Surface Relief Gratings on Azo Polymer Films Through Reversible Photoisomerization by the Irradiation of a Monochromatic Light

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ABSTRACT: Surface relief gratings were induced on azobenzene-functionalized polymer films by exposure to s-polarized and circularly polarized Ar^+-laser (488-nm) irradiation through a photomask. The surface relief structures were investigated with atomic force microscopy. A very regularly spaced surface grating with a modulation depth of about 400 nm was obtained after 30 min of circularly polarized Ar^+-laser irradiation. The diffraction efficiency was measured after irradiation by an Ar^+ laser, and an efficiency of about 2% was achieved. The polymer films also showed a very high period of recording. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3123–3126, 2006

**Key words:** azo polymers; photoisomerization; surface relief gratings

INTRODUCTION

Azobenzene-functionalized polymers, known as azo polymers, have attracted much attention as materials for photonic applications.[1–3] The phenomenon of surface relief gratings (SRGs) was first reported by two research groups independently in 1995.[4,5] Since then, SRGs have been produced by various groups on amorphous side-chain and main-chain azo polymers and on liquid-crystalline azo polymers, mostly in the form of spin-coated films. Azobenzene molecules are known to exist in two isomeric states, a thermodynamically stable trans form and a metastable cis form. Now, it is well known that multiple trans–cis–trans photoisomerizations of the azobenzene moiety are the trigger for the inscription of SRGs. Most of the azobenzene molecules, having electron-donor and electron-acceptor groups at both ends, show a rapid thermal backreaction.[6] To form SRGs, double-beam-exposure experiments are usually used, which combine polarized light and accumulated laser light. Photoinduced SRGs can be formed upon exposure to an interference pattern of Ar^+-laser beams at modest intensities.[4,5,7–12] When modest light intensities are used, mass transport is predominantly light-driven, with negligible thermal effects. SRGs thus fabricated depend on the polarization of the writing beams. Park

and coworkers[13,14] used UV light through a photomask to produce linear and two-dimensional surface gratings on a photosensitive polymer. However, to the best of our knowledge, there are very few reports on the formation of SRGs on polymer films by the illumination of an Ar^+ laser through a photomask. The use of monochromatic light provides easy patterning of the molecules. The low absorbance of the monochromatic light is able to form SRGs on thick polymer films. Thus, SRGs formed by mass transport induced by only photoisomerization of the azobenzene molecules may find potential applications in optical storage, optical communication devices, erasable and rewriteable holographic memory, and so forth.

EXPERIMENTAL

The azobenzene-functionalized, liquid-crystalline polymer used in this study, poly 6-[4-(4′-propoxyphenylazo)phenoxy]hexylacrylate (poly3AB6Ac), was synthesized according to a synthetic route published elsewhere[15] with a good yield and purity. The chemical structure of poly3AB6Ac is shown in Scheme 1. The number-average molecular weight of this polymer was 7000 g/mol. It also showed the following phase-transition behavior: K 80 S 100 N 138 I, where K is the crystalline phase, S is the smectic phase, N is the nematic phase, and I is the isotropic phase. To achieve optimized conditions for SRG formation, the polymer films were prepared through the spin coating of the solution of the polymer in tetrahydrofuran on a glass substrate. Spin coating helped to control the thickness
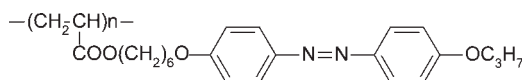
Scheme 1 Structure of poly3AB6Ac.

of the films. The thickness of the films was estimated with ultraviolet–visible spectroscopy measurements. The thickness of the films was about 200 nm.

Figure 1 shows a schematic presentation of the equipment for the irradiation of an Ar$^+$ laser onto nonoriented films through a photomask. SRGs were formed on the polymer films by exposure to s-polarized light parallel to the grating vector of the mask and circularly polarized Ar$^+$-laser irradiation through a photomask. The formation of SRGs was monitored by the diffraction of a low-power, unpolarized He–Ne laser (633 nm) from the spot at which the laser light was irradiated. The surface relief structures were investigated with atomic force microscopy (AFM) and polarized microscopy observations.

RESULTS AND DISCUSSION

A poly3AB6Ac film showed the maximum absorbance at about 345 nm, which corresponded to a strong π–π* transition of the *trans*-azobenzene moiety, and a weak absorption at 450 nm, which originated from the n–π* transition of the *cis*-azobenzene moiety. The polymer film had a little absorbance around 488 nm. This made it possible to record holographic gratings by repeated trans–cis–trans photoisomerization in the polymer film upon exposure to an Ar$^+$ laser of 488 nm. The lower absorbance of the film was better for the inscription of SRGs. If the absorbance had been very high, the light would have been absorbed by the sur-
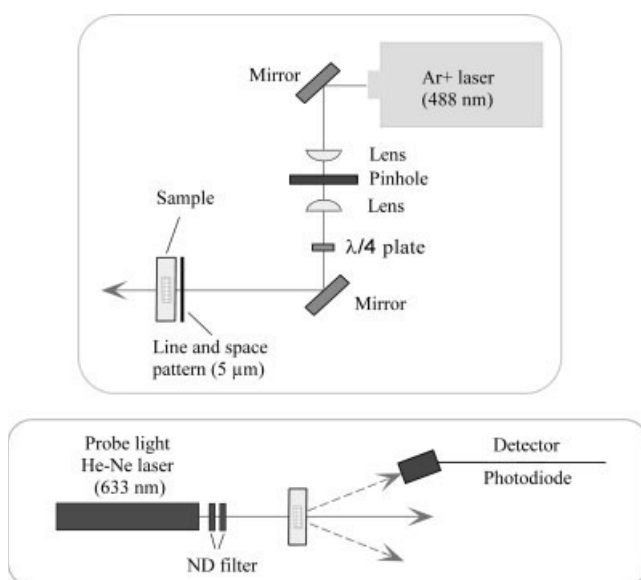
**Figure 1** Experimental setup for the grating inscription.
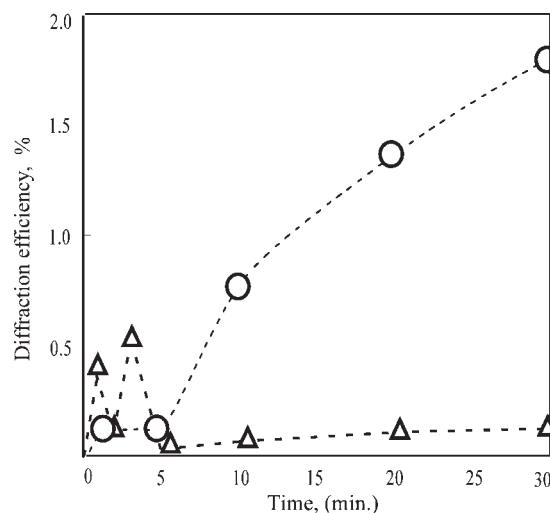
Figure 2 Changes in the diffraction efficiency with time induced by (○) circularly polarized and (△) s-polarized Ar$^+$-laser irradiation on polymer films through a photomask.

face of the film, and further light would not have been permitted into the deeper region of the film.

Figure 2 shows a plot of the diffraction efficiency as a function of the irradiation time. The value of the diffraction efficiency increased with an increase in irradiation time. The diffraction efficiency of the polymer film was about 2% with the irradiation of circularly polarized light for 30 min. High-order diffraction was found clearly with increasing diffraction efficiency. On the other hand, in the case of s-polarized light irradiation, initially a small but very fast increase in the diffraction efficiency was observed. However, it decreased rapidly with time. This was repeated until 5 min. Then, a very slow increase in the diffraction efficiency with time was found, as can be seen in Figure 2. Although the diffraction efficiency was not so high, it was sufficient for the fabrication of various types of diffractive optical components. It was assumed that the dependence of this diffraction efficiency originated from the difference in the hologram formation mechanism. When circularly polarized light was irradiated, SRGs were formed because of the mass transfer of the molecules from the bright region to the dark region. Therefore, the formation of SRGs was slower and better. As a result, the diffraction efficiency of the polymer film increased gradually. On the other hand, by the irradiation of s-polarized light, only molecular orientation in the molecules occurred (no mass transfer). That was the reason that initially the formation of SRGs by s-polarized light was faster. The molecular orientation was confirmed by the measurement of the polarized absorption spectra.

After the formation of SRGs, the exposed regions were scanned with an atomic force microscope. Figure 3(a) shows an AFM image of SRGs that formed on the polymer films. The SRGs had a very regularly spaced, sinusoidal structure with a high modulation
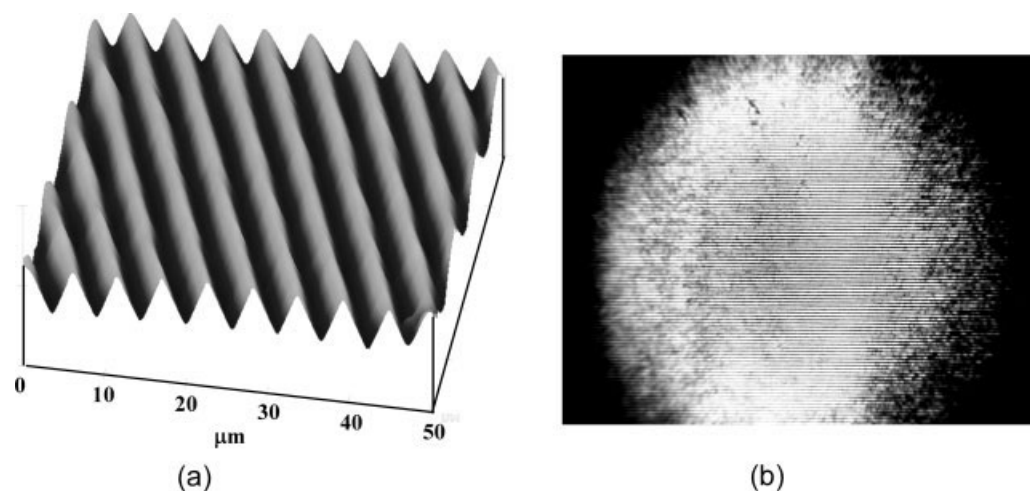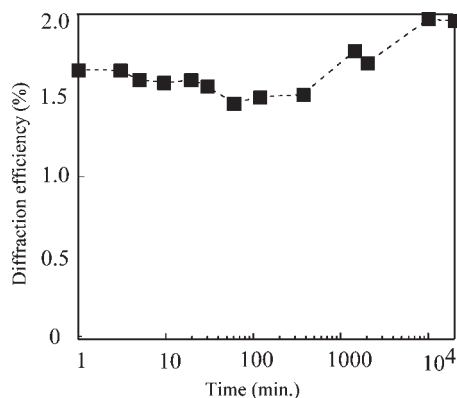
Figure 3 (a) AFM image and (b) POM image of a polymer film irradiated with a circularly polarized Ar^+ laser for 30 min.

depth. Polarized optical microscopy (POM) observations [Fig. 3(b)] also confirmed the formation of SRGs that possessed a periodic structure corresponding to the stripe period of the photomask. The irradiation of circularly polarized light caused continuous trans–cis–trans photoisomerization, which was also proved by the measurement of polarized absorption spectra. Consequently, SRGs were formed on the polymer film by the irradiation of circularly polarized light. Moreover, the formation of SRGs was dependent on the irradiation time. It is said that the formation of SRGs is derived from both trans–cis photoisomerization in the bright domain by excited light irradiation and thermal cis–trans reverse isomerization. The polymer migrates from a bright domain to a dark domain accompanying with the difference in the relative trans form and cis form in the interference stripes of bright and dark domains, respectively. It has been suggested that only light irradiation causing trans–cis–trans photoisomerization induces the formation of SRGs. In the case of irradiation by s-polarized light, the cycle of

trans–cis–trans photoisomerization can be considered to become a photostationary state in which the azo chromophores align in the normal to the direction of the polarization of light. Therefore, the SRG formation mechanism by circularly polarized light irradiation is different from that of linearly polarized light irradiation. The wavelength of the irradiated light was 488 nm, which was different from the absorption maximum of the trans form of the polymer.

The modulation depth of the surface grating on polymer films after irradiation with a circularly polarized Ar^+ laser for 30 min was found to be about 400 nm. The relief period was the same as the photomask stripe period, which was equal to 5 µm. The diffusion of materials from a bright area to a dark area caused the formation of SRGs. This result suggests that the polymer formed a large, convex domain, gathering another one that was transferred from the bright domain. With respect to the depth of the grating, it may depend on the structure of the formed SRG, but it is not clear enough at this stage. We will investigate this in the future.

The time dependence of the diffraction efficiency of the polymer film after circularly polarized Ar^+-laser irradiation was studied at room temperature (Fig. 4). The diffraction efficiency decreased initially, but after a certain time, it started to increase with time to a constant value. AFM observation of the irradiated film showed that the relief structure was retained even after 1 year. This result reveals that the period of recording of the polymer film was very high, more than 1 year.

CONCLUSIONS

Significant SRGs were observed on polymer films by the irradiation of a circularly polarized Ar^+ laser through a photomask for 30 min. The diffraction efficiency induced by s-polarized light was much smaller

Figure 4 Time dependence of the diffraction efficiency of a polymer film after irradiation.

than that induced by circularly polarized light. A diffraction efficiency of about 2% was obtained by the irradiation of a circularly polarized Ar^+ laser for 30 min. AFM and POM observations confirmed the formation of SRGs. The depth of the surface grating formed by the irradiation of a circularly polarized Ar^+ laser was about 400 nm. The period of recording of the polymer film was very high, more than 1 year.

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