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Stability of the surface relief grating on the thin film of the polyurethane and the polymethacrylate containing an aminonitroazobenzene moiety

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Summary

We synthesized the new photosensitive polymers containing an aminonitroazobenzene moiety in the side chain. Azobenzene-containing polyurethane and polymethacrylate were prepared for fabricating the diffraction gratings on the film surface. Two-beam coupling method was employed for fabricating the surface relief gratings. The dynamics of formation of the diffraction gratings was studied in term of the variation of the diffraction efficiency. The erasing behavior of the surface relief gratings was observed under a linearly polarized single beam irradiation. The stability of the diffraction efficiency was also investigated with the change of the sample temperature. The effect of the molecular specific interaction on the thermal stability of the surface relief grating below the glass transition temperature was studied in this work.

Introduction

Polymers containing azoaromatic chromophores have drawn much interest in the field of optical data storage, nonlinear optical, and holographic applications. One of the main properties to be utilized is the photo-induced *trans-cis-trans* isomerization of the azobenzene group. Surface relief gratings (SRGs) can be produced by isomerization and molecular reorientation of the azobenzene chromophore, which is accompanied by large-scale displacement of the molecules, induced by coupling of the two coherent beams. Azobenzene attached to push-pull substituents exhibits fast *trans-cis* photoisomerization and *cis-trans* thermal back reaction, which can be conveniently used in optical storage applications and in the creation of surface relief gratings [1-7].

Erasable gratings formed in the films of azobenzene-containing polymers have been studied extensively since they were first reported by Todorov et. al. [8,9]. Recently, surface relief gratings (SRG) have been fabricated in the side chain azo polymer film through repeated *trans-cis-trans* isomerization upon exposure to the excitation light with an interference pattern [10-12]. Photo-anisotropic materials like the azobenzene-containing polymers respond to variations in both the intensity and polarization state of the total electric field. Topographic relief structures are formed upon exposure to the appropriate optical light source by a single-step process.

Both side chain and main chain azopolymers have been investigated for SRG formation [13-15]. Gratings with large surface modulation depth have been achieved.

SRGs recorded on these polymers are stable when kept below the glass transition temperature (T_g). The patterns can be erased optically even below T_g or by heating the samples above T_g. The understanding of the mechanism responsible for SRG formation is still under study [16-22].

All the polymers that show efficient surface relief gratings reported to date were polymers containing azobenzene chromophores in their side groups. There has been no report on the formation of surface relief gratings on the polyurethane and the effect of the molecular specific interaction on the thermal stability of the gratings.

In this work, we report on the properties of the photosensitive polyurethane (PU) and polymethacrylate (PMA) for fabricating the diffraction grating controlled by a coupled linearly polarized visible light (λ=488 nm). The effect of the hydrogen bond on the stability of the diffraction efficiency was also investigated using the inscribed film of the two polymers below T_g.

Experimental

Synthesis of polymethacrylate (PMA)

Homopolymer of 2-methacrylic acid 6-{methyl-[4-(4-nitro-phenylazo)-phenyl]-amino}-ethyl ester was prepared by radical polymerization. The monomer (3 g, 8.1 mmole) was dissolved in dried NMP (5 ml) in the presence of AIBN(0.07 g, 0.4 mmole). The solution was kept at 70 °C for 48 hr under argon atmosphere. Red polymer was collected and purified by reprecipitation from NMP/hot ethanol until there is no monomer left and dried in vacuum at 90 °C for 48 hr. Yield, 78%. T_g ~117 °C.

Anal. Calcd. for $C_{19}H_{20}N_4O_4$: C, 61.95; H, 5.47; N, 15.21.
Found C, 61.94; H, 5.18; N, 14.94.

^{1}H-NMR ($CDCl_3$) δ (ppm) 0.55-3.92 (12H, $-CH_2-$, $^{\alpha}C-CH_3$, $-N-CH_3$, $-(CH_2)_2-$), 6.71-8.22 (8H, aromatic)

FT-IR (KBR) ν (cm^{-1}) 2984, 2942 (w, C-H), 1728 (s, C=O), 1602, 1588 (s, C=C), 1516, 1338 (s, NO_2)

Synthesis of polyurethane (PU)

2-{(2-Hydroxy-ethyl)-[4-(4-nitro-phenylazo)-phenyl]-amino}-ethanol (3 g, 9.1 mmole) and tetramethyl-1,3-xylene diisocyanate (*m*-TMXDI, 2.22 g, 9.1 mmole) were dissolved in freshly dried dimethylformamide (DMF, 47.2 ml) under argon atmosphere. Dibutyltin dilaurate (DBTDL, 0.012 g, 0.018 mmole) was added into the solution and the reaction mixture was kept under stirring at 85 °C for 72 hr. The product was precipitated into hot ethanol and filtered. It was dried under vacuum at 95 °C for 72 hours. Yield, 55%. T_g~103 °C.

Anal. Calcd. for $C_{30}H_{34}N_6O_6$: C, 62.70; H, 5.96; N, 14.63
Found C, 61.86; H, 5.90; N, 14.57

^{1}H-NMR (DMSO-d_6) δ (ppm) 1.49 (12H, aliphatic 4xCH_3 in *m*-TMXDI unit), 3.67 (4H, $-O-CH_2CH_2-N-$), 4.1 (4H, $-N-CH_2CH_2-O-CO-$), 6.25 (1H, aromatic), 8.00-6.70 (9H, aromatic), 8.34 (2H, aromatic).

FT-IR (KBR) ν (cm^{-1}) (3403 (isolated, -NH-C=O-), 3323 (H-bonded, -NH-C=O-), 1734 (isolated, -NH-C=O-), 1713 (H-bonded, -NH-C=O-), 1601, 1590 (s, C=C), 1515, 1338 (s, NO_2)

Instruments: UV-Vis absorption spectroscopy was performed on a Hewlett Packard 8453 spectrophotometer (PDA type, λ=190-1100 nm). Infrared spectrum was recorded using Bruker IFS66v spectrometer. The thermal behavior of the polymers was investigated by differential scanning calorimetry (DSC) using a Perkin Erlmer DSC7. The heating rate was 10°C/min in all cases.

Film Formation: PU was dissolved in tetrachloroethane and PMA in tetrahydrofuran (THF). The 15 wt% polymer solutions were filtered with 0.2 µm syringe filters and then spin-coated onto glass slides. The films were dried in a vacuum oven at 90°C for 48 hr. The thickness was measured by using the surface profilometer (Tencor P10).

Surface relief grating: SRGs on the thin films were recorded under ambient conditions with the interference pattern produced by a linearly p-polarized argon ion laser at 488 nm. (Lexel model 95) The two linearly polarized laser beams at 488 nm fabricated diffraction gratings with the intensity variation. Laser beams with +45° and -45 ° polarizations were used to be coupled on the film surface. The efficiency of the 1st-order diffracted beam from the gratings in transmission mode was probed with a linearly polarized low power He-Ne laser beam (5 mW) at 633 nm. The angle between the two beams is approximately 5.63°. The polymer film is mounted on a hot stage that enables the temperature of the film to be controlled.

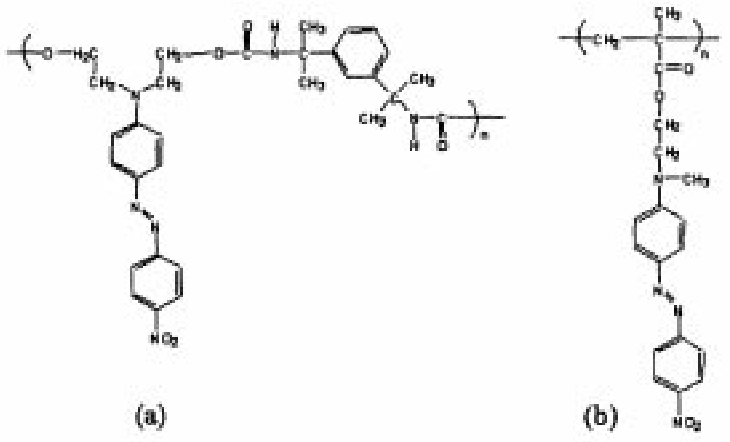
Atomic force microscopy: The AFM investigations of the grating structures in PU and PMA films were carried out with a scanning probe microscope (AFM, Autoprobe, Park Scientific Instrument before and after the gratings were recorded.

Results and discussion

We synthesized polyurethane (PU) and polymethacrylate (PMA) bearing an aminonitroazobenzene as a pendent group (See Scheme 1). The structures of the synthesized polymers were confirmed by elemental analysis, FT-IR, and FT-NMR spectroscopy. The polymer was quite soluble in common organic solvents. The glass transition temperatures (T_gs) of the PU and PMA were determined to be 103°C and 117°C, respectively. Optically transparent films of the PU and PMA were obtained from a solution of tetrachloroethane and THF respectively. UV-Vis absorption spectra of the thin PU and PMA films showed absorption maxima (λ_{max}) at 455 and 448nm, respectively due to π-π^* transition of aminonitroazobenzene chromophore as shown in Figure 1. PMA film showed slightly lower wavelength of λ_{max} that is due to a higher extent of aggregation in which the dipoles are arranged in an antiparallel way [23].

Irradiation Time Dependence of the Diffraction Efficiency

We have observed that the stable surface relief gratings could be fabricated on the polymer film at room temperature that is well below T_g. In Figure 2, we could observe the variation of diffraction efficiency under writing and erasing process. The change of the 1st-order diffraction efficiency was observed at three different intensities of the two pump beams. Under the polarizations (±45°) of the coupled beams we used herein, the interference patterns have both intensity modulation and polarization variation. It is more difficult to remove the diffraction gratings under a single beam irradiation. The oriented polarizable chromophores and hence the polymer is subjected to an electric force field in the light pattern resulting in the surface relief grating formation. Regular grating structures with large surface modulation depth (126-271 nm) were observed. We irradiated the coupled beam on the polymer surface for 300 sec and then the single beam to erase the SRGs for another 300 sec. When we increased the intensity of the two-coupled beams, the diffraction efficiency increased concomitantly. In both polymers, under 20 mW/cm^2 intensity of the two beams, the diffraction efficiency decreased to the lowest level when the +45° linearly polarized beam was irradiated. As the intensity of the coupled beam is higher, the residual diffraction efficiency is higher after optical erasure. This implied that the higher intensity of the coupled beams gives the higher resolved surface gratings that were attributed to the larger scale molecular displacement of the azobenzene group. The intensity of the erasing single beam is just half of the writing coupled beam so that the pre-formed SRGs cannot be diminished totally. It could also show the higher residual optical anisotropy inside the grating period. The diffraction efficiency of the PU showed higher value than the PMA, which is wholly due to the lower T_g of PU.



Scheme 1. Structures of the photosensitive (a) polyurethane and (b) polymethacrylate.

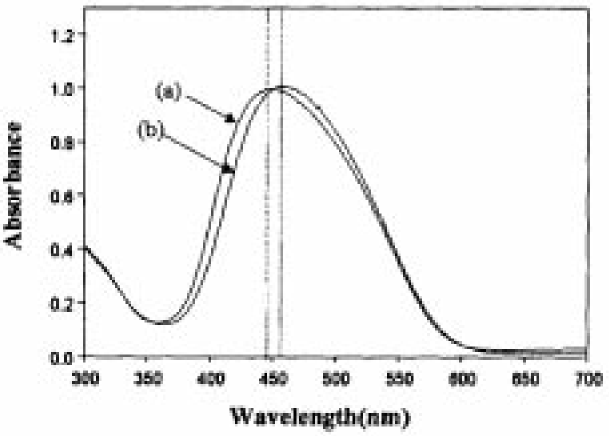


Fig. 1 UV-Vis absorption spectra of the thin films. (a) polymethacrylate; (b) polyurethane.

However, we could observe the different behavior of the increase of the diffraction efficiency during two-beam coupling. The rate of increment in 100 sec irradiation in PMA is much larger than that of PU. It can be thought that the difference of transient behavior results from the hydrogen bond between the main chain themselves in PU. The hydrogen bonds can retard the migration of the side chain azobenzene group so that the rate of increase of the diffraction efficiency in PU is smaller in the initial stage of the irradiation.

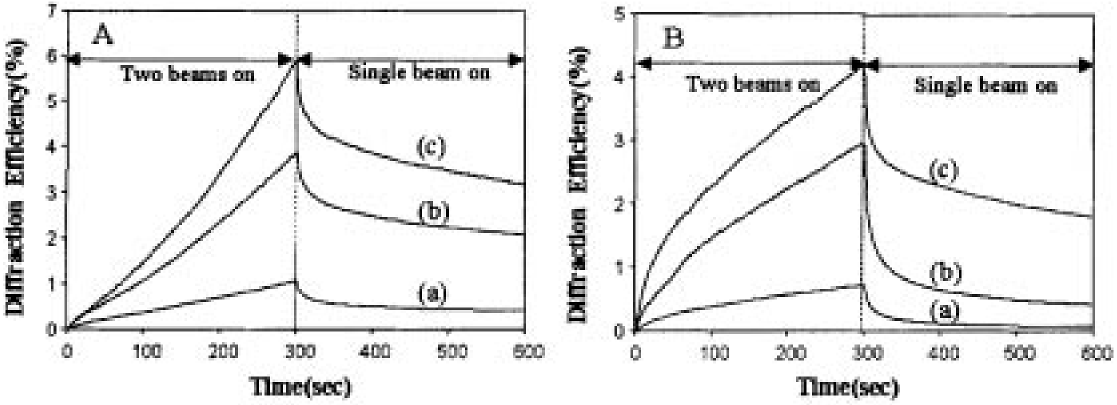


Fig. 2 Diffraction Efficiency as a function of exposure time and erasing behaviors under a single beam irradiation. A: polyurethane, B: polymethacrylate; (a) 20 mW/cm^2, (b) 40 mW/cm^2, (c) 60 mW/cm^2.

Temperature Dependence of the Diffraction Efficiency

Typical erasure temperatures for the two polymers can be defined to be around T_g according to the literatures [12,13]. However, we would like to see the variation of the diffraction efficiency below T_g. The dynamic behavior of the decay of the diffraction efficiency below T_g is thought to be strongly related to the viscoelastic property of the polymers and be affected by the β-relaxation behavior that is associated with the side chain motion. Additionally, the molecular specific interaction in the polymer structure can influence that behavior. Figure 3 shows the temperature dependence of the normalized diffraction efficiency for PU and PMA. The PU films have lower erasure temperatures than the PMA films according to the lower T_g. Examination of the films with an atomic force microscope after recording the grating showed the presence of a surface relief. Heating the films up to a temperature of 130 °C in both cases, which is well above T_g, can erase the surface relief.

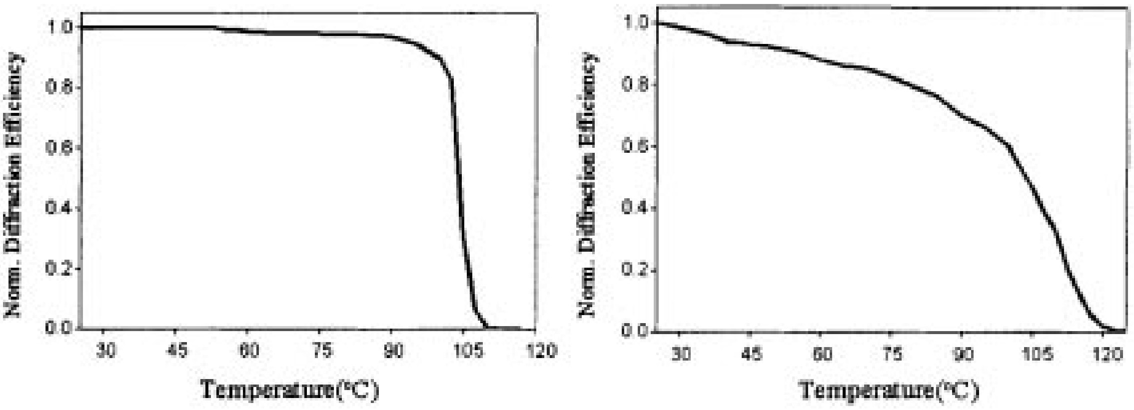


Fig. 3 Stability of the normalized 1st-order diffraction efficiency in polyurethane (A) and polymethacrylate (B) as a function of temperature. The gratings were recorded at a temperature of 25°C. Heating rate is 5°C/min.

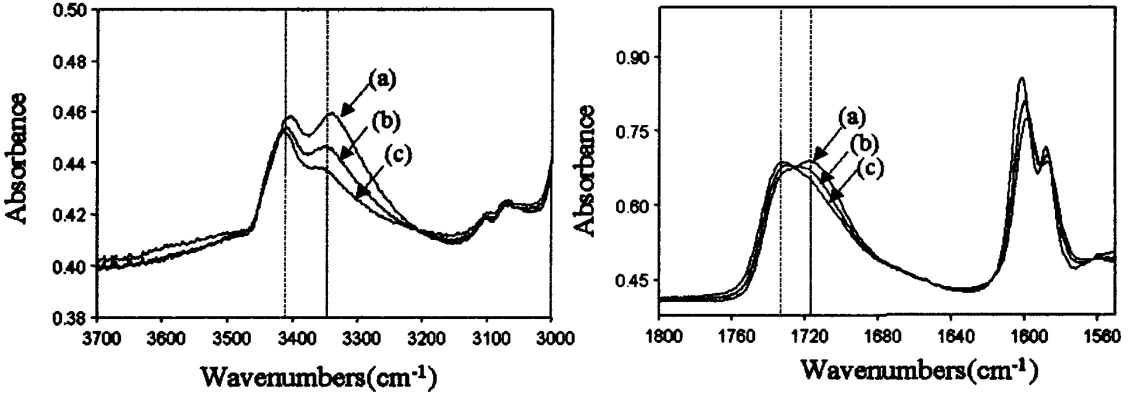


Fig. 4 Infrared spectra of the polyurethane film at different temperatures. (a) 25°C, (b) 120°C, (c) 160°C.

In Figure 3, the diffraction efficiency of the PU fell down to zero at 110°C close to T_g. Of course, the value also showed zero at 125°C in PMA. However, much different decaying behaviors in two polymers were shown below T_g. For example at 90°C, almost 100% and only 65% of the initial diffraction efficiency can be observed in PU and PMA, respectively. Therefore, we can evaluate the thermal stability of the diffraction efficiency in PU to be much higher in the temperature range well below T_g. Assuming that the hydrogen bonds between the main chains in PU played an important role to enhance the stability, we carried out the *in-situ* FT-IR spectroscopy with the change of the sample temperature of the PU thin film. In Figure 4, the IR spectral change of the PU film was shown at three different temperatures. We could figure out that the hydrogen bonds between the secondary amine and carbonyl group in the carbamate unit start to disrupt around 110°C that is slightly higher than T_g of PU. Therefore, the stability of the diffraction efficiency in PU can be though to be affected by the molecular specific interaction particularly below T_g.

Atomic Force Microscopic (AFM) Investigations

The films were examined with an atomic force microscope after recording a grating, optical erasing, and thermal erasing. Figure 5 shows a representative atomic force microscope (20 μm x20 μm) scans of the irradiated area of PU. The grating profile in

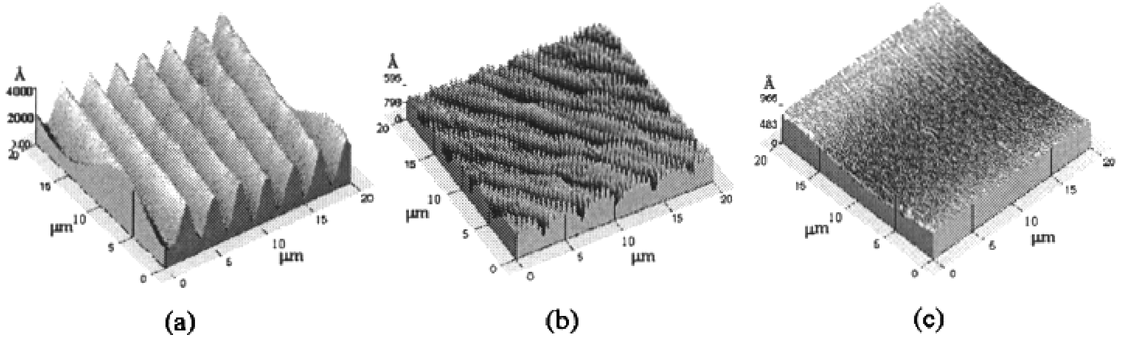


Fig. 5 Atomic force microscopy 3-D image of the surface relief grating on a polyurethane film. (A) after two beam coupling; (b) after optical erasing under a single beam irradiation; (c) after thermal annealing at T_g.

PU shows a regular sinusoidal shape with a depth of about 271 nm and grating spacing of about 2.85 µm that is well consistent with the theoretical calculation (Λ=2.86 µm). The grating depth of PMA was found to be 126 nm that is quite small compared to that of PU because of the higher T_g. The surface topography was observed at the identical time frame employed in Figure 2. Micrograph (a) was taken after 300 sec irradiation of the coupled beams and (b), after 300 irradiation of the linearly polarized single beam. The micrograph (c) was taken after thermal annealing at T_g. The trace of the SRG still exists even after optical erasing under a single beam irradiation. It is well consistent with the results in Figure 2. Finally, the trace of gratings was diminished totally after thermal annealing at T_g even for 10 sec.

Conclusion

Side-chain azobenzene polymers having a polymethacrylate and polyurethane have been synthesized and examined the potential for optical storage. The polymer was amorphous and soluble in many polar solvents. We have observed surface relief gratings on polymer films containing an aminonitroazobenzene chromophore without any subsequent processing steps. After irradiation at 488 nm with a polarized laser beams, these materials present a fairly large diffraction efficiency that is stable at room temperature. The stability of the diffraction efficiency of PU below T_g was observed to be relatively higher than that of PMA owing to the hydrogen bonds between the main chains themselves. Due to the ease with which relief gratings can be recorded on the polymer films, such polymers may have potential applications for optical devices and optical diffractive elements.

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