Photoinduced Surface Relief Gratings in High-*T_g* Main-Chain Azoaromatic Polymer Films

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ABSTRACT: We have synthesized two classes of polyureas with mono- and bisazoaromatic groups in their main chains via reactions between isophorone diisocyanate and the corresponding diamines. Holographic gratings were fabricated on azoaromatic polyurea films prepared by spin-coating from solutions. The effect of high glass transition temperature and dipole moment of azo groups on the formation of gratings was investigated. Although the two polymers have relatively high glass transition temperatures (197 and 236°C), chromophore alignment was induced by laser beam irradiation at modest light intensities. Regularly spaced surface relief gratings on the polymer film were also recorded upon exposure to an interference pattern of two polarized argon laser beams. Erasure could be achieved by heating above T_g or by exposure to one of the beams in a manner similar to low- T_g side-chain azo polymers. © 1998 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem **36**: 283–289, 1998

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INTRODUCTION

Polymers with azoaromatic groups have attracted much attention as materials for optoelectronic applications.¹⁻⁴ Photoisomerization of the azobenzene group resulting in photoinduced changes in the optical properties of the polymer has been extensively studied.^{5,6-9} Stable optically induced birefringence and dichroism has been produced in azoaromatic polymers which forms the basis for reversible optical storage.¹⁰⁻¹³ Various azoaromatic main-chain as well as side-chain polymers have been synthesized, and photochemical *cistrans* isomerization in solution has been investigated.¹⁴⁻¹⁷ Holographic gratings using polymer films have potential applications in various optical elements and devices.^{5,18–19} Surface relief gratings can be fabricated by using polymers such as photoresists²⁰ and thermoplastic photoconductors²¹ or by employing laser ablation techniques with conventional polymer films.²² None of these methods, however, have provided a simple single-step fabrication of erasable surface relief gratings.

There have been reports on the nonlinear optical properties of aromatic polyurea prepared by vacuum deposition polymerization and solution polymerization.^{23,24} Although polyurea films do not show large nonlinear optical coefficients, they have positive features such as short wavelength cut-off and good temporal stability of nonlinearity, among others.^{25,26} These properties may be appropriate for use of polyureas as a matrix material for optical application.

Recently we reported direct optical fabrication

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of erasable surface relief gratings on various epoxy-based polymer films.²⁷⁻²⁹ These polymers had azoaromatic groups in their side chains. Upon exposure to an interference pattern of visible laser beams (argon ion laser at 488 or 514 nm), surface gratings with large surface modulation depth (>6000 Å) could be fabricated. Large-scale molecular motion was thus introduced at least 50°C below the glass transition temperature. Diffraction efficiency higher than 40% could be routinely obtained. The gratings were stable below glass transition temperature (T_g) and could be erased by heating the sample above T_g or exposure to one of the recording beams.²⁹ We have confirmed that this process does not result from photogenerated thermal effects.^{6,29} It was also found that polarization of recording beam has significant influence on the writing and erasure processes.²⁹ Transcis-trans photoisomerization 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. A similar conclusion has been drawn by Natansohn, Rochon, and co-workers from acrylate polymers with azo side groups.^{6,30,31}

All the polymers which showed efficient surface 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 main-chain azoaromatic polymer films. 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 and relatively high T_{g} . In addition, the azo groups have symmetric chemical environments in the main-chain polymer backbone. The permanent dipole moment is due to the urea linkages as opposed to the azo units which were designed to possess push-pull electronic structures in the side chain azo polymers but are symmetrically substituted in the present case. This is the first report on the formation of photoinduced surface grating on high- T_g main-chain diazoaromatic polymer films. The effect of the symmetric azo chromophores positioned in the main chain on the grating formation is discussed.

EXPERIMENTAL

Materials and Reagents

All the starting materials, reagents, and solvents were purchased from Aldrich Chemical Co. and

used without further purification unless otherwise noted. Deuterated *N,N*-dimethylformamide (DMF- d_6), deuterated acetone, and the polymerization medium 1-methyl-2-pyrrolidone (NMP, 99+% anhydrous) were received from Aldrich and used as received. The synthesis of 4,4'-diamino-azobenzene (I) was carried out according to the literature method.^{32,33}

Monomer Synthesis

4-[4'-(4"-Nitrophenylazo)phenylazo]-3,5dimethylaniline (II)

The reaction was accomplished by literature method with modification.³⁴ A 4 g (16.52 mmol) amount of 4-amino-4'-nitroazobenzene (Disperse Orange 3, DO3) was dissolved in ice-cooled 100 mL acetic acid containing 8 mL of 98% sulfuric acid. Sodium nitrite (1.48 g, 21.40 mmol) dissolved in a small amount of water (less than 2 mL) was added dropwise to the stirred solution. The reaction temperature was maintained at 5°C. After 6 h of stirring 3.5-dimethylaniline (5.0 g, 41.30 mmol) in 10 mL of acetic acid was added followed by slow addition of sodium acetate (4.10 g, 50.0 mmol). The resulting red solution was stirred at 5°C for an additional 16 h. A 10% sodium hydroxide solution was slowly added to neutralize the reaction mixture. The precipitates formed were collected by filtration, washed with water several times, dissolved in THF, and dried over magnesium sulfate. Solvent was evaporated, and a dark red powder was obtained by precipitation in n-hexane. The solid was further purified by column chromatography (silica gel; THF : nhexane = 4:6, v/v%), affording 3.51 g (61%) of dark red solid product. ¹H-NMR (DMF): δ 8.58 (d, 2H), 8.20 (m, 4H), 7.99 (d, 2H), 6.55 (s, 2H), 6.15 (s, 2H), 2.60 (s, 6H). FT-IR (KBr): 3335 (m; NH₂), 3008 (w; aromatic CH), 2950–2890 (w; methyl CH), 1625 (s; NH), 1595 (s; aromatic C=C), 1150 cm⁻¹ (s; C–N). FT-Raman: 1445 $cm^{-1}(N=N).$

4-[4'-(4"-Aminophenylazo)phenylazo]-3,5dimethylaniline (III)

To a 20 mL ethanol solution of **II** (0.2 g, 0.53 mmol) under reflux was added sodium hydrosulfide hydrate (0.15 g, 2.71 mmol) dissolved in a small amount of water. The reaction mixture was refluxed for 30 min and then filtered. The residue was washed with chloroform, and the filtrate combined with chloroform was washed with water and



Scheme 1. (a) Synthetic scheme for **II** and **III** and (b) polymerization of **PU1** and **PU2**.

dried over magnesium sulfate. After evaporation of chloroform, the final product (0.14 g, 76%) was obtained by recrystallization in ethanol. ¹H-NMR (acetone): δ 7.93 (m, 6H), 6.84 (d, 2H), 6.50 (s, 2H), 5.46 (d, 4H), 2.55 (s, 6H). FT-IR (KBr): 3333 (m; NH₂), 3010 (w; aromatic CH), 2944–2887 (w; methyl CH), 1634 (s; NH), 1584 (s; aromatic C=C), 1147 cm⁻¹ (s; C–N). FT-Raman: 1443 cm⁻¹ (N=N).

Polymerization

PU1

Into a flask were placed monomer I (1.0 g, 4.71 mmol), isophorone diisocyanate (0.97 g, 4.40 mmol), and NMP (22 mL) under nitrogen purge. The reaction medium was heated at 95°C for 48 h, cooled to room temperature, and then poured into 200 mL of vigorously stirred methanol. The resulting precipitates were filtered out, washed with methanol and acetone thoroughly, and dried

in a vacuum oven, yielding 1.49 g (78%) of dark yellow powder.

PU2

This was synthesized by using a procedure similar to that for the preparation of **PU1**. Diamine monomer **III** (1.0 g, 2.90 mmol), isophorone diisocyanate (0.64 g, 2.90 mmol), and 8 mL of NMP were placed in a flask under nitrogen purge. The polymerization and workup procedures were the same as described above to afford 1.2 g (73%) of red powder.

Characterization

¹H-NMR spectra were taken from a Bruker ARX-250 spectrometer operating at 250 MHz. FT-IR spectra were recorded on a Perkin-Elmer 1760X FT-IR spectrometer using KBr pellets, and the FT-Raman spectra were obtained from a Perkin-Elmer 1700X FT-Raman spectrometer. Absorption spectra were recorded on a Perkin-Elmer Lambda 9 UV-vis-NIR spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using a Du Pont Thermal Analysis Model 2000 equipped with a Model 2950 TGA and a Model 2910 DSC. TGA data were obtained in flowing nitrogen at a heating rate of 20°C/min. DSC thermograms were obtained under nitrogen atmosphere at a heating rate of 10°C/ min. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) using DMF as an eluent and polystyrene as a standard.

Film Formation

PU1 was dissolved in DMF, and **PU2**, in *N*,*N*-dimethylacetamide (DMAc). The 5-10 wt % polymer solutions were filtered with 0.45 μ m syringe filters and then spin-coated onto glass slides. The films were dried in a vacuum oven at 70°C for 48 h. Thickness of the films was measured by ellipsometry.

Measurement of Photoinduced Orientation and Surface Relief Grating Formation

Films of polyureas were irradiated for 30 min with a linearly polarized argon laser beam at 488 nm to investigate dichroism and birefringence in the films. The beam intensity was 50 mW/cm². The polarized UV spectra were recorded by means of

Table I. Properties of the Polymers

	T_{g} (°C)	T_d (°C) ^a	M_n	M_w	Polydispersity
PU1 PU2	$\begin{array}{c} 197.2\\ 236.0 \end{array}$	$\begin{array}{c} 312\\ 320 \end{array}$	7500 7200	7800 7700	$\begin{array}{c} 1.043\\ 1.075\end{array}$

^a On-set decomposition temperature.

a Perkin-Elmer Lambda 9 UV–vis–NIR spectrophotometer. The optically induced birefringence in the exposed films was measured at a wavelength of 633 nm from a low-power He–Ne laser beam as described earlier.²⁸

Holographic gratings were recorded under ambient condition by a simple interferometric apparatus at 488 nm using an argon ion laser with an intensity of 55 mW/cm². The setup of the grating experiment has been reported elsewhere.²⁹ The surface structure of the gratings on the polymer films was investigated by atomic force microscopy (AFM, Autoprobe Cp, Park Scientific Instruments) under ambient condition before and after the holographic gratings were recorded.

RESULTS AND DISCUSSION

Monomer III was prepared by a diazotization-coupling reaction followed by a reduction from nitro to amino groups as shown in Scheme 1a. Byproducts were also obtained during the diazotizationcoupling reaction such as the bisazoamino compound (-N=N-Ar-N=N-NH-Ar) besides an expected aminobisazo compound $(-N=N-Ar-N=N-Ar-NH_2)$.³⁵ Two polyureas with monoazo- or bisazo aromatic groups were synthesized from the simple addition reaction between isophorone diisocyanate and I or III.³³ The chemical structures of PU1 and PU2 are shown in Scheme 1b. The structures of the synthesized polymers were confirmed by FT-IR and FT-Raman spectroscopy.³³ The T_g s of the polymers PU1 and PU2 were determined to be 197 and 236°C, respectively (Table I), which were significantly higher than the side-chain azo polymers reported earlier where relief gratings were fabricated ($\sim 100^{\circ}$ C).²⁷⁻³⁰ No melting points were observed in DSC thermograms of either polymer. On-set decomposition temperatures of PU1 and PU2 were found at 312 and 320°C, respectively. The molecular weights of PU1 and PU2 obtained from GPC are listed in Table I. The molecular weights of **PU1** and **PU2** were found to be lower than those of polyureas reported earlier.²⁵ It is presumed that aromatic diamines containing the azo chromophore has lower reactivity toward diisocyanate than other diamines due to the difference in basicity.³⁶ The polymers were quite soluble in DMF, dimethyl sulfoxide (DMSO), and DMAc. UV-visible absorption spectra of the spin-coated **PU1** and **PU2** films showed absorption maxima (λ_{max}) at 380 and 393 nm, respectively, due to $\pi - \pi^*$ transition of azobenzene chromophore as shown in Figure 1.

We investigated optically induced dichroism and birefringence on the polymer films. Typical thickness of the spin-coated films was from 0.3 to 0.4 μ m. The spin-coated polymeric films were exposed to a linearly polarized beam at 488 nm from an argon laser for 30 min. As shown in Figure 1a,b, dichroism has been optically induced by the laser light in both high- T_g polymers with rigid



Figure 1. Absorption spectra of films of **PU1** (a) and **PU2** (b). The upper curves represent the absorbance for light polarized perpendicular to the polarization direction of the original pump beam, and the lower ones are the absorbance for light polarized parallel to the polarization direction of the original pump beam.



Figure 2. Surface profile of the gratings on PU1 film.

main-chain segments under ambient condition. After irradiation with the laser beam the absorbance in the direction parallel to the polarization of the pump laser light $(A_{//})$ was lower than that in the perpendicular direction (A_{\perp}) . This suggests that azo chromophores in the main-chain have been aligned in the direction perpendicular to the laser beam polarization. Dichroic ratios $(A_{\perp}/A_{\prime\prime})$ of 1.101 (**PU1**) and 1.102 (**PU2**) were obtained, which are somewhat smaller but in the same order of magnitude as some of the side-chain azo polymers with significantly lower T_{g} s.^{5,7} Order parameters, S = (D - 1)/(D + 2), of 0.033 were measured in both PU1 and PU2. The induced birefringence was 0.01 for both **PU1** and **PU2**. This birefringence was also in the same range as those reported from side-chain azo polymers.^{5,28} Induced dichroism and birefringence are attributed to the optically induced alignment of azobenzene groups resulting from *trans-cis* photoisomerization of the azo group followed by a *cis-trans* thermal isomerization or photoisomerization.⁵ This molecular orientation in the film confirmed from the polarized UV spectra (Fig. 1) indicates significant local motion, and the formation of photoinduced surface relief gratings was subsequently explored.

The surface profile of the **PU1** film after the formation of the gratings was investigated by atomic force microscope (AFM). The result is shown in Figure 2. The grating profile shows a regular sinusoidal shape with a depth of about 440 Å and grating spacing of about 900 nm.

Diffraction efficiency from a surface relief grating was monitored 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 Figure 3a. Under the same recording condition as here larger diffraction efficiency and surface modulation could be obtained in a side-chain azo polymer as earlier reported by us.²⁹ In the present study the diffraction efficiency achieved after 30 min 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 *bisazo* aromatic chromophores in its main chain (**PU2**) was also investigated as shown in Figure 3b. The polymer film has a λ_{max} at 393 nm and stronger absorption at 488 nm 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 ef-



Figure 3. Diffraction efficiency as a function of exposure time for **PU1** (a) and **PU2** (b). Incident wavelength of 488 nm with an intensity of 55 mW/cm².

ficiency was lower than that of $\ensuremath{\textbf{PU1}}$ at the same irradiation time.

In spite of the expected restricted mobility of the chromophores in the polymeric chains, a degree of dichroic ratio similar to the side-chain azo polymers was achieved with similar exposure to the polarized laser beams. Even after 1 h of 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 then on the asymmetrically substituted chromophores on their side-chain counterparts. Further, rapid trans-cis-trans isomerization in the pushpull 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_g s are not a detriment.

CONCLUSION

Main-chain azoaromatic polymers were synthesized and characterized as optical recording material and for holographic surface relief grating fabrication. The polymers are amorphous and easily processed into films by use of organic solvents such as DMF and DMAc. Despite high T_{g} s resulting from the rigid main-chain structure these polymers showed strong dichroism and birefringence upon exposure to polarized optical beams due to photoisomerization and reorientation. Formation of surface relief gratings upon exposure to interfering laser beams under ambient condition was demonstrated for the first time in these high- T_{g} main-chain azoaromatic polymers with symmetric azo chromophores.

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