Thickness dependence of the photoinduced birefringence in azodye-doped inorganic–organic hybrid materials by a femtosecond laser

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Abstract
The kinetics of the photoinduced birefringence (PB) induced by a femtosecond laser through two-photon absorption was studied in bulk azodye-doped inorganic–organic hybrid materials derived from the sol–gel method. The effects of the sample thickness on the kinetics of the PB were investigated. The probe transmittance for the saturated PB considerably increased and saturated with increasing the thickness, while the effects of the thickness on the permanent PB were nonsensitive and the saturation effect was not observed. Possible mechanisms, which were associated with the thickness dependence of the probe transmittance for the saturated PB and the permanent PB, were analysed.

1. Introduction

In recent years, the photoinduced birefringence (PB) in azodye-doped materials upon irradiation with a polarized laser has generated much interest due to their potential applications in optical data storage, patterning optical waveguides, and optical switching [1–3]. The mechanisms are based on the selective excitation of the azodye molecules that have a dipole component parallel to the writing beam polarization (so-called angular hole burning, AHB) and the photoinduced reorientation of the azodye molecules that is obtained through a multitude of trans–cis–trans isomerization cycles (so-called angular redistribution, AR). Generally,

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inorganic or polymeric materials are chosen as the supporting matrices for azobenzene molecules. However, a number of significant problems remain to be addressed before the azodye-doped materials can be used as practical photonic-based materials.

One crucial problem is the fact that the wavelength of the writing beam in most studies on this effect is set within the resonant absorption range of azodye molecules that are usually doped into polymer films. This limits the thickness of the sample to several micrometres and makes photoinduced volume birefringence impossible. One excellent method to induce the PB inside transparent bulk materials consists of using femtosecond lasers through multiphoton absorption, because femtosecond lasers have high peak power and ultrashort pulse width [4, 5].

In addition, the relation between the structure of supporting matrices used for loading photoactive molecules and the properties of the PB still remains to be determined, although the rigidity of the polymer matrices, working temperature, and the way of the linkage to the polymers have been investigated extensively for the photoinduced anisotropy [6, 7]. Interestingly, by the replacement of inorganic or polymeric matrices with inorganic–organic hybrids, many practical advantages of the matrix may be gained, such as high versatility for preparing materials whose physical and chemical properties can be modified [8, 9]. By virtue of these advantages the free volume of the hybrid materials can be changed to optimize the isomerization and reorientation of dye molecules.

In view of these problems, photoinduced volume birefringence by an 800 nm femtosecond laser in azobenzene-doped inorganic–organic nanomaterials derived from the sol–gel method has been reported in our group [5]. The maximum probe transmittance obtained for the PB was estimated to be 92% and optical data storage was demonstrated. When we bring these nanomaterials into applications in photonic devices, the effects of the thickness on the growth kinetics rate and the saturation value of the PB should be considered. The above results, however, were achieved without considering the thickness dependence of the PB.

In this paper, the effects of the thickness on the rising rate of the probe transmittance for the PB were investigated under the exciting conditions of 800 nm and 150 fs laser pulses at a repetition rate of 1 kHz, the wavelength of which was outside the linear absorption region of the azodye-doped samples. Additionally, the thickness dependences of both the saturated PB (Δn_{sat}) and the permanent PB (Δn_{perm}) were investigated. The probe transmittance for Δn_{sat} was saturated after reaching a thickness (~ 7 mm), while the effect of the thickness on Δn_{perm} was not as sensitive as that for Δn_{sat} and the saturation effect was not observed.

2. Experiments

2.1. Sample preparation

The azodye used was 4-[N-(2-hydroxyethyl)-N-ethyl] amino-4$'$-nitroazobenzene (disperse red 1, DR1), which was purchased from Aldrich and used as received. The bulk materials of varying thicknesses (0.5, 1, 3, 5 and 7 mm) were prepared by hydrolysis–condensation of the organically modified precursors vinyltriethoxysilane $H_2C{=}CHSi(OC_2H_5)_3$ in ethanol under acid (HCl)-catalysed hydrolysis and basic-catalysed condensation. The azodye was dissolved in acetone/ethanol mixed solvent and then introduced into the sol–gel precursor solution. The weight ratio of the azodye to silica was 3.93 wt%. Details of the preparation processing have been given elsewhere [10]. The derived azodye-doped gel glasses were red and cylindrical transparent materials, 20 mm in diameter. UV–VIS–IR absorption spectra showed that the PB in the bulk materials using an off-resonance wavelength pump beam was based on two-photon absorption (TPA) [11].
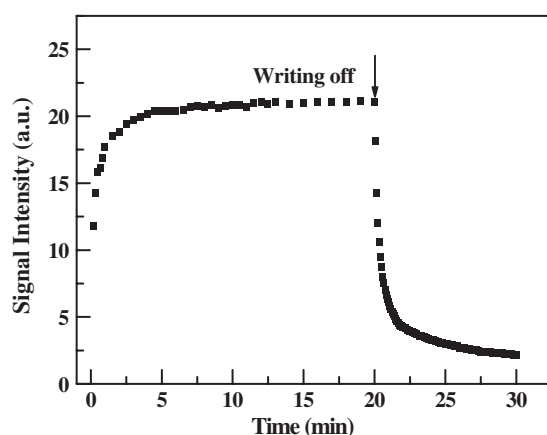
Figure 1. Typical growth and relaxation kinetics of the probe transmittance for the PB in DR1-silica (7 mm) by a 150 fs laser with a power of 150 mW at a rate of 1 kHz.

2.2. Birefringence measurements

An optical Kerr shutter configuration was used for measuring the PB. An 800 nm femtosecond laser with a power of 150 mW and a 633 nm He–Ne laser (0.5 mW cm^{-2}) were used as the writing and probe beams, respectively. The focal length of the lens was 100 mm and the distance between the lens and the sample was 70 mm. The detailed experimental setup for measuring the PB has been described elsewhere [4, 5].

3. Results and discussion

3.1. Photoinduced birefringence kinetics

The typical growth and relaxation kinetics of the probe transmittance for the PB in the DR1-silica (7 mm) is presented in figure 1. The results show that after switching on the writing beam the probe transmittance for the PB is saturated at a value corresponding to Δn_{sat} for a certain time and that after switching off the writing beam, the probe transmittance for the PB decreases to a certain value corresponding to Δn_{perm}. The decay of the probe transmittance for the PB can be characterized by three components: a fastest one, a fast one, and a slow one. The decay times for the faster and fastest components are a few seconds and less than 1 s (the time resolution of the measurement system in this experiment), respectively. These correspond to the lifetime of the cis isomerization and the triplet states of azobenzene molecules [12]. Furthermore, one can see that the AHB is much more important than the AR because the hybrid materials have a rigid three-dimensional inorganic network greatly hindering the reorientation of azodye molecules. The difficulty of reorientation in hybrid materials has been demonstrated [13]. These results are different from those of azodye-doped polymethylmethacrylate (PMMA), in which the PB is mainly due to the reorientation of the azodye molecules [4].

3.2. Thickness dependence of the probe transmittance for the PB

Figure 2 shows the thickness dependence of the growth and relaxation kinetics of probe transmittance for the PB in samples of different thicknesses: 0.5, 3, 5 and 7 mm. From
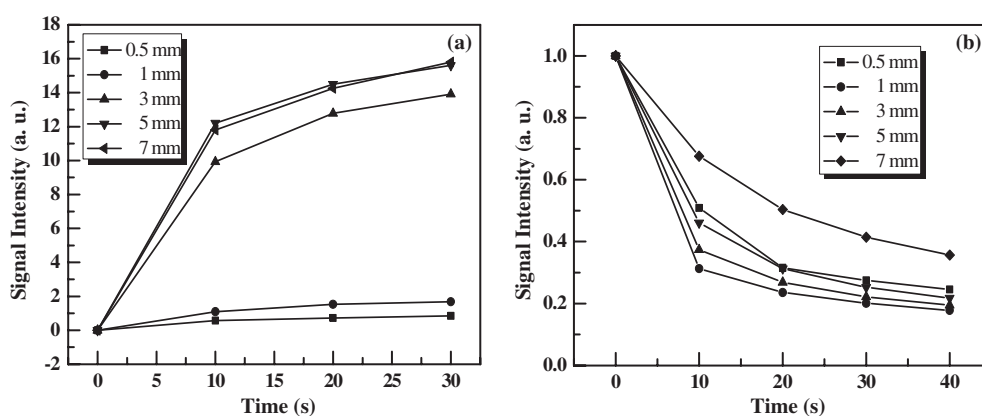
Figure 2. Thickness dependences of the growth and relaxation kinetics of the probe transmittance for the PB. (a) Growth kinetics. (b) Relaxation kinetics.
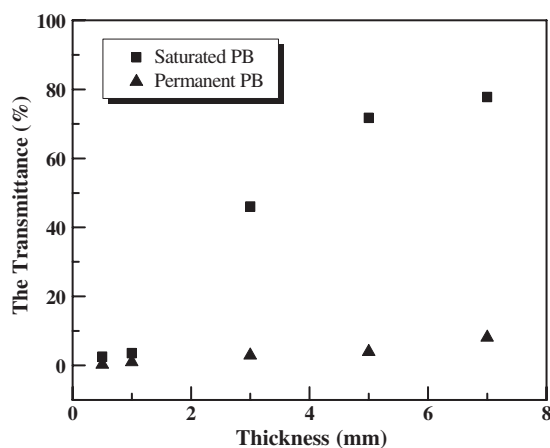

Figure 3. Thickness dependence of the probe transmittance for the saturated PB and the permanent PB. The probe transmittance for the saturated PB will be saturated with increasing the thickness.

figure 2(a), one can see that the growth rate of the probe transmittance for the PB becomes remarkably fast and the saturation value increases considerably with increasing the thicknesses of the samples. However, the saturation time of the probe transmittance for the PB increases dramatically. Similar results are also found in pDR1A polymer thin films using a 514.5 nm argon laser beam as the writing beam [14] and in methyl red doped polystyrene using a 488.0 nm Ar$^+$ laser as the writing beam [15], the writing wavelengths of both of which are inside the linear absorption range of the azodye molecules. The results shown in figure 2(b) indicate that the decay of the probe transmittance for the PB in the thicker sample is a little slower. This is probably because there are more excited azodye molecules attending the trans–cis photoisomerization and thus the PB in the thick sample is larger than that in the thin sample at the same time.

In figure 3 the thickness dependences of the probe transmittance for Δn_{sat} and Δn_{perm} are presented. Obviously, there is a strong thickness dependence for Δn_{sat}. The probe transmittance for Δn_{sat} increases considerably with increasing the thickness and is saturated

after reaching a certain thickness. The maximum probe transmittance for Δn_{sat} is estimated to be 80%. However, we observe a nonsensitive thickness dependence of the probe transmittance for Δn_{perm}. The saturation effect related to the thickness is not found over the range of thickness studied due to low probe transmittance. The probe transmittance for Δn_{perm} is 0.24% at a thickness of 0.5 mm and only 8.09% at 7 mm. These results further demonstrate that in DR1-silica the *trans–cis* photoisomerization effect dominated the effect of photoinduced anisotropy and thus the fast growth and decay of the probe transmittance for the PB are mainly due to the trans–cis photoisomerization effect.

Generally, the probe transmittance for the PB resulting from linear absorption or one-photon absorption can be expressed as [16]

$$I = I_0 \sin^2(\Delta\varphi/2) \sin^2(2\theta), \tag{1}$$

where I and I_0 are the intensity of the incident and transmitted probe beams respectively, $\Delta\varphi$ is the phase change, and θ is the angle between the polarization of the pump beam and that of the probe beam. $\Delta\varphi$ in equation (1) is given by

$$\Delta\varphi = (2\pi \Delta n/\lambda_{\text{p}})(1 - \exp(-\alpha_0 L))/\alpha_0, \tag{2}$$

where λ_{p} is the wavelength of the probe beam, L is the sample thickness, and α_0 is the linear absorption coefficient. Similarly to the linear absorption, in the TPA-induced PB the attenuation of the pump beam should be also considered. Then, the local intensity of the pump beam can be expressed as [17]

$$\frac{\partial I(z, t)}{\partial z} = -\omega\gamma I^2(z, t), \tag{3}$$

where $I(z, t)$ is the local intensity of the writing beam, ω is the frequency, and γ is the TPA coefficient. On the other hand, the two-photon transition rate $W_{\text{gf}}^{(2)}$ using the perturbation method can be expressed as [18]

$$W_{\text{gf}}^{(2)} = \frac{\gamma M}{N_{\text{A}}\rho} I^2(z, t), \tag{4}$$

where N_{A} is the Avogadro number, ρ is the mass density, and M is the molecular mass.

A proposed mechanism is shown to further understand the thickness dependences of the probe transmittance for Δn_{sat} and Δn_{perm}. According to equations (1) and (2), we expect that two cases exist. For $L < L_{\text{c}}$ (L_{c} is a critical sample thickness), the phase change due to the PB is small and equation (1) can be simplified into $I = I_0 \sin^2(2\theta)(\Delta\varphi/2)^2$, in which I is proportional to the square of the thickness; for $L \geqslant L_{\text{c}}$, however, the phase change is so large that the above simplification is no longer appropriate and the probe transmittance is proportional to $\sin^2(\Delta\varphi/2)$ according to equation (1). When the maximum value of the function of $\sin^2(\Delta\varphi/2)$ is obtained, the probe transmittance for Δn_{sat} is saturated. Over the range of the studied thickness, the two cases are demonstrated in figure 3, and L_{c} is estimated to be about 5 mm. However, the relation between the probe transmittance for Δn_{perm} and the sample thickness is not consistent with equation (1) because of the relaxation of the cis-form DR1 molecules. In addition, based on equations (3) and (4), the reason why the saturation time of the probe transmittance for the PB increases dramatically with increasing the thickness can be interpreted as following: the pump intensity becomes weaker and weaker when propagating in the sample and thus the $W_{\text{gf}}^{(2)}$ decreases faster and faster, leading to a longer time to achieve the saturation value.

Our work is important because for practical applications of the inorganic–organic hybrid materials in photonic devices some important parameters must be optimized. Besides the effects of the thickness, the effects of writing conditions on the growth kinetics rate and

the saturation value of the probe transmittance for the PB are also investigated in our group. In addition, complementary experiments are in progress to investigate the effects of the microenvironments on the photoisomerization and reorientation kinetics of the azodye molecules by coupling some flexible oligomers into the rigid network.

4. Conclusions

In conclusion, PB induced by a femtosecond laser through two-photon absorption was demonstrated and the thickness dependence of the probe transmittance for the PB was thoroughly investigated. The growth kinetics of the probe transmittance for the PB showed that the growth rate became remarkably fast with increasing the thickness, while the decay kinetics of the probe transmittance for the PB showed that the decay of the probe transmittance for the PB in the thicker sample became slower. In addition, the probe transmittance for Δn_{sat} was saturated at about 7 mm and the saturation time increased. Analysis showed that the saturation of the probe transmittance for Δn_{sat} resulted from the large thickness and the intensity attenuation of the writing beam due to TPA led to elongation of the saturation time of the probe transmittance for the PB. However, the effect of the thickness on Δn_{perm} was not as sensitive as that for Δn_{sat} and the saturation effect related to the thickness was not observed.

Acknowledgments

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