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Photo-induced Holographic Surface Relief Gratings in High T_g Main-chain Azoaromatic Polymer Films

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We have synthesized two classes of polyureas with *mono-* and *di*azoaromatic groups in their main chains. Holographic gratings were fabricated on the polyurea films prepared by spin-coating from solutions. Regularly spaced surface relief gratings on the polymer film were also recorded upon exposure to an interference pattern of two polarized argon laser beams.

Keywords : azoaromatic polyurea, surface relief grating, holographic material

INTRODUCTION

Photo-isomerization of the azobenzene group resulting in photo-induced changes in the optical properties of the polymer has been extensively studied[1,2]. Stable optically induced birefringence and dichroism has been produced in azopolymers which forms the basis for reversible optical storage[3]. Holographic gratings using polymer films have potential applications in various optical elements and devices[1,4]. Recently our group and Natansohn's group reported direct optical fabrication of erasable surface relief gratings on various epoxy based polymer films almost at the same time[5,6] and these polymers had azoaromatic groups in their side chains. *Trans-cis-trans* photo-isomerization of azobenzene in the polymer is believed to play an important role in the chromophore orientation and subsequent formation of the surface gratings on the polymeric films.

So far efficient surface gratings were recorded on the polymers containing azobenzene chromophores in their side groups. Formation of surface gratings in main-chain azoaromatic polymer might be different from those of side-chain ones due to restricted mobility of the azo chromophore in the backbone, relatively high T_g and symmetric chemical environments around in azo groups in the main-chain polymer backbone.

EXPERIMENTAL

Synthesis

The syntheses of monomers were carried out according to the literature method[7]. Polyureas containing *mono*- and *di*azoaromatic groups were synthesized between isophorone diisocyanate and the corresponding diamines.

Surface relief grating formation

Holographic surface relief gratings were recorded under ambient condition by a simple interferometric apparatus at 488nm using an argon ion laser with an intensity of 55mW/cm^2 [5]. The surface structure of the gratings on the polymer films was investigated by atomic force microscopy (AFM) under ambient condition after the holographic gratings were recorded.

RESULTS AND DISCUSSION

The chemical structure of **PU1** and **PU2** are shown in Fig. 1. The T_gs (197.2°C for **PU1** and 236.0°C for **PU2**) of the polymers were found to be significantly higher than the side-chain azo polymers reported earlier where relief gratings were fabricated[5,6]. UV-visible absorption spectra of the spin-coated **PU1** (from DMF) and **PU2** (from DMAc) films showed λ_{max} at 380nm and 393nm, respectively. Surface profile of the **PU1** film after the formation of the gratings is shown in Fig. 2. The grating profile shows a regular sinusoidal shape with a depth of about 440Å and grating spacing of about 900nm. Diffraction efficiency during the grating formation with respect to exposure time (Fig. 3). Diffraction efficiency of about 1.5 % was obtained in 30 min in the case of **PU1** as shown in Fig. 3 (a). Under the same recording condition as here larger diffraction efficiency and surface modulation could be

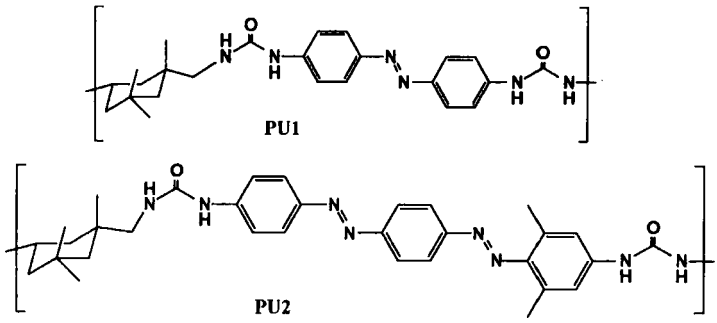

FIGURE 1. Chemical structures of the polymers.

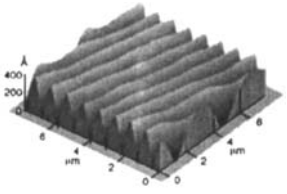

FIGURE 2. 3-Dimensional AFM image of the surface relief gratings in **PU**1 film.

obtained in a side chain azo polymer as earlier reported by us[5]. In the present study the diffraction efficiency achieved after 30 minute exposure was much smaller than that reported earlier but is sufficient for fabrication of various types of diffractive optical components. Grating formation on the film of polyurea with *di*azoaromatic chromophores in its main chain (**PU2**) was also investigated as shown in Fig. 3 (b). The polymer film has a λ_{max} at 393nm and stronger absorption at 488nm than the polyurea with *monoazo*aromatic chromophores (**PU1**). Regularly spaced sinusoidal surface relief gratings could be obtained on a film of **PU2** as well in a manner similar to **PU1**. However, the modulation depth was shallower and the diffraction efficiency was lower than that of **PU1** at the same irradiation time. Even after one hour exposure the diffraction efficiencies are not saturated and the modulation depths appear to be dose dependent in a manner similar to the side chain azo polymers. The formation of the surface relief grating is attributed to spatially varying forces acting on the chromophores due to a spatially varying optical field. This force is responsible for the dragging of the chromophore and hence the polymer in the direction of the optical field gradient. Clearly these forces

are smaller for the symmetric azo and diazo chromophores in the main chain polymers than on the asymmetrically substituted chromophores on their side chain counterparts. Further, rapid *trans-cis-trans* isomerization in the push-pull azo chromophores of the side chain azo polymers and the associated plasticization is significantly reduced in the main chain azo polymers. The fact that grating formation does occur much as dichroism occurs at modest light intensities is indicative that the high T_gs are not a detriment.

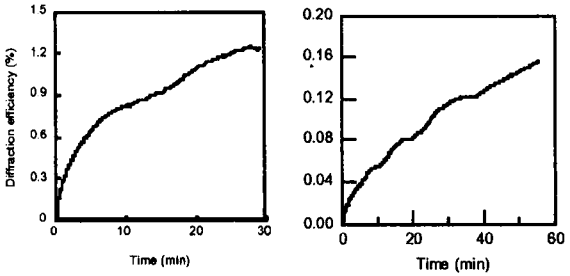

FIGURE 3. Diffraction efficiency of (a) PU1 and (b) PU2.

CONCLUSION

Main-chain azoaromatic polymers were synthesized and characterized as optical recording material and for holographic surface relief grating fabrication. Formation of surface relief gratings upon exposure to interfering laser beams under ambient condition was demonstrated in these high T_g main-chain azoaromatic polymers with symmetric azo chromophores.

Acknowledgment

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