

Note

PHOTOINDUCED HOLOGRAPHIC PHASE GRATINGS BURIED IN AZOBENZENE SIDE-CHAIN POLYMER FILMS WITH A CHIRAL GROUP*

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Abstract An optically active polymer (PM1) containing azobenzene moieties with a chiral group (*s*-2-methyl-butyl) was synthesized by homopolymerization of monomer, 4-[2-(methacryloyloxy)ethyloxy]-4'-(*s*-2-methyl-1-butyloxycarbonyl) azobenzene, using the free radical polymerization method. The polymer dissolved in tetrahydrofuran (THF) could be easily processed into high optical quality films. The optical anisotropy of the polymer films was investigated by polarizing optical microscopy (POM). The experimental results showed that irradiation with a circularly polarized beam could align the orientation of the molecules in the polymer films. Moreover, the holographic phase gratings of photo-induced polymer films were detected by atomic force microscopy (AFM) and POM. In comparison with polymer containing no chiral group, it was found from the preliminary measurement of the photo-induced holographic phase gratings that PM1 containing a chiral group could form holographic phase gratings buried in the films.

Keywords Holographic phase gratings, Azobenzene polymer, Chiral groups

INTRODUCTION

Investigation of optically active polymers is a new and rapidly developing branch of science and technology for nonlinear optics. Among known types of such polymers, side-chain azobenzene polymers combine the conjugate characteristics of azobenzene and processability of organic polymers with thermal stability^[1–3]. Since 1985, when Coles and his co-worker discovered the existence of reversible optical storage properties in some liquid crystalline azobenzene polymer films^[4], there has been a tremendous growth of interest in these materials as media for optoelectronic applications. In the past twenty years a large number of azobenzene polymers have been synthesized and studied, with the main focus being placed on polymers containing azo groups in the side chain^[5]. In 1995 atomic force microscopy (AFM) revealed the surface relief structures due to a substantial mass transport in these materials for the first time^[6, 7]. So great attention has been paid to the study of this phenomenon of photo-induced surface gratings in optical active polymers containing side-chain azobenzene. These polymer systems were shown to be suitable for reversible optical data recording and storage^[8–9]. But there were no reports on the molecular orientation in polymer films containing side-chain azobenzene with a chiral group when the films were irradiated with a circularly polarized beam and the formation of photo-induced holographic phase gratings buried in the films.

It is well known that the key physical process of photo-induced gratings on films is a reversible *cis-trans* photo-isomerization of the azobenzene moieties^[10]. Photo-induced gratings made from polymer films have been

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of keen interest not only because of their potential industrial applications, but also because for scientific reasons. The orientation of the molecules in polymer films caused by irradiation with a circularly polarized beam, which can control the photoalignment of liquid crystals in grating films, is becoming important in technology. On the other hand, the technique of photo-induced holographic phase gratings buried in the films is a promising method for optical data encrypting storage.

The principal aim of this paper was to study the optical anisotropy, photo-induced holographic phase gratings and characterizations of the polymer films. The design and synthesis of the related polymers have been reported previously^[11]. Their structures are depicted in Fig. 1. For the case of the polymers studied here, the optical anisotropy of the films was characterized by POM. Furthermore, the photo-induced holographic phase gratings of the films were characterized by AFM and POM. The formation of photo-induced holographic phase gratings buried in films of an optically active polymer (PM1) containing chiral group is described here.

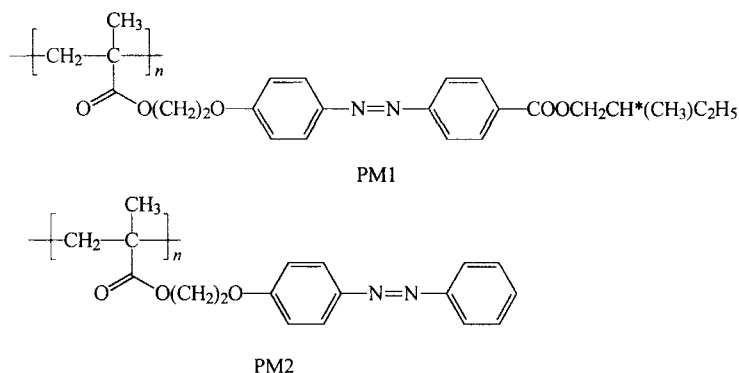


Fig. 1 The structure of polymers PM1 and PM2

EXPERIMENTAL

Film Preparation

An optically active polymer (PM1) containing azobenzene moieties with a chiral group (*s*-2-methyl-butyl) and polymer (PM2) containing no chiral group were used and details of the synthesis and chemical characterization of the polymers have been reported previously^[11]. For the optical studies, thin polymer films were prepared by spin coating on the clear surface of glass or newly cleaved mica plate.

Degenerate Four-Wave Mixing (DFWM)

The optical phase conjugated responses of the polymer films were detected by degenerate four-wave mixing (DFWM). The detailed procedures were described as follows.

An Ar⁺ laser with a wavelength of 514.5 nm was used as incident light. The various input laser beams with different polarization directions of the irradiating beams were directed onto the polymer films. On the basis of photoisomerization of the polymer, the photo-induced holographic gratings were recorded on the polymer films. The schematic diagram of the experimental setup is shown in Fig. 2. Polarization of the laser beams was varied by using three half-wave plates for linear polarization and a quarter-wave plate for circular polarization. Measurements were performed at room temperature.

Characterization

The depth modulation and the pitch of the surface gratings were observed by AFM (Digital Instruments Inc., Nanoscope IIIa) using the tapping mode. The optical anisotropy of the polymer films was investigated by POM (Nikon, Optiphot-2-pol) with a monochromatic filter.

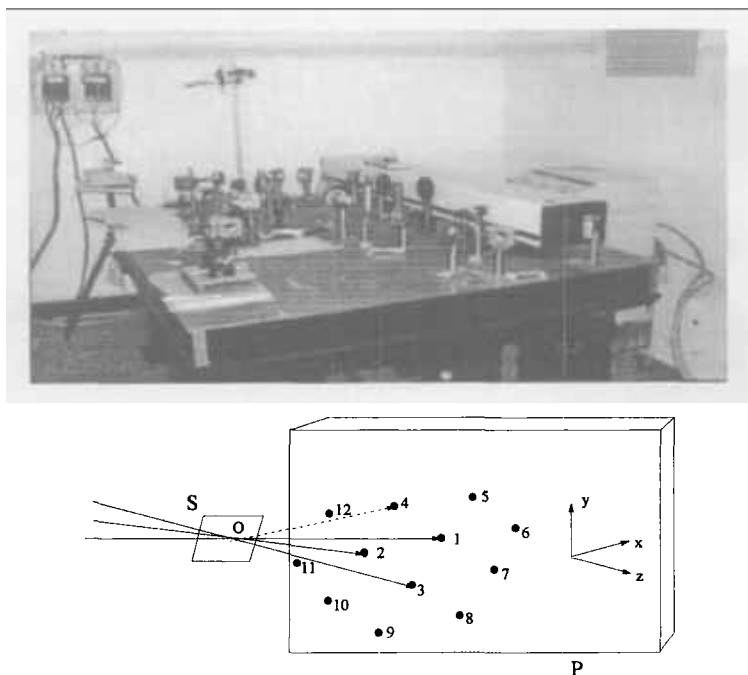


Fig. 2 (a) Experimental optical setup for DFWM; (b) model of the optical experiment in polymer film S = polymer film sample; P = observation plane; 1, 2, 3 represent irradiation beams; 4, 5,....., 12 represent the optical phase conjugated response

RESULTS AND DISCUSSIONS

Optical Anisotropy of the Films

After the DFWM experiments, optical anisotropy of the azobenzene polymer films can be evaluated by POM. After exposing the polymer films to linearly or circularly polarized beams, the response of optical phase conjugated beams could be seen on the observation plane (shown in Fig. 3). Figure 4 shows the relationship between transmittance of the PM1 polymer films with optical anisotropy and the rotation angle on polarizing microscopy. It can be seen from Fig. 4 that the transmitted light intensity changed periodically with a regular 90° separation of the rotation angle. This may be due to the photoisomerization of azobenzene moieties induced by laser beams, since exposure of the polymer films to linearly or circularly polarized beams will result in an anisotropy of molecule orientation and, as a consequence, resulted in the induction of a stable photoinduced birefringence. Also, in our case, images of Figs. 3 and 4 could be obtained from the polymer films containing a chiral group and containing no chiral group, respectively. Furthermore, it was interesting to note that the orientation of the molecules in the polymer films was different, as shown in Fig. 5, when the films were irradiated with linearly polarized beams or circularly polarized beams. Figure 5 shows the POM image of the polymer film containing chiral group exposing to two dextrorotatory beams and one levorotatory polarized beam. In order to compare the optical anisotropy characteristics of different polymers, we adopted polymer PM2 containing no chiral group for comparison. The image of Fig. 5 could not be obtained from polymer PM2 films under the same experimental conditions. The experimental results show that the optical anisotropy of the molecule in the polymer films is related, on one hand, to the presence of azobenzene moieties and, on the other hand, to the short chiral group. Hence, the circularly polarized beams could also influence the optical anisotropy of the molecules in the polymer films significantly, presumably due to the chiral group in the polymer molecular structure.

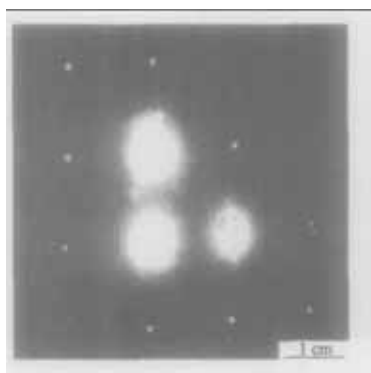


Fig. 3 The response of optical phase conjugated beams shown on the observation plane
Sample PM1 and PM2

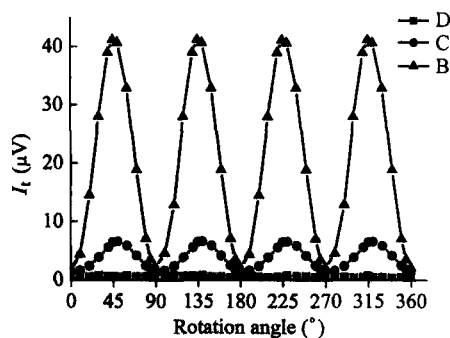


Fig. 4 Optical anisotropy of the PM1 polymer films measured by POM

B: the transmitted light intensity (I_t) of the film exposed to two horizontal beams and one vertical beam

C: the transmitted light intensity (I_t) of the film exposed to two levorotatory polarized beams and one dextrorotatory polarized beam

D: the transmitted light intensity (I_t) of the film without being exposed to beam

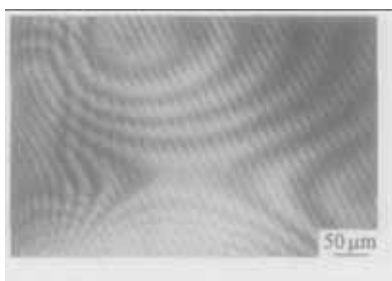


Fig. 5 The POM image of the PM1 film exposed to two dextrorotatory polarized beams and one levorotatory polarized beam

Morphology of Polymer Films

Figure 6 shows the AFM image of the holographic surface relief gratings on the PM2 films containing no chiral group exposed to two horizontal beams and one vertical beam. Figure 7 shows the AFM image on the surface of PM1 films containing a chiral group under the same experimental condition. The PM1 films did not form the same holographic surface relief gratings as did PM2 under the same experimental condition. In other words, polymer films containing no chiral group could easily form the holographic surface relief gratings on the polymer film, while polymer films containing a chiral group are likely to form the holographic phase gratings in the interior of polymer films. In order to illustrate the photo-induced holographic phase gratings buried in the films, the POM image was examined. Figure 8 shows the POM image of films containing chiral group exposed to two horizontal beams and one vertical beam. From Fig. 7 and 8, it is clear that the photo-induced holographic phase gratings occur not on the surface but in the interior of films after irradiation with polarized laser beams. In fact, the results described above show that holographic phase gratings could be preserved only in the polymer films containing a chiral group after irradiation. This phenomenon raises the possibility of realizing reversible recording and encrypting storage of optical information in azobenzene polymer films. It must be pointed out that this photo-process is thermally reversible, and its kinetic features will be considered in a later publication.

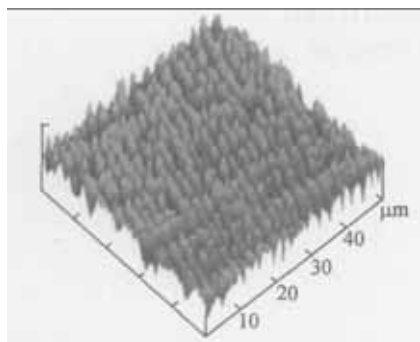


Fig. 6 The AFM image of the film containing no chiral group exposed to two horizontal beams and one vertical beam

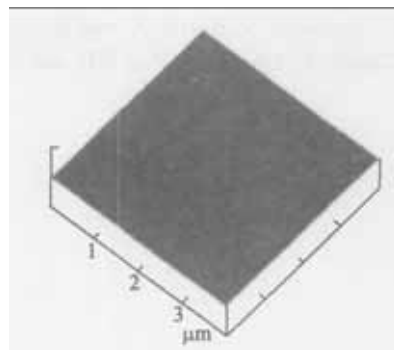


Fig. 7 The AFM image of the surface of PM1 film containing a chiral group exposed to two horizontal beams and one vertical beam

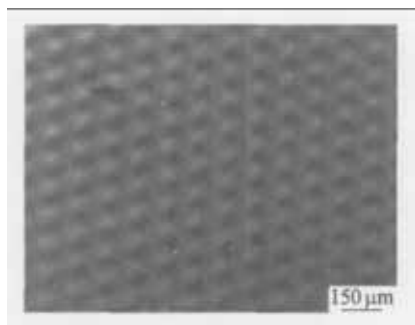


Fig. 8 The POM image of PM1 film containing a chiral group exposed to two horizontal beams and one vertical beam

CONCLUSIONS

In summary, an optically active polymer film could be obtained by spin coating on the clear surface of glass or newly cleaved mica plate. The orientation of the molecules in the azobenzene polymer films containing a chiral group could also be influenced significantly by circularly polarized laser beams. On the other hand, it is interesting that formation of the holographic phase gratings buried in films could be realized by using the polymer films containing a chiral group. The technique is therefore a promising method for accomplishing optical data encrypting storage in the field of optical devices. Further studies on the photo-induced holographic phase gratings buried in the polymer films with a chiral group are in progress.

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