

PHOTOINDUCED BIREFRINGENCE AND NUMERICAL SOLUTION OF A NEW DYNAMIC MODEL IN AN AMORPHOUS COPOLYMER CONTAINING AZOBENZENE GROUPS*

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Abstract Photoinduced birefringence is investigated in a new amorphous copolymer containing azobenzene groups. The levels of birefringence signal are found to depend on the polarization angle between the pump beam and the probe beam, and on the ellipticity of the pump beam. Both the growth and decay processes of the birefringence signal can be described by known biexponential equations. The rate constants and the amplitudes associated with the growth process of the photoinduced birefringence are observed to display a linear dependence with the pump beam intensity. A new dynamic model of the photoinduced birefringence is presented taking into account the contributions of both the *trans* and *cis* isomers of azobenzene groups and the local polymer segments. The numerical treatment of this model shows good agreement with the experimental data in the whole writing-erasing processes of the photoinduced birefringence conducted in our polymer samples.

Keywords Photoinduced birefringence, Azobenzene polymer, Dynamic process, Numerical simulation

INTRODUCTION

Since the pioneering work of Eich and Wendorff on liquid crystalline polymers containing azobenzene groups as reversible optical storage medium^[1, 2], much effort has been devoted to this research field. Probably one of the most significant results presented by Eich and Wendorff is that the optical axis of the liquid crystalline polymer is reoriented perpendicular to the polarization plane following an optically induced *trans-cis* isomerization of azobenzene groups^[2]. It was not long before Gibbons *et al.* showed that the orientation can be produced or changed with a polarized laser beam^[3]. Another important paper published by Natansohn *et al.* showed that liquid crystallinity is not a necessary condition for reversible optical storage and that erasing can be carried out with a circularly polarized laser^[4]. They also performed a computer simulation of the writing-erasing process of the photoinduced anisotropy. Numerous articles were published by them and other authors discussing the dependence of the dynamics of the photoinduced orientation on factors such as the chemical architecture of the azobenzene-containing polymers (including polymer backbone, structure of the azobenzene chromophore and the linkage between the backbone and the azobenzene chromophore), the character of the polymer matrix, the thickness of the polymer films and the wavelength and intensity of the excitation light^[5-10].

What deserves mentioning are recent developments related to the dynamic processes of the photoinduced anisotropy. The cooperative motions of nonphotoactive groups in the side chain or main chain of the azobenzene-containing polymers have been known for some time^[11-13]. Quite recently, not only azobenzene groups but also

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polymer segments (main chain and to a smaller extent flexible side chain) were confirmed experimentally to orient perpendicular to the pump beam polarization by Kulinna *et al.*^[14] These authors discovered this process by performing polarized Fourier transform infrared spectroscopic measurements on deuterated liquid crystalline polyesters containing azobenzene groups. Another important issue concerns the role of the *cis* isomer of azobenzene molecules in the photoinduced anisotropy. In an earlier model proposed by Natansohn *et al.*, the *cis* isomer is assumed to have zero population and makes no contribution to the induced anisotropy^[4]. But in several guest/host azobenzene polymer systems, other investigators have found that the *cis* isomer can exist long enough to contribute to the anisotropy^[15]. To account for their experimental results, the authors hypothesized that both the *cis* and *trans* isomers contribute to the anisotropy in amorphous azobenzene-containing polymers^[16]. In another publication, it was shown that the *cis* isomers can also align perpendicular to the pump beam polarization in an azobenzene-containing polyglutamate film^[17].

In this paper, the photoinduced anisotropy of a new amorphous copolymer of methyl methacrylate (MMA) containing azobenzene groups is reported. The birefringence contributions of the *cis* isomers and the local polymer segments besides the *trans* isomers will be considered in our dynamic model, based on which a numerical solution of the dynamic processes is performed and analyzed relative to our experimental results.

EXPERIMENTAL

The molecular structure of azobenzene polymer of poly(MAZ-*co*-MMA) used in this paper is shown in Fig. 1. The preparation procedures and characterization details were described previously^[18]. The copolymer polymer films of optical quality were prepared by spin-coating the filtered (through a 0.2 μm filter) polymer solution in 1,4-dioxane on a clean glass substrate and dried in a vacuum at 50°C for 20 h. The typical film thickness was about 3 μm as measured by ellipsicity spectroscopy.

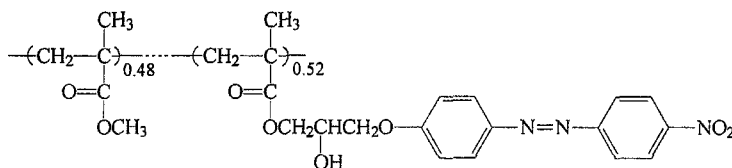


Fig. 1 The chemical structure of the copolymer P(MMA-*co*-MAZ)

Photoinduced birefringence was excited by subjecting the polymer films to a linearly polarized pump (writing) beam at 532 nm generated by a frequency-doubled Q-switched Nd:YAG laser with an intensity of 3 W/cm². The diameter of the pump beam was about 0.2 cm. A low-power He-Ne laser at 633 nm was used as a probe beam. The copolymer films were placed between a pair of crossed polarizers. The experimental set-up is shown schematically in Fig. 2(a). The probe beam was set at a polarization angle of 45° with respect to the pump beam polarization, as shown in Fig. 2(b). To study the pump beam ellipticity dependence of the photoinduced birefringence, elliptically polarized pump beams with different degrees of ellipticity were obtained by rotating a quarter wave plate in the light path.

RESULTS AND DISCUSSION

Photoinduced Birefringence

When the copolymer film was excited by a linearly polarized laser of 532 nm, photoinduced birefringence was produced in the film. The levels of birefringence signal depended on the polarization angle between the pump beam and the probe beam. When the angle was 45°, the birefringence reached its highest level, $\Delta n = 0.083$, as measured in our experiments. Figure 3 shows representative growth curves of the birefringence signal at various polarization angles during the writing process. Unless otherwise stated, all of the following experiments were performed at 45°. As shown in Fig. 4, the growth curve can be fitted with the following biexponential equation^[7]:

$$I(t) = A(1 - e^{-k_a t}) + B(1 - e^{-k_b t}) \quad (1)$$

where $I(t)$ represents the birefringence signal at time t , k_a and k_b are the rate constants for birefringence signal growth, and A and B are the amplitudes associated with the rate processes having k_a and k_b rate constants, respectively. The birefringence signal relaxed when the pump beam was switched off. The relaxed birefringence signal at time t can be expressed as follows^[7]:

$$I(t) = Ce^{-k_c t} + De^{-k_d t} + E \quad (2)$$

where k_c and k_d are the rate constants for the birefringence signal relaxation, C and D are the amplitudes associated with these processes, and E is the residual birefringence signal independent of time. Figure 5 is the relaxation curve fitted with biexponential Eq. (2). Both the growth and the decay curves consist of a fast and a slow process. As mentioned earlier, the *trans* and *cis* isomers of the azobenzene groups, together with the local polymer segments are all involved in the generation of birefringence. In our view, the reorientation of the *trans* and *cis* isomers under laser excitation is associated with the fast growth process, and the orientation of the local polymer segments is associated with the slow process. In the relaxation process, the fast process is due to the orientational relaxation of the *trans* and *cis* isomers while the slow process originates from the relaxation of the anisotropic polymer segments.

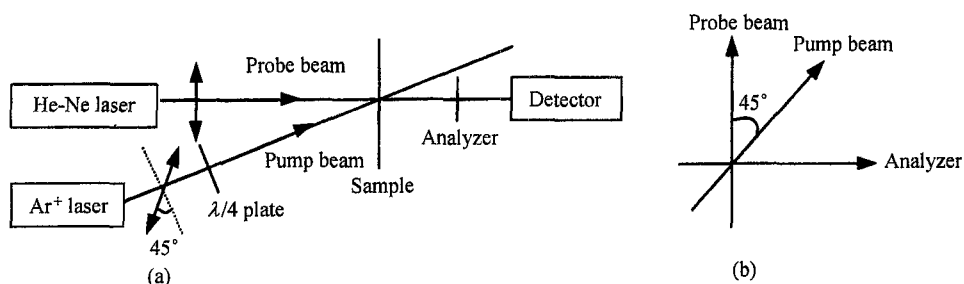


Fig. 2 (a) Geometry of the experimental set-up used for the photoinduced birefringence experiments; (b) the polarization diagram of the pump beam and the probe beam

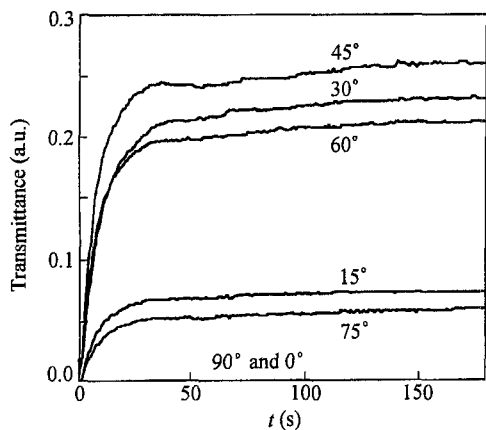


Fig. 3 The growth process of photoinduced birefringence with time for different polarization angles between the pump beam and the probe beam

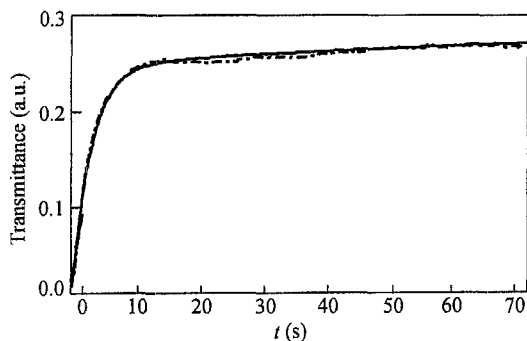


Fig. 4 Typical growth process of photoinduced birefringence with time
The dotted line is a fit to Eq. (1).

We investigated the growth dependence of the birefringence signal on the pump beam intensity. The growth curves obtained at different writing intensities were fitted well with Eq. (1). The fitting parameters of k_a/k_b and

A/B are plotted against the pump beam intensity as shown in Figs. 6 and 7, respectively. The rate constants of k_a and k_b were found to depend on the intensities. They increase linearly with increasing intensities, but k_a is much greater than k_b (Fig. 6). This means that the “writing” time can be controlled by the laser intensity. The local heating effect^[19] of the pump beam may play its part in our experiments. The amplitudes A and B also display a writing intensity dependence. The amplitude of the fast process (associated with k_a) increases, while that of the slow process decreases with increasing writing intensity (Fig. 7). In a recent article^[16], the authors stated that the rate constants k_a and k_b displayed no intensity dependence. In their rate constant/power plot, the intensity variation of the horizontal coordinate is much smaller (almost two orders of magnitude) compared with ours in Fig. 6, while the vertical coordinate variation is almost the same. Therefore, they were not able to perceive, as we did in our experiments, the linear rate constant dependence on laser intensity.

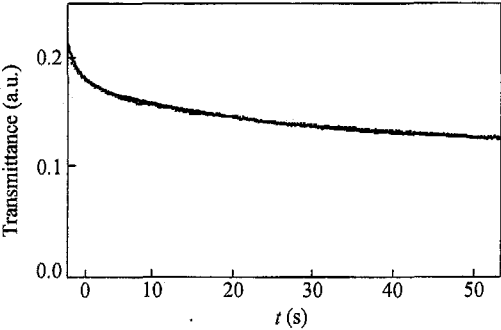


Fig. 5 Birefringence decay after the pump beam is turned off
The dotted line is a fit to Eq. (2).

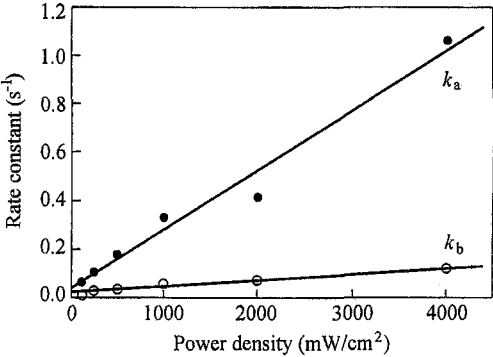


Fig. 6 The pump beam intensity dependence of rate constants of the growth at room temperature

Table 1. Saturated transmittance and photoinduced birefringence dependence on the ellipticity of the pump beam

Angle ϕ	0°	15°	30°	45°	60°	75°	90°
Ellipticity	1	0.732	0.423	0	0.423	0.732	1
Transmittance	0.22	0.145	0.032	0	0.038	0.16	0.22
Δn	0.083	0.058	0.025	0	0.027	0.061	0.083

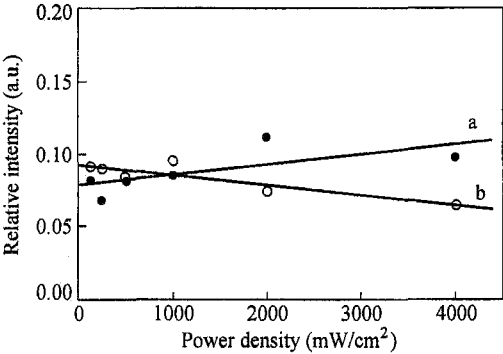


Fig. 7 The pump beam intensity dependence of amplitudes of the growth process at room temperature

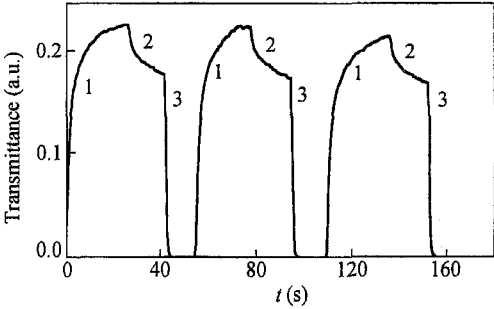


Fig. 8 Three writing-erasing cycles on a P(MMA-co-MAZ) film:
(1) The pump beam is turned on, (2) the pump beam is turned off, (3) the circularly polarized laser (erasing beam) is turned on.

By rotating the angle (Φ) of the axis of a quarter wave plate placed before the sample with respect to the pump beam polarization, various elliptically polarized pump beams can be produced from linearly to circularly polarized light. When excited with these elliptically polarized pump beams, it was found that the induced birefringence depended on the ellipticity of the pump beams. As listed in Table 1, a pump beam with larger ellipticity leads to a higher level of birefringence. The induced birefringence reaches the highest level under the irradiation of the linearly polarized laser, and the birefringence can even be erased over the same recording spot with a circularly polarized laser. Figure 8 shows three writing-erasing cycles, which demonstrates the good reversible recording property in the copolymer film.

Model for Dynamic Processes of Photoinduced Birefringence

So far, several models of photoinduced anisotropy in amorphous polymers^[4, 20, 21] and liquid crystalline polymers^[22–24] have been developed. Among them, a quantum model proposed by Pedersen *et al.* demonstrated that the *cis* isomers are almost isotropic in the plane containing the central C=N=N—C azo bridge. Recently, a stochastic model was also developed to describe photokinetics in amorphous or liquid crystalline polymers. The evolution of the birefringence can be evaluated by this model with additional information about the molecular polarizabilities^[25].

Here, we propose a simple model in which both the *trans* and *cis* isomers and the local polymer segments will be taken into account in the dynamic processes of photoinduced birefringence. The essential point in this paper is to take account of the macroscopic birefringence contribution of the *trans/cis* isomer and the local polymer segments. Our main points are presented as follows:

(1) Not only the *trans* isomers but also the *cis* isomers orient with the transition dipole perpendicular to the pump beam polarization and contribute to the induced birefringence. As previously mentioned, the *cis* isomer of the azobenzene molecule can become aligned perpendicular to the pump beam polarization^[17]. Additionally, we found that the *cis* isomer of the stilbene molecule could be preserved for a few days in a highly crosslinked polymer film after isomerization from its *trans* form^[26]. The azobenzene molecule bearing electron donor-acceptor substituents studied in most cases belongs to the pseudo-stilbene type by Rau's classification^[27] and has very similar photochemical properties to the stilbene molecule. We believe, therefore, that some *cis* isomers can be trapped in the isomerization process depending on the polymeric structural feature and the environment in the polymer matrix, and that their macroscopic contribution should be considered in the dynamic processes of the photoinduced birefringence.

(2) As described in the Introduction section, the local polymer segments can become oriented under the excitation of a linearly polarized laser and contribute to the birefringence. Two driving forces may be involved in this orientation process. One is the mechanical tension due to the reorientation of the azobenzene groups and the other is the local heating effect of the pump beam, which provides an increased free volume for polymer chains to fold regularly into an anisotropic matrix. However, the local heating effect for the local polymer segments makes a lesser contribution to the induced birefringence than the former driving force. Thus, only the isomerization driving force of the azobenzene groups will be taken into account in our following dynamic equations.

(3) Under the irradiation of the pump beam, the photoisomerization and/or the local heating effect will cause an increased degree of freedom of the azobenzene groups themselves^[19, 28]. When the pump beam is turned off, the increased degree of freedom of the azobenzene groups will decrease gradually and return back to the original degree of freedom before laser irradiation.

Based on the above considerations, the signal (proportional to the square of birefringence^[16, 29]) transmitted to the detector behind the analyzer can be given by:

$$S(t) = \left[\sum (k_1 [T]_i + k_2 [C]_i + k_3 [M]_i) \sin 2\phi_i \right]^2 \quad (3)$$

where $[T]_i$, $[C]_i$ and $[M]_i$ are the concentrations of the *trans/cis* isomers and the local polymer segments oriented in the i th direction, respectively, and the summation is performed over the entire angular distribution. k_1 , k_2 and k_3 are the proportionality constants corresponding to the anisotropic contributions of the *trans*, *cis* isomers and the

local polymer segments, respectively. ϕ_i is the angle of the i th direction with respect to the probe beam polarization and is given by $\phi_i = \theta/45^\circ$, as the pump beam is performed at 45° with respect to the probe beam in our experiments. θ_i is the angle between the i th direction and the pump beam polarization. The *trans-cis* isomerization rate for an azobenzene molecule can be described by a term $I \cos^2 \theta_i$, where I is a quantity proportional to the intensity of the pump beam^[30]. Finally, the azobenzene groups will align perpendicular to the pump beam polarization direction after many *trans-cis-trans* isomerization cycles. When $\theta_i = 90^\circ$, they can not be reactivated. Therefore, one can expect a maximum of transmitted signal when the polarization angle between the pump beam and the probe beam is set at 45° , which has been confirmed experimentally as shown in Figure 3.

The dynamics can be described by:

$$\frac{d[C]_i}{dt} = \sum_{j=i\pm 1} \omega_{ji}[T]_j - \sum_{j=i\pm 1} \omega_{cij}[C]_i + \sum_{j=i\pm 1} \omega_{hji}[C]_j - \sum_{j=i\pm 1} \omega_{hij}[C]_i \quad (4)$$

$$\frac{d[T]_i}{dt} = \sum_{j=i\pm 1} \omega_{cji}[C]_j - \sum_{j=i\pm 1} \omega_{tij}[T]_i + \sum_{j=i\pm 1} \omega_{hji}[T]_j - \sum_{j=i\pm 1} \omega_{hij}[T]_i \quad (5)$$

$$\frac{d[M]_i}{dt} = \sum_{j=i\pm 1} ([T]_j + [C]_j) k_m [M]_j - \sum_{j=i\pm 1} ([T]_i + [C]_i) k_m [M]_i \quad (6)$$

where ω_{ji} is the transition rate from the *trans* isomer in the j th direction to the *cis* isomer in the i th direction, ω_{cij} is the transition rate from the *cis* isomer in the i th direction to the *trans* isomer in the j th direction, ω_{hij} , ω_{hji} are the transition rates relative to the pump beam intensity for the *trans* and *cis* isomers orienting to their neighboring direction, respectively. $[M]_i$ and $[M]_j$ are the local polymer segments lying in the i th and j th direction, respectively. It is postulated in this model that the local polymer segments move only in the element of their neighboring positions. As proposed earlier, the isomerization of the azobenzene groups drives the local polymer segments to orient in a certain direction. k_m is a coefficient used to describe the orientation rate of the local polymer segments, which is proportional to the population of the oriented azobenzene groups.

The conditions on the parameters are explained as follows:

(1) When the *trans-cis* isomerization of an azobenzene molecule finishes, the resulting orientation of the *cis* isomer is related to the orientation as its *trans* isomer before changing. It is assumed that the *cis* isomer lies in the same direction as its *trans* isomer with maximum probability, and in the direction perpendicular to the *trans* isomer with minimum probability. Then, the term $\cos^2(\theta_i - \theta_j)$ can be used to describe the reorientation relationship between the *cis* and *trans* isomer, θ_i , θ_j are the orientation angles of the *cis* isomer after isomerization in the i th and j th direction, respectively. While excited by a polarized laser, the *trans-cis* isomerization rate for an azobenzene molecule in θ_i direction is proportional to the term $I \cos^2 \theta_i$, where I is the transition rate proportional to the intensity of the pump beam. Hence for ω_{ji} , $\omega_{ji} = I \cos^2 \theta_i \cos^2(\theta_i - \theta_j)$, as the writing process is taking place. $\omega_{ji} = 0$, as the writing beam is turned off. $\omega_{ji} = I \cos^2(\theta_i - \theta_j)$, for the erasing process with circularly polarized laser beam.

(2) When the *cis* isomer reverts to its *trans* isomer, the term $\cos^2(\theta_i - \theta_j)$ can also be used to describe the reorientation relationship between the *trans* and *cis* isomer. Then the transition rate of the *cis-trans* isomerization is given by $\omega_{cij} = k_i \cos^2(\theta_i - \theta_j)$, where k_i is defined as the rate coefficient during the whole writing-erasing processes. Because the *cis-trans* isomerization is a thermodynamic process, hence a rate-determining step, it is reasonable to assume that k_i is independent of the intensity of the pump beam.

(3) As previously mentioned, the degree of freedom of the azobenzene groups increases under the pump laser irradiation, and has a proportionality coefficient k_h to the pump beam intensity. After removing the pump beam, the degree of freedom decreases gradually, resulting in an exponential decay assumed in our model. This results in $\omega_{hij} = k_h I$, for the writing and erasing processes, $\omega_{hij} = k_h I \exp(-\frac{t_1 - t}{\tau})$, for the relaxation process, where

t_1 is the moment of the time when the pump beam is removed, and τ is the relaxation constant of the degree of freedom of the azobenzene groups.

Table 2. Simulation parameters

Parameter		Value
k_1	The proportionality constant corresponding to the contribution of the <i>trans</i> isomers	0.55
k_2	The proportionality constant corresponding to the contribution of the <i>cis</i> isomers	0.05
k_3	The proportionality constant corresponding to the contribution of the local polymer segments	0.4
k_t	The rate coefficient from <i>cis</i> to <i>trans</i> independent of the pump beam intensity	1/800
k_h	The coefficient proportional to the pump beam intensity reflecting the change of the degree of freedom of the azobenzene groups	60
I	The transition rate proportional to the pump beam intensity	1/249
τ	The relaxation constant of the degree of freedom of the azobenzene groups	0.6

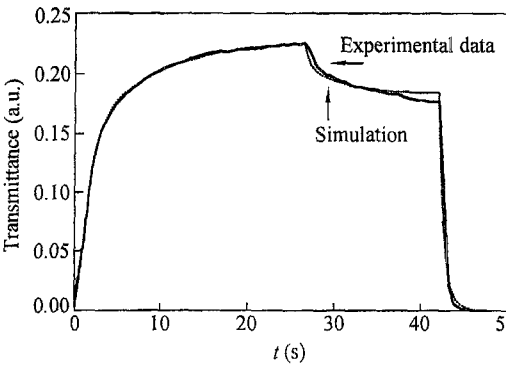


Fig. 9 Comparison between the numerical results based on our model and the experimental data of a birefringence writing-erasing cycle

The above dynamic equations can be solved numerically. The numerical simulation of an experimental writing-erasing cycle (the first cycle in Fig. 8) is performed and is in good agreement with the experimental data (Fig. 9). All the simulation parameters used in the numerical treatments are listed in Table 2. We can conclude from these parameters, that the oriented polymer segments do have a large contribution to the photoinduced birefringence which is reflected by the parameter k_3 (0.4), but less than the contribution of the *trans* isomers (corresponding parameter, $k_1 = 0.55$). Due to the larger geometric volume of the local polymer segments than the azobenzene groups, their mobility and moving rate are smaller than those of the azobenzene groups, thus a relatively smaller value (0.05) of k_m is given in the result of our numerical treatments. It is exactly the slow orientational process of the local polymer segments that results in the comparatively slow process of the photoinduced birefringence. As for the *cis* isomers, it is rather difficult for the oriented *cis* isomers to fold into an anisotropic matrix compactly due to the globular geometry and non-coplanar feature of the phenyl rings of the *cis* isomer^[31]. Therefore, a relatively smaller birefringence contribution is expected for the *cis* isomers. In our model, it is exactly the case that the proportionallity constant (k_2) of the *cis* isomers is much smaller than k_1 and k_3 corresponding to the birefringence contribution of the *trans* isomers and the local polymer segments, respectively. The *cis* isomer has about 5% contribution to the birefringence in our model that is necessary to produce a better fit to the experimental data. It should be noted that our model displays a little deviation from the

experimental data in the birefringence decay process. The simplified monoexponential treatment considering the relaxation process of the degree of freedom of the azobenzene groups may be held accountable for this difference between the experimental data and our numerical results. The decay process has a complicated mechanism in which many factors, such as the thermal *cis-trans* isomerization and the thermal relaxation of the local polymer segments etc. are involved. Thus, further consideration of these factors has to be made to improve our model.

CONCLUSIONS

The photoinduced birefringence has been investigated in a new amorphous azobenzene-containing copolymer of methyl methacrylate. The induced birefringence level reaches a maximum value when the polarization angle between the pump beam and the probe beam is set at 45°. The dependence of the birefringence on the ellipticity of the pump beam is observed, and a higher level of the birefringence is produced on increasing the ellipticity of the pump beam in the polymer film. The linearly polarized pump beam produces the highest birefringence, while the circularly polarized laser erases the induced birefringence. The time dependence of the birefringence growth and decay processes can be described by biexponential equations. The rates and amplitudes of the induced birefringence associated with both the fast and slow processes show a power dependence in our experiments. A new dynamic model including contributions of the *trans* and *cis* isomers of the azobenzene groups and the local polymer segments is proposed, and is in good agreement with the whole writing-erasing cycle of the experimental data. The numerical results of our model show that 55% and 40% of the photoinduced birefringence originate from the contributions of the oriented *trans* isomers of the azobenzene groups and the local polymer segments, respectively. The *cis* isomers make about 5% birefringence contribution, mainly due to the globular geometry and non-coplanar feature of the phenyl rings of the *cis* isomer.

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