

Rapid Communication

OPTICAL PHASE CONJUGATION RESPONSE OF PHOTOINDUCED POLYMER FILMS CONTAINING AZOBENZENE MOIETIES WITH CHIRAL GROUP*

Ze-da Xu, Yong Zhang, Xing-he Fan**, Xin-hua Wan and Qi-feng Zhou**

Department of Polymer Science and Engineering, College of Chemistry and Molecular Engineering,
Peking University, Beijing 100871, China

Abstract An optically active monomer containing azobenzene moieties with chiral group (*s*-2-methyl-butyl), 4-[2-(methacryloyloxy)ethyloxy]-4'-(*s*-2-methyl-1-butyloxycarbonyl) azobenzene (M1) was synthesized. Polymer (PM1) possessing optical phase conjugated response was obtained by homopolymerization of the optically active monomer (M1) using free radical polymerization. The polymer was very soluble in common solvents and good optical quality films could be easily fabricated by spin coating. The optical phase conjugated responses of the polymer PM1 were measured by degenerate four-wave mixing (DFWM). In comparison with polymer containing no chiral group, it was found from the preliminary measurement of photoisomeric change that optical phase conjugated response of the PM1 in the long-range order hexagonal symmetry microstructure could be easily controlled by choosing the appropriate polarization direction of the irradiating beams (514.5 nm) and the irradiating number, presumably due to the chiral group in the PM1 molecular structure. For the case of the polymer investigated here, a chiral group side chain was introduced to increase optical phase conjugated response intensity with different polarization directions of the irradiating beams, which aims originally at searching for a new photo-active material.

Keywords Azobenzene polymer, Chiral groups, Degenerate four-wave mixing, Optical phase conjugation

INTRODUCTION

Side chain liquid crystalline polymers (SCLCPs) exhibiting the desirable mechanical properties and the electro-optical properties have been studied extensively^[1, 2]. SCLCPs with excellent electro-optical properties have potential in electro-optical device applications, such as display, light valve and memory devices^[3–5]. Organic azo-containing compounds are a well-known class of materials characterized by good thermal properties, bright color and high stability. Side-chain azobenzene polymers combine the conjugated characteristics of azobenzene and processability of organic polymers with thermal stability^[6–8]. Since 1993 when Ikeda and co-worker^[9] demonstrated reversible optical storage properties in some liquid crystalline azo-polymer films, there has been a tremendous growth of interest in these materials as media for optoelectronic applications. More recently, a number of groups have synthesized side-chain azobenzene polymers and investigated the structure and physical properties such as electro-optic characteristics^[10–14]. But there has been no report on side-chain azobenzene polymer films with chiral group showing optical phase conjugated characteristics in the long-range order hexagonal symmetry microstructure.

It is well known that linearly polarized light can induce reorientation of azobenzene groups through photochemical *trans-cis-trans* isomerization^[15]. It is believed that the polymer film possessing chirality and

* This work was supported by National Natural Science Foundation of China (No. 59873001) and Scientific Foundation for Returned Overseas Chinese Scholars, Ministry of Education.

** Corresponding authors: Xing-he Fan (范星河), E-mail: fanxh@chem.pku.edu.cn;

Qi-feng Zhou (周其凤), E-mail: qfzhou@pku.edu.cn

Received December 10, 2001; Revised December 21, 2001; Accepted December 22, 2001

azobenzene type nonlinear optical chromophores in the polymer side-chain shall possess good optical phase conjugated characteristics in the long-range order hexagonal symmetry microstructure. Materials of this kind are of considerably theoretical and practical interest and are well suited for a variety of "smart" applications.

In this paper, the principal task was to study the influence of side-chain azobenzene polymer with chiral group on optical characteristics. For the polymer studied here, we introduced chiral group side chain to increase optical phase conjugated response intensity with different polarization directions of the irradiating beams, which aimed originally at searching for a new kind of photo-active materials. We reported here, for the first time, an investigation of optical phase conjugated response of side-chain azobenzene polymer films with chiral group at different polarization directions of the irradiating beams. To introduce chiral groups on the side-chain polymer matrix, azobenzene side-chain polymer with chiral group (*s*-2-methyl-butyl) was synthesized. Moreover, in order to study the photoisomerization of the polymer films, two dimensional phase grating of the polymer film was characterized using degenerate four-wave mixing (DFWM). Furthermore, photoinduced behaviors (optical phase conjugated response) were discussed in terms of the polymer compositions of polymer film and chiral group dependence.

EXPERIMENTAL

Degenerate Four-Wave Mixing (DFWM)

An Ar⁺ laser with wavelength of 514.5 nm was used as incident light and three input laser beams (1, 2 and 3) with different polarization directions of the irradiating beams were irradiated to the polymer films. The two dimensional optical lattices were studied using degenerate four-wave mixing (DFWM). After changing the polarization directions of the irradiating beams, then on the base of photoisomerization of the polymer, we got the different responding curves of the optical conjugated response on the films. The optical phase conjugated response (I_4) of the films in the long-range order hexagonal symmetry microstructure was recorded with a digital storage oscilloscope. The schematic diagram of the experimental setup was shown in Fig. 1. Measurements were performed at room temperature.

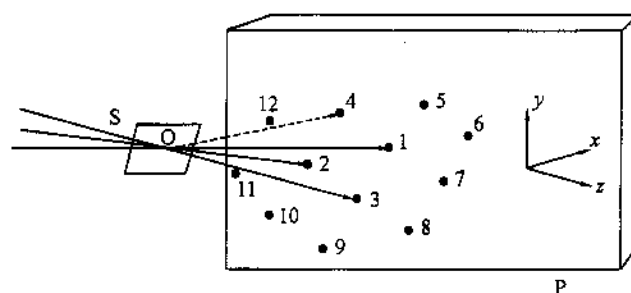


Fig. 1 Schematic experiment optical setup diagram, S = polymer film sample, P = observation plane, 4, 7, 10 represent the optical phase conjugated response on the films in the long-range order hexagonal symmetry microstructure

Reagents

Tetrahydrofuran (THF) was purified by refluxing, distilling from calcium hydride. All the solvents and reagents, of analytical-grade quality, were commercial products and used as received unless otherwise stated. The (*s*)-(-)-2-methyl-1-butanol (Aldrich 99%) was used without any further purification.

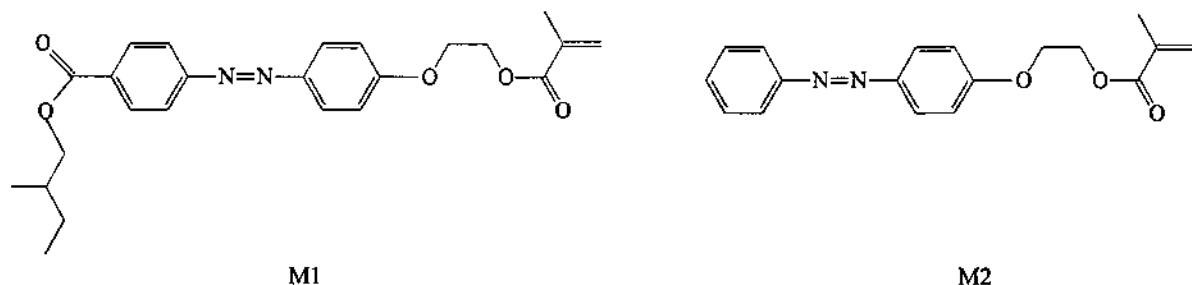
Characterization

¹H-NMR spectra were recorded with a Varian-Unity Plus-200 operating at 200 MHz in CDCl₃ and chemical shifts were reported in δ units with TMS as an internal standard. The polymers were characterized by gel permeation chromatography (GPC) (Waters 510 instrument) with tetrahydrofuran as eluent. Optical activities of polymer and monomer were measured using circular dichroism (CD) on a JOBIN-YUON CD6 dichrograph in

CHCl_3 solution at 25°C .

Synthesis of Monomers

In comparison with M1 containing azobenzene moieties with a chiral group, M2 containing no chiral group was designed. The molecular structures of the polymerizable monomers were presented in Scheme 1. The detailed procedures were as follows.



Scheme 1

4-[2-(Methacryloyloxy)ethoxy]-4'-(s-2-methyl-1-butyloxycarbonyl)azobenzene (M1)

The synthesis of M1 was performed according to the literature methods described by S'heeren^[16] and Shibaev^[17], through 5 reactions. The raw product was purified by column chromatography using CH_2Cl_2 as eluent and recrystallized from ethanol as shiny, orange needle crystals (mp $98-100^\circ\text{C}$) with a yield of 22%. $^1\text{H-NMR}$ (d -DMSO, TMS): $\delta = 0.97$ (t, 3H, CH_2CH_3), 1.05 (t, 3H, CHCH_3), 1.35–1.40 (m, 2H CH_2CH_3), 1.90 (m, 1H, CHCH_3), 1.97 (s, 3H, $-\text{CH}_3$), 4.19 (d, 2H, OCH_2CH), 4.34, 4.53 (t, t, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 5.61, 6.15 (s, s, 2H, $\text{H}_2\text{C}=\text{C}$), 7.03 (d, 2H, Ar-H), 7.91, 8.01 (d, d, 4H, Ar-H), 8.16 (d, 2H, Ar-H).

2-(4-Oxy-azobenzene) ethyl methacrylate (M2)

The synthesis of M2 was prepared by using the same method as for the preparation of M1. The raw product was purified by column chromatography using CH_2Cl_2 as eluent and recrystallized from ethanol as shiny, orange needle crystals (mp $63-64^\circ\text{C}$) with a yield of 35%. $^1\text{H-NMR}$ (d -DMSO, TMS): $\delta = 1.89$ (s, 3H, $-\text{CH}_3$), 4.41, 4.46 (t, t, 4H, $-\text{CH}_2-\text{CH}_2-$), 5.71, 6.05 (s, s, 2H, $\text{H}_2\text{C}=\text{C}$), 7.18 (s, 2H, Ar-H), 7.57 (s, 3H, Ar-H), 7.87 (s, 4H, Ar-H).

Polymer Synthesis

The homopolymers PM1 and PM2 were synthesized by a free radical polymerization method using AIBN as initiator. The polymerization procedure was as follows.

A 200.0 mg sample of monomer (M1 or M2) and 2% mol of AIBN (based on the monomer) were dissolved in 3–5 mL of freshly distilled chlorobenzene. The solution was thoroughly degassed by several freeze-pump-thaw cycles and heated in a sealed ampoule at 60°C for 24h. The resulting polymer solution was cooled and poured into vigorously agitated methanol to precipitate the polymer. The obtained polymer was purified by several reprecipitations from THF solutions into methanol. After filtration and vacuum drying, an orange colored solid polymer was obtained. The structure of the polymers shown was consistent with $^1\text{H-NMR}$ spectroscopic data. After the polymerization was completed, the vinyl proton peaks of the monomer in the methacrylic group at $\delta = 5.50$ and 6.15 had completely disappeared. The molecular weight of PM1 and PM2 were determined by GPC to be $M_n = 18,600$ ($M_w/M_n = 1.82$) and $M_n = 18,200$ ($M_w/M_n = 1.60$), respectively. These two polymers have good solubility in common organic solvents, such as THF, CHCl_3 and DMF, etc.

Film Preparation

For the optical studies, thin polymer films were prepared by spin coating on the clear surface of glass or newly cleaved mica plate. For this purpose appropriate amounts of polymers were dissolved in freshly distilled THF. The solution was filtered through a $0.45\ \mu\text{m}$ Teflon filter to remove insoluble particles. It was then spin coated,

depending on the desired thickness, onto a glass or a mica plate. Residual solvent was removed by heat treating the films first at 35°C for 3h and then at 60°C, 266.6–666.6 Pa vacuum overnight.

RESULTS AND DISCUSSION

Characterization of Circular Dichroism (CD) Spectra

The optical rotatory (chiroptical) properties of monomer and polymer PM1 were measured from experiments. However, no reliable measurements of optical rotatory power on azobenzene-containing monomer and polymer PM1 could be obtained due to their high absorption, but their chirality (chiroptical properties) can be identified from CD spectra^[18]. The result is shown in Fig. 2. The CD spectra in CHCl₃ solution were recorded at a concentration of 500 mg/L. From these spectra (Fig. 2), by comparison of the CD peaks before and after the polymerization, we can see that polymer PM1 and monomer M1 exhibit a broad negative band around 360 nm and 370 nm, respectively. From these CD spectra, it can also be concluded that monomer M1 and polymer PM1 both possess chirality.

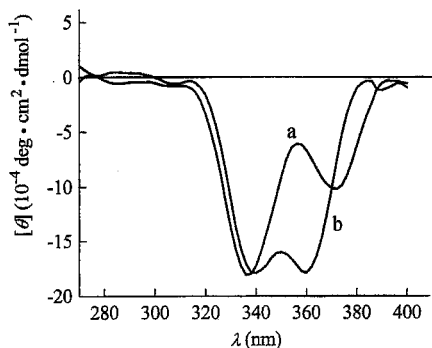


Fig. 2 The circular dichroism (CD) spectra at 25°C of M1 (a) in CHCl₃ (500 mg/L) and PM1 (b) in CHCl₃ (500 mg/L)



Fig. 3 The response of optical phase conjugated beams on the observation plane

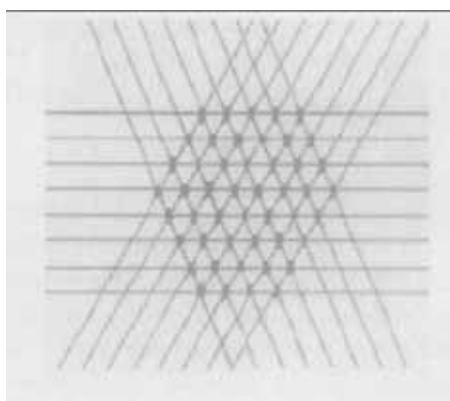


Fig. 4 Physical picture of hexagonal pattern

Degenerate Four-Wave Mixing

The optical phase conjugated response (I_4) of the polymer film was measured using a degenerate four-wave mixing (DFWM) technique with a laser beam (514.5 nm) as the fundamental light source. Through the DFWM experiments on the azobenzene polymer films, we have carried out research on the formation of the two dimensional phase grating. After no more than 3 s, the response of optical phase conjugated beam could be seen on the observation plane (shown in Fig. 3). The results proved that the photoisomerization of azobenzene group helped to form the two dimensional phase grating structure in the films. The physical picture of this hexagonal

pattern is shown in Fig. 4. As shown in Fig. 3, we think this may be due to photoisomerization by laser beams of the azobenzene group, since exposure of the polymer film to linearly polarized light resulted in an anisotropy of molecular orientation and, as a consequence, in the induction of a stable photoinduced birefringence. In this way the polymer film could be “written” and then “erased” several times, and the physical property of this structure was very stable. Below the glass transition temperature (T_g), no difference in the structure would occur after a long period of time. The report by D.C Neckers helped to prove this point^[19].

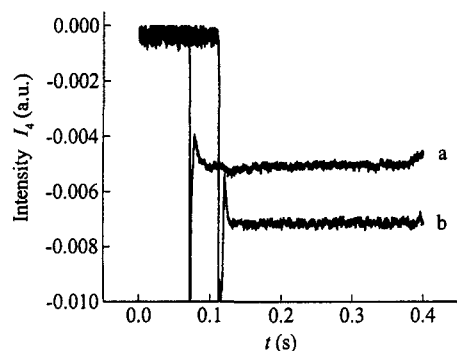


Fig. 5 The optical phase conjugated response intensity (I_4) of the PM1 films,
a) Three dextrorotarily polarized beams
b) Three levorotarily polarized beams

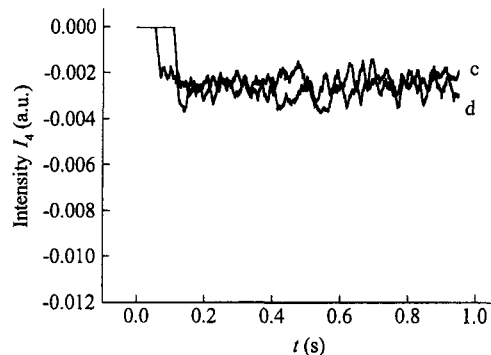


Fig. 6 The optical phase conjugated response intensity (I_4) of the PM2 films
c) Three levorotarily polarized beams
d) Three dextrorotarily polarized beams

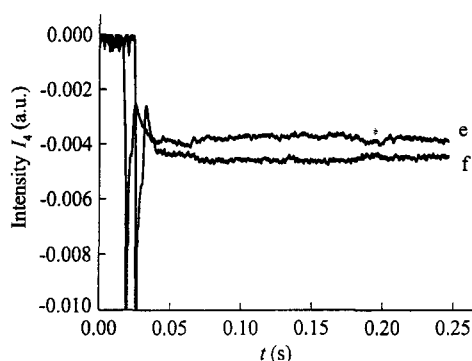


Fig. 7 Influence of the numbers and directions of irradiating beams on the optical phase conjugated response (I_4) of the PM1 film
e) Three horizontal beams
f) Two horizontal beams and one vertical beam

The Influence of Photoinduced Behaviors by Chiral Groups

The optical phase conjugated characteristics measurements were performed on films with a laser beam (514.5 nm) as light source, and recorded with a digital storage oscilloscope. Figures (5)–(7) show the relationship between optical phase conjugated response (I_4) and polarization direction of the irradiating beams, the irradiating numbers and directions, respectively. From Fig. 5, we note that I_4 of polymer PM1 with a chiral group in the molecular structure film depends strongly on the polarization direction of the irradiating beams. The optical phase conjugated response intensity (I_4) of the PM1 films exposed to three levorotarily polarized beams (b) is greater than that for three dextrorotarily polarized beams (a). As shown in Fig. 7, after changing the irradiating numbers and directions, I_4 was essentially constant. In order to compare optical phase conjugated characteristics of different polymers, we adopted the polymer PM2 containing no chiral group for comparison. It could be seen from Fig. 6 that for the same experimental condition I_4 of polymer PM2 was independent of the polarization

direction of the irradiating beams, and the optical phase conjugated response intensity (I_4) of the PM2 films exposed to three levorotarily polarized beams (c) is equal to the response intensity for three dextrorotarily polarized beams (d). After changing the polarization direction of the irradiating beams, the irradiating numbers and directions, I_4 was essentially constant. It was interesting to note that I_4 for a given polymer (PM1) film was influenced significantly by the chiral group. The mechanism of this spontaneous behavior was not clear. The chiral group in side-chain azobenzene polymer film may be reasonably viewed as a driving force for the optical phase conjugated response (I_4).

Finally, we conclude that chiral group in side-chain azobenzene polymer film plays an important role in responding to the polarization direction of the irradiating beams and the irradiating number. The chiral group is found to effectively change physical properties such as optical phase conjugated characteristics (I_4). Further studies on the photoinduced properties of side-chain azobenzene polymer films with chiral group are in progress.

Acknowledgements The authors would like to express thanks to the group of Prof. L.H. Lai of Peking University for their help in the circular dichroism (CD) measurement.

REFERENCES

- 1 Dinescu, L. and Lemieux, R.P., *Adv. Mater.*, 1999, (1): 42
- 2 Rochon, P., Gosselin, J., Natansohn, A. and Xie, S., *Appl. Phys. Lett.*, 1992, 60: 4
- 3 Liu, Z.F., Hashimoto, K. and Fujishima, A., *Nature*, 1990, 347: 658
- 4 Ikeda, T. and Tsutsumi, O., *Science*, 1995, 268: 1873
- 5 Herr, B.R. and Mirkon, C.A., *J. Am. Chem. Soc.*, 1994, 116: 1157
- 6 Beattie, M.S., Jackson, C. and Jaycox, G.D., *Polymer*, 1998, (12): 2597
- 7 Wu, Y., Ikeda, T. and Zhanget, Q., *Adv. Mater.*, 1999, (4): 300
- 8 Park, B., Jung, Y. and Choi, H., *Jpn. J. Appl. Phys.*, 1998, 37: 5663
- 9 Ikeda, T., Sasaki, T. and Ichimura, K., *Science*, 1993, 361: 4281
- 10 Bobkovsky, A.Y., Boiko, N.I. and Shibaev, V.P., *J. Photochemistry and Photobiology A: Chemistry*, 2001, 138: 2617
- 11 Yoshida, M., Fan, X.H., Yoshizawa, H., Itahara, T., Kawano, Y., Uemura, Y. and Hatate, Y., *J. Appl. Polym. Sci.*, 2001, 8(10): 2490
- 12 Dai, X.M., Goto, H., Aksgj, K. and Shirakawn, H., *Synthetic Materials*, 1999, 102: 1291
- 13 Yoshida, M., Fan, X.H., Yoshizawa, H., Itahara, T., Kawano, Y., Uemura, Y. and Hatate, Y., *Chem. Eng. Comm.*, 2001, 185: 183
- 14 Simonov, A.N., Larichev, A.V., Shibaev, V.P. and Stakhanov, A.I., *Optics Communication*, 2001, 197: 175
- 15 Wiesner, U., Reynolds, N., Boeffel, C. and Spiess, H.W., *Liq. Cryst.*, 1992, (11): 251
- 16 S'heeren, G. and Samyn, C., *Eur. Polym. J.*, 1993, (7): 981
- 17 Kostromin, S.G., Shibaev, A.I. and Shibaev, V.P., *Polym. Sci. Ser., A*, 1996, 38: 1030
- 18 Angiolini, L., Caretti, D., Carlini, C., Giorgini, L. and Salatelli, E., *Macromol. Chem. Phys.*, 1999, 200: 390
- 19 Sudesh kumar, G. and Neckers, D.C., *Chem. Rev.*, 1989, 89: 1915