PHOTOINDUCED SURFACE RELIEF GRATINGS ON AZOCELLULOSE FILMS

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Dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

Surface relief gratings (SRG) on films of azobenzene–modified cellulose (azocellulose) with ultrahigh molecular weight were holographically recorded in a single step. Surface modulation depth of the SRGs increased with the degree of substitution (DS) of the azobenzene chromophores in the cellulose as well as with the grating spacing. Large surface modulations over 500 nm on all samples were obtained with a grating spacing of 4 μm. A linear increase of photoinduced birefringence with the azobenzene chromophore concentration in these photodynamic polymers was also observed. The maximum birefringence of 0.11 was achieved for an azocellulose polymer with a DS of 0.99.

Key Words: Surface relief grating; Azobenzene chromophore; Cellulose; Birefringence

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INTRODUCTION

Polymers containing azobenzene chromorphores have been extensively explored as potential optical storage materials [1-7]. It is known that azobenzene chromophores upon irradiation with polarized light undergo photoinduced reorientation through trans-cis-trans isomerization. This reorientation can also initiate an unusual light-induced mass transport process [1-3], which results in surface relief gratings (SRG) on the thin films of azobenzene chromophore functionalized polymers at temperatures well below the glass transition temperature (Tg). SRG formation begins on the free surface of the polymer film and continues through into the bulk. The surface modulation depth can be controlled by adjusting the light exposure time and the polarization state of the writing beams. Thus this facile single step process has a significant advantage over other techniques, which always involve multiple steps (such as baking, exposure and developing, etc.). SRGs have been investigated on a variety of azobenzene functionalized polymers, such as epoxy polymers, polyacrylates, polyesters, conjugated polymers, poly(4-phenylazophenol) [1-7]. However, all previous researches focused on azobenzene polymers with low or moderate molecular weights, and the investigation on inscribing SGRs with ultrahigh molecular weight azobenzene polymer has not been reported.

Cellulose is a linear polymer consisted of anhydroglucose ring units. The anhydroglucose units are jointed together by β-1,4-glycosidic bonds and alternate up and down along the main chains of cellulose. The molecular weight of natural cellulose is typically around 10^6 or even higher depending on the delignification process. Because of the bulky D-glucopyranose rings and the strong intra- and intermolecular hydrogen bonding, cellulose has a high Tg of around 230°C [8]. Thus, covalently attaching azobenzene chromophores to these kinds of natural polymers of high molecular weight and high Tg will provide us a new class of polymer materials for further understanding the unusual photo driven deformation process.

Recently, we successfully synthesized an azobenzene-modified derivative of cellulose: azocellulose. These polymers were obtained by covalently linking 4-cyanophenylazophenol to ultra high molecular weight natural cellulose polymer (9). These novel photodynamic polymers with different degree of substitution (DS) were obtained by varying the ratios of reactants. In this paper, we report on the experimental results of the photoinduced birefringence and holographically fabricated SRGs on these polymers.

EXPERIMENTAL

Materials

A series azocellulose polymers were synthesized by covalently attaching 4-cyanophenylazophenol to cellulose (around 5.8×10^8, Aldrich Chemical Co.) by
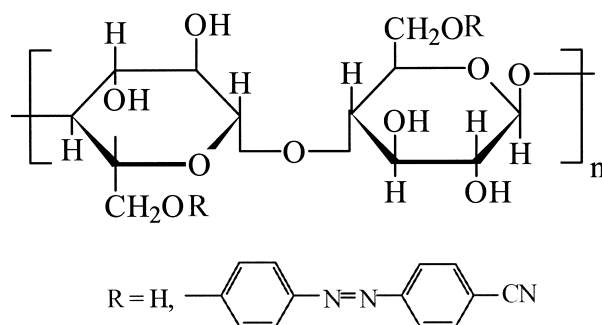
Figure 1. Chemical structure of the azocellulose polymers.

Mitsunobu ether formation reaction [9]. The chemical structure of the polymers is shown in Figure 1. The DS, which is the average content of azobenzene chromophores in each glucose unit, ranges from 0.13 to 0.99. Theoretically, the maximum DS would be 3 if all the hydroxyl groups were substituted by azobenzene chromophores in each glucose ring. No Tg was observed in these polymers even when the temperature reached up to decomposition (230°C).

Sample Preparation

The synthesized azocellulose polymers were dissolved in mixed solvents of hexafluroisopropanol and trifluroacetic acid (80:20 by volume). The solutions were cast on glass substrates in a vacuum oven at room temperature, and vacuum was immediately applied for twenty minutes. Then the films were dried at 90°C in vacuum over 12 hours. The thickness of the films was controlled between 0.5-3.0 μm by adjusting the solution concentration and measured using a Sloan Dektak IIA profiler. The UV-visible absorption spectra were recorded using a Perkin-Elmer Lambda 9 spectrophotometer.

Optically Induced Birefringence

The optically induced birefringence in polymer films was measured as described in Reference 4. The film on the glass substrate was placed between two crossed polarizers in the path of a low-power unpolarized He-Ne laser beam at 633 nm. The birefringence was induced in the polymer film by a linearly polarized beam at 488 nm from an Ar^+ laser with an intensity of 100 mW/cm^2. The polarization angle of the Ar^+ laser beam was set at 45° with respect to the orientation of the polarizers. An increase in transmission of the He-Ne laser beam resulting from induced birefringence in the polymer film was measured. The birefringence was then calculated from the intensity of the transmission by the following equations [10]:

$$I = I_0 \sin^2 (\delta\varphi/2) \tag{1}$$

$$\delta\varphi = 2\pi\delta n \, d/\lambda \tag{2}$$

where δn, d and λ are the photoinduced birefringence, the sample thickness and the wavelength of probe beam, respectively. I_0 is the intensity of the transmitted light with a phase difference $\delta\varphi$ of π before the birefringence is photoinduced.

SRG Fabrication

SRGs were fabricated using a simple interferometric set-up (4) at 488 nm with an intensity of 200 mW/cm^2. The grating spacing (Λg) can be controlled by changing the incidence angle (θ) according the relation:

$$\Lambda g = \lambda/2\sin\theta \tag{3}$$

where λ is the wavelength of the writing beam. The polarization of the two writing beams was selected to be $\pm45°$ with respect to the s-polarized beams. The gratings formed on the polymer films were monitored by measuring the power of the first order diffracted beam in the transmission mode from the unpolarized low power probe He-Ne laser beam. The SRGs were investigated by an atom force microscopy (AFM) in the contact mode under ambient conditions. The surface topology and surface profiles provided the spacing and the surface modulation depth of the surface gratings.

RESULTS AND DISCUSSION

Figure 2 shows the UV-visible absorption spectrum of an azocellulose polymer film with a DS 0.99. The maximum at 350 nm corresponds to the π-π* transition of the azobenzene chromophores [11]. Since the absorption for the azocellulose polymers at 633 nm is negligible, the He-Ne laser beam at 633 nm was chosen as the probe beam. The birefringence was optically induced in the azocellulose polymer films by exposure to a linear polarized Ar$^+$ laser beam. Figure 3 shows a typical increase of the transmission for the probe beam as a function of time when the writing beam was turned on. Prior to exposure to Ar$^+$ laser beam, the polymer film was isotropic. This was confirmed by placing the sample between the two crossed polarizers (which allowed no transmission of the probe beam). The polarized writing beam induced a preferred orientation of the azobenzene chromophores in the direction perpendicular to the polarization of the writing beam through trans-cis-trans isomerization [10], thus leading to birefringence in the amorphous polymer films.
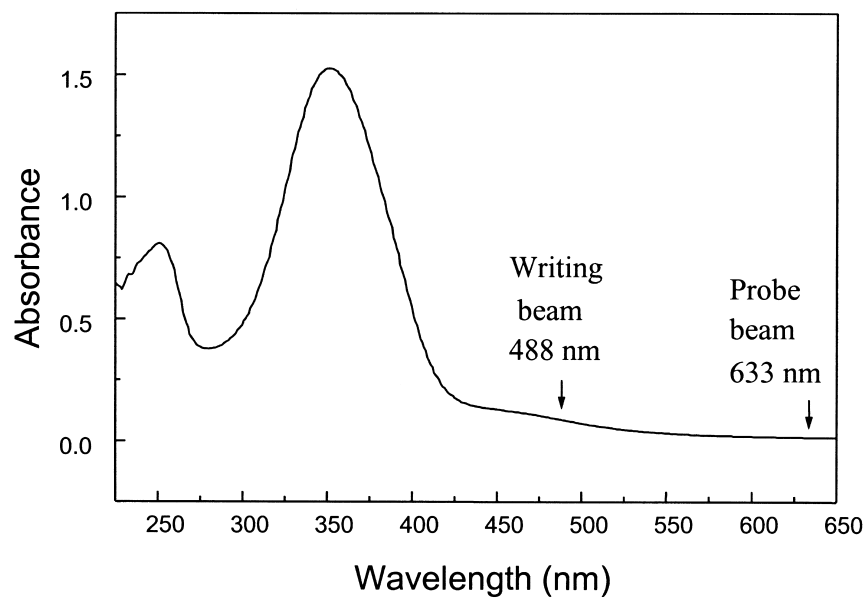
Figure 2. UV-visible spectrum of a thin film for an azcellulose with a DS of 0.99.
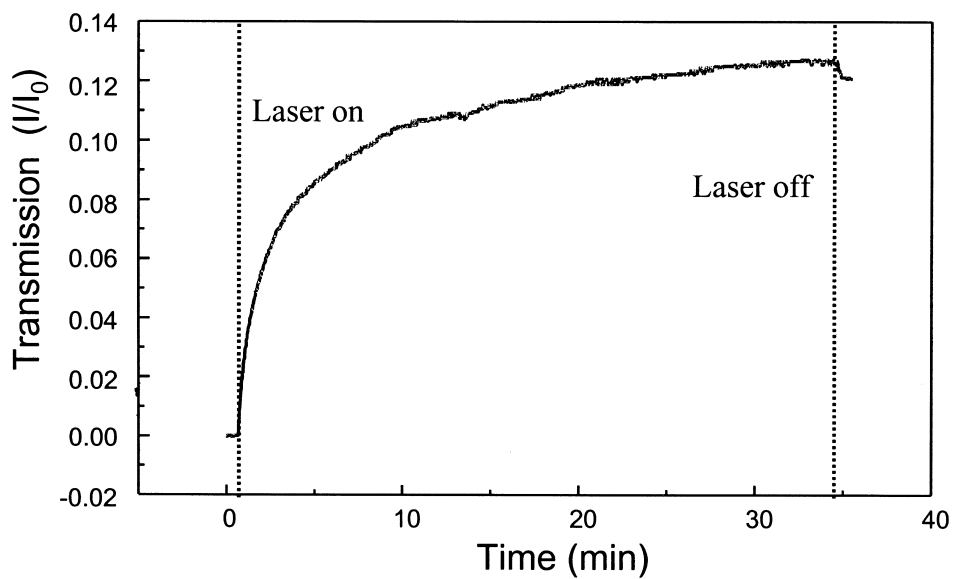
Figure 3. Transmission of the probe He-Ne laser beam through two crossed polarizers as a function of time for a sample with a DS of 0.99 under a laser illumination at 488 nm.

The photoinduced birefringence (δn) for the azocellulose polymers as a function of DS is shown in Figure 4. I/I_0 was obtained at the saturation stage as shown in Figure 3. This value was used to calculate $\delta\varphi$ and δn was then calculated by Equation 2. The results indicate that photoinduced birefringence increased linearly with the content of azobenzene chromophores. This observation is proportional to the amount of photodynamic elements per volume in the azocellulose polymer films. The higher DS an azocellulose polymer has, the more the number of azobenzene chromophores that take part in the photo isomerization process in the acocellulose films, giving rise to higher birefringence. For the polymer with a DS of 0.99, photoinduced birefringence as large as 0.11 has been obtained.

The grating recording was performed with linearly polarized beams with polarization $\pm45°$ respect to the s-polarization direction. Figure 5 represents the typical time evolution of the probe beam diffraction intensity during the SRG formation on the film of azocellulose polymer with a DS of 0.99. The initial steep rise is attributed to the bulk refractive index grating, which saturated in several tens of seconds and gave rise to a maximum diffraction efficiency of about 1%. At latter times, the much slower process, attributed to surface transformation, evolved over several tens of minutes and finally saturated giving maximum diffraction efficiency. With this film and writing with a grating spacing of 1μm, the diffraction efficiency saturated at about 25% in each of the ±1 order.

Figures 6 and 7 present typical AFM three-dimensional images of the SRGs with grating spacings of 1 and 4 μm on the films of azocellulose with a DS of 0.99. The effects of DS and grating spacing on the surface modulation depth of the SRGs are shown in Table 1. The SRGs on all samples were recorded at an
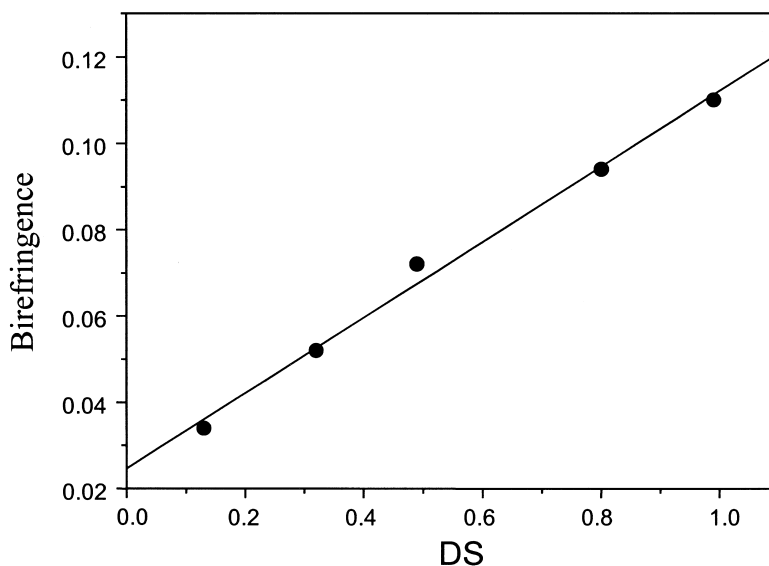

Figure 4. Photoinduced birefringence of azocellulose polymers as a function of DS.
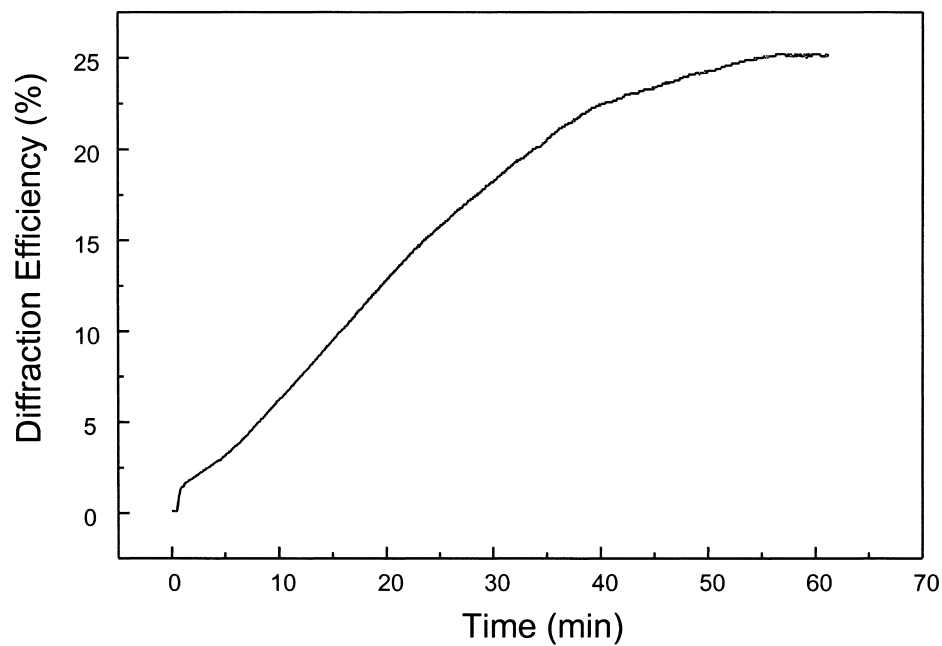
Figure 5.   First order diffraction efficiency of a polymer film with a DS of 0.99 as a function of time at a grating spacing of 1μm.
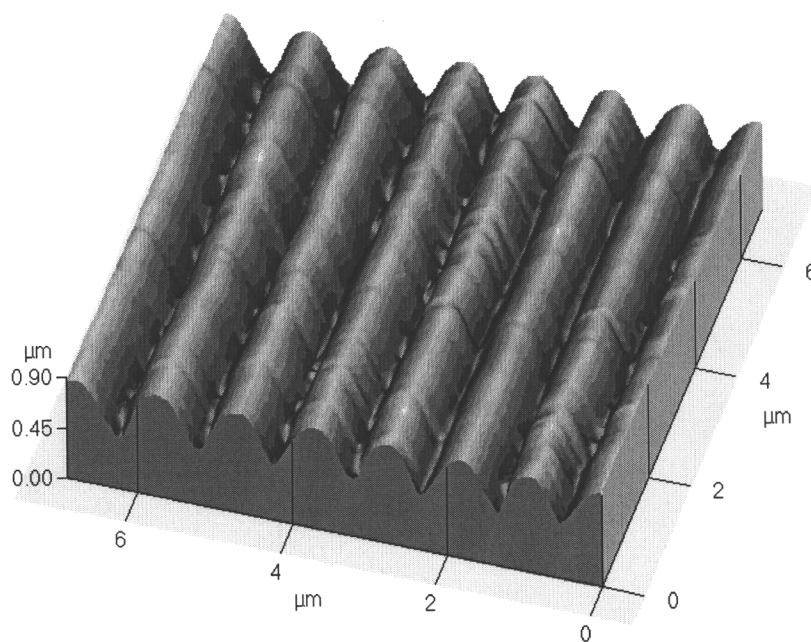

Figure 6.   Three-dimensional view of the SRGs with a grating spacing of 1 μm on the film of azo-cellulose with a DS of 0.99.
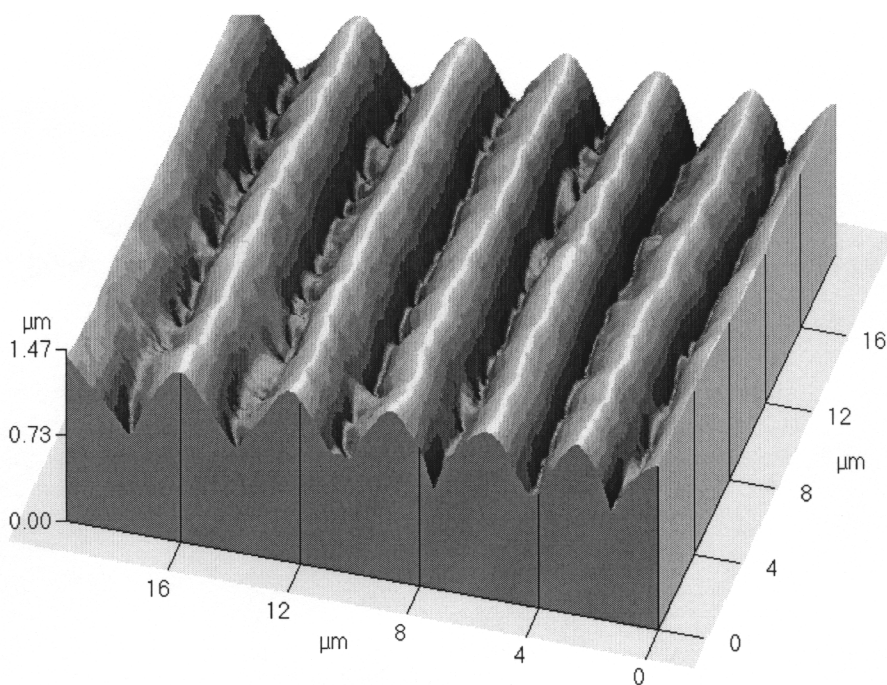
Figure 7.   Three-dimensional view of the SRGs with a grating spacing of 4 µm on the film of azo-cellulose with a DS of 0.99.

intensity of 200 mW/cm², and the writing beams were turned off after the diffraction efficiency saturated. For SRGs with smaller grating spacings (1 µm and 2 µm), the amplitude of the surface modulation increased with DS. For SRGs with larger grating spacing of 4 µm, Larger surface modulation of over 500 nm could be induced on all azocellulose films with different DS. These results suggest that for smaller grating spacings, the higher DS or degree of functionalization of the azocellulose polymer, the larger the mass transport of the polymer chains. However, the DS effect is insignificant at larger grating spacing of 4 µm. As the grating spacing became larger, the amplitude of the surface modulation increased,

Table 1. Effects of DS and Grating Spacing on the Surface Modulation Depth

| | Modulation Depth (nm) | | |
| | Grating Spacing | | |
DS	1µm	2µm	4 µm
0.32	170	391	550
0.49	270	410	500
0.80	290	450	550
0.99	450	500	600

especially for the films of azocellulose with lower DS. For the film with a DS of 0.32, an increase from 170 nm to 550 nm was observed. Surface modulation around 550 nm could be inscribed on all the samples with a grating spacing of 4 μm.

Earlier papers reported that high molecular weight azobenzene functionalized polymers do not inscribe gratings efficiently because of large number of entanglement of polymer chains (5). The experiments reported here are on ultrahigh molecular weight polymers exhibiting no glass transition temperature even up to the temperature of decomposition.

CONCLUSION

SRGs on the films of azocellulose polymers with very high molecular weight and different degree of substitution were holographically induced in a single step. The surface modulations of the photofabricated SRGs were found to depend strongly on the DS for the azobenzene chromophores on the cellulose and grating spacing. The photoinduced birefringence in these polymers has also been measured. This is the first report of SRGs inscribed on ultrahigh molecular weight polymers.

ACKNOWLEDGMENT

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