

Synthesis of Aniline-Based Azopolymers for Surface Relief Grating

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Received January 5, 2008; Revised January 31, 2008; Accepted February 1, 2008

Abstract: Epoxy-based azopolymers were synthesized by the reaction of the diglycidyl ether of bisphenol A (DGEBA) or *N,N*-diglycidyl aniline (DGA) with disperse orange 3 (DO3) to give poly(DGEBA-*co*-DO3) or poly(DGA-*co*-DO3), respectively. Aniline-based azopolymers prepared from poly(DGA-*co*-An) precursors, synthesized by the reaction of DGA with aniline, were produced by the post-azo coupling reaction with diazonium salts containing various substituents. Holographic gratings were carried out to measure the diffractive efficiencies (DE) for the interference patterns of the Ar⁺ laser from 50 to 300 mW/cm² intensity. The shorter repeating unit with higher chromophore density induced deeper surface relief gratings (SRG). Large surface gratings were observed for the aniline-based azopolymers with -COOH substituents, as compared with those for epoxy-based azopolymers. The aniline-based azopolymers with dimerized chromophores and various substituents were also synthesized to observe the effect of chromophore substituents and dimerization on the holography. The dimerized chromophores were more sensitively photoisomerized by the Ar⁺ laser beam, and demonstrated a larger grating than that with one azo bond.

Keywords: surface relief grating, holography, azopolymer, diglycidyl aniline, post azo coupling.

Introduction

Holography is an optical recording method of photosensitive materials with the surface relief on recording media using various patterns of coherent light beams. Much attention has been paid to the surface relief grating (SRG) since Todorov *et al.* had demonstrated that chromophore molecules had a tendency to make large optical birefringence by photoisomerism when irradiated by a polarized light.¹ The trans-cis photoisomerization of azobenzenes and thermal relaxation of main chains from cis to trans isomers resulted in birefringence gratings on epoxy-based azopolymers^{2,3} and polyacrylates^{4,6} with disperse red azobenzene dyes. In particular, azopolymers possessed processibility enough to create an excellent quality of thin films for the SRGs. The SRGs were initiated by the photoisomerism of the azobenzenes to transfer electrons from electron donating groups, such as -N=, to electron acceptor groups like -NO₂, -CN, -COOH, -CHO and -SO₂H. When a light beam was illuminated on a recording medium, the polymer chains were migrated toward both surface sides around an illumination spot, whose migration was driven by the photoisomeriza-

tion, thermal relaxation or gradient force.^{4,7} The effects of main chains, such as poly(vinyl alcohol),⁸ polythiophenes,⁹⁻¹² peptide oligomers¹³ and epoxy-based polymers,^{14,15} chromophores and electron acceptors,¹⁶ on the holography have been reported. The chromophore density of the azopolymers could influence the SRG, and the secondary bonding between the functional groups in the main chains and the chromophore substituents was one of the main factors to restrict the migration of the azopolymers. The aniline-based azopolymers had the higher chromophore density than the epoxy-based azopolymers reported so far.

In this work, the aniline-based azopolymers with various substituents and dimerized chromophores were synthesized for the first time and the effects of the chromophore structures on the SRG were studied in comparison with epoxy-based azopolymers.

Experimental

Synthesis of Poly(DGEBA-*co*-DO3). The epoxy-based azopolymers of poly(DGEBA-*co*-DO3) were prepared with bulk polymerization of diglycidyl ether of bisphenol A (DGEBA) (Exxon 834) with 4-[(4'-nitrophenyl)azo] aniline [disperse orange 3 (DO3), Aldrich] on an equimolar basis at 110 °C

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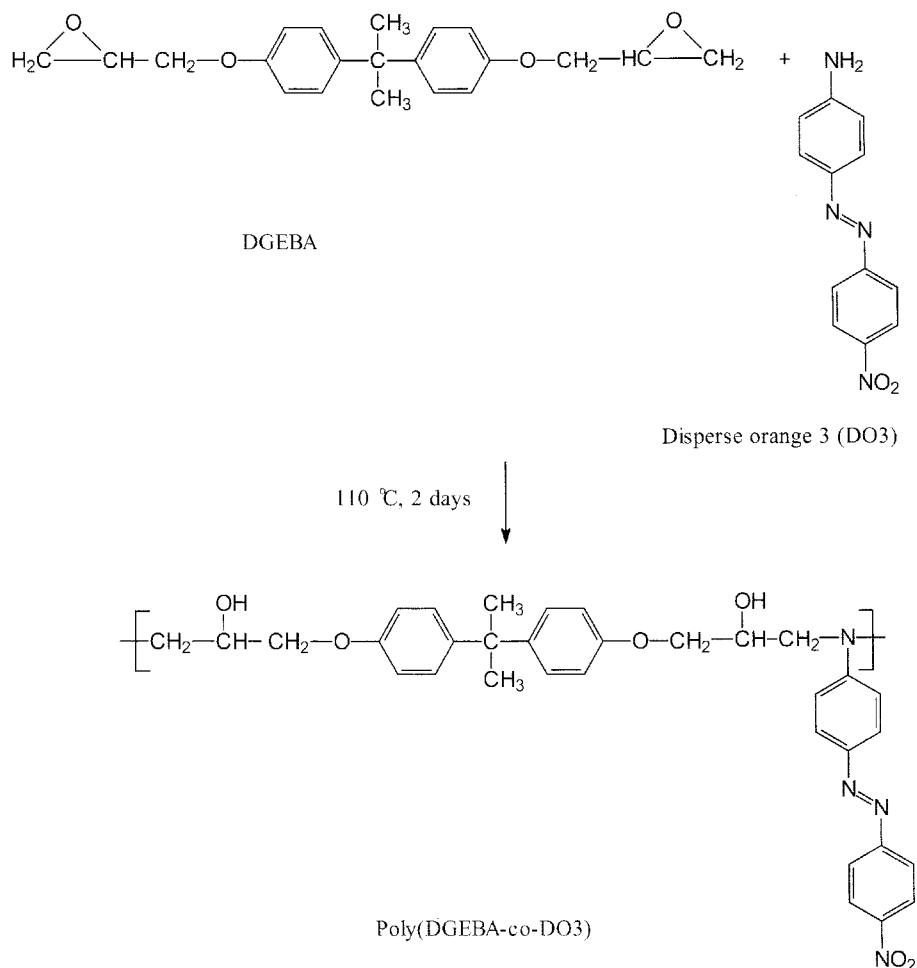


Figure 1. Synthetic scheme of poly(DGEBA-co-DO3).

for 2 days to prevent the undesired ring opening reactions of secondary hydroxyl groups with glycidyl groups, as reported by B. K. Mandal, *et al.*¹⁷ The resultants were dissolved in acetone, filtered and dried under vacuum for purification. The reaction scheme is shown in Figure 1.

Synthesis of Poly(DGA-co-DO3). The epoxy-based azopolymers of poly(DGA-co-DO3) were prepared with the bulk polymerization of *N,N*-diglycidyl aniline (DGA, Aldrich) with DO3 on the equimolar basis at 110 °C for 2 days.¹⁷ The resultants were purified as the same method as for poly(DGEBA-co-DO3) (Figure 2).

Synthesis of the Precursor Poly(DGA-co-An). The precursors poly(DGA-co-An) were synthesized from DGA with aniline (An) through bulk polymerization at the temperature ranges of 110-150 °C for 2 days.¹⁴ The number average molecular weight (M_n) and polydispersity index (PDI) were measured to be 1,200 g/mole and 1.4 using gel permeation chromatography (GPC, Waters 712 WISP) equipped with a refractometer/viscometer dual detector (Viscotek Model 250) and UV detector (Water 486) in THF as an eluent with 1 mL/min flow rate at room temperature.

Synthesis of Aniline-Based Azopolymers with an Azo Bond. A solution of 4-aminobenzoic acid (ABA, Aldrich) (2.74 g, 20 mmol) in 4 mL HCl (0.131 mol) was reacted with a solution of 2.15 g (31 mmol) of sodium nitrite (Aldrich) in 10 mL H₂O. An excess nitrous acid was decomposed by adding sulfamic acid (0.2 g in 2 mL H₂O). The diazonium salt solution was added dropwise into poly(DGA-co-An) (2.38 g, 8 mmol) dissolved in 20 mL dimethyl formamide (DMF) and then stirred at 0 °C for 12 h. The mixture was then poured into water under agitation with a few drops of hydrochloric acid. The precipitated poly(DGA-co-An-azo-ABA) was collected by filtration and washed with an excess of water until the filtrates were clear. The resultants were further purified by repeatedly extracting with chloroform and dried under vacuum for 24 h. 4-Aminobenzonitrile (ABN, Aldrich), 4-aminobenzaldehyde (ABAl, Aldrich) or 4-nitroaniline (NA, Aldrich) (20 mmol, respectively) was reacted with 2.15 g (31 mmol) of sodium nitrite (Aldrich) in 10 mL H₂O to produce the aniline-based azopolymers called as poly(DGA-co-An-azo-ABN), poly(DGA-co-An-azo-ABAl) or poly(DGA-co-An-azo-NA). The azo coupling reactions

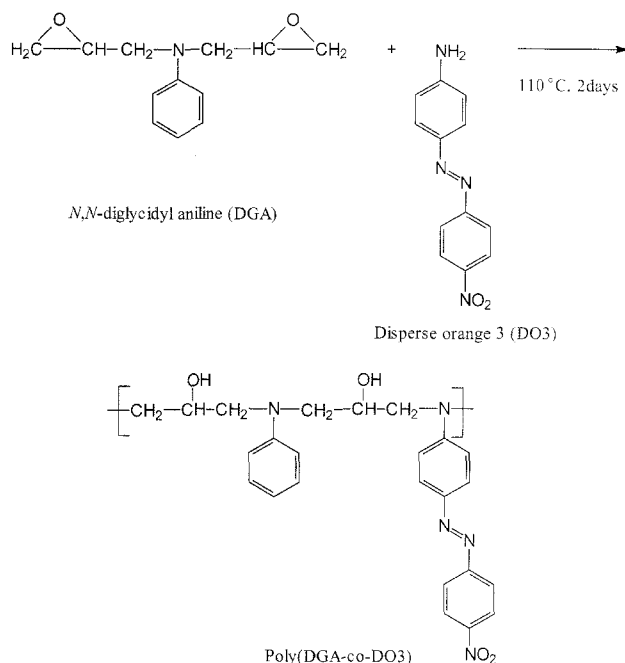


Figure 2. Synthetic scheme of poly(DGA-co-DO3).

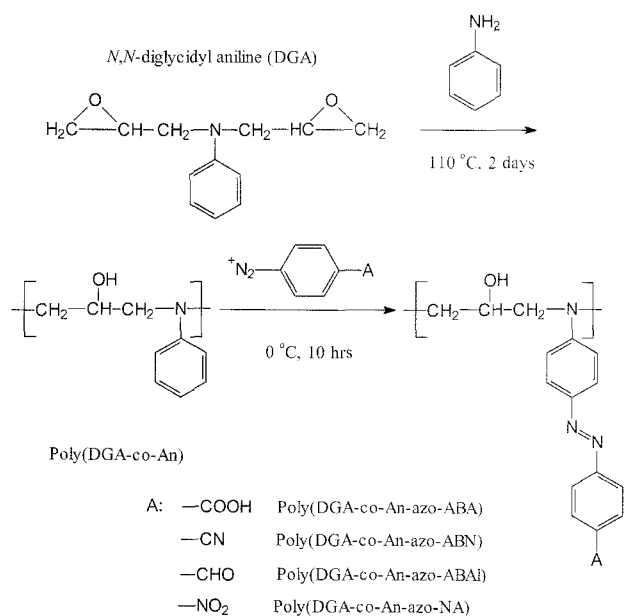


Figure 3. Synthetic scheme of the aniline-based azopolymers prepared with the post azo coupling reactions.

and separations were carried out as the same method as for poly(DGA-co-An-azo-ABA) (Figure 3).

Synthesis of Precursor Poly(DGA-co-An-azo-An). A solution of 2.94 g (0.03 mol) aniline in 6 mL HCl (0.393 mol) was reacted with a solution of 3.21 g (45 mmol) NaNO₂ in 15 mL H₂O. An excess nitrous acid was decomposed by adding sulfamic acid (0.2 g in 2 mL H₂O), and then the diazonium salt solution was added dropwise into poly(DGA-co-An) (3.57 g, 12 mmol) dissolved in 30 mL

DMF. The precipitated poly(DGA-co-An-azo-An) was collected by filtration and washed until the filtrates were clear. The precursor azopolymers were further purified by repeatedly extracting with acetone and dried under vacuum for 24 h.

Synthesis of Aniline-Based Azopolymers with Two Azo Bonds. A solution of 1.37 g (10 mmol) 4-aminobenzoic acid in 4 mL HCl was reacted with a solution of 1.0 g (15 mmol) sodium nitrite in 5 mL H₂O for 15 min. The diazonium salt solution was added dropwise into poly(DGA-co-An-azo-An) (2.0 g, 8 mmol) dissolved in 15 mL DMF solution. The solution was stirred at 0 °C for 12 h, and then poured into water under agitation. The resultant poly[DGA-co-(An-azo)₂-ABA] was filtered, washed, further purified by repeatedly extracting with acetone and dried under vacuum for 24 h. Poly[DGA-co-(An-azo)₂-ABN] or poly[DGA-co-(An-azo)₂-NA] was prepared with adding 10 mmol of 4-aminobenzonitrile or 4-nitroaniline as the same procedure as for poly[DGA-co-(An-azo)₂-ABA] (Figure 4).

Spin Coating Process. The azopolymers were dissolved in propylene glycol monomethyl ether acetate (PGMEA)/dioxane (8/2 w/w) for poly(DGEBA-co-DO3) and poly(DGA-co-DO3), and THF or THF/dioxane (8/2 w/w) for poly(DGA-co-An-azo-ABA) and poly[DGA-co-(An-azo)₂-ABA]. The solutions with 10 wt% concentration were spin-coated under

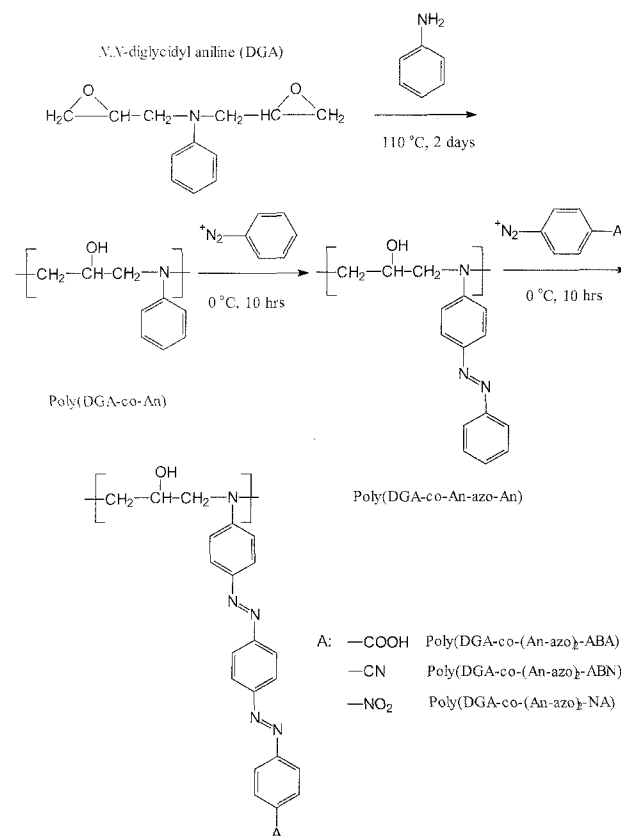


Figure 4. Synthetic scheme of the aniline-based azopolymers with two azo bonds and different substituents through the post azo coupling reactions.

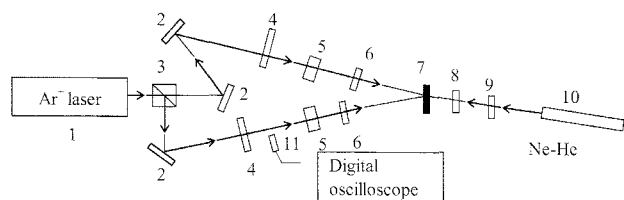


Figure 5. Holographic optical elements for grating: 1, Ar⁺ laser; 2, mirror; 3, beam splitter; 4, attenuator; 5, half wave plate; 6, polarizer; 7, recording medium; 8, wave plate; 9, attenuator; 10, He-Ne laser; 11, photo sensor.

800 rpm for 60 sec and dried at room temperature, creating about 1 μm thickness.

Surface Relief Grating (SRG) and Diffractive Efficiency (DE). The gratings were fabricated using an interference of two linearly *p*-polarized beams from an Ar⁺ laser (Coherent Innova) at 488 nm with 1 μm pitch, as shown in Figure 5. A half wave plate was used to provide equal intensity in the two beams split at a beam splitter, rotating the polarization direction of the recording beams that were *p*-polarized at a polarizer plate. Diffractive efficiency (DE), η , was defined as the intensity ratio of a diffracted beam to an incident beam as follows.

$$\eta = I_{+1}/I_0 \quad (1)$$

where I_{+1} and I_0 are the intensities of a +1 order (first order) diffracted beam and a probe transmission beam,¹⁸ respectively. The DE was measured through a digital oscilloscope by monitoring an unpolarized low power He-Ne laser beam at 633 nm.

Measurement of Second Harmonic Generation Coefficient d_{33} . Polings of thin films were carried out at 85 °C with 2.5 mA for 20 min. The d_{33} coefficients were measured both at 1.063 and 1.54 μm of Nd:Yag laser, compared with Y-cut quartz reference ($d_{11}=0.364$ pm/V). The thickness of the polymer films were measured with an ellipsometer (Rudolph Research) using a UV intensity at 532 μm .

Atomic Force Microscopy (AFM). The surface relief views and profiles were measured using an atomic force microscopy (AFM) (Park Scientific Instrument Auto Probe Cp) with a contact mode. The spin-cast films on glass slides were cut into 1 cm wide and 2 cm long, and the surface roughness was observed without any surface treatment at 2 Hz scanning rate using a 10 μm range scanner with a Si_3N_4 tip. The contact mode was normally used with an applied force of around 10 nN. The two- and three-dimensional images of the surface topologies and profiles were obtained with controlled spacing and surface modulation depths.

Nuclear Magnetic Resonance (NMR) Spectroscopy. The azo coupling reactions and molecular structures were confirmed by a ¹H-NMR spectroscopy (250 and 350 MHz Bluka ARX-200) with a deuterated dimethyl sulfoxide ($\text{d}^6\text{-DMSO}$)

solution. The NMR samples were prepared with a concentration ranging from 5 to 10 wt%.

Ultraviolet (UV)-Visible Spectroscopy. The absorbances of benzene rings of the azopolymers were confirmed with THF solutions using an ultraviolet spectroscopy (GBC UV/Vis 916). The solutions were scanned at 2 nm slit with 120 nm/min scan rate at a glass tube.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Weight losses were observed by a thermogravimetric analyzer (Hi-Res TGA 2950 Thermogravimetric Analyzer, TA Instruments) at 10 °C/min heating rate under nitrogen gas. The glass transition temperatures (T_g) of the azopolymers were measured using Du Pont Instrument DSC 2910 from a 2nd run scan after the first cycle of heating above their glass transition temperatures and cooling to room temperature at a heating rate of -10 °C/min.

Results and Discussion

Mechanism of Surface Relief Grating (SRG). The polarized laser activated the photoisomerization to transform the chromophores from *trans* to *cis* configuration through an electronic flow system between the electron-donating and electron-withdrawing groups. Hydrogen bonding was a typical secondary bonding to affect additional photoisomerizations and determine a grating scale by decreasing the mass transfer of the main chains, directly related to polymer viscosity, plasticity and T_g values. A nitro group substituent had two oxygen atoms that easily induced hydrogen bonding with an intrachain or interchain, requiring a higher beam intensity to create the surface relief grating (SRG) than a carboxyl acid or cyano group substituents with one oxygen or nitrogen atom.

Thermal and Optical Properties. The molecular weights of the repeating unit containing one chromophore (M_0) of poly(DGABA-*co*-DO3), poly(DGA-*co*-DO3) and poly(DGA-*co*-An-azo-NA) were 582, 447 and 298 g/mol, respectively. The profile depths of the azopolymers increased greatly according to the repeating unit molecular weight (Table I). The effect of repeating unit length on forming profiles of the surface relief indicated that the space length between the chromophores was one of significant factors influencing profile shapes. The migration of the main chain, induced by the photoisomerization, was accelerated by the high chromophore density, leading to the high profiles.

The effects of electron acceptors on non-linear optical (NLO) properties have been studied before, but how the space between chromophores influenced NLO properties has never been known, yet.^{12,16,17,19,20} Table I also lists the second harmonic generation coefficients (SHG, d_{33}) and glass transition temperatures (T_g) of the azopolymers with various repeating units.²¹ As the repeating unit length of the azopolymers decreased, the T_g increased, because the closely packed chromophores increased the steric hindrance of the

Table I. Various Properties of the Azopolymers

Azopolymers	M_o (g/mole)	Profile Height(Å)		d_{33} (pm/V)	T_g (°C)
		200 mW	300 mW		
Poly(DGEBA- <i>co</i> -DO3)	582	1,012	1,510	76.6	59
Poly(DGA- <i>co</i> -DO3)	447	1,527	2,140	39.0	70
Poly(DGA- <i>co</i> -An-azo-NA)	298	1,570	2,160	0	-
Poly(DGA- <i>co</i> -An-azo-ABA)	297	1,780	2,230	0	99

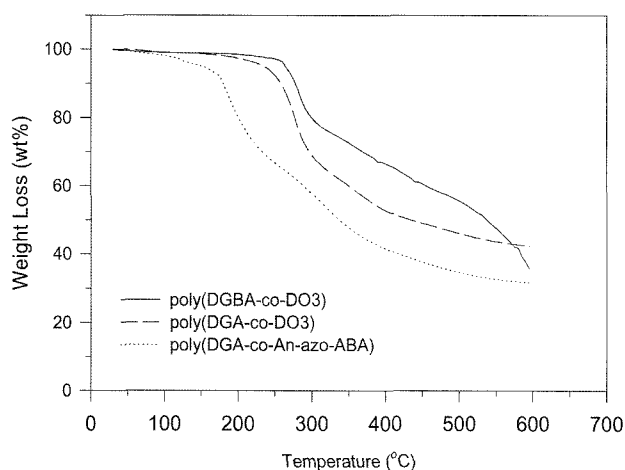
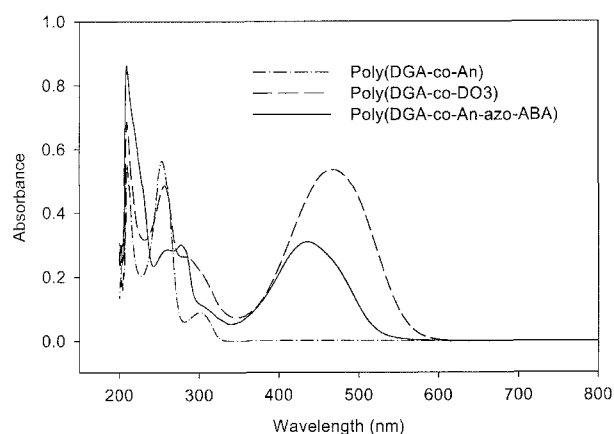
main chains, and the chromophore pendent groups possibly protected the main chains from heat flow. The more and larger pendent groups were more effective to prohibit the heat transfer to the main chains, leading to increasing the T_g of the azopolymers. The broader space between chromophore molecules in poly(DGEBA-*co*-DO3) allowed them more easily aligned in parallel, resulting into a higher d_{33} value than the others. The sufficient spaces between chromophores potentially provided a good condition for NLO properties by easy orientation of chromophores. The dense spaces between chromophores did not cause proper alignments of chromophores. So when poly(DGA-*co*-An-azo-ABA) was irradiated by the laser beam, it will have zero d_{33} value. The main chains of poly(DGA-*co*-An-azo-ABA) protected by a high chromophore density, with theoretically 297 g/mol per repeat unit at a complete coupling reaction, had the increased heat resistance and the T_g of 99 °C (Table I).

The thermal stability, reported to vary by the type of electron acceptors,¹² was also affected by the chromophore density. The thermal stability of the azo polymers decreased as the length of their repeating unit decreased. Poly(DGEBA-*co*-DO3) was thermally stable up to 260 °C under nitrogen atmosphere, as shown in Figure 6. As the chromophore density of the azopolymers increased, their thermal stability decreased gradually due to increasing azo bond density. The thermal decomposition of poly(DGEBA-*co*-DO3) and

poly(DGA-*co*-DO3) started from 267 and 245 °C, respectively. The thermal stability of poly(DGA-*co*-An-azo-ABA) was lower than that of poly(DGA-*co*-DO3), because poly(DGA-*co*-An-azo-ABA) containing higher chromophore density was basically more sensitive to heat and subjected to decomposition at a lower temperature than poly(DGA-*co*-DO3). The decomposition of poly(DGA-*co*-An-azo-ABA) started from 175 °C.

The post azo reactions were also confirmed by an azo bond-containing benzene absorbance peak (435 nm) at the UV spectra (Figure 7). The absorbance peak of poly(DGA-*co*-An) observed at 270 nm wavelength was assigned to a benzene ring absorbance with no azo bonds. The 475 nm peak of an azo bond-containing benzene absorbance, not observed for poly(DGA-*co*-An), appeared at the spectrum of poly(DGA-*co*-DO3). The benzene absorbance, observed at 435 nm for poly(DGA-*co*-An-azo-ABA), confirmed the post azo coupling reaction with poly(DGA-*co*-An). The ratios of the absorbance at 250 nm to that at 435 or 475 nm wavelength of poly(DGA-*co*-An-azo-ABA) or poly(DGA-*co*-DO3) were close to one, indicating that one benzene ring of the main chain contained one azo bond connected with another benzene ring.

Effect of Substituent of Chromophore. The substituents potentially interacted with the adjacent -OH groups of the main chains through hydrogen bonding according to their

**Figure 6.** TGA thermograms of the azopolymers.**Figure 7.** UV spectra of poly(DGA-*co*-An), poly(DGA-*co*-DO3), and poly(DGA-*co*-An-azo-ABA) in THF solution.

electronegativity. The hydrogen bonding between the substituents of the chromophores and the hydroxyl groups of the main chains possibly delayed or decreased the photoisomerization. The initial slope of diffractive efficiency (DE) versus exposure time increased in the order of $-\text{CHO}$, $-\text{NO}_2$, $-\text{CN}$ and $-\text{COOH}$ substituents. The initial response of the DEs for the azopolymers with $-\text{COOH}$ or $-\text{CN}$ substituents was faster than that with $-\text{NO}_2$ or $-\text{CHO}$ substituents. This may imply that their chromophores responded to the laser beam more sensitively so as to create the photoisomerization faster. As one of the desirable properties for the holography, the fast initial response could reduce a writing time on a recording medium. The aniline-based azopolymers with the aldehyde or cyano group substituents showed relatively good SRGs, compared with the epoxy-based azopolymers, and the profile height of poly(DGA-co-An-azo-ABN) increased slightly more than that of poly(DGA-co-An-azo-ABA), which may be ascribed to the less interactivity of the cyano groups for hydrogen bonding (Figure 8). Because the nitrogen atoms of the cyano groups had less electronegativity than the oxygen atoms of the aldehyde groups, the aldehyde group substituents, showing the higher tendency to do the hydrogen bonding, resulted in the lower grating. The carboxyl acid of poly(DGA-co-An-azo-ABA) was obviously the best substituent to create the largest grating among them because the carboxyl acid had a low effect on hydrogen bonding due to containing one oxygen atom to induce the hydrogen bonding and one hydroxyl group to repel it. The initial gradient of the DE for poly(DGA-co-An-azo-ABA) was also the highest among them.

Effect of Azo Bond Dimerization. PMMA-based azopolymers with two azo bonds were reported to show larger photoisomerization and deeper surface relief than their

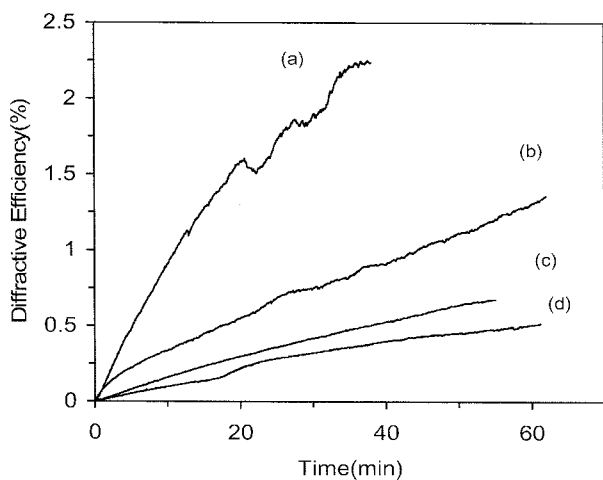


Figure 8. Diffractive efficiency versus exposure time for (a) poly(DGA-co-An-azo-ABA), (b) poly(DGA-co-An-azo-ABN), (c) poly(DGA-co-An-azo-NA), and (d) poly(DGA-co-An-azo-ABAl), prepared with the THF/dioxane (8/2 w/w) solution and 800 rpm and irradiated with 50 mW/cm².

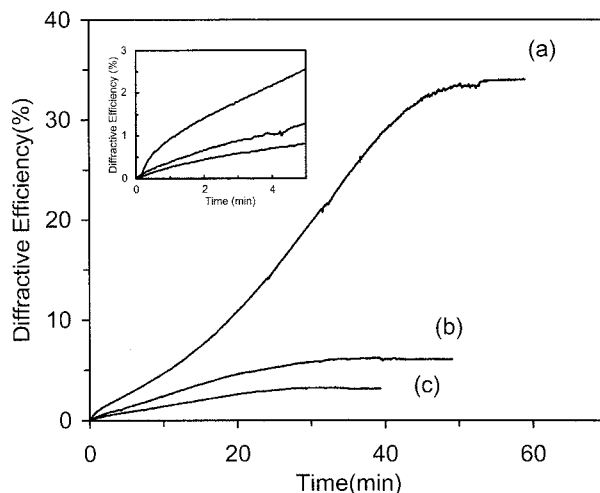


Figure 9. Diffractive efficiencies versus exposure time for (a) poly[DGA-co-(An-azo)₂-ABA], (b) poly[DGA-co-(An-azo)₂-ABN], and (c) poly[DGA-co-(An-azo)₂-NA], prepared with the THF/dioxane (8/2 w/w) solution and irradiated with 50 mW/cm².

azopolymers with one azo bond.²² The aniline-based azopolymers with two azo bonds and $-\text{NO}_2$ substituents apparently showed deeper surface relief than those with one azo bond. The chromophore substituents also significantly influenced the SRGs since each substituent had different withdrawing and interacting strengths with the adjacent hydroxyl groups of the main chains according to their electronegativity. Figure 9 shows DE versus exposure time for three azopolymers with dimerized chromophores and various substituents. The azopolymers with $-\text{NO}_2$ or $-\text{CN}$ substituents basically attained the saturation with a lower maximum DE and a slower initial gradient than those with $-\text{COOH}$ substituents. The azopolymers with $-\text{COOH}$ substituents, poly[DGA-co-(An-azo)₂-ABA], exhibited the highest maximum DE of 34% in 60 min exposure time. The chromophore dimerization, substantially influencing the photoisomerization of azobenzenes, also contributed directly to the deep grating and high diffractive efficiency saturation. The DE of the dimerized chromophores was also greatly affected by the type of substituents that was also critical of the initial response and deep grating. The dimerized chromophores with the carboxyl acid substituents showed the faster initial response at a short exposure time than those with cyano or nitro group substituents (the inset in Figure 9). As shown in Figure 10, the average profile height of poly[DGA-co-(An-azo)₂-ABA] was observed to be as much high as ca. 4,500 Å as compared with that of poly(DGA-co-An-azo-ABA) of 1,800 Å. The chromophores containing the carboxyl acid substituents were the most effective for the photoisomerism, so that the azobenzenes with the dimerized chromophores and carboxyl acid substituents created the largest photo-induced isomerization, leading to the highest surface relief.

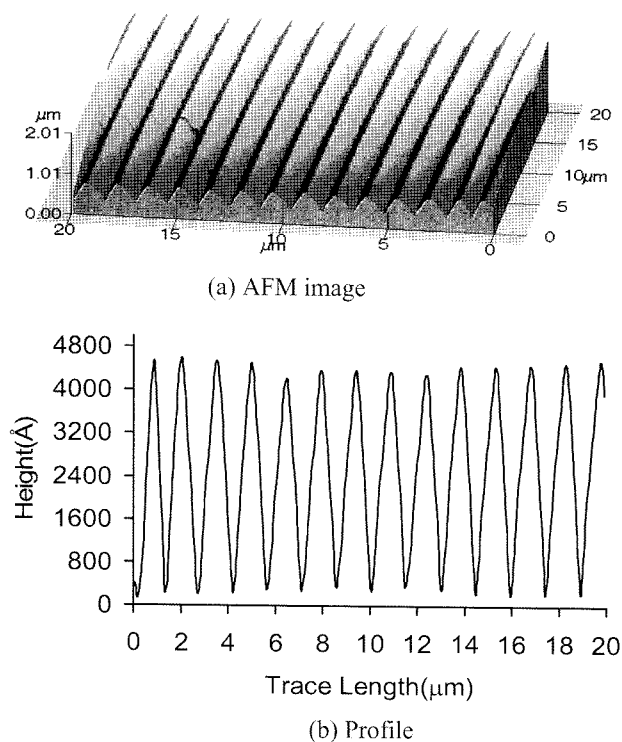


Figure 10. AFM image and profile of poly[DGA-co-(An-azo)₂-ABA] prepared with a THF solution and irradiated with 100 mW/cm² for 60 min.

Conclusions

The aniline-based azopolymers with various substituents were synthesized using the bulk polymerization and post azo coupling reactions. Holographic gratings were carried out to measure the diffractive efficiencies (DE) for the interference patterns from 50 to 300 mW/cm² intensity of the Ar⁺ laser. The aniline-based azopolymers with carboxyl acid substituents, poly(DGA-co-An-azo-ABA), prepared from the precursor poly(DGA-co-An) via the post azo coupling reaction with 4-aminobenzoic acid, had the fastest initial response, deepest interference profile and highest diffractive saturation compared to the epoxy-based azopolymers and the aniline-based azopolymers with other substituents. The maximum saturation of the DE was significantly affected by the type of substituents, increasing in the order of -CHO, -NO₂, -CN and -COOH substituents. Such a tendency was also confirmed by the azopolymers with the dimerized chromophores.

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