dichroism. Because the transition dipole moment of such molecules is oriented nearly along their long axis, light absorption depends on the angle between this axis and light polarization. Trans isomers of elongated shape are characterized by the maximum absorption dichroism. Cis isomers in the folded state are characterized by a lower dichroism that, to a first approximation, can even be disregarded.

Photoinduced optical anisometry (POA) of azo dyes is based on photochromism and dichroism. This anisometry manifests itself as birefringence and absorption dichroism of the irradiated films. This effect is well pronounced for irradiation with polarized light, even though it can be observed also during the inclined irradiation with a nonpolarized light beam [4, 5].

The mechanisms of POA in azo compounds were studied in detail by Dumont [6, 7]. He analyzed two limiting cases. When the lifetime of cis isomers of azo molecules is long (one minute or longer) and the absorption of excitation light is small (this case is possible when absorption bands corresponding to trans and cis isomers are markedly spaced), the mechanism of angular photoselection comes into play. In this case, anisotropy in the distribution of trans isomers arises owing to the transition of azo molecules, whose long axes are parallel to the polarization of excitation light, into the cis form. As was mentioned above, cis isomers are quasi-isotropic; hence, the initial isotropic distribution of trans isomers becomes anisotropic, and the direction of their preferential orientation is perpendicular to the direction of light polarization.

In the opposite case, when the lifetime of cis isomers is short or they effectively absorb the excitation light, azo fragments repeatedly undergo isomerization transitions during the period of anisotropy development. As a result of the repeated cycles of trans-cistrans isomerization, the molecules change their spatial location and are aligned along the direction perpendicular to the direction of light polarization, because, along this particular direction, their absorption is minimized. This mechanism is coined the *mechanism of reorientation*. In practice, the above mechanisms usually appear to be coupled.

The phenomenon of POA has been initially observed for viscous [8] and solid [9] solutions of azo dyes. In the latter case, the principal attention has been focused on polymer solutions of azo compounds. However, the use of mixed compositions of polymers and dyes has evident disadvantages. Because of the poor solubility of the dyes, the dye content in polymer matrices rarely exceeds 1–5 mol % and loading with higher concentrations of photochromic compounds leads to their phase separation. In such systems, the efficacy of POA is small. Furthermore, the POA-based recording is unstable, a circumstance that does not allow any long-term data recording.

Another situation is typical of polymers containing azo fragments that are chemically linked to macromolecules. In this case, the concentration of added azo dyes in polymer systems can be increased by an order of magnitude, without any loss in their homogeneity. From the standpoint of the efficacy of POA, polymers containing side fragments belonging to the class of azobenzene species appear to be the best. At high concentrations of azo fragments, these polymers often show LC phases. In such systems, the efficacy of POA is exceptionally high (birefringence achieves 0.3) and its stability lasts for many years [4, 5, 10–15].

Photoinduced orientational ordering in polymer films is often assumed to be uniaxial. However, in the general case, this order is biaxial and three-dimensional orientation of optical axes is controlled by the geometry of irradiation. Hence, orientational ordering of side fragments should be studied in a real threedimensional space. A commonly used simplification to a two-dimensional case (ordering in the film plane) does not always reflect a real pattern of ordering of azo fragments.

Recently, we proposed an effective method for studying three-dimensional orientational structures. This method is based on the combination of null ellipsometry and polarization UV spectroscopy [15, 16]. The first technique makes it possible to establish the character of ordering, either uniaxial or biaxial, as well as to ascertain the three-dimensional orientation of axes; the second technique allows determination of the components of the orientational order parameter. which, in the general case, is the tensor value. This approach was applied for studying self-ordering and photoinduced ordering in polyesters containing side azobenzene fragments [17]. This evidence makes it possible to formulate several empirical rules that establish the relationships between the structure of a polymer molecule and tendencies in its photo- and self-ordering. In this case, the fulfillment of the above relationships is not evident for some other classes of polymers.

The objective of this study is to investigate the spontaneous and photoinduced three-dimensional orientation of azo fragments in the three-dimensional space of methacrylic azo polymers. To this end, methacrylic homopolymers and copolymers with side azobenzene fragments containing various end substituents were synthesized.

EXPERIMENTAL

Synthesis and Characterization of Compounds

The structure of monomers of the studied azo polymers is shown below.



Polymers were synthesized by acylation of azo benzene derivatives by methacrylic acid chloroanhydride and subsequent radical polymerization or copolymerization with methylmethacrylate (MMA). The details

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Fig. 1. Optical layout of null ellipsometer.

of this synthesis procedure will be presented in the next section. The structure of the synthesized compounds was confirmed by the corresponding NMR spectra. The glass-transition temperature and molecular mass of the synthesized polymers were determined with the help of DSC measurements and exclusion chromatography, respectively.

Preparation of Films and Irradiation of the Samples

Polymers were dissolved in dichloroethane up to a concentration of 3 wt % and deposited onto molten quartz substrates by ultracentrifugation (1500 rpm, 30 s). The deposited films were annealed at 90°C for 1 h; then, they were allowed to stay at room temperature for 1 day until all solvent traces were evaporated. Film thickness *d* was measured with a profilometer and varied from 300 to 500 nm.

In films, anisotropy was induced by irradiation with UV light from a mercury lamp with $\lambda_{ir} = 365$ nm and I = 4.3 mW/cm². The wavelength band at 365 nm was filtered by an interference band filter. The light was linearly polarized by a Glan prism. The thus filtered beam of the polarized monochromatic light was directed along the normal direction onto the polymer film so that the excitation-light polarization was parallel to film axis x (Fig. 1). Irradiation was performed in several steps and measurements were conducted in between irradiation runs. The total irradiation time was calculated via summing the times of all irradiation runs.

Polarization Spectroscopy. Estimation of the Orientational Order Parameter

Polarization absorption spectra of polymer films were collected in a spectral interval from 250 to 600 nm on an Ocean Optics spectrometer (USA). The samples were positioned perpendicular to the direction of the test polarization light beam from a deuterium lamp in two positions so that both the x and y axes (Fig. 1) were parallel to the polarization of the reference light. In this way, the optical densities at the absorption maximum, D_x and D_y , were measured.

When POA was induced via the mechanism of photoreorientation, the total absorption of the film, $D_t = D_x + D_y + D_z$, before and after each irradiation step should be the same. With the knowledge of the total absorption and measured values of D_x and D_y , it is possible to find absorption component D_z . Let us assume that, at a certain step of irradiation, uniaxial orientation in the film plane is achieved: $D_x = D_z < D_y$. In this case, total absorption $D_t = 2D_x + D_z$; hence, this parameter is controlled only by the experimentally measured values. With the use of D_t , it is possible to calculate D_z for any irradiation dose.

The values of D_x , D_y , and D_z can be used for the calculation of the main components of the tensor of orientational order parameter *S* of azo fragments. For example, component S_{xx} can be estimated through the following equation:

$$S_{xx} = \frac{D_x - 0.5(D_y + D_z)}{D_x + D_y + D_z},$$
(1)

In addition, S_{yy} and S_{zz} can be obtained by cyclic permutations of D_x , D_y , and D_z in this equation. In the case of the uniaxial orientation, for example, along direction x, the order parameter is a scalar value and can be expressed as $S \equiv S_{xx} = -1/2 S_{yy} = -1/2S_{zz}$.

Transmission Null Ellipsometry. Determination of the Type of Orientational Ordering

This method was used for the determination of the orientation of the optical axis and the phase difference both in the film plane and in the perpendicular direction $((n_y - n_x)d$ and $(n_z - n_x)d$, respectively).

Comparison of phase differences helps establish whether an anisotropic film is uniaxial or biaxial.



Fig. 2. Experimental (points) and calculated (curves) dependences $\phi(\theta)$ for poly-II. Curves *1* and *1*' correspond to a nonirradiated film; curves *2* and *2*' correspond to a film irradiated for 10 min. In cases *1* and *2*, the *x* axis in the optical layout (Fig. 1) is vertical; in cases *1*' and *2*', horizontal.

The optical setup of this method is shown in Fig. 1. The polymer film was sandwiched between a crossed polarizer and an analyzer so that the projection of the polarization plane of excitation light on this film (the x axis) was oriented either vertically or horizontally. A plate with a thickness of a quarter-wavelength was placed in front of the analyzer; the plate's optical axis is parallel to the polarization direction of the polarizer. During passage through an anisotropic sample, the linearly polarized light becomes elliptically polarized. The quarter-wavelength-thick plate produces a reverse light-polarization transformation from elliptical to linear. In this case, the direction of linear light polarization after passing the plate is different from the direction of light polarization before the plate. The rotation of the light-polarization plane coincides with the rotation angle of the analyzer in order to provide minimum transmission. Angle ϕ is related to the phase difference in the sample as $\phi = \pi (n_v - n_x) d/\lambda$, where λ is the wavelength of the test light ($\lambda = 628$ nm) and d is the thickness of the sample.

With the use of an inclined incidence of the test beam, $(n_z - n_x)d$ was estimated. To this end, we measured the dependence of analyzer rotation angle ϕ on the angle of incidence of the test beam, θ . These curves are describes by the dependences $\phi(\theta)$ that are calculated for this specific optical setup and for different types of orientations of the optical axis and different phase differences. Figure 2 presents curves $\phi(\theta)$ typical for the films based on the polymers under study.

RESULTS AND DISCUSSION

Synthesis of Monomers

Azo compounds were synthesized according to the classical scheme of dinitrogenation of aniline derivatives and their further azo combination with phenol [18]. The synthesized azo compounds were acylated with methacrylic acid chloroanhydride through hydroxyl group in the presence of triethylamine (see the above scheme), and the corresponding azo monomers were isolated.

4'-methacryloxy-4-nitroazobenzene was synthesized according to the one-step procedure: To a solution of 6 g (0.025 mol) of 4'-hydroxy-4-nitroazobenzene in 75 ml of dry THF in the presence of 4 ml of triethylamine at -5° C and under constant stirring, 3.9 g (0.04 mol) of methacrylic acid chloroanhydride was added dropwise. The reaction mixture was allowed to stay at room temperature for another 3 days; then, this mixture was precipitated in 0.5 l of distilled water. After repeated rinsing with water, the precipitate was filtered, dried, and crystallized from ethanol in the presence of activated carbon. As a result, 5 g of 4'-methacryloxy-4-nitroazobenzene was obtained.

The azo monomers 4'-methacryloxy-4-butoxycarbonylazobenzene and 4'-methacryloxy-4-pentoxyazobenzene were prepared according to similar procedures from 4'-hydroxy-4-butoxycarbonylazobenzene and 4'-hydroxy-4-pentoxyazobenzene, respectively.

4'-(methacryloxy)ethyloxy-4-nitroazobenzene was synthesized in two stages: 6 g (0.025 mol) of 4'-hydroxy-4-nitroazobenzene was dissolved in 50 ml of dry acetone, and equimolar amounts of potassium carbonate and 2-bromoethanol were added. The mixture was refluxed in a boiling-water bath for 40 min and precipitated with 0.51 of distilled water. The bright red precipitate was filtered, dried, and crystallized from ethanol. As a result, 8 g of 4'-(hydroxy)ethyloxy-4-nitroazobenzene was obtained; then, 4'-(hydroxy) ethyloxy-4-nitroazobenzene was methacrylated similarly to 4'-hydroxy-4-nitroazobenzene. 4'-(methacryloxy)hexyloxy-4-nitroazobenzene was synthesized according to a similar procedure, but 6-bromohexanol was used as an alkylating agent.

Characteristics of the synthesized methacrylic azo monomers are presented below.

4'-methacryloxy- 4-butoxycarbonylazobenzene (I). $T_{\rm m} = 336 \text{ K}$; $R_f = 0.57$ (methanol : chloroform : hexane eluent = 0.15 : 1 : 1). ¹H NMR (400 MHz, DMSOd₆); ppm: 7.89 (d, 2H, Ar), 7.73 (d, 2H, Ar), 7.93 (d, 2H, Ar), 6.94 (d, 2H, Ar), 6.34 (s, 1H, =CH₂), 5.90 (s, 1H, =CH₂), 2.10 (s, 3H, -CH₃), 1.72 (m, 9H, C₄<u>H₂</u>). Electron spectrum (ethanol): $\lambda_{\rm max}$: 355, 495 nm.

Found, %: C, 67.40; H, 5.90; N, 7.61.

For $C_{21}H_{22}O_4N_2$

calcd., %: C, 67.38; H, 5.88; N, 7.65.

4'-methacyloxy-4-nitroazobenzene (II). $T_m = 413$ K; $R_f = 0.72$ (methanol : chloroform : hexane eluent =

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Fig. 3. (a, c) Phase differences and (b, d) components of optical density plotted against irradiation time for the films based on (a, b) poly-II and (c, d) poly-V. Irradiation parameters: $\lambda_{ir} = 365 \text{ nm}$, $I = 4.5 \text{ mW/cm}^2$, x polarization. (a, c) (I) $(n_y - n_x)d$, (2) $(n_z - n_x)d$; (b, d) (I) D_y , (2) D_x , and (3) D_z .

0.15 : 1 : 1). ¹H NMR (400 MHz, DMSO-d₆), ppm: 8.43 (d, 2H, Ar), 8.07 (d, 2H, Ar), 8.03 (d, 2H, Ar), 7.40 (d, 2H, Ar), 6.34 (s, 1H, =CH₂), 5.91 (s, 1H, =CH₂), 2.05 (s, 3H, -CH₃). Electron spectrum (ethanol): λ_{max} : 360, 485 nm.

Found, %: C, 61.70; H, 4.16; N, 13.52.

For $C_{16}H_{13}O_4N_3$

Calcd., %: C, 61.74; H, 4.18; N, 13.50.

4'-(methacryloxy)ethyloxy-4-nitroazobenzene (III). $T_{\rm m} = 403 \text{ K}, R_f = 0.72 \text{ (methanol : chloroform : hex$ ane eluent = 0.15 : 1 : 1). ¹H NMR (400 MHz,DMSO-d₆), ppm: 8.37 (d, 2H, Ar), 8.02 (d, 2H, Ar),7.92 (d, 2H, Ar), 7.08 (d, 2H, Ar), 6.28 (s, 1H, (c, 1H,=CH₂), 5.85 (s, 1H, =CH₂), 4.13 (m, 4H, -OCH₂-), $2.00 (s, 3H, -CH₃. Electron spectrum (ethanol): <math>\lambda_{\rm max}$: 366, 490 nm.

Found, %: C, 60.88; H, 4.81; N, 11.85. For C₁₈H₁₇O₅N₃ Calcd., %: C, 60.85; H, 4.79; N, 11.83.

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4'-(methacyloxy)hexyloxy-4-nitroazobenzene (IV). $T_{\rm m} = 345 \text{ K}, R_f = 0.74 \text{ (methanol : chloroform : hexance eluent = 0.15 : 1 : 1). ¹H NMR (400 MHz, DMSO-d_6), ppm: 8.39 (d, 2H, Ar), 8.01 (d, 2H, Ar), 7.93 (d, 2H, Ar), 7.07 (d, 2H, Ar), 6.02 (s, 1H, =CH₂), 5.59 (s, 1H, =CH₂), 4.09 (m, -OCH₂-), 1.9 (s, 3H, CH₃), 1.82 (m, 2H, Ph-O-CH₂-C<u>H₂-), 1.69 (m, 2H, -CO-O-CH₂-CH₂-), 1.52 (m, 2H, Ph-O-(CH₂)₂-C<u>H₂-), 1.47 (m, 2H, -CO-O-(CH₂)₂-C<u>H₂-), 1.47 (m, 2H, -CO-O-(CH₂)₂-C<u>H₂-). Electron spectrum (ethanol): <math>\lambda_{max}$: 370, 490 nm.</u></u></u></u>

Found, %: C, 61.70; H, 4.16; N, 13.52.

For C₂₂H₂₅O₅N₃

Calcd., %: C, 61.74; H, 4.18; N, 13.50.

4'-methacryloxy-4-pentoxyazobenzene (V). $T_m = 345 \text{ K}$; $R_f = 0.73 \text{ (methanol : chloroform : hexane elu$ ent = 0.15 : 1 : 1). ¹H NMR (400 MHz, DMSO-d₆),ppm: 8.21 (d, 2H, Ar), 8.01 (d, 2H, Ar), 7.83 (d, 2H,Ar), 7.33 (d, 2H, Ar), 6.35 (s, 1H, =CH₂), 5.9 (s, 1H,



 $n_x = n_y = n_z$

Fig. 4. Ellipsoids of the refractive indexes for the films based on azo polymers before and after the development of anisotropy by the action of polarized UV light. (a) State before irradiation: a uniaxial film with optical axis z (positive film C). (b) Intermediate stage of irradiation: biaxial film. (c) Saturation state for homologs with an azo fragment containing an acceptor substituent: a uniaxial film with optical axis x (negative film A). (d) Saturation state for homologs with an azo fragment containing a donor substituent: isotropic film.

=CH₂), 4.11(s, 3H, OCH₃), 2.06 (s, 3H, CH₃). Electron spectrum (ethanol): λ_{max} : 350, 500 nm.

Found, %: C, 71.62; H, 6.80; N, 7.93.

For C₂₁H₂₄O₃N₂

Calcd., %: C, 71.59; H, 6.82; N, 7.95.

The synthesized azo monomers dissolve well in DMF, acetone, chloroform, and dioxane. They can be dissolved in ethanol upon heating but remain water insoluble.

Preparation of Homopolymers and Copolymers

Radical homopolymerization of the synthesized monomers was performed in 10% solution of toluene in the presence of AIBN as an initiating agent (1% with respect to the weight of monomer) at 80°C. The polymerization time was 30–90 h. The synthesized homopolymers were purified by repeated precipitation with DMF into methanol and dried at room temperature for several days. The final products were solid powders at room temperature; they can be dissolved in

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benzene, toluene, DMF, and dichloroethane. Copolymerization of methacrylic azo monomer **II** with MMA was performed according to a similar procedure; the polymerization time was 20–30 h.

Table 1 lists the main temperature and molecularmass characteristics of homopolymers and copolymers. All synthesized polymers show only one phase transition, which corresponds to the transition of the polymer from the glassy state to the amorphous state. For all polymers, glass-transition temperature T_g is found to be sufficiently high (above 373 K). This result may be related to the presence of donor or acceptor end substituents in azo fragments, which can interact with the polymer backbone and suppress its mobility. In the presence of an alkyl spacer, T_g decreases, a phenomenon that can be explained by the reduced rigidity of linkages between macrochain and side units. As a result, the degree of freedom of polymer fragments increases.

Introduction of MMA units into the polymer chain of azo polymers decreases its rigidity and thus increases mobility. As a result, T_g of polymers is changed: This temperature is lower than that of the corresponding homopolymers and monotonically decreases as the concentration of azo fragments, c_a , decreases.

As follows from Table 1, the synthesized azo polymers are characterized by a low degree of polymerization, as is typical of oligomer compounds. According to [10, 11, 19], a low degree of polymerization is characteristic of azo polymers prepared by radical polymerization, a situation that is related to the ability of azo groups in azo monomers to serve as "traps" for radicals. As a result, in the course of polymerization, the role of termination and chain-transfer reactions markedly increases. In particular, this conclusion is confirmed by the results on the synthesis of copolymers based on azo monomer II and MMA: As the concentration of azo monomer in the reaction mixture decreases, the molecular mass of copolymers increases.



Fig. 5. Components of order parameter (1) S_{xx} , (2) S_{yy} , and (3) S_{zz} plotted against irradiation time for poly-II calculated from experimental curves $D_{x, y, z}(t)$ (Fig. 3b).

Despite their low molecular masses, the synthesized compounds show good film-forming characteristics and can be successfully applied for studying POA. Similar situation was observed for POA in poly(azoesters) [17].

POA in Homopolymers

During study of the three-dimensional ordering in the synthesized polymers, their behavior can follow two different scenarios, which are controlled by the type of azo fragments. The first scenario is characteristic of homologs containing azobenzene fragment with the acceptor substituent (slightly accepting $COOC_4H_9$ or strongly accepting NO_2) (poly-I, poly-II, poly-III, poly-IV), whereas the second scenario is observed for the homologs with azobenzene fragment containing the donor substituent (OC_5H_{11}) (poly-V).

Let us consider the development of anisotropy through the first scenario for the poly-II homolog and through the second scenario for the poly-V homolog. Figures 3a and 3c show the phase differences for the

Polymer	<i>T</i> _g , K	λ _{max} , nm (in film)	$M_{\rm n} imes 10^{-3}$	$M_{ m w} imes 10^{-3}$	$M_{\rm w}/M_{\rm n}$	\overline{P}_n
Poly-I	396	350	4.5	5.7	1.26	12
Poly-II	434	352	5.6	7.8	1.39	18
Poly-III	386	355	4.1	5.6	1.39	11
Poly-IV	385	362	3.0	4.2	1.38	9
Poly-V	396	348	2.0	2.5	1.24	6
II-co-MMA (50 mol % II)	423	350	5.8	7.9	1.36	
II-co-MMA (35 mol % II)	401	350	6.0	8.1	1.35	
II-co-MMA (15 mol % II)	384	350	6.1	8.2	1.35	
II-co-MMA (5 mol % II)	381	350	7.2	9.5	1.35	

Table 1. Characteristics of homopolymers and copolymers based on methacrylic azo monomers

films based on the above polymers. As is seen in Fig. 3, before irradiation, both cases obey the following relationship for the main refractive indexes, $n_z > n_x = n_y$, a result that suggests a preferential homeotropic orientation of azo fragments.

Optical characteristics of anisotropic films are traditionally compared with the characteristics of standard crystalline phase sheets. Nonirradiated films based on the polymers under study are equivalent to positive film C, which is a slab of a positive uniaxial crystal with the principal axis oriented along the normal direction with respect to this plate. The ellipsoid of the refractive index of this slab is shown in Fig. 4a. This is an ellipsoid of revolution with the long axis directed along normal z to the slab plane.

A common feature of both types of polymers is the fact that their irradiation with polarized light leads to the development of biaxial orientation $(n_x \neq n_y \neq n_z)$ (Fig. 4b). The kinetics of anisotropy development experiences saturation, but the character of this saturation is controlled by the type of polymer. In homologs with an acceptor-containing azobenzene fragment, $(n_y - n_x)d$ and $(n_z - n_x)d$ are compared at saturation; here, the following relationship holds: $n_x < n_y = n_z$. This fact indicates the development of a uniaxial oriented structure, and its optical equivalent is negative slab A, which is based on a negative uniaxial crystal whose optical axis lies in the plane of the sample. For this slab, the ellipsoid of the refractive index is oblate along the direction of optical axis x (Fig. 4c).

In the homologs with the donor-containing azobenzene substituent, saturation implies that $(n_y - n_x)d$ and $(n_z - n_x)d$ tend toward zero. Hence, in the saturation interval, $n_x = n_y = n_z$, i.e., the film is spatially isotropic. Figure 4d shows the ellipsoid of the refractive index for this film.

Figures 3b and 3d show the corresponding kinetic curves illustrating the components of optical density D_i (*i* = *x*, *y*, *z*). Qualitatively, the kinetics of anisotropy development in the poly-II polymer corresponds to the mechanism of photoreorientation; in the poly-V polymer, to the mechanism of photoselection [6, 7]. Usually, in the case of photoreorientation, cis isomers are short-lived species; in the case of photoselection, they are long-lived. Lifetime τ_i (*i* = II, V) of cis isomers in the above polymers was estimated by the analysis of the spectral relaxation at the maximum of the $\pi\pi^*$ band after irradiation with nonpolarized UV light. The relaxation times are $\tau_{II} = 4$ s and $\tau_V > 12$ h. By its order of magnitude, relaxation time τ_{II} corresponds to the mechanism of reorientation, while relaxation time $\tau_{\rm v}$ corresponds to the mechanism of angular selection.

In the case of the poly-II sample, a short relaxation time makes it possible to invoke the method of full absorption for the estimation of component D_z . Figure 3b presents the calculated kinetic curve for D_z . The development of a uniaxial structure is accompanied by a slight decrease in the concentration of azo fragments along the direction normal to the film plane due to the partial reorientation along some other directions. In the saturation state, the following relationship holds: $D_x < D_y = D_z$; in other words, all azo fragments are uniformly distributed in the plane perpendicular to the polarization vector of the excitation light. Hence, the distribution of azo fragments is fully controlled by the geometry of irradiation, a behavior that is different from that observed for polyesters, which show wellpronounced processes of photoinduced self-ordering [17]. This behavior is likely related to higher glasstransition temperatures of azo derivatives of poly(methacrylate) when the self-ordering process is less efficient. Note also the absence of any LC mesophases that dramatically enhance the processes of self-ordering.

Substitution of D_i (i = x, y, z) into Eqs. (1) makes it possible to estimate the principal components of orientational order parameter \hat{S} for a poly-II sample at different irradiation doses. Figure 5 presents the corresponding curves. In the saturation state, azo fragments show negative orientational order, which is characterized by the scalar $S \equiv S_{xx} = -0.07$. Order parameter S_{xx} indicates how well azo fragments are aligned in the plane perpendicular to the polarization vector of the excitation light (the x axis). Prior to irradiation, the films experience uniaxial positive ordering of azo fragments along axis z. This case is characterized by the scalar $S \equiv S_{zz} = 0.06$.

Hence, irradiation of the poly-II polymer films leads to the transformation of the uniaxial structure with a positive orientational order (a thermodynamically favorable structure arising owing to self-ordering) into the uniaxial structure with a negative orientational order (a metastable structure with the symmetry of the light field). All intermediate states are biaxial. In turn, irradiation of polymer V breaks down the orientational order. The cause of this behavior is related to the photoinduced transformation of anisotropic trans isomers into the quasi-isotropic cis form in all directions and not only along the direction of excitation light polarization, as in the first stage of irradiation.

By analogy with poly-II, the order parameter in the saturation state can be calculated for all homologs with azo fragments that contain the acceptor substituent. These data are listed in Table 2. This table shows also the birefringence in the saturation state, $\Delta n = n_y - n_x = n_z - n_x$, and the time required for the attainment of this state, τ_s . These data correspond to films of approximately similar thickness, close to 300 nm. For all materials, the measurements were performed at room temperature or well below the glass-transition temperature. With allowance for this fact and the existence of similar phases in all compounds under study, it seems reasonable to compare the corresponding parameters.

Table 2 shows that the length of the spacer in the side group of azo polymers effects the efficacy of POA, and this efficacy can be estimated from the birefrin-

gence or order parameter; for homologs with an alkyl spacer, the efficacy of POA is somewhat lower than that of homologs without any spacers. In the saturation state, the absolute order parameter decreases with an increase in length of the alkyl spacer, a fact that is explained by an increased mobility of azo chromophores, which activates thermodynamic processes of orientational relaxation. The spacer increases the mobility of polymer fragments, and this mobility increases with an increase in the spacer length. This tendency is confirmed by the depressed glass-transition temperature of polymers. This observation is confirmed also by an early attainment of the saturation stage (Table 2).

Relaxation of the photoinduced state in azo fragments can lead either to their complete orientational disordering (isotropic state) or to an alternative mode of ordering that is more thermodynamically favorable than the first mode. Long axes of rodlike azo fragments are spontaneously oriented along one direction. This type of self-ordering is most pronounced in liquid crystals and in calamitic LC polymers [13, 14]. This self-ordering is characterized by positive orientational order parameter *S*.

Indeed, in azomethacrylates with glass-transition temperature exceeding 400 K, the processes of orientational relaxation cannot dominate in the macrovolume, as occurs in LC azo polymers based on polyesters with low crystallization temperatures [17, 20, 21]. At the same time, local relaxation processes are allowed. These processes are likely to occur in the vicinity of photoexcited azo fragments, because relaxation of their electron excitation is accompanied by a local temperature rise [22], which increases the mobility of molecular fragments. The lower the glass-transition temperature of an azo polymer, the more intensive the above processes.

To ascertain the fact that processes of orientational relaxation (disordering or spontaneous ordering) dominate in the polymers under study, the following experiments have been performed.

The films based on azo polymers with the photoinduced structure that is shown in Fig. 4b were heated to 450 K for 1 h and cooled to room temperature. In this way, we endeavored to model the local temperature rise during the relaxation of photoexcitation energy. After the thermal treatment, the films were studied by the method of null ellipsometry. These studies show that the ellipsoid of their refractive index corresponds to that shown in Fig. 4a. This observation implies that the photoinduced order relaxes down to the initial positive order of films.

Therefore, it may be anticipated that irradiation with light is accompanied by competition between concurrent photoinduced and spontaneous ordering rather than by the competition between photoinduced ordering and disordering. Therefore, the development of negative photoinduced order in azo polymers can be presented as follows. In the vicinity of the azo frag**Table 2.** Order parameter S_x and birefringence $n_y - n_x$ for photo-oriented films of azo polymers in the saturation state and time τ_s for attainment of saturation in $n_y - n_x$

Polymer	$ S_x $	$n_y - n_x$	τ_s , min
Poly-I	0.042	0.115	240
Poly-II	0.067	0.125	150
Poly-III	0.060	0.119	85
Poly-IV	0.051	0.101	60
II-co-MMA (50 mol % II)	0.045	0.081	170
II-co-MMA (35 mol % II)	0.043	0.075	255
II-co-MMA (15 mol % II)	0.038	0.062	360
II-co-MMA (5 mol % II)	0.032	0.041	430

ment supplying the energy of its photoexcitation to the environment, the processes of self-ordering are activated. As a result, clusters of azo fragments with positive orientational order arise. Orientation of the axes of the above clusters is controlled by the geometry of the light field. In the case of the irradiation under study, the axes are distributed in the plane perpendicular to the direction of light polarization. Therefore, macroscopic negative order in the irradiated films is formed owing to the negative ordering of clusters composed of azo fragments with positive orientational order in the light field. The higher the degree of positive ordering of azo fragments in clusters, the higher the degree of photoinduced negative order. In amorphous azo polymers, one can hardly expect a high level of orientational self-ordering; hence, activation of these processes should weaken the photoinduced negative order.

POA in Copolymers

We studied the specific features of POA for poly-II-MMA copolymers with a concentration of azo chromophores in the polymer chain ranging from 5 to 50 mol %. Figure 6 illustrates the kinetics of phase differences in the above copolymers. The dependences of $(n_v - n_r)d$ and $(n_z - n_r)d$ on irradiation time appear to be qualitatively similar to the corresponding curves for homopolymer II: They increase monotonically, tend to saturate, and merge in the saturation state. This behavior suggests the development of the negative uniaxial order with the x axis along the direction of excitation light polarization. As the concentration of azo fragments decreases, the efficacy of POA monotonically decreases (Table 2); however, even at low concentrations of azo fragments (5 mol %), photoinduced ordering is induced. The time until POA saturation increases with a decrease in the concentration of azo fragments. Photoinduced anisotropy is stable in time for all homologs of this series.

The measurements of components D_x and D_y show that, as in the case of poly-II, photoinduced ordering



Fig. 6. Phase differences (dashed curves) $(n_y - n_x)d$ and (solid lines) $(n_z - n_x)d$ plotted against irradiation dose for the films based on poly-II-co-MMA copolymers; contents of poly-II are (1) 50, (2) 35, (3) 15, and (4) 5 mol %. Irradiation parameters: $\lambda_{ir} = 365$ nm, I = 4.5 mW/cm²; *x* polarization.

of azo fragments in copolymers proceeds via the mechanism of reorientation. Similarly to poly-II, for all copolymers, orientational order parameter S_{xx} in the saturation state was estimated. For all homologs, parameters $(n_y - n_x)$, $|S_{xx}|$, and τ_s are listed in Table 2.

As in the case of homopolymers, a decrease in order parameters $|S_{xx}|$ in the copolymers with a decrease in the concentration of azo fragments, c_a , may be related to enhanced processes of orientational relaxation. Indeed, the lower c_a , the lower the glass-transition temperature of polymers and, hence, the higher the mobility of their chains.

When the concentration of azo fragments decreases, the development of anisotropy slows down, a behavior that can be explained by the collective character of their orientation. As was shown above, the azo chromophore is reoriented under light excitation and relaxation, a process that is accompanied by the orientation of its nearest neighborhood and by the formation of a cluster composed of positively ordered fragments. The probability of the collective orientation increases with an increase in c_a . Hence, the higher c_a , the sooner the saturation of the photo-ordering process is attained. Note that collective orientation can involve also nonphotosensitive fragments of both the backbone chain and side chains [17, 20. 21], a circumstance that should minimize the free energy of the system.

In conclusion, note that all polymers and copolymers under study preserve their induced orientational order over a long-term shelf life (for months) at room temperature. This finding opens up new advantages for the efficient use of synthesized azo polymers as materials for long-term storage and static holography.

CONCLUSIONS

We have studied the specific features of threedimensional photoinduced orientational ordering in azo polymers under light excitation corresponding to the absorption $\pi\pi^*$ band of azo fragments. To this end, several methacrylic polymers and copolymers containing side azobenzene fragments with different substituents have been synthesized. Prior to irradiation, azo fragments in all polymers tend to orient along the normal to the film plane. During irradiation, their three-dimensional orientation is changed and these changes tend to saturate. In the saturation state, orientation is controlled by the end substituent in the azo fragment. In the case of acceptor substituents $(NO_2,$ $COOC_4H_9$), azo fragments adopt a uniaxial orientation and a uniform distribution in the plane perpendicular to the direction of excitation-light polarization. In the case of donor substituents (OC_5H_{11}) , the distribution of azo fragments in the saturation state is isotropic. This difference is related to the predominant mechanism of photo-ordering, which is controlled by the lifetime of photoexcited cis isomers. The existence of a flexible spacer that links the azo fragment and macrochain somewhat decreases the photoinduced order, a behavior that is provided by enhanced processes of orientational relaxation with an increase in the mobility of azo chromophores. Among copolymers, photoinduced order monotonically decreases with a decrease in the concentration of azo fragments. This tendency can be provided also by the enhanced processes of orientational relaxation, a result that is confirmed by the depression in the glass-transition temperature of azo polymers.

The revealed features of photo-ordering broadens our knowledge concerning photoinduced processes in methacrylic azo polymers and can be used for further optimization of this class of polymers and their application in optical systems for data recording, storage, and processing; in holography; and in information displays.

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