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The Initial and Photoinduced 3D Orientational Order in Polymethacrylates with Azobenzene Side Groups

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The combination of the transmission null ellipsometry and total absorption method, earlier approved for several polymer classes, is applied to study 3D orientational configurations of azochromophores in polymethacrylates with azobenzene side groups. The transformation of the initial orientation due to the photoexcitation of azochromophores is investigated. The dependence of the orientational configuration on the structure of azochromophore fragments and its concentration in the polymers are also studied. In the non-irradiated films, azochromophores strive to be aligned normally to the film plate. Under irradiation, if reorientation mechanism of the photoinduced ordering prevails, the azochromophores reorient perpendicularly to the polarization direction of the exciting light, \mathbf{E}_{ex} , and in the saturation state they are randomly distributed in the plane perpendicular to \mathbf{E}_{ex} . This implies that the induced structure is mainly influenced by the photoordering, while selfordering of polymer chains is not effective or overcome, presumably because of high T_g of polymethacrylates. In case when photoselection ordering mechanism dominates, 3D distribution of azochromophores in the saturation state of irradiation is isotropic due to a strong exhaustion of the number of anisotropic trans isomers. The transient photoinduced orientations are biaxial independently on the dominating ordering mechanism. The reduction of the azochromophore's concentration in polymers reduces the anisotropy rate but not influence the trends described above. The observed regularities were earlier described for several other

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classes of photosensitive polymers and so they may be common rules for photoordering in the photochromic media.

Keywords: azopolymer; 3D orientational order; photoinduced anisotropy; polymethacrylate

1. INTRODUCTION

The last decade observes increased interest to azopolymers, i.e., polymers containing azochromophores (usually, azobenzene derivatives) in the side or main polymer chain. The most attractive feature of azopolymers is an effective photoinduced optical anisotropy (POA), which reveals itself in a linear dichroism and photoinduced birefringence. This feature makes azopolymers rather attractive for a number of photonic applications such as polarization holography, optical memory, integrated optical circuits, and liquid crystal (LC) aligning substrates, etc [1,2].

On microscopic level, POA in azopolymers is explained by the orientational ordering of azochromophores. The widely accepted model of this photoorientation is based on the specific photochemistry (*trans-cis* isomerization) and strong absorption dichroism of azochromophores in the *trans* configuration. According to theory of Dumont [3,4], the mechanism of POA is determined by the molecular extinctions (along the long and short molecular axis) of *trans* and *cis* azochromophores on the wavelength of excitation, lifetime of *cis* isomers and coefficient of the rotational diffusion. M. Dumont selects two elementary mechanisms. First mechanism, *photoselection or angular hole burning*, is realized if lifetime of *cis* isomers is long while their molecular extinction is low, so that azochromophores undergo only one or few cycles of isomerization over the irradiation period. At these conditions, if rotational diffusion rate is not very high, the anisotropic distribution of azochromophores appears due to the angularly selective conversion of *trans* chromophores into the less anisotropic (isotropic in the first approximation) *cis* form. The strongest conversion is observed for the fragments oriented along the polarization direction of exciting light, \mathbf{E}_{ex} . So, due to photoselection, azochromophores will be mainly aligned perpendicularly to \mathbf{E}_{ex} . If photoproducts are thermally and photochemically stable, the saturation of hole burning leads to a total depletion of *trans* form and so to isotropy of azopolymer film. In the opposite case, if lifetime of *cis* isomers is short and/or their molecular extinction is high, azochromophores undergo many isomerization cycles over excitation period. The change of the

molecular shape leads to the change of the molecular orientation. Due to the many cycles of isomerization a random-walk rotation of azochromophore appears. The chromophores accidentally aligned perpendicularly to \mathbf{E}_{ex} will be excluded from the further rotation, because their absorption is minimized. Thus, photoinitiated random-walk rotation leads to accumulation of azochromophores in the direction perpendicular to polarization of the exciting light. This mechanism is known as *photoreorientation* or *angular redistribution*. More generally, through both photoselection and photoreorientation the system tends to minimize the probability of optical excitation. The final distribution of azochromophores is a result of competition between the above ordering process and the thermal diffusion in the ground state, which tends to establish isotropy.

Let us pay attention to the angular distributions of azochromophores in the real (3D) space. According to the model described above the symmetry of the angular distribution of azochromophores is imposed by the exciting light. If the exciting light is only the factor of photoorientation, the symmetry of angular distribution is fully determined by the symmetry of photoexcitation. For instance, in case of excitation with polarized light, the chromophores should be randomly aligned in the plane perpendicular to light polarization \mathbf{E}_{ex} (oblate order with \mathbf{E}_{ex} symmetry axis). The real orientational structures can be quite different from the oblate order described, because of the influence of other factors. One of them is self-ordering of polymers, which can be stimulated with heating or photoexcitation [5–7]. Due to the competition of various factors big variety of orientational distributions can be obtained. In our previous studies this variety was mainly investigated using a series of azopolyesters. A number of experimental rules were established allowing us to predict photoinduced distribution proceeding from the molecular structure and thermodynamic characteristics of azopolymers as well as from the irradiation conditions [8–10]. A theory of 3D ordering was suggested [9,11], which gave theoretical interpretation of some empiric rules.

In the present research we elucidate the ordering regularities in azogroups containing polymethacrylates (p-AzoMA). This is the most popular class of azopolymers quite attractive for practical uses because of enhanced thermal stability, excellent film forming properties, relatively simple synthesis, *etc.* In spite of this popularity, the studies on the photoinduced anisotropy in these polymers were mainly restricted to 2D case, which cannot give a complete notion about ordering peculiarities. Regarding 3D consideration, one can admit only few studies based on different variations of prism coupling method [3,12,13] and works of Spiess with coworkers [14] used a total absorption method

briefly described in the following section. Besides, 3D order in one polymer of this class has been studied in our previous works [8,9,11]. In the present paper we apply transmission null ellipsometry supported by the modified total absorption method to investigate the 3D order in a big series azopolymers based on polymethacrylate. As we earlier proved this combination is effective and practical tool for the study of the orientational molecular distributions. We consider the induced orientational order as a function of molecular structure, supramolecular organization and irradiation conditions. The regularities obtained are compared with those earlier established for other kinds of azopolymers.

2. EXPERIMENTAL

2.1. Polymers

We use a series of homopolymers and copolymers with a general formula presented in Figure 1. The x , y , n , and m values as well as a structure of the end group R for all homologues of the studied series are given in Table 1.

The corresponding monomers were synthesized by general methods. The azocompound (0.06 mol) and triethylamine (9.0 mL) were dissolved in THF (200 mL). The solution was kept in an ice bath for 10 min. A solution of distilled methacryloyl chloride (6.0 mL, 0.06 mol) was added slowly to the above mixture. After the addition of methacryloyl chloride, the resulting mixture was stirred at room temperature overnight. Then the solution was poured into distilled water (1 L) and the obtained residue was filtered and air-dried. Recrystallization of monomers was carried out in ethanol.

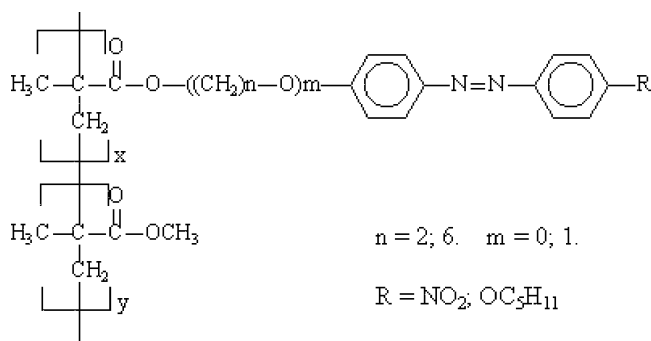


FIGURE 1 General structure of the studied azopolymers.

TABLE 1 Characteristics of Polymers. G, N and I Denote Glassy, Nematic and Isotropic Phase, Respectively. $\lambda_{\pi\pi^*}$ Defines the Maximum of the $\pi\pi^*$ Absorption Band

Code	R	n	m	x, %	y, %	Transition temperatures, °C	$\lambda_{\pi\pi^*}$, nm
Homopolymers							
P1	NO ₂	0	0	100	0	G 147 I	460
P2	OC ₅ H ₁₁	0	0	100	0	G 123 I	345
P3	NO ₂	2	1	100	0	G 113 I	357
P4	NO ₂	6	1	100	0	G 112 I	354
P5	OC ₅ H ₁₁	6	1	100	0	G 112 N 140 I	340
Copolymers							
P6	NO ₂	0	0	35	65	G 137 I	453
P7	NO ₂	0	0	10	90	G 128 I	450

Copolymers as well as homopolymers were synthesized by free-radical polymerization in toluene. The polymerization was carried out in 10 wt.% toluene solution of comonomers or monomer with AIBN as free radical initiator (10 wt.% of comonomers or monomer) at 80°C over more than 30 hours. Polymers were isolated from the reaction solution by precipitation into excess of methanol followed by reprecipitation from toluene into methanol and then dried at 20°C overnight. The synthetic work is described in more details in a separate paper [15].

The synthesized azopolymers were characterized by ¹H NMR spectroscopy. The obtained results were in agreement with the proposed structures.

The phase transitions were studied by differential scanning calorimetry (DSC) using Perkin Elmer DSC-2 instrument equipped with a IFA GmbH processor at the scan rate of 20°K/min.

2.2. Films

The polymers were dissolved in DMF (2 wt%) and filtered using a 0.2 μm Teflon filters. The prepared solution was spin coated on the plates of fused quartz allowing us to measure polymer absorption in a UV range. The films were dried at 90°C over 1h. A thickness of the films was measured by profilometer. It was varied within 300–1000 nm.

The photo-ordering processes were initiated with a polarized UV light from the high-pressure mercury lamp. The propagation direction of light corresponded to *z*-axis, while polarization of light was always chosen along the *x*-axis of the Cartesian coordinate system with *x*- and *y*-axis parallel to the verges of the rectangular polymer film

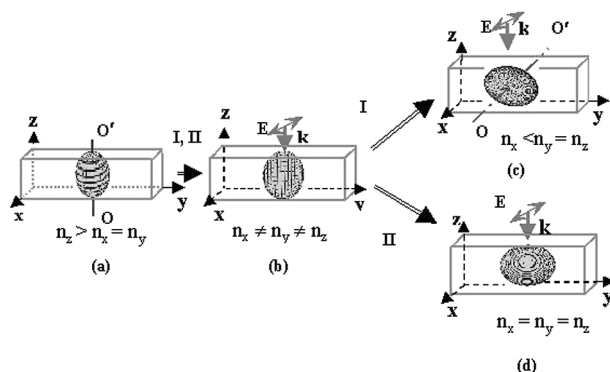


FIGURE 2 The transformations of the 3D orientational distributions of *trans*-azochromophores in the p-AzoMA films due to $\lambda = 365$ nm irradiation. (a) before irradiation; (b) biaxial transient distribution; (c) oblate distribution with the symmetry axis parallel to \mathbf{E}_{ex} (P1, P3, P4, P6, P7, photosaturation state); (d) isotropic distribution (P2, P5, photosaturation state).

and z -axis normal to this film (Fig. 2). The line 365 nm was selected with an interference filter. The light was directed normally to the films. The irradiation was carried out stepwise. After each irradiation step the photoinduced order was evaluated. The time period between irradiation and measurements was about 10 min to ensure relaxation of *cis* isomers (at least their short living fraction).

2.2. Methods

The key method of our studies was the *transmission null ellipsometry* (TNE). This is a modified version of Senarmont method extended for the measurement of the out-of-plane retardation. The obtained in-plane and out-of-plane retardation values $((n_y - n_x)d$ and $(n_z - n_x)d$, Fig. 2) allowed us to judge about the ellipsoid of refractive index n_{ij} and, finally, about the orientational configuration of azochromophores assuming that directions of maximal values of n_{ij} correspond to the maximally populated directions of azochromophores. The details of this method can be found in our previous works [8,9].

As a complementary characterization method, we also perform **2D** dichroism measurement in the UV/Visible spectral range. The optical densities, D_x and D_y , corresponding to x and y in-plane polarizations, are measured with a probe beam propagating perpendicularly to the sample. The third, out-of-plane component, D_z , can be estimated by the *total absorption (TA) method*, if total absorption,

$D_{total} = D_x + D_y + D_z$, is the same for all measuring steps. This is, for instance, true if the photoinduced *cis* isomers quickly relax back to a *trans* form and the loss of azochromophores due to a photodegradation is negligible. The D_{total} can be easily obtained, if at some instant of time t_0 the sample is uniaxial, with an in-plane orientation of the axis of anisotropy, say y . Then

$$D_{total} \equiv D_x(t_0) + D_y(t_0) + D_z(t_0) = 2D_x(t_0) + D_y(t_0) \quad (1)$$

Since we assumed that number of azobenzene units in *trans* configuration remains constant at each instant of time t , $D_z(t)$ can be estimated as:

$$D_z(t) = D_{total} - D_x(t) - D_y(t) \quad (2)$$

where $D_x(t)$ and $D_y(t)$ are experimentally measured in-plane components.

Then, the diagonal terms of the tensor of orientational order S_{ij} can be estimated. For example:

$$S_{xx} = \frac{D_x - \frac{1}{2}(D_y + D_z)}{D_x + D_y + D_z} \quad (3)$$

The components S_{yy} and S_{zz} can be obtained by cyclic permutation in expression (3).

In the original version of TAM, D_i ($i = x, y, z$) corresponded to the maximum of the vibration bands (IR spectral range) characteristic for azochromophore. In our version the absorption in the UV/Vis range is measured. We operated with the D_i ($i = x, y, z$) values corresponding to the $\pi\pi^*$ absorption maximum of *trans* chromophores.

The UV/Vis absorption measurements were carried out using a diode array spectrometer S2000 from Ocean Optics Co. The samples were set normally to the testing light from a low intensity deuterium lamp. A Glan-Thomson prism was used to polarize the probe beam.

3. RESULTS AND DISCUSSION

First of all we measured the UV/Vis absorption spectra of azopolymers before and after irradiation with unpolarized UV light (365 nm, normal incidence). These measurements confirmed that major photo-reaction is *trans-cis* isomerization revealed itself in strong depletion of $\pi\pi^*$ band and increase of $n\pi^*$ band, which is much more intensive for *cis* isomers. The $\lambda_{\pi\pi^*}$ values corresponding to maximum of $\pi\pi^*$ absorption band are shown in Table 1. As usually, bathochromic shift of $\pi\pi^*$ band is observed by substituting alkoxy chain with a polar

NO_2 group in a chromophore's tail (push-pull chromophores). In spite of this shift, in all polymers, 365 nm excitation wavelength corresponds to effective adsorption within the $\pi\pi^*$ absorption band.

With regard to results on 3D ordering, two types of the ordering behavior can be selected. We describe them on an example of P1 and P2, representatives of these two types. The values of the in-plane, $(n_y - n_x)d$, and the out-of-plane $(n_z - n_x)d$ retardation for the films of P1 and P2 are presented, respectively, in Figure 3a and Figure 4a. The data correspond to successive exposure doses (x polarization of UV irradiation). Several conclusions from this curves can be drawn. First of all, before irradiation, azochromophores demonstrate slight

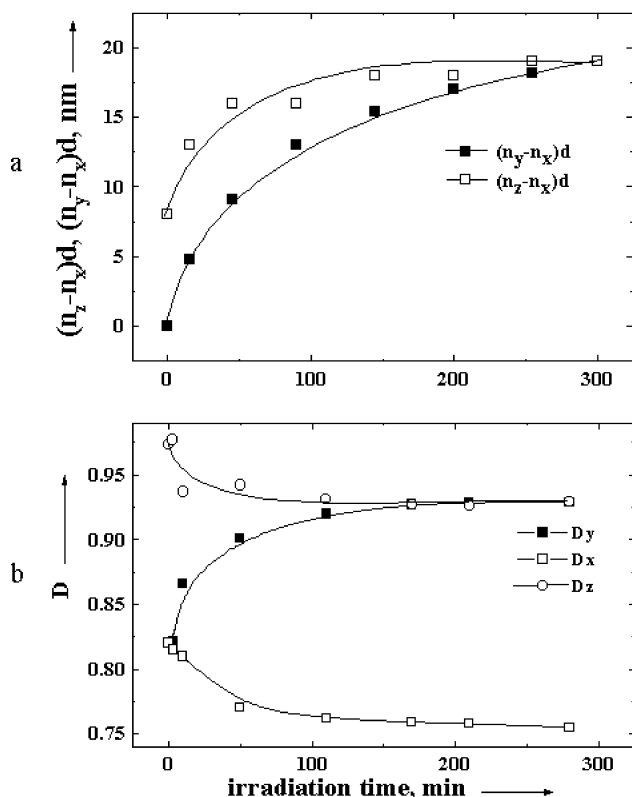


FIGURE 3 The kinetics of the absorption components D_x , D_y and D_z (a) and phase retardation components $(n_y - n_x)d$ and $(n_z - n_x)d$ (b) for successive exposure doses for polymer P1. Irradiation is with $\lambda_{\text{ex}} = 365$ nm ($I = 5$ mW/cm², x polarization).

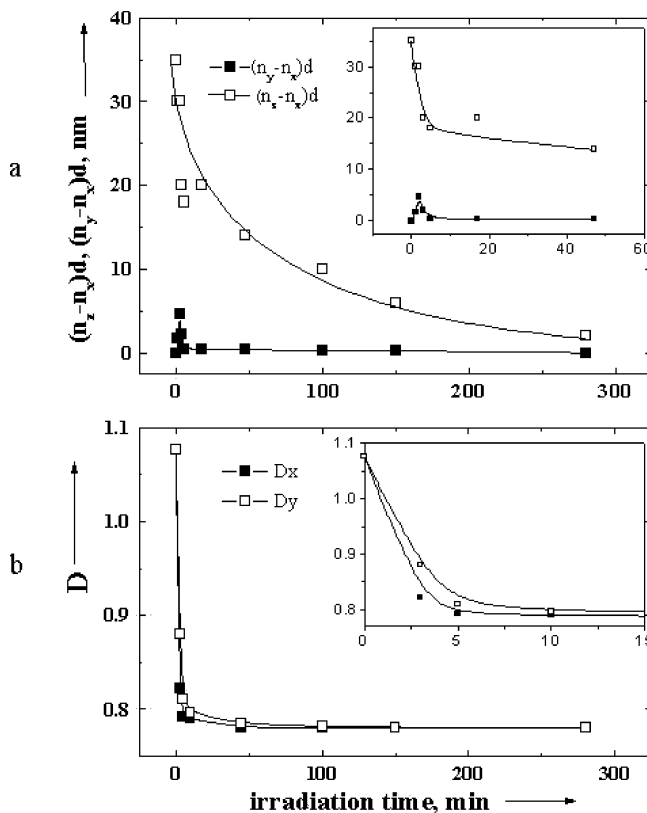


FIGURE 4 The kinetics of the absorption components D_x , D_y and D_z (a) and phase retardation components $(n_y - n_x)d$ and $(n_z - n_x)d$ (b) for successive exposure doses for polymer P1. Irradiation is with $\lambda_{\text{ex}} = 365 \text{ nm}$ ($I = 5 \text{ mW/cm}^2$, x polarization).

preference to the out-of-plane alignment ($n_z > n_x = n_y$, Fig. 2a). This rule was true for all homologues studied. The irradiation, however, induces different kinds of transformation of this initial order in two different polymer classes we selected. This difference is especially clear for the structures realized in the saturated states of irradiation reached for all polymers. In P1 film, the irradiation results in an oblate order with the x ordering axis ($n_x < n_y = n_z$, Fig. 2c). In contrast, in P2 film isotropic order is formed ($n_x = n_y = n_z$, Fig. 2d). In general case, the transient orientational structures are biaxial ($n_x \neq n_y \neq n_z$, Fig. 2b). In P2 films, between biaxial and isotropic orientation, the uniaxial out-of-plane alignment ($n_z > n_x = n_y$, Fig. 2a) can be observed, as a

result of faster degradation of the in-plane anisotropy $(n_y - n_x)d$ compared with the out-of-plane anisotropy $(n_z - n_x)d$. The D_x and D_y absorption components as the functions of exposure time measured for P1 and P2 are presented in Figure 3b and Figure 4b. The behavior of $D_x(t)$ and $D_y(t)$ curves is typical for reorientation mechanism: increase of $D_y(t)$ and simultaneous decrease of $D_x(t)$ ($x \parallel \mathbf{E}_{\text{ex}}$) is an evidence of redistribution of azochromophores with the increase of their concentration in the y direction perpendicular to the light polarization \mathbf{E}_{ex} [3,4]. In turn, simultaneous decrease of $D_x(t)$ and $D_y(t)$ curves is typical for the angular photoselection [3,4]. The conversion of *trans* isomers in the long living *cis* form first in the direction of light polarization \mathbf{E}_{ex} and then in all other spatial directions may explain isotropic order realized in P2 film at high irradiation doses.

As we discussed in Introduction, the reorientation mechanism may be an evidence of short lifetime of *cis* isomers. If it is really so, the total absorption of azochromophores D_{total} can be practically kept constant after successive irradiation steps. In conjunction with a fact of the uniaxial ordering in a stationary state ($n_y = n_z$) this may allow us to apply TA method to calculate D_z component. To estimate the lifetime of *cis* chromophores, the transmission of P1 film at $\lambda_{\pi\pi^*}$ was measured as a function of relaxation time after the exposure with unpolarized light (365 nm, 15 mW/cm², 10 min). The testing and exciting light were directed almost normaly to the film. The obtained relaxation curve is presented in Figure 5. It can be satisfactorily fitted with three exponents with the parameters shown in Figure 5. Different exponents may reflect relaxation of the different fractions of *cis* isomers situated in the polymer sites with different free volume [16]. As one can see, the major relaxation occurs over several seconds after switching off the irradiation, while the more living *cis* isomers relax over next 5 minutes of relaxation. Hence, 10 min period between irradiation and measuring steps is sufficient for practically complete relaxation of *cis* isomers and so keeping D_{total} constant. The calculated $D_z(t)$ curve is shown in Figure 3b.

The D_i ($i = x, y, z$) values were used to calculate the diagonal components S_{xx} , S_{yy} and S_{zz} of the order parameter tensor \hat{S} according to (3). The $S_{xx}(t)$, $S_{yy}(t)$ and $S_{zz}(t)$ curves are shown in Figure 6. The uniaxial oblate distribution of azochromophores with the x ordering axis, realized in the stationary state of irradiation, is characterized by the scalar $S \equiv S_{xx} = -0.07$. The initial order of azochromophores (uniaxial ordering along the film normal) is also characterized by scalar: $S \equiv S_{zz} = 0.06$. The latter value indicates that initial out-of-plane ordering is rather weak. The transient structures between the uniaxial structures in the initial state and in the stationary state of excitation

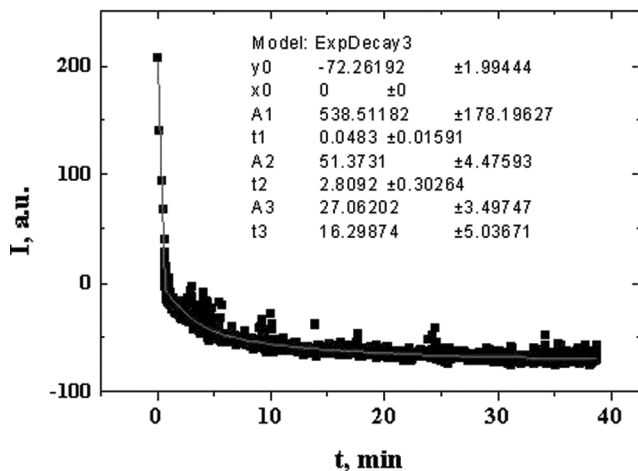


FIGURE 5 The relaxation kinetics of the transmission of P1 film ($\lambda = \lambda_{\pi\pi^*}$) after irradiation with non-polarized UV light (365 nm, 15 mW/cm², 10 min).

are biaxial and so can be described at least with three (diagonal) elements of \hat{S} .

Note again, that the TA method can not be applied for P2 because of strong exhaustion of *trans* chromophores possible for rather stable *cis* isomers. This automatically excludes conditions needed for TA method.

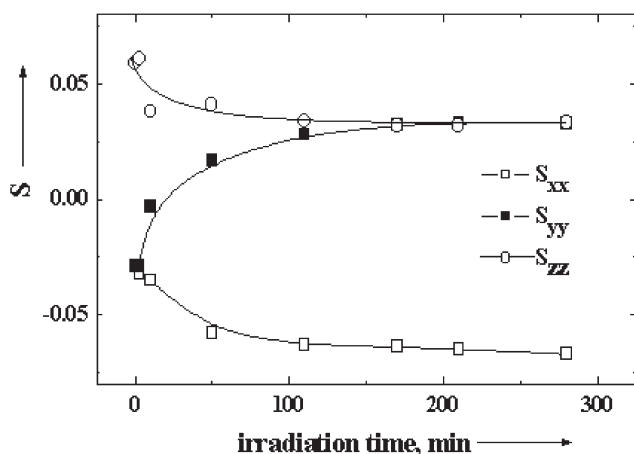


FIGURE 6 Kinetics of S_{xx} , S_{yy} , S_{zz} for successive exposure doses (polymer P1) calculated from the data of Figure 3b according to formula (3).

Qualitatively, the ordering peculiarities of P1 inhere in the following series P3, P4, P6, P7, i.e., in all homologues containing NO₂ acceptor group (push-pull azochromophore). The transformation of the 3D order under irradiation for these polymers is schematically presented in Figure 2 as transformation way I. This general tendency does not depend on the length of the side-chain spacer as well as on the concentration of azochromophores in co-polymers. At the same time, the mentioned molecular variations influence the induced birefringence and dichroism which determine ordering rate of azochromophores. These quantitative regularities will be considered in the forthcoming publications.

The ordering features of P2 are also inherent in P5; on the initial stage of irradiation, the biaxial alignment is observed, which transforms, with irradiation dose, in the spacially isotrop distribution. These transformations are presented as transformation way II in Figure 2.

The general tendencies of the photoinduced ordering allows us to conclude that in the p-AzoMA the photoinduced order is mainly influenced by the molecular photoordering through the photoselection and reorientation mechanisms described above. The clear evidence of it is the fact that realized orientational configurations of azochromophores reflect geometry of photoexcitation. Energetically this configurations can be not profitable (as in our experimental case), counter to self-organization of anisotropic molecules aimed on the achievement of uniaxial prolate order to minimize free energy of polymer. So, in strong contrast to azobenzene polyesters earlier studied [10], the self-ordering under photoirradiation in p-AzoMA at the ambient temperatures is rather weak. This might be caused by rather high temperatures of glass transition ($T_g > 100^\circ\text{C}$) that testify to deep "freezing" of p-AzoMA chains so that they can not be involved in the processes of self-organization stimulated with UV light. Contrary to this, in the azopolyesters, the glass transition temperatures are low ($T_g < 20^\circ\text{C}$) and so both azochromophores and polyester chains participate in the collective processes of self-organization. The "freezing" of polymer chains in p-AzoMA polymers may also explain why liquid crystallinity (observed in polymer P5), as a particular feature of self-organization, does not influence substantially the order in these polymers. According to Ref. [17], the contribution of the intrinsic self-organization to the orientational order in p-AzoMA may strongly increase if the film is irradiated at the temperature a little lower T_g . Thus competition of the molecular photoorientation and self-organization in the 3D order can be achieved for elevated temperatures close to 100°C . This can be rather interesting subject for the future studies.

Since a light ordering factor at the ambient temperatures strongly prevails, the induced orientation depends rather on the molecular photochemistry than on the self-ordering processes. If the photoreorientation mechanism dominates, the oblate order with the symmetry axis parallel to \mathbf{E}_{ex} is formed. In the opposite case, if photoselection mainly influences the order, spatially isotropic alignment is realized.

4. CONCLUSIONS

Thus, studying the 3D orientational ordering in the azogroups containing polymethacrylates we revealed the regularities earlier established for the other kinds of azopolymers [10] as well as polymers containing cinnamoyl photosensitive group [18]. The main rule says that under photoexcitation the initial orientational distribution (frequently, uniaxially ordered due to the self-ordering of photosensitive groups) is transformed into some other uniaxially ordered distribution (in case of photoreorientation mechanism) or isotropic distribution (in case of photoselection). The transient structures from the initial to the final uniaxial (isotropic) distributions are biaxial. In case of photoselection, the transient uniaxial homeotropic alignment can be observed if the in-plane depletion rate of *trans* chromophore-sand is substantially higher than the out-of-plane one. Before irradiation, the azochromophores in the studied p-AzoMA demonstrate preference to the out-of-plane alignment that can be caused by the self-ordering in the diluted polymers under the film formation. The final photoinduced alignment is a result of concurring photoorientation and self-organization. The latter factor in p-AzoMA at the ambient temperatures is weak, presumably, because of high T_g . This excludes collective self-organization processes under photoexcitation playing important role, for example, in azopolyesters [19]. The regularities observed may predict alignment tendencies in other kinds of photopolymers showing POA.

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