Nonlinear optical properties of an azobenzene polymer*

Zeng Yi(曾 艺), Pan Zhi-Hua(潘志华), Zhao Fu-Li(赵付丽),
Qin Mu(秦 苜), Zhou Yan(周 延), and Wang Chang-Shun(王长顺)†

State Key Laboratory of Advanced Optical Communication Systems and Networks, Department of Physics, Shanghai Jiao Tong University, Shanghai 200240, *China*

(Received 27 January 2013; revised manuscript received 4 July 2013; published online 20 December 2013)

The nonlinear optical properties of an azobenzene polymer azo12–MO were investigated by a Z-scan technique. The polymer was synthesized by assembling the liquid-crystalline polymer azo12 with methyl orange. The nonlinear refractive index (1.39×10^{-15} cm^2/W) and the nonlinear absorption coefficient (0.11 cm/GW) of azo12–MO were determined with 532-nm picosecond laser pulses at the irradiance of 92.40 GW/cm^2. When compared to the nonlinear properties of azo12 and methyl orange, azo12–MO possesses the advantages of its two constituents and shows larger nonlinear optical properties.

Keywords: nonlinear optics, reverse saturable absorption, azobenzene polymer

PACS: 42.65.–k, 78.20.Ci, 42.70.Gi **DOI:** 10.1088/1674-1056/23/2/024212

1. Introduction

Materials with excellent nonlinear optical characteristics have been proven to be quite advantageous for various photonic device applications. For example, photosensitive materials have received much attention as a fundamental-research aspect of nonlinear optical technologies because of their applications in information storage,[1] optical processing,[2] optical limiters,[3,4] holographic gratings,[5,6] and so on. Photoresponsive polymers containing azobenzene chromophores have simulated considerable interest for their promising nonlinear optical properties during recent years.[7–9] The detailed investigation of linear and nonlinear optical coefficients in optical materials enables us to fabricate optical materials, appropriately designing their structure at the molecular level for a specific device. In this work, we designed a novel polymer azo12–MO, which possesses the advantages of both methyl orange and a liquid crystal polymer azo12.[10] We synthesized the polymer and measured its nonlinear optical properties, finding both the nonlinear refraction index and the nonlinear absorption properties to be larger than those of methyl orange and azo12. Furthermore, azo12–MO showed a reverse saturable absorption and optical limiting effect.

2. Experimental

Trimethylammonium-functionalized 1-bromo-12-(4-methoxyazobenzene-4'-oxy) do-decane (azo12) was synthesized according to the method of Xiao *et al.*,[10] and analytical reagent grade 4-((4-(dimethylamino)phenyl)diazenyl) benzenesulfonate (MO) was obtained commercially. For the preparation of azo12–MO, 8-mg/mL mo aqueous solution was added dropwise to azo12 aqueous solution with the concentration of 3 mg/mL, in a 1:1 molar charge ratio. The precipitated complex was filtered and washed several times with doubly distilled water to remove residual salts and then dried in a vacuum at 50 °C for 12 h. Figure 1 shows the linear absorption spectra of azo12, MO and azo12–MO in dimethyl sulfoxide (DMSO); the inset is the molecular structure of azo12–MO. The absorption bands of azo12–MO were at 375 nm and 425 nm, which correspond to the absorption bands of azo12 at 365 nm and MO at 430 nm, respectively, showing that the absorption spectrum of azo12–MO consists of the absorption spectra of azo12 and MO. Figure 2 shows images of azo12 (a) and azo12–MO (b) at 400x magnification without polarized light irradiation, indicating that azo12–MO has a good crystalline structure.

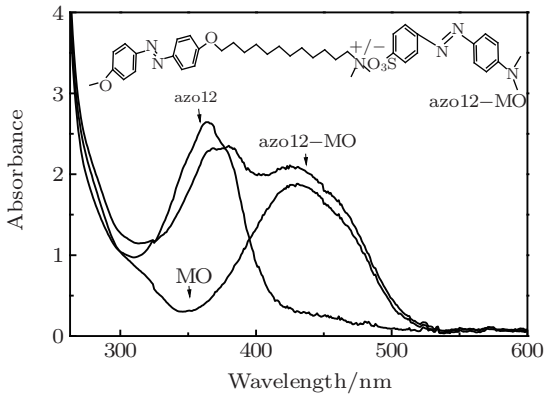


Fig. 1. Linear absorption spectra of azo12, MO, and azo12–MO; inset: molecular structure of azo12–MO.

The Z-scan technique[11] was utilized to investigate the nonlinear optical properties of the polymers, including the measurement of the nonlinear refraction index and nonlinear

*Project supported by the National Natural Science Foundation of China (Grant No. 11174203).
†Corresponding author. E-mail: cswang@sjtu.edu.cn
© 2014 Chinese Physical Society and IOP Publishing Ltd

absorption. In the Z-scan measurement, the Gaussian beam was focused on the sample by a lens with a 30-cm focal length. By translating the sample through the focus, the change of intensities at the far-field intensity pattern was monitored by using the open aperture (OA) and closed aperture (CA) measurements. This experiment was performed with the mode-locked Nd:YAG laser (38 ps and 10 Hz) at a wavelength of 532 nm.

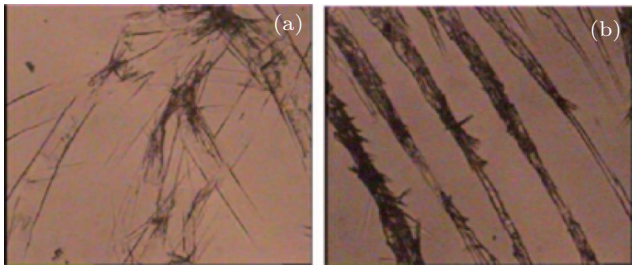


Fig. 2. (color online) Images of polymers with 400x magnification without polarized light irradiation: (a) azo12; (b) azo12–MO.

3. Results and discussion

Figure 3(a) shows the OA data of azo12–MO in DSMO at 532 nm and Fig. 3(b) gives the Z-scan experimental result of CA divided by OA measurements. Figure 3(a) shows that transmittance is enhanced with decreasing light intensity and is reduced with increasing light intensity. The solid curve in Fig. 3(a) is the result of theoretical fit according to the form[11]

$$T(z,s=1)=\sum[-q_0(z,0)]^m/(m+1)^{3/2},\quad (q_0(0)<1),\quad (1)$$

where $q_0(z,0)=\beta I_0 L_{\rm eff}/\left(1+z^2/z_0^2\right)$, $z_0=k\omega_0^2/2$ is the diffraction length of the beam, ω_0 is the beam waist radius at the focal point and $k=2\pi/\lambda$ is the wave vector. The nonlinear absorption coefficient was calculated by the fit result as -0.11 cm/GW. In Fig. 3(b), the peak to valley configuration of the curve suggests a negative nonlinear refractive index, indicating a self-defocusing effect. In the experiment, the peak intensity of the incident laser at the focal point was 92.40 GW/cm^2. The solid curve in Fig. 3(b) is a theoretical fit using

$$\Delta T\left(z,\Delta\Phi_0\right)=1-4\Delta\Phi_0 x/\left(x^2+9\right)\left(x^2+1\right),\quad (2)$$

where $z_0=k\omega_0^2/2$, $|\Delta\Phi_0|=kL_{\rm eff}n_2I_0$ is the on-axis phase shift at the focus, I_0 is the intensity of the laser beam at focus $z=0$, $L_{\rm eff}=[1-\exp(-\alpha L)]/\alpha$ is the effective thickness of the sample, $x=z/z_0$, z_0 is the diffraction length of the beam. From the theoretical fit results in Fig. 3(b), the nonlinear refractive index was found to be -1.39×10^{-15} cm^2/W.

Figures 4(a) and 4(b) show the OA and CA/OA curves of MO. The peak intensity of the incident laser at the focal point was 131.38 GW/cm^2 for the MO sample. The solid curve is the theoretical fit. The nonlinear absorption coefficient and nonlinear refractive index were calculated as 0.06 cm/GW and 1.01×10^{-15} cm^2/W. Meanwhile, the valley to peak characteristic shape shown in Fig. 4(b) indicates a self-defocusing effect. The nonlinear optical process given in Figs. 3(a) and 4(a) is taken to be reverse saturable absorption (RSA),[12,13] i.e., the medium absorption coefficient increases with input intensity.

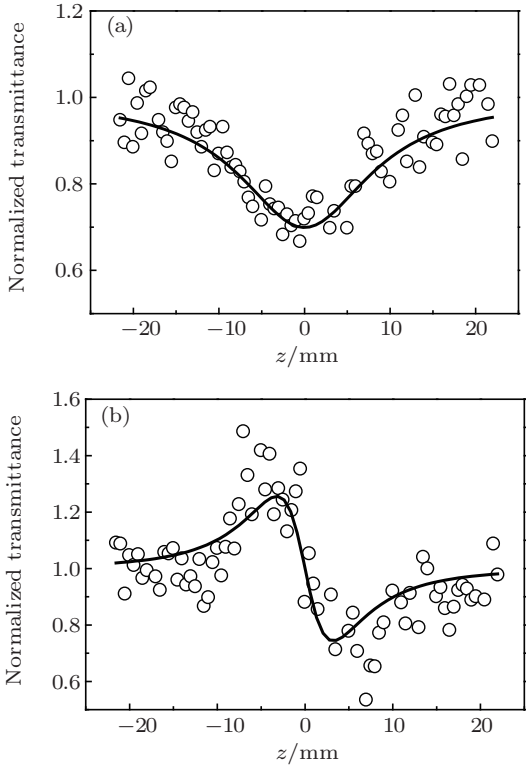


Fig. 3. Z-scan traces of the polymer azo12–MO in DSMO at ps 532 nm. (a) Open aperture. (b) Closed aperture divided by open aperture. The solid curves are the fitting curves.

Figure 5 shows the CA Z-scan signals of azo12 in DMSO under the excitation light of 532 nm. In the experiments, the peak intensity of the incident laser at the focal point was enlarged to get data with a higher signal to noise ratio. The value was 566.14 GW/cm^2. The inset is OA Z-scan results of azo12 in DMSO, which indicate that the nonlinear absorption can be neglected. With the solid theoretical fitted curve, the nonlinear refractive index was calculated as 6.40×10^{-17} cm^2/W. The measured nonlinear optical parameters are summarized in Table 1. Furthermore, the valley to peak configuration of the curve in Fig. 5, which differs from that of azo12–MO and MO, indicates a self-focusing effect. The self-focusing effect in azo12 is mainly caused by an electronic effect induced by either population redistribution or distortion of electronic clouds.[14] In contrast, the self-defocusing effects in azo12–MO and MO are mainly due to laser heating. Note that the measured values of the nonlinear refractive index and absorption coefficient of azo12–MO are larger than those of azo12 and MO. Therefore, it is clear that azo12–MO has the advantages of nonlinear optical properties of both azo12 and MO.

Further, it is obvious that the nonlinear optical properties of azo12–MO polymer can be adjusted by assembling azo12 with MO at the molecular level.

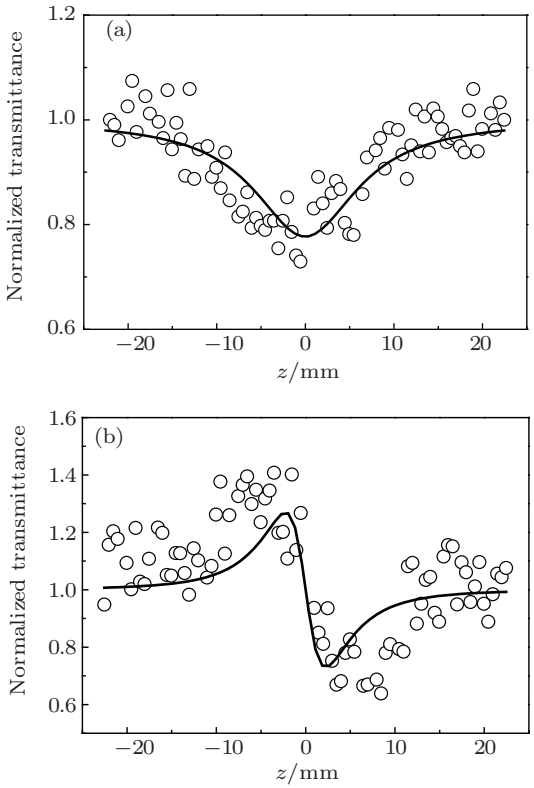


Fig. 4. Z-scan traces of the polymer MO in DSMO at ps 532 nm. (a) Open aperture. (b) Closed aperture divided by open aperture. The solid lines are the fitting curves.

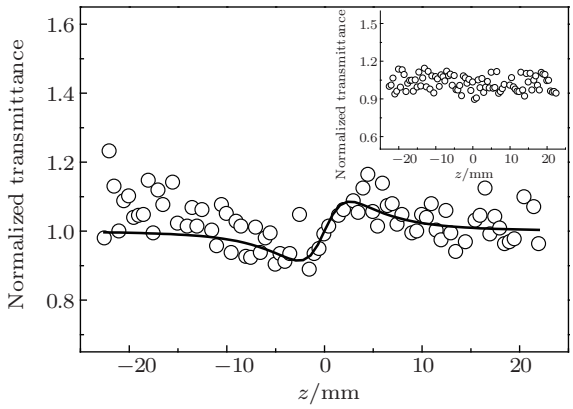


Fig. 5. Closed aperture Z-scan traces of the polymer azo12 in DSMO; inset: open aperture Z-scan results of azo12.

Table 1. Estimated values of nonlinear optical parameters of azo12, MO, and azo12–MO at ps 532 nm.

Sample	I_0/(GW/cm^2)	β/(cm/GW)	n/(cm^2/W)
azo12–MO	92.60	0.11	-1.39×10^{-15}
MO	131.18	0.06	-1.01×10^{-15}
azo12	566.14	–	6.40×10^{-17}

In order to analyze the nonlinear absorption property of azo12–MO and MO further, we studied the two polymers with different input intensities of the picosecond laser using an OA Z-scan technique. Figure 6 shows the nonlinear optical absorption coefficients β (dots) of azo12–MO and MO under different excitation levels; solid curves are sketched as a guide for the eyes. Note that the values of β decrease with increasing on-axis input intensity I_0 for both polymers, which probably results from the excited-state absorption effect.[15,16] This excited-state absorption induced RSA might be the origin of the optical limiting property of polymers. Optical limiting experiments were performed by placing the sample at the focus of the laser beam and measuring the transmitted energy for different input laser energies. Figure 7 shows the optical limiting response of the polymers in DMSO solutions. The solid line is a guide for the eyes, which indicates that the linear transmittance of azo12–MO and MO is 2% and 2.9%, respectively. This indicates that the two polymers both exhibit optical limiting behaviors in response to picosecond laser pulses in DMSO solution. Therefore, the polymer investigated here seems to be a promising material for making nonlinear photonic devices.

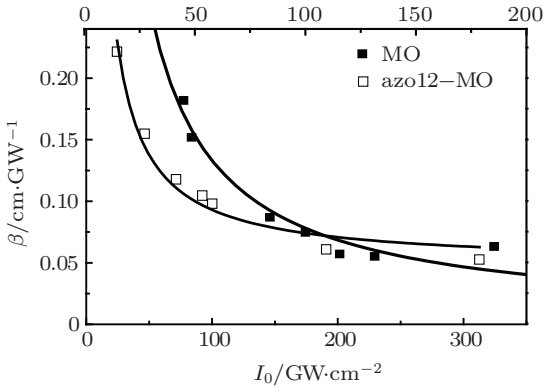


Fig. 6. Nonlinear absorption coefficients of azo12–MO and MO under different irradiances; the solid curves are sketched as a guide for the eyes.

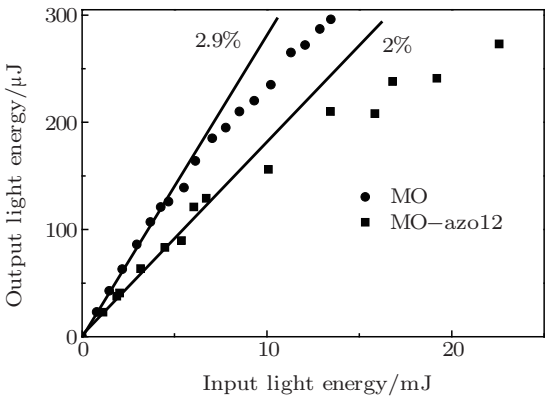


Fig. 7. Optical limiting response of azo12–MO and MO; the solid line is a guide for the eyes.

4. Conclusion

An azobenzene polymer, azo12–MO, was synthesized and its nonlinear optical properties were investigated by a Z-

scan technique. The measured nonlinear refractive index coefficient was found to be larger than that of either of the two constituents, azo12 and MO. Reverse saturable absorption was observed and the nonlinear absorption coefficient was measured to be larger than that of either of the two constituents. This indicates that azo12–MO possesses the advantages of nonlinear optical properties of both of its two constituents and has greater nonlinear optical properties. Furthermore, azo12–MO was measured to exhibit optical limiting behaviors under picosecond laser pulses. These experimental results make azo12–MO a candidate for applications in all-optical switching modulators and it seems to be a promising material for making nonlinear photonic devices.

References

[1] Yao Y P, Liu Y K, Dong S N, Yin Y W, Yang S W and Li X G 2012 *Appl. Phys. Lett.* **100** 193504

[2] Haripadmam P C, Kavitha M K, John H, Krishnan B and Gopinath P 2012 *Appl. Phys. Lett.* **101** 071103

[3] Almosawe A J and Saadon H 2013 *Chin Opt. Lett.* **4** 041902

[4] Niu Y X, Yang H L, Zhang P, Shen X J, Jiang N, Chen Y and Tang F 2008 *Chin. Phys. B* **17** 3367

[5] Gai X, Choi D Y, Madden S and Luther-Davies B 2012 *Opt. Express* **20** 13513

[6] Chen K, Cheng J Q, Wang Y and Huang M J 2010 *Chin. Phys. B* **19** 014204

[7] Brzozowski L and Sargent E H 2001 *J. Mater. Sci. Mater. Electron.* **9** 483

[8] Fuh A Y G, Lin H C, Mo T S and Chen C H 2005 *Opt. Express* **26** 10634

[9] He T C, Wang C S, Pan X, Zhang C Z and Lu G Y 2009 *Appl. Phys. B: Lasers Opt.* **94** 653

[10] Xiao S, Lu X, Lu Q and Su B 2008 *Macromolecules* **41** 3884

[11] Sheik-Bahae M, Said A A, Wei T H, Hagan D J and Van Stryland E W 1990 *IEEE J. Quantum Electron.* **26** 760

[12] Sreekumar G, Frobel P G L, Muneera C I, Sathiyamoorthy K, Vijayan C and Mukherjee C 2009 *J. Opt. A: Pure Appl. Opt.* **11** 125204

[13] Couris S, Renard M, Faucher O, Lavorel B, Chaux R, Koudoumas E and Michaut X 2003 *Chem. Phys. Lett.* **369** 318

[14] Gurudas U, Brooks E, Bubb D M, Heiroth S, Lippert T and Wokaun A 2008 *J. Appl. Phys.* **104** 073107

[15] Poornesh P, Umesh G, Hegde P K, Manjunatha M G, Manjunatha K B and Adhikari A V 2009 *Appl. Phys. B: Lasers Opt.* **97** 117

[16] Yang Q G, Si J H, Liu X C, Xu G, Ye P X, Lei Z Q, Zhan X W and Yang M J 1998 *Chin. Phys. Lett.* **15** 3