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The Behavior of Surface Relief Grating Formation on Organic Glass Films Containing Azo Chromophores

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The surface of azobenzene polymer films could be photo-fabricated into various surface relief structures. Most of surface grating formation studies were focused on polymeric materials because of the easy film formation. In this work, we investigated the photo-manipulation of low molecular weight tri-isocyanate cyclic compounds containing azobenzenes which form glassy films upon spin casting. These non-polymeric films were capable of forming efficient surface gratings when irradiated to an interference pattern of polarized laser beams. We examined the difference of the grating formation behaviors between the isocyanate trimer and polyisocyanate films containing azobenzene groups with the same chemical compositions. The surface grating formation on the trimer film was more efficient than on the polymer films even though both films have similar T_g s.

Keywords surface relief grating; azobenzene; polyisocyanate

INTRODUCTION

The photo-fabrication of surface relief gratings on azobenzene functionalized polymer films has been investigated lately for the potential application to the optical storage and devices [1]. When irradiated to an interference pattern of polarized laser beams, polymer films containing azobenzenes showed the large amplitude of surface

modulation [2, 3]. All the results reported in this field so far have used polymer films due to its capability of easy optical film formation. In this report, we synthesized isocyanate organic glass materials which form optical quality films upon spin coating. We investigated the formation of surface relief grating in these isocyanate materials and compared with the polyisocyanate with the same azobenzene contents.

EXPERIMENTAL

The chemical structures of trimer and polymer were shown in figure 1.

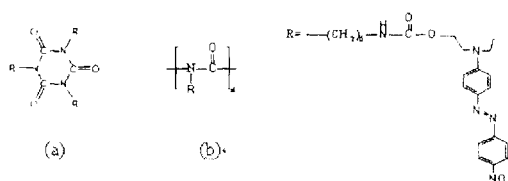


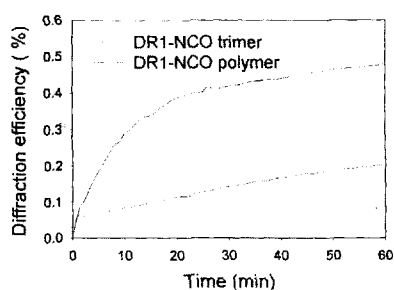
FIGURE 1. The chemical structures of (a) DR1-NCO trimer and (b) polymer.

The syntheses of DR1-NCO trimer and polymer will be reported elsewhere [4]. The molecular weight of DR1-NCO trimer was 1446 and the glass transition temperature (T_g) of trimer was 44°C. The number (M_n) and weight average molecular weight (M_w) of the polymer were 9726 and 12534, respectively. The polydispersity was 1.29. T_g of the polymer was 49°C. DR1-NCO trimer and polymer films were fabricated by spin casting of a filtered solution 3.85 wt% in THF. The prepared films were baked near T_g of the samples for 20 hrs. The thickness of the films was about 0.3 μm . The UV-Vis absorption spectra of DR1-NCO trimer and polymer thin films showed the maximum at 466 nm and 463 nm, respectively. The surface relief grating was fabricated by exposure of the interference pattern of polarized Ar⁺ laser

beams at 488 nm [2]. The power of Ar^+ laser during this experiment was about 50 mW/cm^2 . The polarization of writing beams during this experiment was 45° . The incident angle of the writing beams was 14° for the grating spacing of about $1 \text{ }\mu\text{m}$. The efficiency of the diffraction was detected by He-Ne laser at 633 nm.

RESULTS AND DISCUSSION

The diffraction efficiencies of DR1-NCO trimer and polymer are shown in figure 2. The increase rate of diffraction efficiencies in trimer with low molecular weight was larger than that of polymer probably due to the less entanglement of trimer molecules than that of polymer chains.



The grating structures on DR1-NCO trimer and polymer by the atomic force microscopy are shown in figure 3. The surface relief gratings of trimer and polymer are erasable upon heating above T_g .

FIGURE 2. The diffraction efficiencies of trimer and polymer

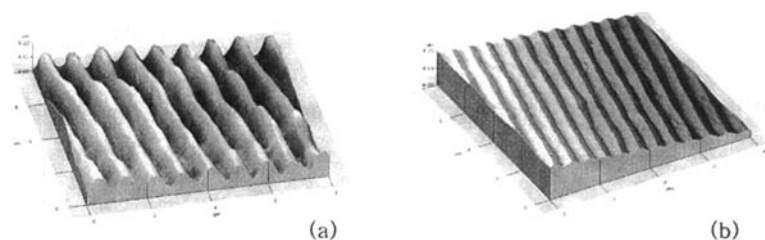


FIGURE 3. AFM 3-D view of the surface gratings fabricated on (a) the DR1-NCO trimer film and (b) the polymer film.

CONCLUSION

Azobenzene functionalized isocyanate cyclic trimers and polyisocyanate with the same chemical composition were synthesized. Even with its low MW, DR1-NCO trimer containing azobenzene chromophores could form optical quality amorphous films by the simple spin coating process. The surface relief grating could be fabricated on both DR1-NCO trimer and polymer films upon exposure to an interference pattern of Ar⁺ laser beams. The gratings were erasable on heating above T_g . The diffraction efficiency of DR1-NCO trimer with low molecular weight was larger than that of polymer under the same fabrication conditions.

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