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Light-Induced Anisotropy in Azobenzene Doped Copolymer Films

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In this study, an azobenzene dye, Dispersion Red 1 (DR1) was doped into the copolymers of methyl methacrylate(MMA) and butyl acrylate(BA) to obtain five bulk composites with varied ratios of methyl methacrylate to butyl acrylate. An experimental setup, in which the He-Ne laser produced signal beams and Ar^+ laser, the pump beams was employed to investigate the photoinduced anisotropic properties of these samples. The results show that, the lower rigidity of the copolymers chains caused by the increased BA content would lead to a lower extent of birefringence for the samples. With the increased pump beam power, the extent of birefringence first slightly increased, reached a maximum value, and then decreased. These increases and then decreases would be caused by the co-effects of both orientation and saturation mechanism. On the other hand, the optical dichroism properties can be detected in the bulk samples with photoinduced anisotropic property. The birefringence and dichroism properties exhibited by the dye-doped bulk composites have great potential in optical devices and optical communication systems; in particular, these bulk polymeric materials are very important for three-dimensional optical applications.

Keywords: Azobenzene, isomerization, dye-doped, light-induced anisotropy

1 Introduction

In recent years, there has been increasing interest in photoresponsive polymers in which light can be controlled by light as a stimulus. Among them, the azobenzene-containing polymers have received more and more attention because of their unique and excellent properties which allow various applications in information processing by photonics (1–6). One of the attractive phenomena is photoinduced orientation of the azobenzene moieties. When the azobenzene-containing polymers are under the excitation of polarized laser at a certain wavelength, the laser beam can cause the photo-isomerization of the azobenzene moieties, from*trans* isomers to *cis*, and then the *cis* ones photochemically and/or thermally back to the *trans* states. The *trans* isomers parallel to the polarization plane of the laser have a greater tendency to isomerize and reorientate. Therefore, during the *trans*-*cis*-*trans* isomerization cycles, a substantial portion of azobenzene groups would reach the more stable state in which the *trans* isomers aligned perpendicular to the polarization plane of the laser beam. The resulting anisotropy in polymer samples generated optical birefringence (7, 8) and dichroism properties. This photoinduced anisotropy in azobenzene polymers has been studied a great deal as promising applications in optical data storage, all-optical switching, as well as optic-optic controlling devices (9–15). So far, most studies involve samples of polymer membranes or films. Compared with the azo-dye containing polymer films, bulk materials have inneglectable thickness (usually in millimeters), which is very important for three-dimensional optical applications, such as the three-dimension optical storage, optical waveguides and other nonlinear optical devices (16–18). As for three-dimension optical storage, it is attractive that the effective area storage density can be significantly increased by using a thick recording layer to record multiple, independent pages of data. A recording medium of millimeter thickness or more is required to achieve high storage density by recording multiple volume holograms (18).

In order to investigate photoinduced birefringence and dichroism in azo-dye doped copolymer bulk materials, we synthesized five copolymers of methyl methacrylate and butyl acrylate [Poly(MMA-BA)]. They were all doped with azo-dyes DR1 [Disperse Red 1, 4′-(2-hydroxyethyl)ethylamino-4-nitroazobenzene], to yield DR1/poly(MMA-BA) bulk composite materials. By

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*Address correspondence to: Fang Zeng, College of Materials Science and Engineering, South China University of Technology, Guangzhou, China, 510640. E-mail: mcfzeng@scut.edu.cn adjusting the contents of butyl acrylate (BA) moieties in the copolymers, the flexibilities of polymer chains in the matrixes can be controlled. Optical experiments were conducted to investigate photoinduced birefringence and dichroism of these bulk samples.

2 Experimental

Disperse Red 1 (DR1), Methyl methacrylate (MMA) and butyl acrylate (BA) were purchased from Aldrich Chemical Company. The monomers of MMA and BA were purified by distillation under vacuum to remove inhibitors. The initiator, 2,2′-isoazobutyronitrile (AIBN), was purchased from Acros Organics and used as received. MMA and BA were mixed to obtain five monomer mixtures, with the BA weight percentages, namely BA/(BA+MMA), being 5, 10, 15, 20 or 30%, respectively. The initiator AIBN and DR1 chromophores were added into these monomer mixtures with their concentration of 2.0 wt% and 1.0 wt%, respectively. These mixtures were pre-polymerized at 70°C for about 40 min to yield viscous pre-polymers. Then the pre-polymers were injected through a 3.0 mm × 3.0 mm opening into glass molds, which were assembled with two parallel glass plates and 3.0 mm-thick spacers. The molds were then heated to 110°C by increasing the temperature by 10°C after every 2 h. Then, the molds were cooled to ambient temperature. The composite plates were carefully taken out of the molds, cut into 10 × 10 × 3.0 (in millimeters) cuboid blocks and polished for optical experiments. The five samples were denoted as BA-*i* ($i = 5$, 10, 15, 20 and 30, respectively), with the number *i* indicating the BA percentage.

The molecular weight for the samples were determined on a Waters 2410 gel permeation chromatography (GPC) using THF as the eluent (1.0 ml/min) at 30°C. The calibration curve was established by using polystyrene (PS) as the standard. The UV spectrum for DR1 monomers was measured in N,N-dimethylformamide (DMF) solution on a Hitachi U-3010 UV-Vis spectrophotometer. The photoinduced birefringence investigations were conducted at 25°C on an experimental setup illustrated in Figure 1.

The Ar^+ laser beam ($\lambda = 514$ nm) with a diameter of 0.5 mm was used as the pump beam. The sample was placed between two orthogonal polarizers (P1 and P2), in the path of a He-Ne laser beam ($\lambda = 632.8$ nm, 0.5 mW, diameter of 0.3 mm), which was used as the probe beam. The polished 10 mm×10 mm faces of the samples were perpendicular to the pump beam and signal beam as the test surfaces. The angle between the polarization directions of polarizers P1 and P3 was 45°. The change of optical property in the samples induced by the pump beam was monitored by detecting the intensity of the probe beam transmitting through polarizer P2. The intensity was automatically recorded with a digital oscilloscope. The pump beam was controlled by the shutter, turning on at the time of 0 s and turning off at the time of 200 s. All five samples were examined under different pump beam powers, in the range of 1.0 mW∼22.4 mW. The property of photoinduced dichroism was also investigated on the setup as shown in Figure 1, except that the polarizer P2 was removed and the detector recorded the intensities of the transmitted probe beam directly. In this test, the pump beam was turned on at 0 s and turned off at 50 s.

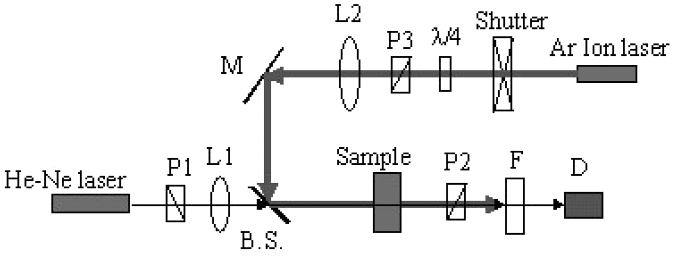

Fig. 1. The laser setup for the examination of photoinduced birefringence.

3 Results and Discussion

3.1 UV-Vis Absorption

Figure 2 shows the UV-Vis absorption spectrum of DR1 chromophores. The peak at about 502 nm corresponds to the absorption of the azobenzene moieties in DR1 molecules, and the smaller peak at 286 nm corresponds to the absorption of the phenyl moieties. This figure also shows the wavelengths of Ar^+ laser beam (514 nm), which is within the range of absorption of azobenzene; and the wavelength of He-Ne laser beam (633 nm), which is out of this range. Thus, Ar^+ laser was chosen as the pump beam to excite the isomerization in azobenzene groups to cause the anisotropy in the polymer, and He-Ne laser was chosen as the probe beam, whose transmittance in the polymer would indicate the extent of the photoinduced anisotropy.

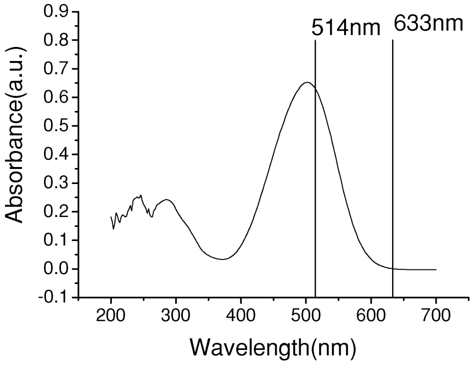

Fig. 2. The UV-Vis spectrum of DR1 chromophore and the wavelengths of Ar^+ laser and He-Ne laser.

3.2 Birefringence under Varied Pump Beam Powers

We investigated the properties of photoinduced birefringence of all five samples by using the experimental setup shown in Figure 1.

It is well known that azobenzene groups can exist in two configurations: the *cis* form and the more stable *trans* form. Upon exposure to the pump beam, the stable *trans* form can be photo-isomerized into *cis* form, and *cis-trans* back isomerization can occur thermally and/or photochemically. With repeated *trans-cis-trans* isomerization processes, the chromophore moieties would align perpendicular to the polarization plane of pump beam, and photoinduced anisotropy will occur. In our birefringence test, when the pump beam was turned off, the transmitted intensity of the probe beam was nearly zero because the angle between polarizers P1 and P2 is 90°. However, when the pump beam was turned on, the sample underwent optical anisotropy caused by the irradiation of the pump beam. Consequently, the polarization state of the probe beam is changed while passing through the sample, from the linear polarization state to the elliptical polarization state due to the anisotropy of the composite. Therefore, a vector of probe beam could be detected through P2 in a very short time after the turning on of the pump beam.

The extent of the birefringence can be calculated from the intensity I of the transmitted probe beam as shown in the following equation (15):

$$I = I_0 \sin^2(\pi \Delta n D/\lambda) \sin^2(2\theta) \tag{1}$$

Where, I_0 is the intensity of incident probe beam, I is the intensity of the transmitted probe beam, D is the thickness of the polymer sample (3.0 mm), λ is the wavelength of the probe beam (633 nm), Δn is the birefringence index, and θ is the angle between the polarization of the pump beam (after polarized by P3) and that of the probe beam (after polarized by P2). In this experimental setup, $\theta = 45°$, therefore, $\sin^2(2\theta) = 1$. So the increase in Δn of the polymeric film causes the monotonic increase in the intensity of the received probe beam I, and *vice versa*.

Figure 3 shows the intensity of the transmitted probe beam I for sample BA-5 under varied pump beam powers (I_{pump}). The intensity of incident probe beam was 0.5 mW and the pump beam powers (I_{pump}) were 1.0 mW, 3.1 mW, 5.6 mW, 8.2 mW, 11.2 mW, 14.8 mW, 18.4 mW and 22.4 mW, respectively. The pump beam was turned on at the time of 0 s, and turned off at the time of 200 s.

We can see from this figure that, turning on and off the pump beam can cause a gradual increase in the transmitted probe beam intensity at the time of 0 s and a swift decrease at 200 s, respectively, with a rising time and a falling time of about tens of seconds, which indicates that it takes a relatively long time for chromophore molecules to transform from the random ones into the ordered states (or from ordered ones into random states). And within the observation period between 200 s and 400 s, the samples can't thoroughly recover to the initial random state and exhibit a residual birefringence effect. The similar phenomena were also observed in our previous studies on the azo-dyes doped polymer films, but which showed relatively swift responses (19–21).

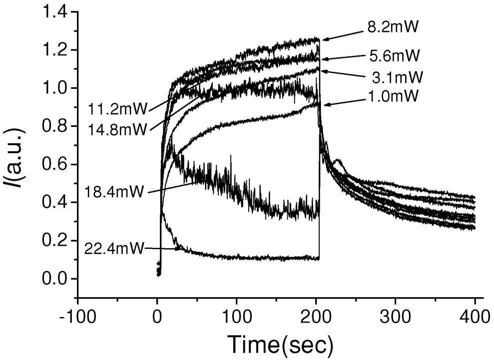

Fig. 3. The intensity of transmitted probe beam (I) for sample BA-5 under different pump beam powers (I_{pump}).

We calculated the averaged values of the transmitted probe beam intensity I over the whole irradiation period (0 s~200 s) to reflect the average extents of birefringence in sample BA-5 during excitation. The relationship between the averaged intensity (I_a) for BA-5 and the pump beam power (I_{pump}) are shown in Figure 4.

From both Figures 3 and 4, we can observe that, with increasing pump beam power, the birefringence extents, which is defined as the averaged intensities of transmitted probe beam (represented by I_a), first slightly increase, reach a maximum and then decrease. This phenomenon can be explained as follows: the first slight increase in the averaged intensity (I_a) (or the birefringence extents) with the pump beam power was mainly caused by a reorientation process. That is, when the pump beam became stronger, a higher population of chromophores were excited to undergo the repeated processes of the *trans-cis-trans* isomerizations so

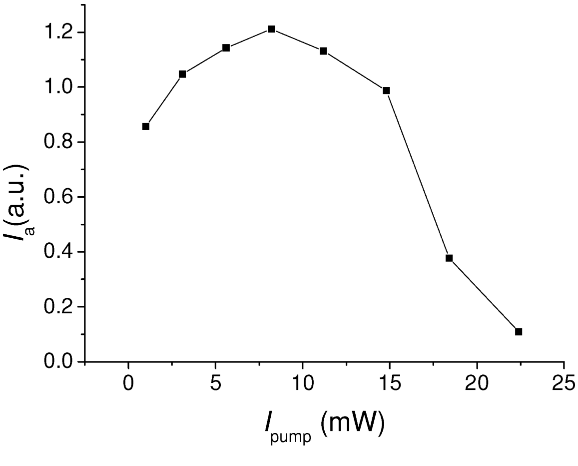

Fig. 4. The averaged intensities (I_a) in sample BA-5 as the function of the pump beam powers (I_{pump}).

that the reorientation effect of the azobenzene groups became stronger, thus causing the higher birefringence extents (19–21).

From Figures 3 and 4, we can see that, as the pump beam further increased to 18.4 mW and 22.1 mW, the birefringence dropped to a relatively low level. The possible mechanism is thought to be as follows: As a result of the further increase in the pump beam power, the reorientation would reach a saturated level. At this level, almost all the azobenzene groups were excited to the *cis* states, and it was very difficult for them to return to the stable *trans* states due to the continuous strong irradiation, and the sample was abundant in *cis* isomers and lack of oriented *trans* ones. Consequently, the repeated processes of *trans-cis-trans* isomerizations were restrained, causing the reduction of the birefringence extents. It can be also seen from Figure 3 that, as the pump beam was turned off, the intensities under 18.4 mW and 22.1 mW abruptly jumped to a high level, and then gradually decreased. The reason would be, that as the pump beam was just turned off, the strong excitation was promptly stopped, and the *cis-trans* back isomerization re-occurred and suddenly generated large quantities of orientated *trans* isomers from *cis* ones, resulting in the abrupt increase of birefringence.

Therefore, the effect of pump beam power on the birefringence behavior of the composite shown in Figure 4 was determined by both the effects of orientation and saturation.

3.3 Effect of Chain Rigidity of Polymer Matrix

To investigate the effect of chain rigidity on the photoinduced birefringence, we prepared a series of polymer samples with different butyl acrylate content and listed their molecular weights and glass transition temperatures in Table 1. It can be seen that the five samples have closed molecular weights; however, they exhibit different glass transition temperatures owing to different BA contents, thus at 25°C, at which the birefringences were measured, the five samples exhibit different chain flexibilities. The birefringence curves of all five samples under the same pump beam power of 14.8 mW are shown in Figure 5. In this figure, the birefringence differences caused by polymer matrixes with varied chain flexibilities can be observed. The lower weight percentage of BA in copolymers would cause more rigidity in the polymer chain segments. For rigid polymer chain segments, their thermal motion would be less active. The averaged transmitted intensities I_a for the five samples are in the decreasing order of: BA-5 > BA-10 > BA-15 > BA-20 > BA-30. These experimental results indicate that the polymer chains with higher rigidity favor the higher birefringence extent. After the chromophores were orientated through *trans-cis-trans* circles, the random thermal motions of chromophores themselves and the neighboring chain segments would also interrupt the ordered chromophore moieties. So, the rigid polymer chains in BA-5 and BA-10 made the composites exhibit higher photoinduced birefringence, while the flexible chains in BA-20 and BA-30 tended to reduce the birefringence.

Table 1. Molecular weight and glass transition temperature (T_g) of MMA/BA copolymers

Sample	*BA-5*	*BA-10*	*BA-15*	*BA-20*	*BA-30*
BA content (wt%)	5.0	10.0	15.0	20.0	30.0
M_w^a	1.6×10^5	1.7×10^5	1.5×10^5	1.5×10^5	1.8×10^5
T_g (°C) ^{b}	89	75	62	51	32

[a] Determined by GPC.
[b] Determined by DSC.

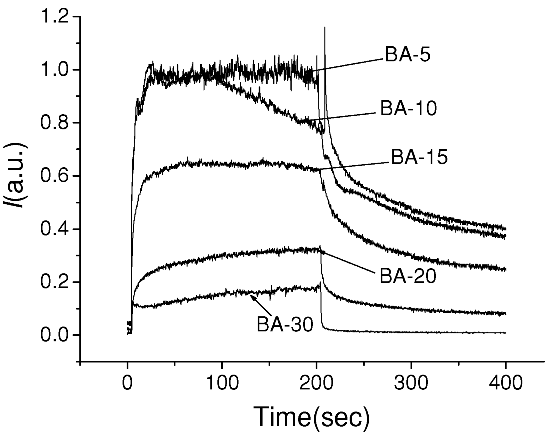

Fig. 5. The birefringence curves of five samples under the same pump beam power of 14.8 mW.

The averaged intensity (I_a) for five samples were also calculated and plotted against the pump beam power (I_{pump}) in Figure 6. The pump beam powers are in the range of 1.0 mW∼14.8 mW in the investigation. This figure also indicates that for different samples, the birefringence extent generally decreases with the increased BA content in the composites under every pump beam power in this investigation, due to the different rigidity of polymer chains. On the other hand, for each sample, the birefringence gradually increases, first due to the reorientation process and reaches a maximum; and then decreases as a result of saturation mechanism. So we can conclude that, the differences of copolymer chain structure leads to significant changes in the photoinduced birefringence, with an extent even greater than that of the contribution of pump beam powers.

3.4 Photoinduced Dichroism

To further investigate the photoinduced anisotropy in the samples, we conducted the dichroism measurements. The dichroism represents the different light transmittance along different axes in the anisotropic sample. In our case, it means different transmittance in different polarization

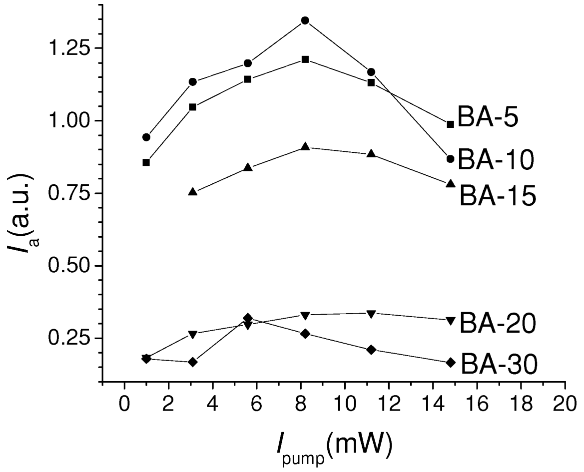

Fig. 6. The averaged intensities (I_a) in five samples under different pump beam powers (I_{pump}).

direction of laser beams. This photoinduced dichroism property would play an important role in such applications as optic-optic switching, wave filtering and optical modulation. As an example, BA-5 was investigated in this study since BA-5 has the greatest photoinduced anisotropy according to the birefringence measurements above.

The experimental setup was similar to that of the birefringence investigation, except that the polarizer P2 was removed so that the detector directly records the intensities of the transmitted intensity of the probe beam. The intensity of the probe beam and pump beam was 40 μW and 15 mW, respectively. The experiments for recording the photoinduced dichroism of the composites were conducted with the polarized planes of pump beam and probe beam (1) parallel to each other, or (2) perpendicular to each other.

The dichroism experimental results are shown in Figure 7. It clearly indicates that the curves for the above-mentioned two arrangements (parallel and perpendicular) are different. When the pump beam was turned on at the time of 0 s, the transmittance of the parallel arrangement (arrangement 1) increased, while that of the perpendicular arrangement (arrangement 2) decreased. When the pump beam was turned off at the time of 50 s, the intensities in both arrangements recovered quickly to their initial values.

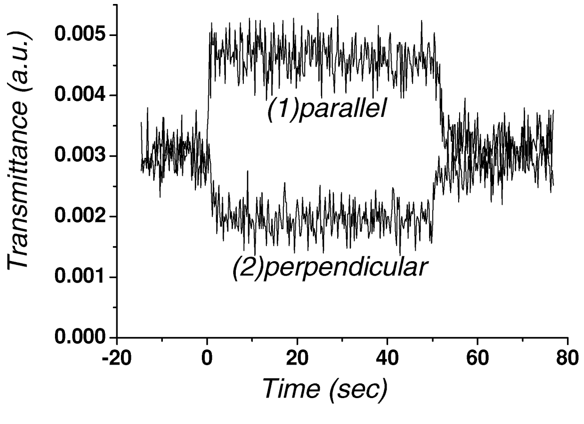

Fig. 7. Photoinduced dichroism for sample BA-5. The polarized planes of pump beam and probe beam are (1) parallel to each other, or (2) perpendicular to each other.

The azobenzene molecule has two isomers, the *trans* and the *cis* one. Previous studies have proved that the *cis* isomers have absorption at the probe beam wavelength of 633 nm (17). On the other hand, the *trans* isomers have positive dichroism, which will cause much stronger absorption in the polarized direction parallel to the molecular dipole moment of azobenzene moieties (17). When the pump beam was turned on, *cis* isomers were generated and then some *cis* isomers isomerize back to the *trans* form, and the continuous excitation of the sample led to the combination of *cis* and the reoriented *trans* forms (with the molecular geometrical axis perpendicular to the pump beam polarization direction). Thus, when the sample was being excited, there were two effects on the transmittance of the materials. First, the appearance of *cis* isomers would increase the absorption of the probe beam and decreases its transmission. Secondly, due to the positive dichroism in the reoriented *trans* isomers, the absorption of the probe beam would increase in the polarization direction along the aligned molecular geometrical axis, but decrease in the cross polarization direction. This effect of reoriented *trans* isomers played the primary role in the changes of transmittance. In the parallel arrangement as shown in Figure 7 (1), the polarization direction of probe beam was parallel to that of the pump beam and consequently, perpendicular to the reoriented *trans* isomers, causing a remarkable increase in transmittance. On the other hand, the contribution from the *cis* isomers, which would decrease the transmittance, is of little importance for the recorded values. While in the perpendicular arrangement shown in Figure 7 (2), the polarization direction of the probe beam was perpendicular to that of the pump beam and consequently, parallel to the reoriented*trans* isomers, resulting in the decrease in the transmittance. In addition, the absorption caused by the *cis* isomers also contributed to the decrease in transmittance. When the pump beam was switched off, the anisotropy in the sample recovered quickly, because the random molecular thermal motion destructed the alignment of *trans* isomers. Thus, the transmittance of sample in both cases returned to the initial value.

4 Conclusions

In this study, five bulk samples of azo-dye doped copolymers with varied ratios of MMA/BA monomers were fabricated. Their photoinduced birefringence properties were investigated experimentally under different pump beam powers and with varied rigidity of chain segments. Swift photoinduced birefringence was observed for these polymers. With increasing pump beam power, the extent of birefringence first slightly increased due to reorientation mechanism, and then decreased due to the saturation mechanism. The flexibilities of polymer chains in the samples play an important role in the photoactive properties. Higher rigidity in the polymer chains would favor the photoinduced birefringence.

The investigation of photoinduced dichroism also proved the anisotropy in the optic-excited sample, and these photoinduced changes in transmittance could find wide applications in optic sensitive polymers.

Compared with previous research on azo-dye doped thin films, these bulk materials showed larger birefringence extents (I_a), though the concentration of azo-dye is relatively low; but they have a relatively longer period of relaxation (about tens of seconds) in the reorientation/recovery processes.

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