

Azo Chromophore-Functionalized Polyelectrolytes. 1. Synthesis, Characterization, and Photoprocessing

Xiaogong Wang, Srinivasan Balasubramanian, Jayant Kumar,[†] and Sukant K. Tripathy*

Departments of Chemistry and Physics, Center for Advanced Materials, University of Massachusetts–Lowell, Lowell, Massachusetts 01854

Lian Li

Molecular Technologies Inc., Westford, Massachusetts 01886

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A series of azobenzene chromophore-functionalized polyelectrolytes have been synthesized by a post-azo-coupling reaction. An epoxy-based precursor polymer (CH-AN) was synthesized by the reaction of 1,4-cyclohexanedimethanol diglycidyl ether (CH) with aniline (AN). For comparison purposes, another epoxy-based precursor polymer (BP-AN) was prepared from the diglycidyl ether of bisphenol A (BP) and aniline (AN). These precursor polymers were then postfunctionalized by an azo-coupling reaction to form polymers containing donor–acceptor type azo chromophores. The azo chromophores were designed to contain ionizable groups to impart self-assembling and photoprocessing capabilities to the polymers. The structure and properties of the newly synthesized polymers are reported in this paper. CH-AN-based azo polymers exhibit typical properties of polyelectrolytes. The polymers containing 4-(4-(carboxylic acid)phenylazo)aniline chromophores can be directly photofabricated to form surface relief gratings with large surface modulations. Charge interactions had a strong influence on the details of the writing process.

Introduction

Design and synthesis of polymers containing aromatic azo units have attracted considerable interest in several research fields.^{1–9} The highly conjugated azobenzene groups can act as efficient nonlinear optical (NLO) chromophores. A variety of NLO azo polymers have been developed in the past decade.^{1–5} The rigidity of azobenzene groups has been widely used in the design of mesogenic units for liquid crystal polymer (LCP) studies.⁶ Optically induced trans–cis isomerization of aromatic azo groups is being investigated for diverse potential applications.^{7–9} When exposed to light or heat, azobenzene and many of its derivatives undergo reversible transformation between the generally more

stable trans form and the less stable cis form.^{10,11} The rate of isomerization of the azo groups depends on the structure of the azo compounds and polymer matrixes incorporating the aromatic azo chromophores.^{12,13} The photoinduced conformational changes can significantly influence the bulk and surface properties of the polymer.^{7–9} This mechanism is being actively explored for potential applications such as optical switching, command surface generation, and information storage.^{14–20}

For reversible optical storage and related applications, polarized light has been used to induce reorientation of the azobenzene groups through repeated trans–cis photoisomerization and subsequent cis–trans relaxation

[†] Department of Physics.

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of azobenzene groups.^{21–23} Reversible holographic phase gratings have been formed by optically induced birefringence.^{24–26} Recently, direct formation of surface relief grating on azobenzene polymer films has been reported.^{27–31} The surface relief gratings were formed upon exposure to an interference pattern of Ar⁺ laser beam at modest intensities without any subsequent processing steps. The large-scale macromolecular motion is attributed to the photoinduced trans–cis–trans isomerization cycles of azobenzene chromophores and the forces experienced by the chromophore dipoles in the electric field gradient of the standing wave pattern.^{29,31} At the present stage, the photoprocessability of different types of polymer matrixes containing azobenzene moieties and the photoresponse behavior of different systems are being pursued to fully understand the structure–property correlation and to develop more versatile new materials.

In this work, a series of epoxy-based aromatic azo polymers have been synthesized by a post-azo-coupling reaction.^{32,33} The polymers were designed to include donor–acceptor type azo chromophores containing ionizable groups. Under appropriate pH conditions, the polymers can be ionized into azo polyions in water. The structure and properties of the newly synthesized epoxy-based aromatic azobenzene polyelectrolytes were extensively studied in this work. Surface relief gratings with large surface modulations were photofabricated on films of the polymer containing 4-(4-(carboxylic acid)-phenylazo)aniline chromophores. Besides the photoprocessability, the newly synthesized azobenzene polyelectrolytes can form aggregates with species containing opposite charges and result in a highly organized structure under suitable conditions. By a layer-by-layer dipping process recently established by Decher,³⁴ the polyelectrolyte containing 4-(4-(carboxylic acid)-phenylazo)aniline chromophores has been assembled into multilayer films along with an oppositely charged polyelectrolyte. The azo chromophores in the multilayer structure self-assemble into a noncentrosymmetric alignment and demonstrate macroscopic second-order optical nonlinearity.³⁵ In this paper, synthesis of precursor polymers, postfunctionalization of the precursor poly-

mers by an azo-coupling reaction, and properties of synthesized polyelectrolytes including optical, thermal, and photoprocessing capabilities are discussed.

Experimental Section

Characterization. Infrared spectra were measured using a Perkin-Elmer 1720 FT-IR spectrometer by incorporating samples in KBr disks. The UV–vis absorption spectra of the polymers in DMF solution or as spin-coated films were determined on a Perkin-Elmer Lambda 9 spectrophotometer. ¹H nuclear magnetic resonance (NMR) spectra of polymers in methyl sulfoxide-*d*₆ were obtained on a Bruker ARX-250 MHz FT-NMR spectrometer. The thermal properties of the polymers were investigated with a TA Instrument DSC 2910 and Hi-Res TGA 2950 at a heating rate of 10 °C/min. The molecular weights were determined by gel permeation chromatography (GPC) utilizing a Waters model 510 pump and model 410 differential refractometer with 500-, 10³-, 10⁴-, and 10⁵-Å Ultrastaygel columns placed in series. Chloroform was used as the eluent for precursor polymer CH-AN at a flow rate of 1.0 mL/min. Dimethylformamide (containing 0.1 w/v LiBr) was used as the eluent for precursor polymer BP-AN at a flow rate of 1.0 mL/min. Calibration curve was generated by low-dispersity polystyrene standards (Polysciences).

Materials. Commercially available amino compounds purchased from Aldrich were directly used for the azo-coupling reaction. All other starting materials, reagents, and solvents, purchased from Aldrich, VWR, and Shell, were used without further purification. The syntheses of polymers were carried out according to the reaction schemes shown in Schemes 1–3 as described in detail below.

Preparation of CH-AN. Equimolar quantities of 1,4-cyclohexanedimethanol diglycidyl ether (5.127 g, 0.02 mol) and aniline (1.863 g, 0.02 mol) were homogeneously mixed under gradual heating and polymerized at 110 °C for 48 h. The product (7 g) was dissolved in acetone (20 mL) and precipitated in excess methanol. The polymer was collected by filtration and dried under vacuum for at least 24 h. The typical IR absorption bands of the epoxide groups at 915 and 3058 cm⁻¹ nearly disappeared. The *T*_g of the polymer was determined to be 41 °C. Number average molecular weight of the polymer was estimated to be 3500, with a polydispersity index of 1.57 by GPC characterization. ¹H NMR (DMSO): δ 7.11 (CH, 2H, br), 6.74 (CH, 2H, br), 6.57 (CH, 1H, m), 5.06 (OH, 1H, br), 4.79 (OH, 1H, br), 3.84 (CH, 2H, br), 3.68–3.32 (CH₂, 12H, br), 1.78–0.94 (cyclohexyl, 10H, br).

Preparation of BP-AN. Equimolar quantities of the diglycidyl ether of bisphenol A (7.6 g, 0.02 mol) and aniline (1.86 g, 0.02 mol) were homogeneously mixed under gradual heating and polymerized at 110 °C for 48 h. The product (9.4 g) was dissolved in CHCl₃/CH₃OH mixed solvent (4:1, 50 mL) and precipitated in 500 mL of acetone. The polymer was collected by filtration and dried under vacuum for at least 24 h. The typical IR absorption bands of the epoxide groups at 915 and 3058 cm⁻¹ nearly disappeared. The *T*_g of the polymer was determined to be 91 °C. Number average molecular weight of the polymer was estimated to be 57 400, with a polydispersity index of 1.56 by GPC characterization. ¹H NMR (DMSO): δ 7.08 (CH, 6H, d), 6.82 (CH, 4H, d), 6.74 (CH, 2H, d), 6.55 (CH, 1H, m), 5.27 (OH, 1H, d), 5.08 (OH, 1H, d), 4.06 (CH, 2H, m), 3.89 (CH₂, 4H, s), 3.75–3.34 (CH₂, 4H, m), 1.56 (CH₃, 6H, s).

Preparation of CH-1A-NS. A diazonium salt of 2-amino-5-nitrobenzenesulfonic acid was prepared by adding an aqueous solution of sodium nitrite (0.04 g, 0.578 mmol) in 0.1 mL of water) dropwise into a solution of 2-amino-5-nitrobenzenesulfonic acid sodium salt dihydrate (0.1381 g, ca. 0.5 mmol) in a homogeneous mixture of 0.05 mL of sulfuric acid and 1 mL of glacial acetic acid. The mixture was stirred at 5 °C for

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5 min before the excess nitrous acid was decomposed by addition of 0.05 g of sulfamic acid in a suitable amount of water. The diazonium salt solution was added dropwise into a solution of CH-AN (0.14 g, 0.4 mmol) in 30 mL of *N,N*-dimethylformamide at 0 °C. After the solution was stirred at 0 °C for 12 h, the mixture was poured into water under agitation while adding a few drops of hydrochloric acid. The precipitated CH-1A-NS was collected by filtration and washed with plenty of water until neutral stage was achieved. The polymer was further purified by extraction with chloroform several times and dried under vacuum for at least 24 h. IR (KBr, cm⁻¹): 3446, 2965, 2937, 2877, 1742, 1596, 1566, 1510, 1472, 1436, 1396, 1362, 1322, 1285, 1234, 1192, 1167, 1143, 1096, 1048, 998, 968, 928, 875, 826, 722, 653, 634, 573, 554, 403. ¹H NMR (DMSO): δ 8.68 (CH, 1H, s), 8.24 (CH, 1H, d), 7.82 (CH, 2H, d), 7.54 (CH, 1H, d), 7.04 (CH, 2H, d), 5.15 (OH, 2H, br), 3.92 (CH, 2H, br), 3.74–3.35 (CH₂, 12H, ov), 1.81–0.96 (cyclohexyl, 6H, br).

Preparation of CH-1A-CA. The diazonium salt of 4-aminobenzoic acid (0.0686 g, 0.5 mmol) was prepared via a procedure similar to that described above for 2-amino-5-nitrobenzenesulfonic acid. The diazonium salt solution was added dropwise into a solution of CH-AN (0.14 g, 0.4 mmol) in 30 mL of *N,N*-dimethylformamide at 0 °C. After the solution was stirred at 0 °C for 12 h, the mixture was poured into water under agitation while adding a few drops of hydrochloric acid. The precipitated CH-1A-NS was collected by filtration and washed with plenty of water until neutral stage was achieved. The polymer was further purified by extraction with chloroform several times and dried under vacuum for at least 24 h. IR (KBr, cm⁻¹): 3446, 2965, 2937, 2877, 1742, 1596, 1566, 1510, 1472, 1436, 1396, 1362, 1322, 1285, 1234, 1192, 1167, 1143, 1096, 1048, 998, 968, 928, 875, 826, 722, 653, 634, 573, 554, 403. ¹H NMR (DMSO): δ 8.06 (CH, 2H, d), 7.80 (CH, 4H, ov), 6.91 (CH, 2H, br), 3.92 (CH, 2H, br), 3.72–3.34 (CH₂, 12H, ov), 1.78–0.98 (cyclohexyl, 10H, br).

Preparation of CH-1A-Sp. The diazonium salt of sulfanilic acid (0.0866 g, 0.5 mmol) was prepared via a procedure similar to that described above for 2-amino-5-nitrobenzenesulfonic acid. The diazonium salt solution was added dropwise into a solution of CH-AN (0.14 g, 0.4 mmol) in 30 mL of *N,N*-dimethylformamide at 0 °C. After the solution was stirred at 0 °C for 12 h, the mixture was poured into water under agitation while adding a few drops of hydrochloric acid. The precipitated CH-1A-NS was collected by filtration and washed with plenty of water until neutral stage was achieved. The polymer was further purified by extraction with chloroform several times and dried under vacuum for at least 24 h. IR (KBr, cm⁻¹): 3446, 2965, 2937, 2877, 1742, 1596, 1566, 1510, 1472, 1436, 1396, 1362, 1322, 1285, 1234, 1192, 1167, 1143, 1096, 1048, 998, 968, 928, 875, 826, 722, 653, 634, 573, 554, 403. ¹H NMR (DMSO): δ 7.77–7.68 (CH, 4H, ov), 7.57 (CH, 2H, d), 7.00 (CH, 2H, d), 3.91 (CH, 2H, br), 3.78–3.35 (CH₂, 12H, ov), 1.79–0.98 (cyclohexyl, 10H, br).

Preparation of CH-1A-Sm. The diazonium salt of metanilic acid (0.0866 g, 0.5 mmol) was prepared via a procedure similar to that described above for 2-amino-5-nitrobenzenesulfonic acid. The diazonium salt solution was added dropwise into a solution of CH-AN (0.14 g, 0.4 mmol) in 30 mL of *N,N*-dimethylformamide at 0 °C. After the solution was stirred at 0 °C for 12 h, the mixture was poured into water under agitation while adding a few drops of hydrochloric acid. The precipitated CH-1A-NS was collected by filtration and washed with plenty of water until neutral stage was achieved. The polymer was further purified by extraction with chloroform for several times and dried under vacuum for at least 24 h. IR (KBr, cm⁻¹): 3446, 2965, 2937, 2877, 1742, 1596, 1566, 1510, 1472, 1436, 1396, 1362, 1322, 1285, 1234, 1192, 1167, 1143, 1096, 1048, 998, 968, 928, 875, 826, 722, 653, 634, 573, 554, 403. ¹H NMR (DMSO): δ 8.00 (CH, 1H, s), 7.74 (CH, 1H, d), 7.35 (CH, 1H, d), 7.24 (CH, 2H, d), 6.98 (CH, 2H, d), 6.95 (CH, 1H, t), 3.90 (CH, 2H, br), 3.71–3.32 (CH₂, 12H, ov), 1.78–0.94 (cyclohexyl, 10H, br).

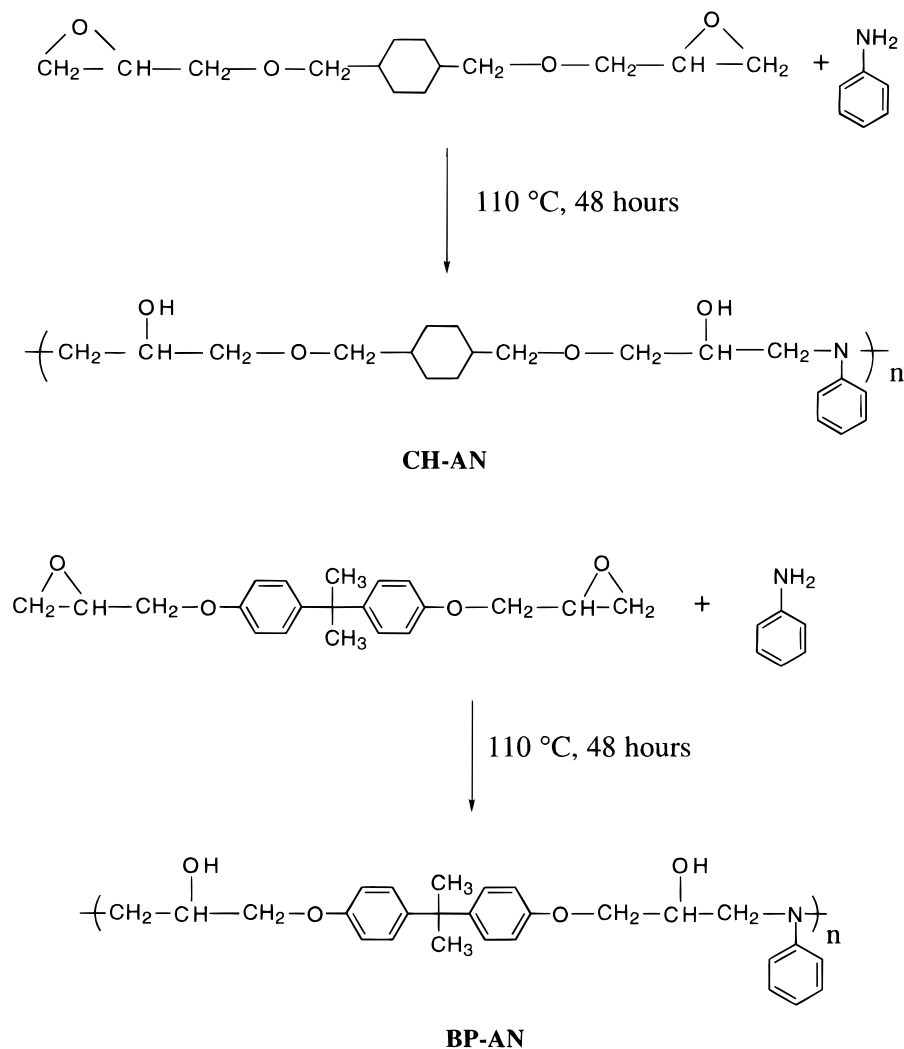
Preparation of CH-1A-PY. Nitrososulfuric acid was prepared by adding sodium nitrite (0.04 g, 0.578 mmol) carefully and with stirring to 0.08 mL of sulfuric acid at 70 °C. The temperature was strictly controlled not to exceed 75 °C during the addition. The resulting solution was cooled in an ice bath and diluted with 1 mL of glacial acetic acid. A diazonium salt of 4-aminopyridine was prepared by adding the solid of 4-aminopyridine (0.0471 g, 0.5 mmol) directly into the above nitrososulfuric acid solution. The mixture was stirred at 5 °C for 5 min before the excess nitrous acid was decomposed by addition of 0.05 g of sulfamic acid in a suitable amount of water. The diazonium salt solution was added dropwise into a solution of CH-AN (0.1892 g, 0.4 mmol) in 50 mL of *N,N*-dimethylformamide at 0 °C. After the solution was stirred at 0 °C for 12 h, the mixture was poured into water under agitation. The precipitated CH-1A-PY was collected by filtration and washed with plenty of water until neutral stage was achieved. The polymer was further purified by extraction with acetone for several times and dried under vacuum for at least 24 h. IR (KBr, cm⁻¹): 3446, 2965, 2937, 2877, 1742, 1596, 1566, 1510, 1472, 1436, 1396, 1362, 1322, 1285, 1234, 1192, 1167, 1143, 1096, 1048, 998, 968, 928, 875, 826, 722, 653, 634, 573, 554, 403. ¹H NMR: δ 8.71 (CH, 2H, br), 7.78 (CH, 2H, br), 7.71 (CH, 2H, br), 6.94 (CH, 2H, br), 4.96 (OH, 2H, br), 3.92 (CH, 2H, m), 3.74–3.36 (CH₂, 12H, ov), 1.78–0.94 (cyclohexyl, 10H, br).

Preparation of BP-1A-NS. The diazonium salt of 2-amino-5-nitrobenzenesulfonic acid (0.1381 g, 0.5 mmol) was prepared via the procedure described above. The diazonium salt solution was added dropwise into a solution of BP-AN (0.1892 g, 0.4 mmol) in 30 mL of *N,N*-dimethylformamide at 0 °C. After the solution was stirred at 0 °C for 12 h, the mixture was poured into water under agitation while adding a few drops of hydrochloric acid. The precipitated BP-1A-NS was collected by filtration and washed with plenty of water until neutral stage was achieved. The polymer was further purified by extraction with chloroform several times and dried under vacuum for at least 24 h. IR (KBr, cm⁻¹): 3446, 2965, 2937, 2877, 1742, 1596, 1566, 1510, 1472, 1436, 1396, 1362, 1322, 1285, 1234, 1192, 1167, 1143, 1096, 1048, 998, 968, 928, 875, 826, 722, 653, 634, 573, 554, 403. ¹H NMR (DMSO): δ 8.65 (CH, 1H, s), 8.26 (CH, 1H, br), 7.81 (CH, 1H, d), 7.61 (CH, 1H, br), 7.13 (CH, 4H, d), 7.04 (CH, 2H, ov), 6.88 (CH, 4H, d), 4.18 (CH, 2H, br), 3.98 (CH₂, 4H, br), 3.85–3.68 (CH₂, 4H, ov), 1.59 (CH₃, 6H, s).

Preparation of BP-1A-CA. The diazonium salt of 4-aminobenzoic acid (0.0686 g, 0.5 mmol) was prepared via the procedure described above. The diazonium salt solution was added dropwise into a solution of BP-AN (0.1892 g, 0.4 mmol) in 30 mL of *N,N*-dimethylformamide at 0 °C. After the solution was stirred at 0 °C for 12 h, the mixture was poured into water under agitation while adding a few drops of hydrochloric acid. The precipitated BP-1A-NS was collected by filtration and washed with plenty of water until neutral stage was achieved. The polymer was further purified by extraction with chloroform several times and dried under vacuum for at least 24 h. IR (KBr, cm⁻¹): 3446, 2965, 2937, 2877, 1742, 1596, 1566, 1510, 1472, 1436, 1396, 1362, 1322, 1285, 1234, 1192, 1167, 1143, 1096, 1048, 998, 968, 928, 875, 826, 722, 653, 634, 573, 554, 403. ¹H NMR: δ 8.06 (CH, 2H, d), 7.81 (CH, 2H, d), 7.75 (CH, 2H, ov), 7.07 (CH, 4H, br), 6.92 (CH, 4H, ov), 6.85 (CH, 4H, d), 5.49 (OH, 2H, br), 4.12 (CH, 2H, br), 3.92 (CH₂, 4H, br), 3.80–3.49 (CH₂, 4H, br), 1.55 (CH₃, 6H, s).

Polymer Film Preparation. The homogeneous solutions of polymers in spectroscopic grade *N,N*-dimethylformamide were filtered through 0.2- μ m membranes. The solutions were spin-coated onto glass slides. The film thickness was controlled to be 0.4–1 μ m by adjusting the solution concentration and the spin speed. The spin-coated films were dried under vacuum for 48 h at 40–50 °C and were stored in a desiccator for further measurements.

Surface Relief Grating Formation. The experimental setup for the grating formation has been reported elsewhere.^{28,29} A linearly polarized laser beam at 488 nm from

Scheme 1. Synthetic Scheme for the Precursor Polymers CH-AN and BP-AN

an Ar⁺ laser was used as the recording source. The polarized laser beam was passed through a halfwave plate and was then expanded and collimated. Half of the collimated beam is incident on the film directly. The other half of the beam is reflected onto the film from a mirror. The polarization condition of the recording beam can be adjusted by rotating the halfwave plate. The angle α , which is defined as the angle between the polarization with respect to s-polarization, was selected to be 45° for optimal recording. The intensity of the recording beams ranged from 50 to 100 mW/cm². The incident angle θ of the recording beam was adjusted to control grating space. The diffraction efficiency of the first-order diffracted beam from the gratings in transmission mode was probed with an unpolarized low-power He-Ne laser beam at 633 nm.

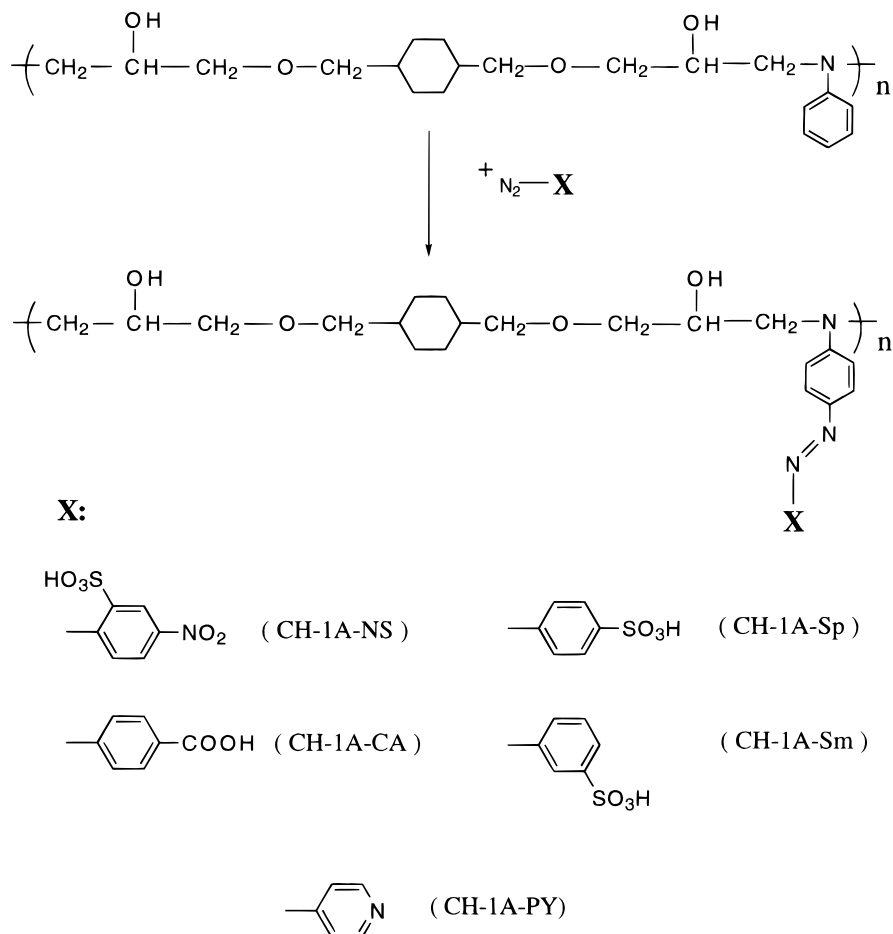
Results and Discussion

Polymer Synthesis. Precursor polymers were prepared as shown in Scheme 1. The precursor polymer CH-AN was synthesized from 1,4-cyclohexanedimethanol diglycidyl ether (CH) and aniline (AN). Precursor polymer BP-AN was synthesized from the diglycidyl ether of bisphenol A (BP) and aniline (AN). BP-AN with a more rigid backbone was prepared for comparison purpose. At relatively high temperatures, both amino groups and the hydroxyl groups formed during the polymerization react with unreacted epoxide rings, resulting in cross-linked, insoluble polymers. Therefore, a relatively low (110 °C) polymerization temperature

was selected. The polymers obtained were linear polymers with good optical transparency and good solubility in polar organic solvents including dimethylformamide (DMF) and tetrahydrofuran (THF). Low-molecular-weight oligomers, which are mainly cyclic oligomers, were removed by the fractionation method as described in the Experimental Section. Number average molecular weights of the polymers CH-AN and BP-AN were determined to be 3 500 and 57 400 g/mol, respectively, with respective polydispersity indices of 1.56 and 1.57, by gel permeation chromatography (GPC).

The precursor polymers were functionalized to incorporate different azobenzene chromophores by a post-azo-coupling reaction (Schemes 2 and 3). The precursor polymers were reacted directly with the diazonium salts of the corresponding amino compounds in organic solvent. Stable diazonium salts can easily be formed for amino compounds containing acid groups such as 4-aminobenzoic acid and 2-amino-5-nitrobenzenesulfonic acid, among others. However, post-azo-coupling by diazotizing 4-aminopyridine in the normal method results in a very low degree of functionalization. One possible reason is that the equilibrium between amine and ammonium salt favors the former even in a strong acidic solution of 4-aminopyridine. In this study, 4-aminopyridine was diazotized by adding the solid compound

Scheme 2. Post-Azo-Coupling Reaction of the Polymer CH-AN To Form Azobenzene-Functionalized Polyelectrolytes



directly to nitrosylsulfuric acid in acetic acid solution. By this method, stable diazonium salt solutions were formed and post-azo-coupling reactions were carried out with satisfactory yield. Diazonium salt readily reacts with the phenyl ring at electron-rich positions. As shown in the following NMR results, the electrophilic substitution takes place exclusively at the 4-position of aniline moieties, due to the steric crowding at the 2-position.

The azobenzene polymers synthesized in this work are listed in Table 1. The first part of the polymer nomenclature is an abbreviation to distinguish between precursor polymers from 1,4-cyclohexanedimethanol diglycidyl ether (CH) and the diglycidyl ether of bisphenol A (BP). The subsequent parts refer to the different conjugation bridges, electron acceptors, and ionizable groups of the chromophores.

Polymer Characterization. ^1H NMR spectroscopy was used to characterize the precursor polymers and postfunctionalized polymers to determine the position of electrophilic substitution and the degree of functionalization. ^1H NMR spectra of CH-AN-based precursor and azo polymers are shown in Figure 1. ^1H NMR spectra of BP-AN-based precursor and azo polymers are shown in Figure 2. In Figure 1a, resonances at 7.11, 6.74, and 6.57 ppm correspond to chemical shifts of protons at meta, ortho, and para positions of aniline moieties in the case of precursor polymer CH-AN. Similar protons of aniline moieties of precursor polymer BP-AN exhibit almost the same chemical shift as shown

in Figure 2a. The 7.11 ppm resonance overlaps with the resonance of benzene ring protons from bisphenol A moieties which appear at 7.10 ppm (doublet) and 6.84 ppm (doublet).

^1H NMR spectra of the postfunctionalized azo polymers are shown in Figures 1b–d and 2b,c. As inferred from NMR spectra, azo-coupling substitution preferentially occurs at the para positions of aniline moieties in the precursor polymers with high yield. The following changes in the chemical shift can be observed for aniline moieties in precursor polymer upon azo-coupling reaction. The resonance (6.57 ppm) corresponding to the protons at the para position of the amino group disappears. The chemical shifts of protons ortho and meta to the amino groups shift to lower magnetic field, due to the presence of electron-withdrawing groups introduced by the azo-coupling reaction. Moreover, additional resonances corresponding to chemical shifts of the benzenoid ring protons introduced through the post-azo-coupling reaction appear at lower magnetic field. The assignments were confirmed by using a two-dimensional NMR technique (^1H – ^1H correlational spectroscopy, COSY45).

The degree of functionalization depends on the amino compounds. The resonances (7.11, 6.74, 6.57 ppm) corresponding to the protons of unreacted aniline moieties totally disappear for CH-1A-NS, CH-1A-CA, and CH-1A-PY. The degree of functionalization for these three polymers was estimated to be near 100%. This result was further confirmed by comparing the peak

Scheme 3. Post-Azo-Coupling Reaction of the Polymer BP-AN To Form Azobenzene-Functionalized Polymers

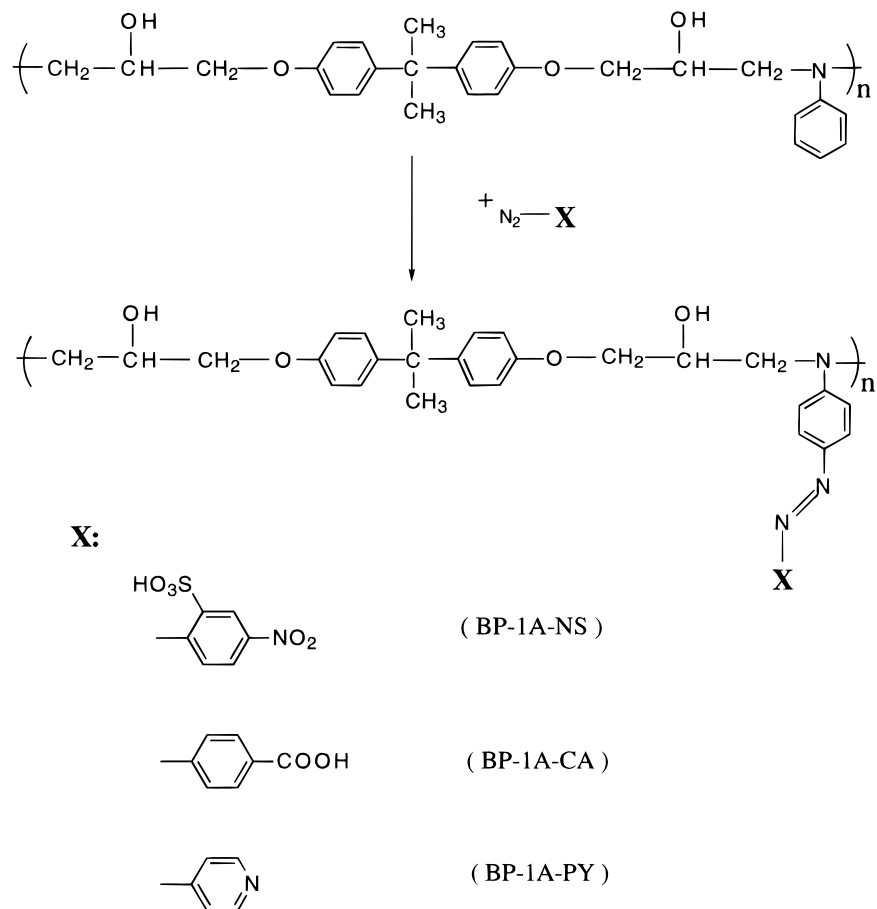


Table 1. Polymers Containing Ionizable Azobenzene Chromophores Synthesized by Post-Azo-Coupling Reaction

polymer	DF ^a (±3%)	λ_{\max}		T_g (°C)	T_d (°C)
		sol	film		
CH-1A-NS	100	482	508	144	209
CH-1A-CA	100	437	428	90	217
CH-1A-Sp	69	429	514	98	206
CH-1A-Sm	54	424	464	143	213
CH-1A-PY	100	440	437	88	194
BP-1A-NS	100	483		105	216
BP-1A-CA	100	438		105	224

^a Degree of functionalization measured by ¹H NMR. ^b In DMF solution.

areas for the benzenoid protons introduced by the azo-coupling reaction and the peak area at 1.78–0.94 ppm that corresponds to the protons of backbone cyclohexane moieties. The resonances corresponding to the protons of unreacted aniline moieties can still be seen for CH-1A-Sp and CH-1A-Sm. The degree of functionalization for these two polymers was determined to be 50–60% by comparing the peak areas for the proton of substituted and unsubstituted aniline moieties. A high degree of substitution was also observed for the precursor polymer BP-AN. The degree of functionalization for BP-1A-NS and BP-1A-CA was determined to be near 100%, which was obtained from the peak areas for the proton meta to the amino group in substituted aniline moieties and the peak area at 1.58 ppm that corresponds to the methyl protons of bisphenol A moieties.

The solubility characteristics of the synthesized polymers were greatly influenced by the chromophore and backbone structures. All of the polymers discussed above were able to form homogeneous solution in polar organic solvents such as DMF. CH-AN-based azo polymers containing an acid group such as CH-1A-NS and CH-1A-CA are highly soluble in aqueous alkaline medium. CH-1A-PY is soluble in aqueous acid solution. BP-AN-based azo polymers containing an acid group such as BP-1A-NS are highly soluble in polar organic solvents but can hardly be dissolved in even strong alkaline water solution. BP-1A-PY containing 4-(4-pyridylazo)aniline chromophores is not soluble in any solvents tested in our laboratory. The insolubility of BP-1A-PY is presumed to be due to the presence of physical cross-links caused by strong hydrogen-bonding interaction between the pyridine nitrogen and the hydroxyl groups on the main chain. Similar phenomenon has been reported for low-molecular-weight pyridine derivatives. According to the solubility characteristics described above, only CH-AN-based azo polymers can be considered as polyelectrolytic and were the main object of this study.

Thermal behavior of the precursor and azo polyelectrolytes was studied by using differential scanning calorimetry (DSC). All the polymers exhibit thermal behavior typical of amorphous polymers. The glass transition temperatures (T_g 's) for various polymers determined by DSC are listed in Table 1. The T_g of precursor polymer CH-AN is relatively low (41 °C) due

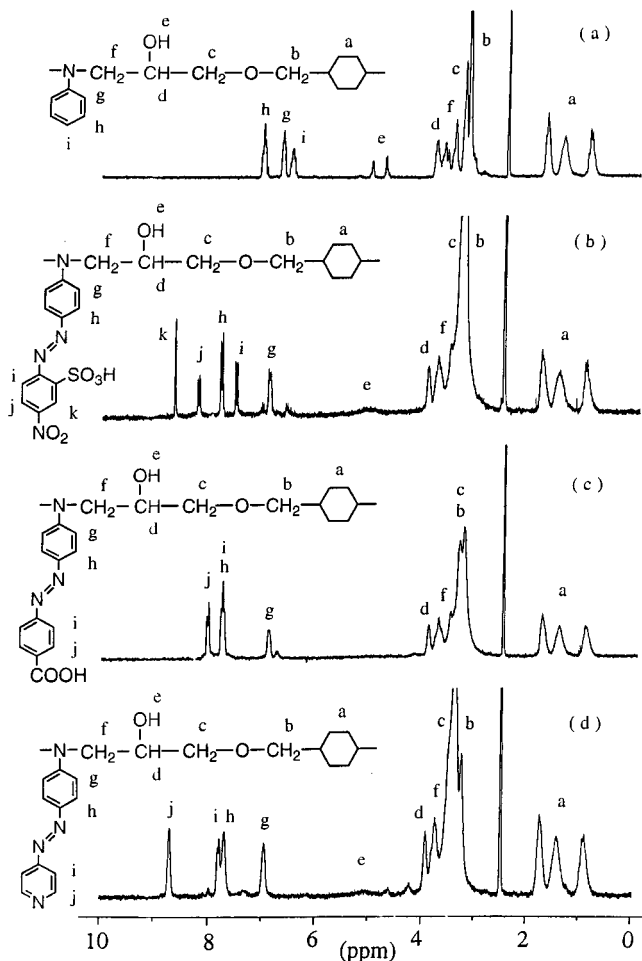


Figure 1. ^1H NMR spectra of (a) CH-AN, (b) CH-1A-NS, (c) CH-1A-CA, and (d) CH-1A-PY, in methyl sulfoxide- d_6 .

to the flexible backbone. The T_g 's of the functionalized polymers are much higher than that of the precursor polymer and are highly dependent on the structure of the azo chromophores. CH-1A-CA and CH-1A-PY show T_g 's of about 90 °C, and the increase in T_g is attributed to the significant increase in both the size and the dipole moment of the side groups. CH-1A-NS and CH-1A-Sm show much higher T_g 's (144, 143 °C). As shown by the following UV-vis spectroscopic studies, the polyelectrolytes containing sulfonic groups exhibit strong inter- and intramolecular interactions in the solid state.

Thermal stability of the polymers was characterized by thermogravimetric analysis (TGA). The precursor polymer CH-AN is thermally stable up to 290 °C under nitrogen atmosphere. Upon azo functionalization, the thermal stability of the polymers declines. All of CH-AN-based azo polymers start to lose weight in the temperature range from 190 to 220 °C. The thermal degradation temperature depends on the type of azo chromophore present in the polymers. CH-1A-CA and CH-1A-PY have the highest and lowest thermal degradation temperatures in the series, respectively. The precursor polymer BP-AN starts to lose weight at 330 °C. The higher thermal stability is due to rigid backbone structure. The thermal degradation temperatures of BP-AN-based azo polymers are also higher than those of CH-AN-based azo polymers (Table 1).

The UV-vis spectra of the azo polyelectrolytes in DMF solution and as spin-coated thin films are shown

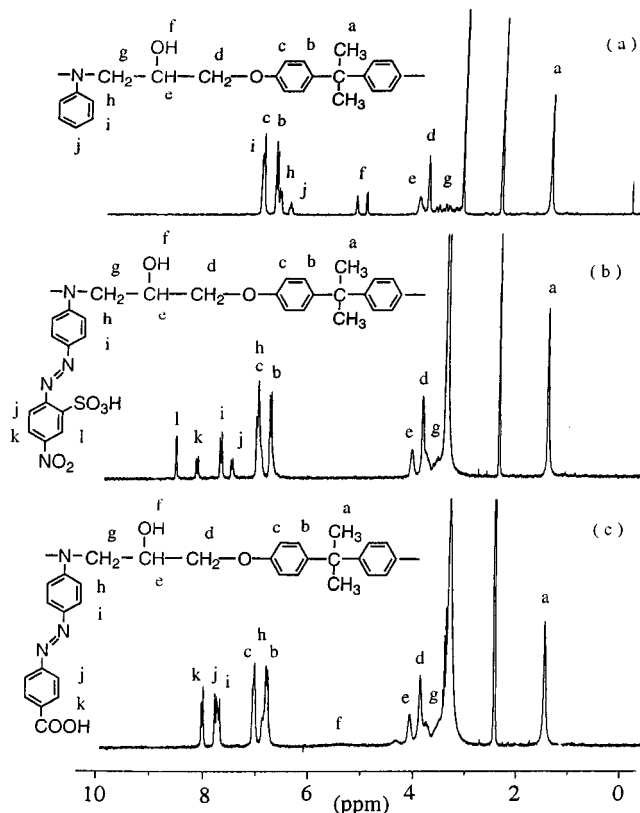


Figure 2. ^1H NMR spectra of (a) BP-AN, (b) BP-1A-NS, and (c) BP-1A-CA, in methyl sulfoxide- d_6 .

in Figure 3, and absorption maxima (λ_{max}) of the polymers are listed in Table 1. In DMF solution, the polymers show color ranging from yellow to red (Figure 3a). CH-1A-NS has the longest λ_{max} of 482 nm in the series due to the strong electron-withdrawing effect of the nitro substituent. Compared to spectra in solution, some of the polymer films exhibit broader absorption and more complicated characteristics. In the case of spin-coated film, CH-1A-CA shows a red shift of about 10 nm (437 vs 428 nm in solution) as expected from solvatochromic effect. However, films of polymers with sulfonic acid substituents exhibit significant blue shift compared to the same polymer in DMF solution. The λ_{max} values of CH-1A-NS and CH-1A-Sp shift from 507 and 514 nm in solution to 482 and 441 nm, respectively, in the case of spin-coated films. CH-1A-Sm shows a more complex spectrum with a λ_{max} of 464 nm and another absorption band at longer wavelength. Although λ_{max} of CH-1A-PY remain almost unchanged, a broad shoulder can be seen in the range from 480 to 540 nm. This spectral change can be attributed to the possible interaction between the pyridine ring and hydroxyl group on the main chain. In the system mentioned above, the proton-donating and -accepting processes accompanied by local charge separation result in strong inter- or intramolecular interaction.

Polymer Photoprocessing. Spin-coated thin films of newly synthesized azo polymers were used to carry out photoprocessing experiments. Surface relief gratings with designed dimension and patterns can be formed on the film surfaces. The grating formation efficiency depends on the type of polymer and also on the recording conditions. The experimental setup and recording conditions have been previously reported²⁷⁻²⁹

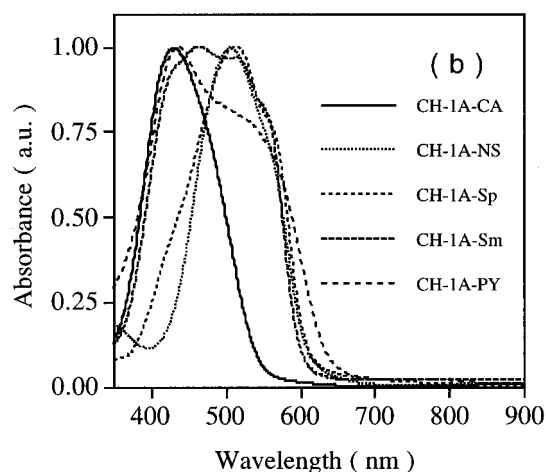
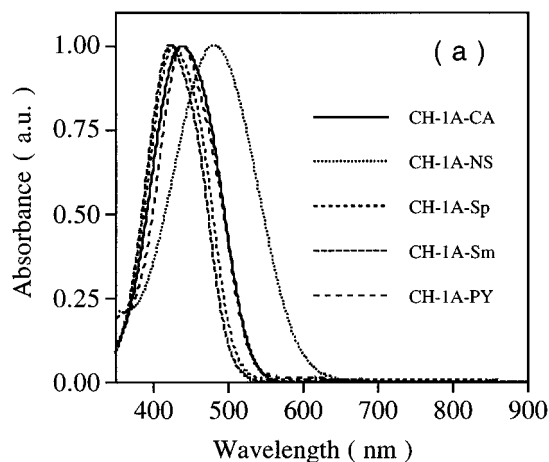


Figure 3. UV-vis absorption spectra of the azo polyelectrolytes (a) in DMF solution and (b) as spin-coated film.

and also described briefly in the Experimental Section of this paper.

The polymer films were exposed to an interference pattern formed by two polarized Ar^+ laser beams at a wavelength of 488 nm. Polymers undergo photodriven transport, and a surface relief pattern is formed. The surface modulation profile is dose-dependent, and the periodicity is determined by the writing geometry and wavelength. It was found that the azo polymers depending upon chromophore structures show significantly different photoprocessability. The polymers containing 4-(4-(carboxylic acid)phenylazo)aniline chromophores such as CH-1A-CA and BP-1A-CA form surface relief gratings with large surface modulations and high diffraction efficiencies. As CH-1A-CA and BP-1A-CA possess polymer backbones with quite different rigidities, the similar recording efficiency for both polymers implies that the azo chromophores play the defining role in the grating formation process. Chromophore densities being similar, the two polymers are subjected to similar forces and are equivalently plasticized in the writing process. The polymer containing 4-(2-(sulfonic acid)-4-nitrophenylazo)aniline and 4-(pyridinylazo)aniline chromophores such as CH-1A-NS and CH-1A-PY can form surface relief grating with low efficiency. In the case of CH-1A-Sp and CH-1A-Sm, surface grating was hardly observed under the same

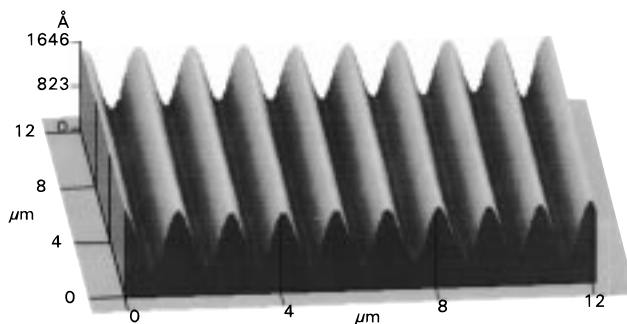


Figure 4. Atomic force microscopy image of surface relief grating on CH-1A-CA polymer film.

recording conditions. It is believed that the driving force, resulting from localized variations of magnitude and polarization of the resultant electric field in the film, is counterbalanced by the strong intermolecular interaction mentioned above. In the companion paper, electric field-induced poling of these NLO polymers is reported. While the side chain azo polymers CH-1A-CA, BP-1A-CA, and CH-1A-PY could be effectively poled, poling was inefficient for sulfonic acid-functionalized azo polymer systems. It has been observed before that high-molecular-weight polymers with possible entanglements and cross-linked polymers hinder the process of photo-induced surface relief grating formation.³¹

The atomic force microscopy (AFM) image of the surface relief grating formed on CH-1A-CA film is shown in Figure 4. Similar grating can be fabricated on the polymer BP-1A-CA film also. Regularly spaced sinusoidal surface relief structures can be seen in both cases. The spacings depend on the period of interference pattern, which can be adjusted in range between 0.3 and 5 μm by changing the angle (2θ) between the two writing beams. The depths of the gratings formed in typical cases were in the range of 1000–3000 Å. Large surface modulation (>6000 Å) and high diffraction efficiency (>40%) were obtained under optimized conditions. The gratings were stable when stored below the polymer T_g and could be erased by heating the polymer above T_g . One of the interesting properties of the azo polyelectrolytes such as CH-1A-CA is the unique ability to form both surface relief grating upon exposure to an interference pattern of laser beam and formation of multilayer structures by a layer-by-layer deposition process discussed in detail in the second paper of this series.

In summary, two epoxy-based precursor polymers have been functionalized to form a series of side-chain azo polymers which contain ionizable groups on the chromophores. The CH-AN-based azo polymers show typical behaviors of a polyelectrolyte. Surface relief gratings with large surface modulation were obtained on the polymer film containing 4-(4-(carboxylic acid)-phenylazo)aniline chromophores.

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