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All-optical switching properties of poly(methyl methyacrylate) azobenzene composites

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In this paper, the all-optical switching polymer composites based on poly(methyl methacrylate) (PMMA) and azobenzene dyes were prepared. The optical switching effects of the composites were measured by using 514 nm pump beam and 632.8 nm probe beam. The composites' photoinduced reversible and repeatable change in the transmittance of the probe beam is attributed to the photoisomerization of the azobenzene dyes. The influencing factors of the optical switching properties, such as the modulation frequency, pump beam intensity and temperature, were studied experimentally. The effects of pump beam power and temperature on the optical switching response were also studied experimentally. © *2003 Kluwer Academic Publishers*

1. Introduction

In recent years, much attention has been paid to photonics in which light can be controlled by light as a stimulus as future technology for various photonic applications such as optical switching, high-speed information processing, optical image storage, and optical display [1]. Light has a lot of properties such as intensity, polarization, and wavelength, and these properties are quite useful for information processing. Therefore, by photonics, it may be possible to process much information quickly. In photonics, switching devices play an important role in the control of light, changing their own physical properties with the stimulus light.

Azobenzene-containing polymer systems have received increasing attention because of their unique and unexpected properties which allow various applications triggered by light [2–6]. One of the attractive phenomena is photoinduced alignment of the azobenzene moieties upon irradiation of linearly polarized light. The photoinduced anisotropy of azobenzene dyes has been studied quite a lot for promisingapplications in optical data storage and all-optical switching [6–13]. As for optical data storage, polymer systems containing azobenzene dyes have been reported by many researchers, e.g. surface relief gratings and photoinduced birefringence resulted from the photoinduced anisotropy of azobenzene in these systems [7, 8, 14–16]. As for all-optical switching, various polymer liquid crystal (LC) composites containing azobenzene dyes have been studied; in these composites, phase transitions of the LCs induced by the photoinduced anisotropy of azobenzene are the keys to optical switching effects; orientation of azo dyes induced by irradiating the polarized light is considered to be a driving force for the alignment of the liquid crystals [17–19]. Few composite systems containing only an inert host polymer and azobenzene dyes have been reported for the all-optical switching effect. In the present paper, we report long-term stable all-optical switching devices based on composites consisting of poly(methyl methacrylate) (PMMA) and the donor-acceptor type azobenzene dyes 4′-(2-hydroxyethyl)ethylamino-2-chloro-4-nitroazobenzene (Disperse Red 13, DR 13).

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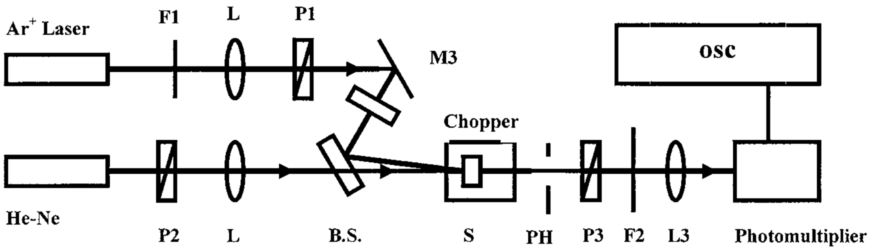

Figure 1 Experimental setup for measurement of optical switching effect: F—filter; L—lens; P—polarizer; M—mirror; B.S.—beam splitter; S—sample; PH—diaphragm.

The all-optical switching effects of these composites were studied by using the 514 nm pump beam and 632.8 nm probe beam. In addition, the effects of the modulation frequency of the chopper, the pump beam intensity and temperature on the optical switching properties of the composites were investigated experimentally as well. Long-term stability of over one year of the devices was accomplished by carefully eliminating impurities, residual solvents, and air pockets in the material.

2. Experimental

2.1. Sample preparation

Poly(methyl methacrylate) (PMMA, $M_W = 93000$), and 4′-(2-hydroxyethyl)ethylamino-2-chloro-4-nitroazobenzene (Disperse Red 13, DR 13) were purchased from Aldrich Chemical Company.

The film samples were prepared as follows: PMMA was dissolved in toluene. A clear solution was obtained. To this clear solution, DR 13 (equivalent to 2.5% of PMMA by weight) was added. Then the mixture was heated and stirred for 5–6 h until a clear, red solution was obtained. Afterwards, the solution was filtered (5.0 μm, Teflon) into another beaker. Later, the solution was heated on a hotplate to evaporate some of the solvents. After the solution volume was reduced to about 3×10^{-6} m^3 (this solution is used as the solution sample in the experiment), the remaining solvents were removed by heating the solution on a piece of stainless steel. The stainless steel plate was placed on a hotplate and heated to 60°C–70°C. The solution was pipetted onto the stainless steel plate drop by drop and stirred with a stainless steel spatula until all of the solvents appeared to have evaporated. The soft polymeric material was then rolled into a ball and cut into small pieces for film preparation.

Prior to film preparation, the above-mentioned material was placed in the vacuum oven and dried at 65°C for 4 days just before use. The drying was found to be necessary for preventing formation of bubbles in the film due to residual solvent. Then the dried material was placed on the glass slide, 4 Teflon spacers (50 μm thick) were placed on the four corners of the glass slide. The glass slide was placed on the hotplate, until the material softened. Afterwards, a second glass slide was used to sandwich the material in between the two glass slides. At the same time, pressure was applied to the glass slides. Finally, the device was allowed to cool to room temperature in air.

2.2. Measurement

The all-optical switching effect of the composites were measured by using the experimental setup as shown in Fig. 1. An argon laser beam (514 nm) with a diameter of 0.5 mm was used as the pump beam. The sample was placed between two orthogonal polarizers (P2 and P3) in the path of a He-Ne laser beam (632.8 nm, probe beam, 1.16 mW, with a diameter of 0.3 mm). The angle between the polarization direction of polarizers P1 and P2 is 45°. The optical change of the samples induced by pump beam was monitored by detecting the intensity of the probe beam transmitting through polarizer P3. The intensity was automatically recorded with a digital oscilloscope.

3. Results and discussion

Fig. 2 shows the intensity of the transmitted probe beam as a function of time at different modulation frequencies (pump beam power = 27.4 mW). In the figure, at the peak points of the curves, the pump beam was turned off; while at the valley points of the curves, the pump beam was turned on. When the pump beam was blocked, the transmitted intensity of the probe beam was quite low; this is because the angle between polarizers P2 and P3 is 90°. When the pump beam was unblocked, the probe beam could be detected. This is because the polarization of the probe beam is changed while passing through the sample due to the photoinduced anisotropy resulted from the irradiation of the pump beam. It is well known that, azobenzene groups can exist in two configurations: the *cis* form and the more stable *trans* form. When exposed to light of a certain wavelength, the stable *trans* form can be photoisomerized to the *cis* form. *Cis-trans* isomerization can occur thermally and/or photochemically. By the repetition of the *trans-cis-trans* isomerizations, photoinduced anisotropy will occur. In our composite systems, the photoinduced anisotropy changes the polarization of the probe beam.

From Fig. 2, we can see that, as the pump beam is turned on, the intensity of the probe beam increases rapidly; while as the pump beam is turned off, the intensity of the probe beam decreases quickly. This indicates the all-optical switching effect has quick response. As the modulation frequency increases (from 300 to 1000 Hz), the switching response becomes quicker, but the modulation depth (all-optical switching effect) becomes less. This is because, at higher modulation frequency, there might be in sufficient time for the oriented

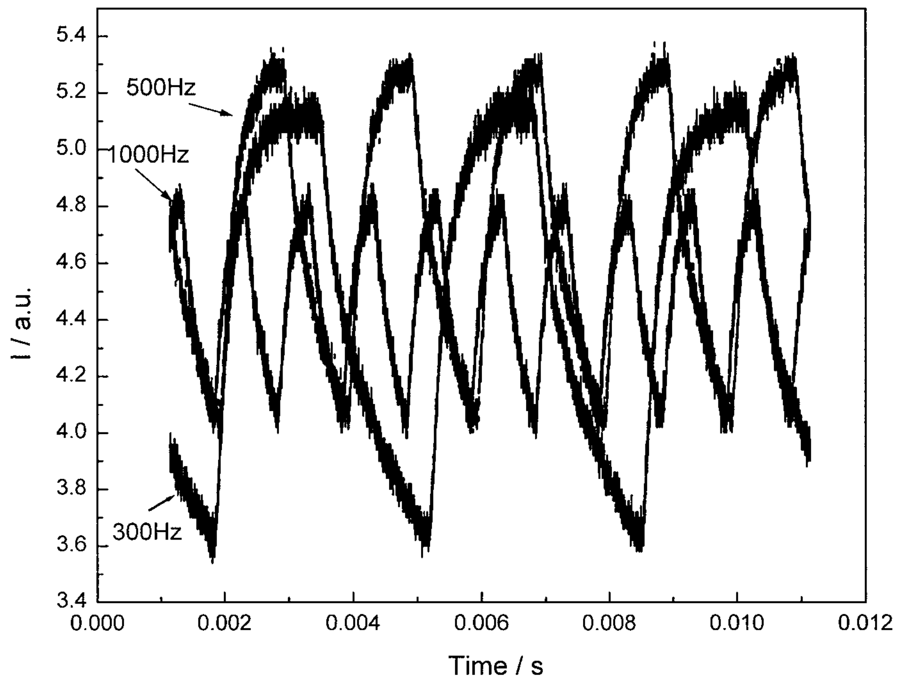

Figure 2 The intensity of the transmitted probe beam as a function of time under different modulation frequencies.

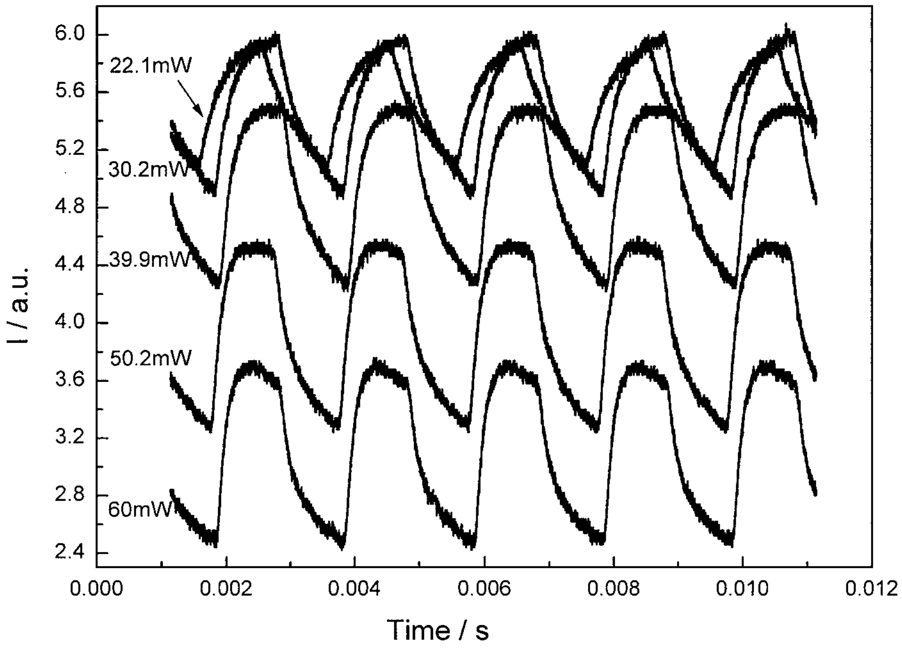

Figure 3 The intensity of the transmitted probe beam as a function of time at different pump beam powers.

azobenzene molecules to relax to their fully random structure; hence the modulation depth becomes less.

Fig. 3 shows the intensity of the transmitted probe beam as a function of time at different pump beam powers (modulation frequency = 500 Hz). It can be seen that, under a given modulation frequency, the modulation depth becomes greater as the pump beam intensity is increased. This is because, at higher pump beam intensities, the photoanisotopy of the composites is stronger, which in turn leads to greater modulation depth. From Figs 2 and 3, it also can be seen that, under different modulation frequencies and pump beam intensities, there is no obvious crosstalk for the device.

Fig. 4 shows the optical switching effect of the sample under different temperatures (modulation frequency = 500 Hz, and pump beam power = 39.3 mW). It can be seen that, as temperature increases, the optical switching becomes less obvious. The glass-transition temperature of the system is 104°C (measured by using a Perkin Elmer DSC 7 differential scanning calorimeter (DSC) with a heating rate of 10°C/min under nitrogen). In this experiment, the testing temperatures are under the glass-transition temperature of the system. The experimental phenomenon is probably because, as temperature is increased, the *cis-trans* back isomerization of the azobenzene molecules occurs more quickly. In this experiment, in addition to film samples, we

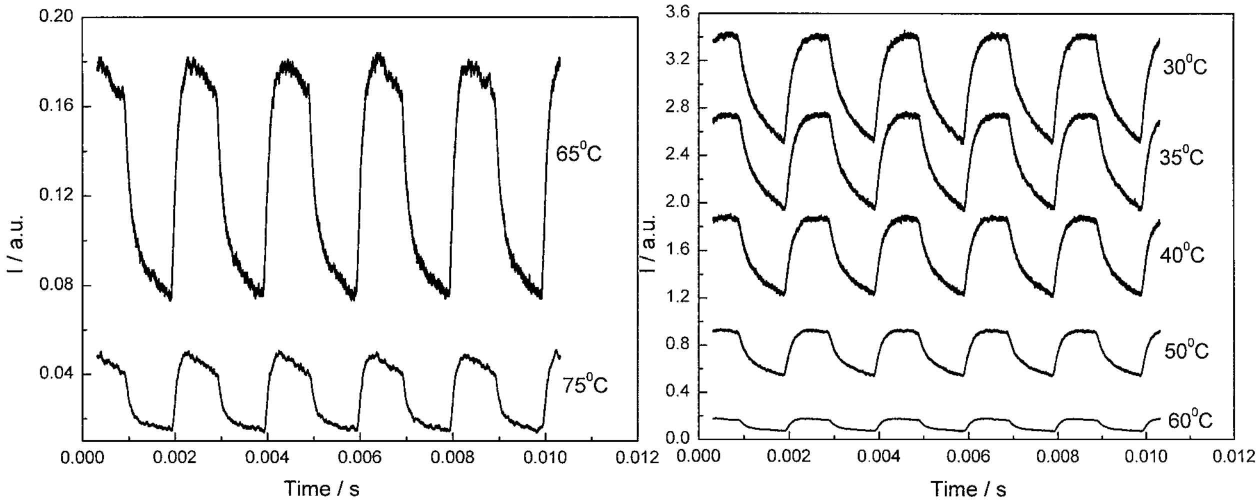

Figure 4 The intensity of the transmitted probe beam as a function of time at different temperatures.

also measure the optical switching effect of the solution sample. No optical switching effect could be observed for the solution sample. This may be explained as follows: Upon exposure to the pump beam, in film samples, through the *trans-cis-trans* transitions, azo dye molecules are arranged in an ordered way, thus photoinduced anisotropy occurs. Compared with film samples, in solution, the *cis-trans* back isomerization of azo molecules is much easier, and the polymer chain segments are also in free motion, so no significant photoinduced anisotropy could occur.

In the present study, the effects of the pump beam power and temperature on the system's optical switching response were also investigated, and the experimental results are shown in Figs 5 and 6. Fig. 5 shows the intensity of the transmitted probe beam as a function of time at different temperatures when the pump beam is kept turned on (pump beam power = 38.7 mW). Fig. 6 shows the intensity of the transmitted probe beam as a function of time at different pump beam powers when the pump beam is kept turned on. It can be seen that, under lower temperatures or lower pump beam powers, the intensity of the probe beam intensity first increases with time, then levels off; under higher temperatures or higher pump beam powers, the intensity of the transmitted probe beam first quickly reaches a maximum value, then decreases with time; as the temperature or the pump beam power increases, the peak of the transmitted probe beam intensity becomes more obvious, but the peak value becomes smaller. These experimental phenomena can be explained as follows: under lower pump beam power, photoinduced anisotropy due to *trans-cis-trans* isomerizations of azo dyes occurs, and the intensity of the transmitted probe beam increases with time and finally levels off; as the pump beam power or temperature is increased, the intensity of the transmitted probe beam decreases, this might be caused by thermal effects. As for lower pump beam power, thermal effects in the sample may be neglected; while under higher pump beam powers, the sample's temperature could be changed due to thermal effects, and the relaxation of the orientated molecules in the sample could be induced. As the temperature is increased, thermal disturbance of the oriented molecules due to the linearly-polarized pump beam is increased, thus the randomness in the sample is increased; in turn, the photoinduced anisotropy decreases, and the intensity of the transmitted beam decreases.

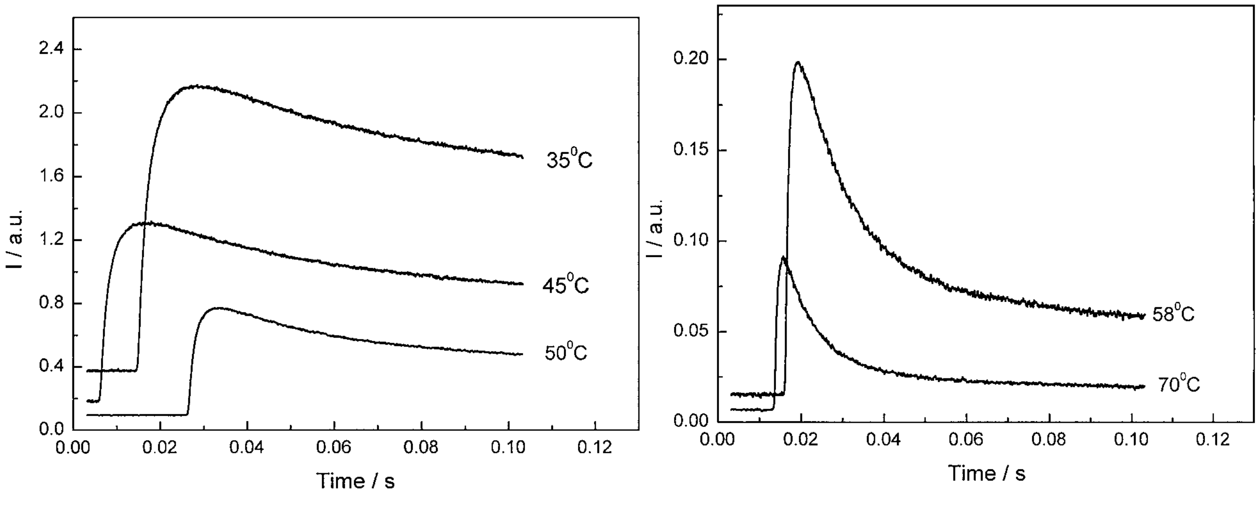

Figure 5 Response characteristic at different temperatures.

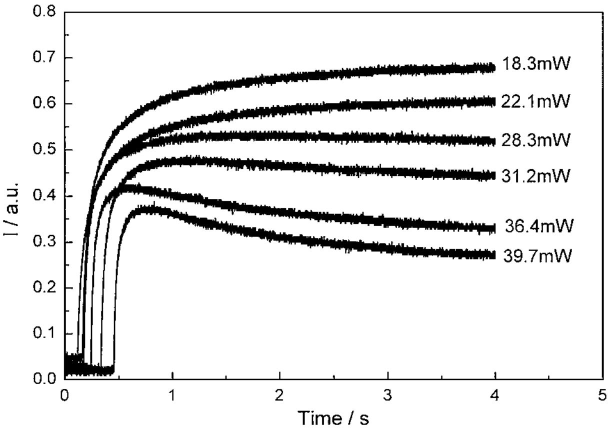

Figure 6 Response characteristic at different pump beam powers.

4. Conclusions

In this article, we have prepared PMMA-based azobenzene composites. The composites' photoinduced reversible and repeatable change in the transmittance of the probe beam is attributed to the photoisomerization of the azobenzene dyes. As the modulation frequency increases, the switching response becomes quicker, but the modulation depth becomes less. At a given modulation frequency, the modulation depth becomes greater as the pump beam intensity is increased. Under lower temperatures or pump beam powers, the intensity of the transmitted probe beam first increases with time, then levels off. As temperature or pump beam power is increased, the intensity of the transmitted probe beam decreases.

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References

1. A. SHISHIDO, O. TSUTSUMI, A. KANAZAWA, T. SHIONO and T. TAMAI, *J. Phys. Chem.* B **101** (1997) 2806.
2. W. M. GIBBONS, P. J. SHANNON, Sh. T. SUN and B. J. SWETLIN, *Nature* **351** (1991) 49.
3. D. EATON, *Science* **253** (1991) 281.
4. T. IKEDA and O. TSUTSUMI, *ibid.* **268** (1995) 1873.
5. S. BIAN, J. A. HE, L. LI, J. KUMAR and S. K. TRIPATHY, *Adv. Mater.* **12** (2000) 1202.
6. R. ROCHON, E. BATALLA and A. NATANSOHN, *Appl. Phys. Lett.* **66** (1995) 136.
7. D. Y. KIM, S. K. TRIPATHY, L. LI and J. KUMAR, *ibid.* **66** (1995) 1166.
8. M. S. HO, C. BARRETT, J. PATERSON, M. ESTEGHAMATIAN, A. NATANSOHN and P. ROCHON, *Macromolecules* **29** (1996) 4613.
9. X. WANG, S. BALASUBRAMANIAN, L. LI, X. JIANG, D. J. SANDMAN, M. F. RUBNER, J. KUMAR and S. K. TRIPATHY, *Macromol. Chem. Rapid Commun.* **18** (1997) 451.
10. T. S. LEE, D. Y. KIM, X. L. JIANG, L. LI, J. KUMAR and S. K. TRIPATHY, *J. Polym. Sci. Part A: Polym. Chem.* **36** (1998) 283.
11. S. HVILSTED, F. ANDRUZZI and P. S. RAMANUJAM, *Opt. Lett.* **17** (1992) 1234.
12. S. HVILSTED, F. ANDRUZZI, C. KULINNA, H. W. SIESLER and P. S. RAMANUJAM, *Macromolecules* **28** (1995) 2172.
13. C. EGAMI, Y. KAWATA, Y. AOSHIMA and S. ALASFAR, *Jpn. J. Appl. Phys.* **39** (2000) 1558.
14. U. PIETSCH, P. ROCHON and A. NATANSOHN, *Adv. Mater.* **12** (2000) 1129.
15. D. Y. KIM, L. LI, X. L. JIANG, V. SHIVSHANKAR, J. KUMAR and S. K. TRIPATHY, *Macromolecules* **28** (1995) 8835.
16. H. K. LEE, K. DOI, A. KANAZAWA, T. SHIONO, T. IKEDA, T. FUJISAWA, M. AIZAWA and B. LEE, *Polymer* **41** (2000) 1757.
17. H. K. LEE, A. KANAZAWA, T. SHIONO, T. IKEDA, T. FUJISAWA, M. AIZAWA and B. LEE, *Chem. Mater.* **10** (1998) 1402.
18. *Idem., J. Appl. Phys.* **86** (1999) 5927.
19. A. SHISHIDO, O. TSUTSUMI, A. KANAZAWA, T. SHIONO and T. TAMAI, *J. Am. Chem. Soc.* **119** (1997) 7791.

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