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PHOTOFABRICATION OF SURFACE RELIEF GRATINGS USING POST FUNCTIONALIZED AZO POLYMERS

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ABSTRACT

A series of azobenzene functionalized polymers has been synthesized by post polymerization azo coupling reaction. Photo-fabrication of surface relief gratings were studied on the polymer films. Epoxy based azo polymers were prepared by post 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 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. A new soluble polydiacetylene, post-functionalized with azobenzene groups was also prepared. Large amplitude surface gratings could be fabricated on this polydiacetylene film as well.

INTRODUCTION

Polymers containing aromatic azo units have attracted considerable interest in various research fields.¹⁻⁸ The mesogenic azobenzene groups have widely been used in the design of liquid crystal polymer (LCP) studies.¹ The highly conjugated azobenzene groups can act as efficient nonlinear optical (NLO) chromophores. A variety of NLO azo polymers have been developed in the last decade.²⁻⁵ Optically induced trans-cis isomerization of aromatic azo groups is being investigated for diverse potential applications.⁶⁻⁸ Upon exposure to light, azobenzene groups undergo reversible photoisomerization between the generally more stable trans form and the less stable cis form.⁹⁻¹⁰ The rate of isomerization of the azo groups depend on the structure of azo compounds and polymer matrices incorporating the aromatic azo chromophores.^{11,12} This photo-induced geometrical or conformational change can significantly influence the bulk and surface properties of the polymer.⁶⁻⁸ Therefore, this photoisomerization of the azobenzenes in polymer matrices and its related property changes are being actively explored for potential applications, such as in optical switching and optical information storage.¹³⁻¹⁶

Upon exposure to a polarized light reorientation of the azobenzene groups in polymer matrices can be induced through repeated trans-cis photoisomerization and subsequent cis-trans relaxation of the azobenzene groups.¹⁷⁻²⁰ Reversible holographic phase gratings have been

demonstrated using this optically induced orientation or birefringence.^{19,20} Recently, our group²¹⁻²⁶ and several other groups²⁷⁻²⁹ have shown that large surface modulation can be photo-induced on azobenzene polymer films. The surface relief gratings were formed upon exposure to an interference pattern of Ar⁺ laser beam at modest intensities without any subsequent processing steps. We have found that this process is due to the large scale macromolecular translational motion, which may be 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 superimposed standing wave pattern. At the present stage, the photoprocessibility of different types of polymer matrices containing azobenzene moieties and the photo-response behavior of different systems are being pursued to fully understand the structure-property correlation and to develop versatile new materials.

Recently we have synthesized a series of polymers functionalized with aromatic azo groups by post polymerization azo coupling reaction for the study of their NLO properties and surface relief grating formation.³⁰⁻³² Post polymerization azo coupling reaction can provide a convenient way to synthesize various azo functionalized polymers. It is often the simplest path to prepare azo functionalized polymers. The extent of the functionalization also could be easily controlled using post azo-coupling reactions. In addition, versatile functional groups can be incorporated on the azobenzene groups. Polymers containing azo chromophores with ionizable groups could also be synthesized. Under appropriate pH condition the polymers can be ionized into azo polyions in water. By a layer-by-layer dipping process, along with an oppositely charged polyelectrolyte, the azobenzene polyelectrolyte can be assembled into multilayer films. A number of important potential applications are expected in these self assembled multilayer films.

In this paper, we report the photo-fabrication of surface gratings on various azo polymers prepared by post polymerization azo-coupling reactions. A series of epoxy based azopolymers with various substituents were prepared and the structure-property relationship in photo-fabrication is discussed. We have also prepared a novel soluble polydiacetylene (PDA) functionalized with azobenzene groups in the side chain. Surface grating formation in this conjugated polymer was also demonstrated.

EXPERIMENTAL SECTION

Materials

The chemical structures of the epoxy based polymers post-functionalized with various azobenzene groups are shown in Fig. 1. The synthesis and structure characterization of the epoxy based polymers were reported elsewhere.³³

Azobenzene functionalized PDA was prepared by post polymerization azo coupling reaction on the precursor PDA. The precursor PDA was reacted with the diazonium salt of *p*-aminobenzoic acid in N,N'-dimethylformamide (DMF) to give a quantitative yield (Fig. 2). The detailed synthesis of the precursor and functionalized PDAs are reported elsewhere.³⁴

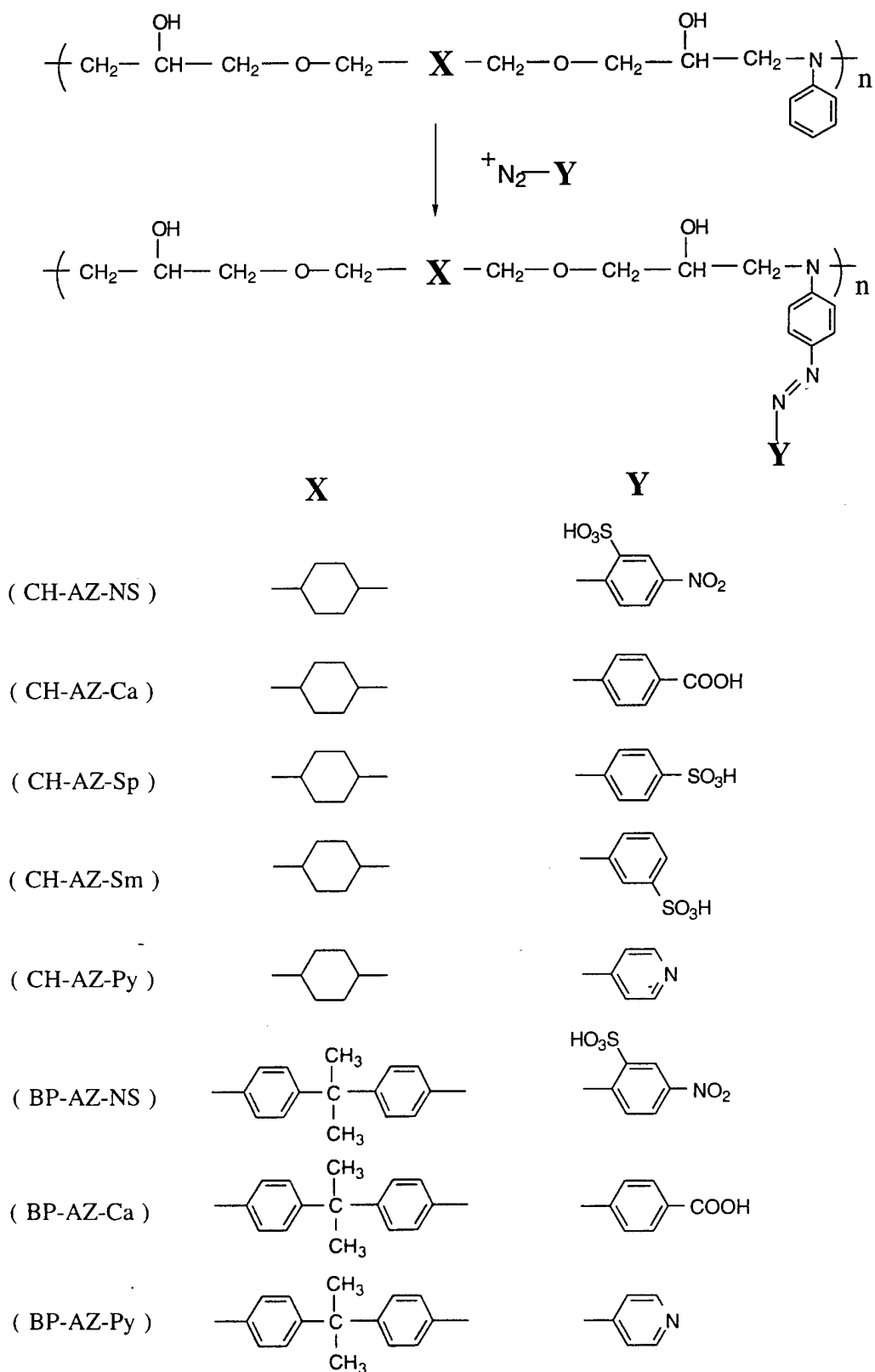


Figure 1. Synthetic scheme and chemical structures of epoxy-based polymers post-functionalized with various azobenzenes.

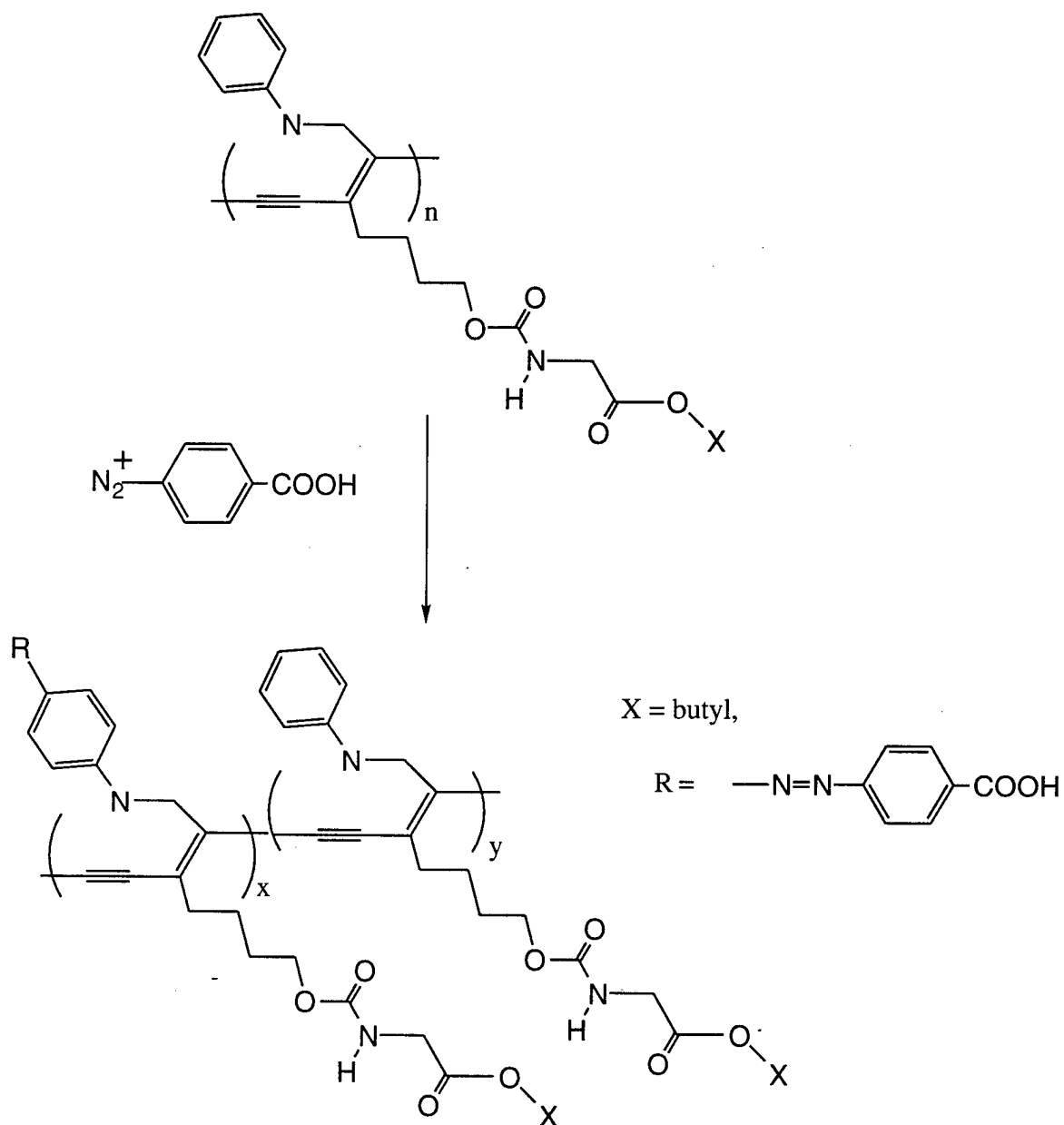


Figure 2. Synthetic scheme of the polydiacetylene post-functionalized with azobenzene groups.

Polymer Film Preparation

The homogeneous solutions of polymers in spectroscopic grade DMF were filtered through 0.2 μm membranes. The solutions were spin-coated onto glass slides. The film thickness was controlled to be 0.4-1 μm by adjusting the solution concentration and the spin speed. The spin-coated films were dried under vacuum for 48 h at 40-50 $^\circ\text{C}$ and were stored in a desiccator for further measurements.

Surface Relief Grating Formation

The experimental setup for the grating formation has been reported elsewhere^{22,23}. A linearly polarized laser beam at 488 nm from an Ar⁺ laser was used as the recording source. The polarized laser beam passes through a halfwave plate, and is 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 between the polarization with respect to s-polarization, was selected to be 45° for optimal recording²³. 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 spacing. 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

The precursor polymers were functionalized to incorporate different azobenzene chromophores by post azo coupling reaction (Fig. 1). Optical and thermal properties of these azobenzene polymers 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 diglycidyl ether of bisphenol-A (BP). The subsequent parts refer to different conjugation bridges, electron acceptors and ionizable groups of the chromophores.

Table 1. Optical and thermal properties of azobenzene post functionalized polymers.

Polymer	D.F. ^a (%±3%)	λ_{\max}^b (sol.)	λ_{\max} (film)	T _g (°C)
CH-AZ-NS	100	482	508	144
CH-AZ-Ca	100	437	428	90
CH-AZ-Sp	69	429	514	98
CH-AZ-Sm	54	424	464	143
CH-AZ-Py	100	440	437	88
BP-AZ-NS	100	483		105
BP-AZ-Ca	100	438		105

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

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 acid groups such as CH-AZ-NS and CH-AZ-Ca are highly soluble in aqueous alkaline medium. CH-AZ-PY is soluble in aqueous acid solution. BP-AN based azo polymers

containing acid groups such as BP-AZ-NS are highly soluble in polar organic solvent, but can hardly be dissolved even in strong alkaline aqueous solution. BP-AZ-PY containing 4-(4-pyridylazo)aniline chromophores is not soluble in any solvent tested in our laboratory. The insolubility of BP-AZ-PY is presumed due to the interaction between the pyridine nitrogen and the hydroxyl groups on the main chain.

Thermal behavior of the precursor and azo polyelectrolytes were studied by using differential scanning calorimetry (DSC). All the polymers exhibit thermal behavior typical of amorphous polymers. The T_g s for various polymers determined by DSC are listed in Table 1. The T_g of the precursor polymer CH-AN is relatively low (41 °C) due to the flexible backbone. The T_g s of the functionalized polymers are much higher than the precursor polymer and are highly dependent on the structure of the azo chromophores. CH-AZ-CA and CH-AZ-PY show T_g s of about 90 °C and the increase in T_g is attributed to significant increase both in the size and the dipole moment of the side groups. CH-AZ-NS and CH-AZ-Sm show much higher T_g s (144°C, 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.

Absorption maxima (λ_{max}) of the polymers from UV-Vis spectra are listed in Table 1. The λ_{max} values of CH-AZ-NS and CH-AZ-Sp shift from 482 and 441 nm to 507 and 514 nm respectively in case of spin coated films. CH-AZ-Sm shows a more complex spectrum. λ_{max} of 464 nm and a second absorption band can be seen at a longer wavelength. It is believed that the reason for the color change is similar to halochromism effect of aminoazobenzene caused by protonation of the β -Nitrogen atom of the azo group. Although λ_{max} of CH-AZ-PY remain almost unchanged, a broad shoulder can be seen in the range from 480 to 540 nm. One possible reason for the spectral change is caused by 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 reported and also described briefly in the experimental part 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 angle and wavelength. It was found that these azo polymers show significantly different photoprocessibility depending upon chromophore structures. The polymers containing 4-(4-(carboxylic acid) phenylazo)aniline chromophores such as CH-AZ-CA and BP-AZ-CA form surface relief gratings with large surface modulations and high diffraction efficiencies. As CH-AZ-CA and BP-AZ-CA possess polymer backbones with quite different rigidities, the similar recording efficiency for both polymers imply 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-(pyridineazo)aniline chromophores such as CH-AZ-NS and CH-AZ-PY can form surface relief grating with low efficiency. In case of CH-AZ-Sp and CH-AZ-Sm, surface grating was hardly observed under the same recording condition. It is believed that the driving force, resulting from localized variations of magnitude and polarization of the resultant electric field in the film, are counterbalanced by the strong intermolecular interaction mentioned above. Electric field induced poling experiment of these NLO polymers also proved this strong intermolecular interaction present in sulfonic acid functionalized azo polymer systems. While the side chain azo polymers CH-AZ-CA, BP-AZ-CA and CH-AZ-PY could be effectively poled, poling was inefficient for sulfonic acid functionalized azo polymer systems. We also investigated the surface grating formation on the guest-host system. A PMMA film doped with an azo dye (Disperse Orange 3) with 20 wt% dye content was prepared and exposed to an identical exposure condition. Amplitude of surface modulation was much smaller ($<100 \text{ \AA}$) than those of functionalized polymer films.

The atomic force microscopy (AFM) images of the surface relief gratings formed on CH-AZ-CA and BP-AZ-CA films are shown in Figure 3, and Figure 4, respectively. 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 depth of the gratings formed in typical cases were in the range of 1000 to 3000 \AA . Large surface modulation ($>6000 \text{ \AA}$) and high diffraction efficiency ($>40\%$) were obtained under optimized condition. 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-AZ-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.³²

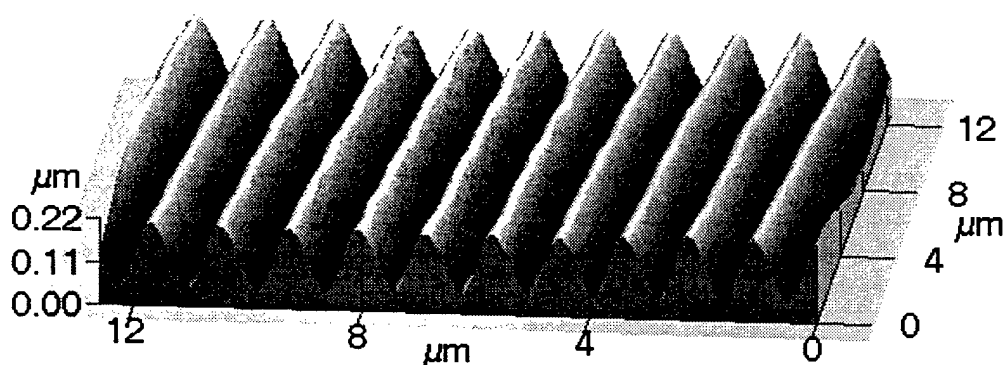


Figure 3. Atomic force microscopy image of surface relief gratings on the CH-AZ-CA film.

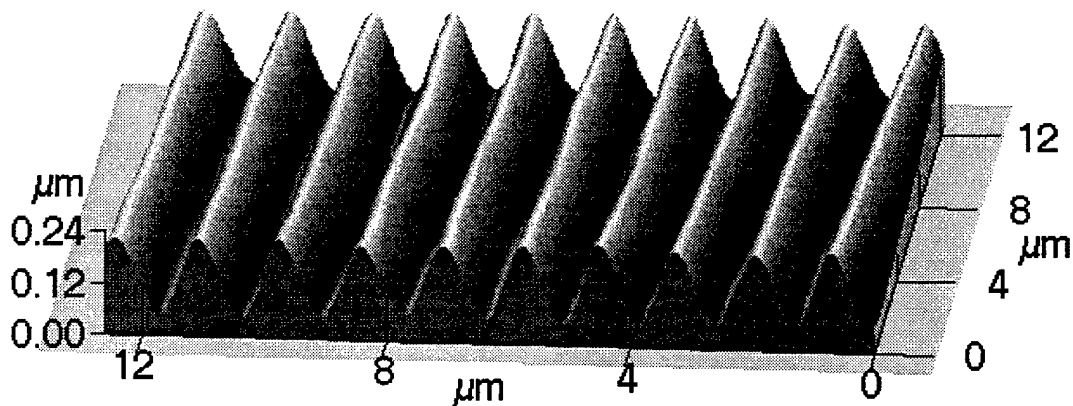


Figure 4. Atomic force microscopy image of surface relief gratings on the BP-AZ-CA.

We also investigated surface grating formation in a PDA system which was post functionalized with azobenzene groups by a post azo coupling reaction. The precursor PDA was reacted with the diazonium salt of *p*-aminobenzoic acid in DMF to give a quantitative yield of the azobenzene functionalized PDA (Fig. 2). The polymer was found by ^1H NMR to have 60% of the aromatic rings functionalized. No T_g was observed from DSC studies of this polymer. Exposure of a spin-coated film to an interference pattern from two polarized argon-ion laser beams at 488 nm leads to formation of a surface grating. As shown in Figure 5, the surface relief grating shows very regularly spaced surface structure similar to other epoxy based systems with depth modulation of over 800 Å. The grating spacing can be adjusted by changing the angle between the two writing beams.

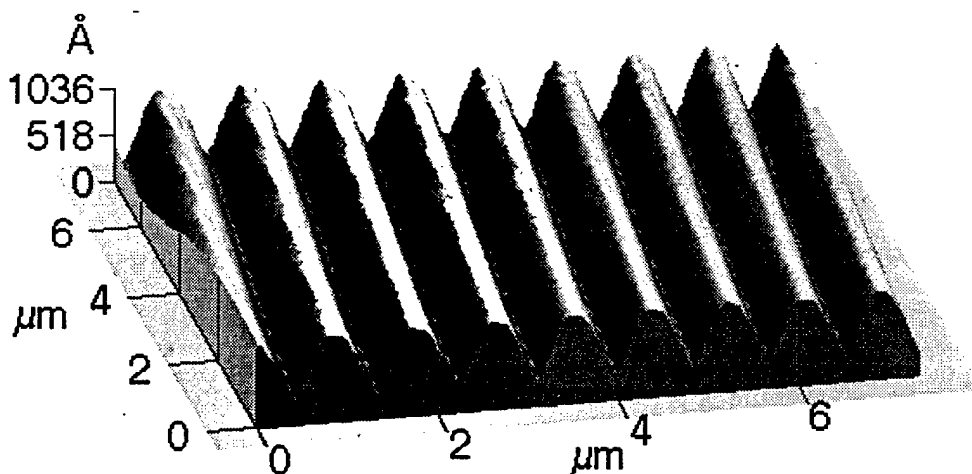


Figure 5. AFM 3-D image of the surface grating fabricated on an azobenzene functionalized PDA film.

Even though the surface grating formation was less efficient than other epoxy based systems such as CH-AZ-CA and BP-AZ-CA, it is very interesting to observe such a large and smooth surface modulation in a conjugated polymer system which is generally believed to possess a very rigid polymer backbone. This provides the first example of such laser-induced grating formation in a conjugated polymer lacking a glass transition.

CONCLUSIONS

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. In case of the polymers containing azobenzenes with sulfonyl groups surface modulation could not be observed due to the strong intermolecular interactions. Surprisingly, large photo induced surface modulation was also observed on a conjugated polydiacetylene polymer functionalized with azobenzene side groups. We have demonstrated post azo coupling reaction is a convenient and versatile synthetic procedure for the preparation of various kinds of azo polymers. Due to the presence of ionic groups in our azo polymers self assembled polymer multilayers can be readily fabricated and characterization of optical, electronic and other interesting properties are being explored in our group.

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