Macromolecules **1995,** *28,* 8835−8839

Polarized Laser Induced Holographic Surface Relief Gratings on Polymer Films

D. Y. Kim,[†] Lian Li,[‡] X. L. Jiang,[‡] V. Shivshankar,[†] J. Kumar,[‡] and S. K. Tripathy*[,†]

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

Received April 7, 1995; Revised Manuscript Received August 8, 1995[⊗]

ABSTRACT: Large-amplitude holographic surface relief gratings on azobenzene-containing polymer films were optically induced without any subsequent processing steps. The surface relief structures were observed upon exposure to an interference pattern of polarized Ar^+ laser beams. The surface relief structures were investigated using atomic force microscopy. A very regularly spaced surface grating with a surface modulation depth of over 1000 Å was obtained. The gratings were stable at ambient conditions, and the samples were reusable after erasing the gratings by heating the film above the glass transition temperature. The orientation of the azobenzene groups was induced first and followed by the surface deformation process. The polarization of the writing beam had a significant effect on the surface modulation process. The relation between the surface change and optically induced orientation of the azobenzene groups is discussed. Thermal effects were also investigated by studying the dependence of the writing intensity and grating spacing on the grating formation process.

Introduction

It has been a decade since Todorov *et al.* demonstrated that azo dyes in polymeric matrices could give rise to large optical birefringence when excited by polarized light.[1] The mechanism of this process involves repeated trans−cis photoisomerization of azobenzene groups and thermal cis−trans relaxation, resulting in the alignment of azobenzene groups in the direction perpendicular to the polarization of the incident light. Numerous researchers have investigated this phenomenon in various polymer matrices such as guest−host,[1] liquid crystalline,[2−6] semicrystalline,[7] and amorphous polymers.[8−10] The photoinduced alignment of the azobenzene groups was stable in polymers with high glass transition temperatures (T_g). This photoinduced orientation could be erased by exposure to unpolarized or circularly polarized lights or by heating the polymer above its T_g. Therefore, the birefringence resulting from this photoinduced alignment of the azobenzene groups has been used for producing erasable holographic gratings.[1−4,7] However, those gratings have been known to be produced due to the birefringence, and the formation of surface relief gratings in azo dye containing polymers had never been reported.

Recently, we observed the direct formation of large-amplitude surface relief gratings on spin-coated films of a cross-linkable epoxy-based nonlinear optical (NLO) polymer containing Disperse Orange 3 azobenzene side groups (PMDO3, shown in Figure 1).[11] Rochon *et al.* also independently reported very similar results of the formation of the surface relief gratings on an acrylate polymer with Disperse Red 1 azobenzene groups.[12] We have observed that large-amplitude and stable surface relief gratings were produced upon exposure to an interference pattern of polarized laser beams at modest intensities without any subsequent processing steps. The intensities of the writing beams were well below the power required for ablation of the polymer. The gratings could be erased by heating the polymer film above its T_g, and the writing and erasing cycles could be repeated. A surface modulation depth of more than 1000 Å was obtained. While irradiation of a polarized laser beam at 488 nm resulted in orientation of the azobenzene groups, leading to birefringence in the polymer film, such a large surface change on the polymer film solely due to the alignment of molecules was not expected and seems to have its origins due to new optically induced processes which have not been explained so far. Large-scale molecular motion and volume change caused by the orientation of the azobenzene moieties seemed to be occurring simultaneously.

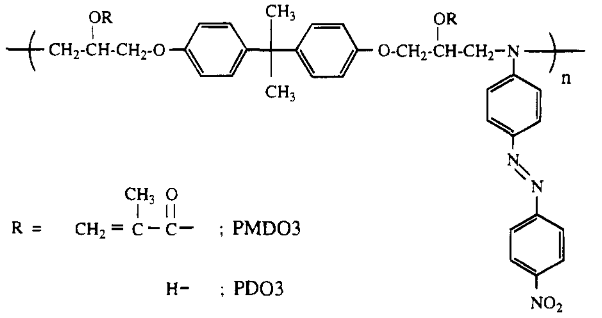

Figure 1. Chemical structures of the epoxy-based NLO polymers.

This new process of direct surface relief grating formation has considerable significance from both technological and polymer physics points of view. It provides several advantages over other conventional surface grating formation processes such as photoresist development, laser ablation techniques, and a process using thermoplastic photoconductor materials.[13−15] Since the amplitude of the surface variation is large and the relief gratings can be conveniently recorded on the polymer films, such polymers may have significant potential applications for optical devices and optical elements. Optically induced large nondestructive periodical volume change of the high-T_g polymer film evokes questions about the mechanism of this process.

In order to understand the mechanism of the process, the structure of the polymer should be simplified and modified to identify the role of each structural element to the process. In our previous study, an azobenzene-

---

[†] Department of Chemistry.

[‡] Department of Physics.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

0024-9297/95/2228-8835$09.00/0

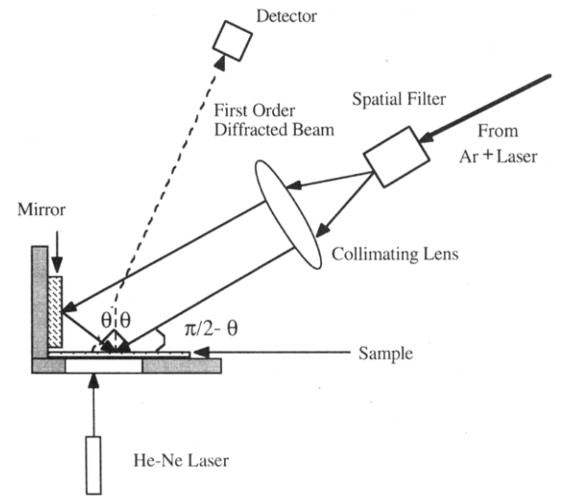

Figure 2. Schematic setup of the grating experiment.

containing polymer with a cross-linkable functionality was employed.[11] Our recent study confirmed that the cross-linkable functionality is not a necessary condition for the surface relief grating formation. In this paper, we report the detailed investigation of the surface relief grating formation of an azobenzene side chain polymer with a simplified structure. The effects of a number of important parameters on the process are investigated and possible mechanisms are also discussed.

Experimental Section

An epoxy-based polymer (PDO3) was synthesized from the diglycidyl ether of Bisphenol A (Shell, Epon 828) and Disperse Orange 3 (Aldrich). The synthesis of the polymer was previously reported.[16] The chemical structure of the polymer is presented in Figure 1. A differential scanning calorimeter (DSC) was used to measure the T_g of the polymer.

The polymer films were obtained by spin coating of a filtered polymer solution in 1,4-dioxane (5% w/w) on clean microscope glass slides. The films were dried in a vacuum oven at 60 °C overnight. The thickness of the film was measured by using an ellipsometer and a scanning electron microscope. UV−visible absorption spectra of the films were obtained on a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer. The refractive index of the polymer film was measured by using an ellipsometer.

The optically induced birefringence was measured by placing the samples between two crossed polarizers in the path of a low-power He−Ne laser beam at 633 nm. The birefringence was induced in the polymer film using a plane-polarized Ar^+ laser beam at 488 nm with a polarization angle of 45° with respect to the orientation of the polarizer. The transmission of the He−Ne laser beam at 633 nm resulting from induced birefringence was measured. The birefringence were calculated from the intensity of the transmission using the equation described earlier.[1]

Holographic gratings were recorded by a simple interferometric apparatus at wavelengths of 488 and 514 nm from an Ar^+ laser with intensities ranging from 5 to 70 mW/cm^2. The schematic setup of the grating experiment is shown in Figure 2. The grating spacing (Λ_g) could be adjusted by varying the angle (2θ) between the two writing beams according to the relation

$$\Lambda_g = \lambda/2 \sin \theta$$

where λ is the wavelength of the writing beam. Gratings with a spacing ranging from 0.35 to 3 μm have been recorded. The polarization of two writing beams was selected to be p-polarized except when the polarization effect was studied. Grating formation was monitored with a low-power unpolarized He−Ne laser beam at 633 nm by measuring the power of the +1-order diffracted beam in the transmission or reflection mode. The probe beam was incident at normal to surface of the polymer film.

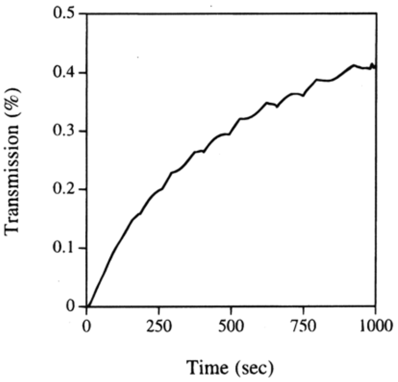

Figure 3. Transmission of the birefringence probe He−Ne laser beam through two crossed polarizers as a function of time.

The surface structure of the gratings on the polymer films was investigated by atomic force microscopy (AFM, Autoprobe Cp, Park Scientific Instruments) under ambient conditions before and after the holographic gratings were recorded. For all measurements, an 80 μm scanner was used in the contact mode. A microlever of force constant 0.05 N/m was used. A scan rate of 2 Hz was employed.

Results and Discussion

The polymer, PDO3, has a high concentration of azobenzene chromophores with strong electron donor−acceptor substituents, leading to large second-order NLO effects upon poling. The polymer can be further functionalized by incorporation of a desirable side group because a free hydroxyl moiety is available in the polymer. For example, the temporal stability of second-order NLO properties of the poled polymer film could be improved by cross-linking of the poled polymer through the reaction of cross-linkable side groups. The second-order NLO properties of these types of polymers have extensively been studied by our group.[17,18] The polymer functionalized with methacryloyl groups, PMDO3, is the polymer from which the formation of the surface relief gratings was observed earlier.[11]

The T_g of polymer PDO3 from a first heating scan of DSC was established as 106 °C. No crystalline transition was detected. This indicates that the polymer is amorphous. The polymer is soluble in common organic solvents and can form optical-quality films by spin coating. The films were found isotropic when viewed between two crossed polarizers. The typical thickness of the polymer films spin coated on glass slides was 0.6 μm. The refractive index of the polymer film was 1.75 at a wavelength of 633 nm. The UV−visible absorption spectrum of the spin-coated film showed a maximum at 462 nm, which corresponds to the $\pi-\pi^*$ transition of the azobenzene chromophores. The optical densities of the films at 488 and 514 nm were 2.2 and 1.7, respectively. Absorption at 633 nm was negligible. Therefore, an Ar^+ laser at either 488 or 514 nm was used as the writing beam, and a He−Ne laser at 633 nm was chosen as the reading beam.

The birefringence was optically induced in the polymer PDO3 films by exposure of a plane-polarized Ar^+ laser writing beam at 488 nm. As shown in Figure 3, transmission of the probe beam was increased as the writing beam was turned on. Initially the polymer film was isotropic, and no transmission of the probe beam was observed. The polarized writing beam induced the

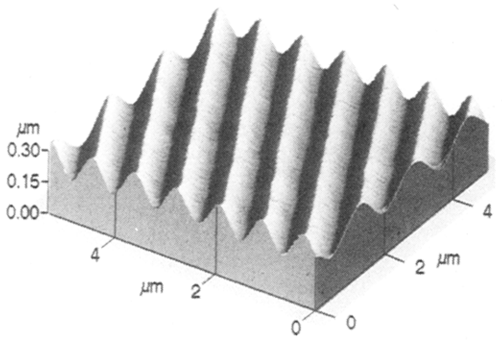

Figure 4. AFM three-dimensional view of the grating on the polymer film.

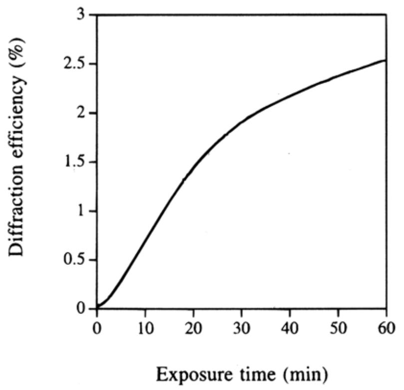

Figure 5. Effect of exposure time on the diffraction efficiency of the polymer film exposed with an intensity of 70 mW/cm^2 at 488 nm.

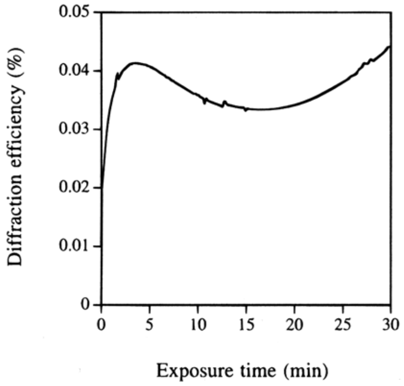

Figure 6. Diffraction efficiency of the polymer film as a function of time when exposed with 12 mW/cm^2 at 488 nm.

preferred orientation of the azobenzene side groups in the direction perpendicular to the polarization of the writing beam through trans−cis−trans isomerization steps, which consequently gave rise to birefringence in the amorphous polymer film. The time required for the saturation of the birefringence depended on the intensity of the writing beam. With an intensity of 25 mW/cm^2, it reached saturation in about 1000 s. The induced birefringence calculated from the transmission at saturation was about 0.02. This birefringence was in the same range as those reported from other azobenzene-containing amorphous polymers.[9]

The holographic surface relief gratings were optically created on the polymer films by exposure to an interference pattern of a polarized Ar$^+$ laser beam at 488 or 514 nm. Figure 4 shows a typical example of the three-dimensional view of the surface relief gratings observed from AFM. In this case, the polymer film was exposed for 30 min to a p-polarized Ar$^+$ laser beam at 488 nm with an intensity of 50 mW/cm^2. Very regularly spaced sinusoidal surface relief structures with large surface modulation depths were observed. The surface modulation depth was about 1300 Å, and the grating spacing was about 0.8 μm. The grating spacing measured from AFM was consistent with the theoretically calculated spacing. The surface of the film prior to the exposure to laser beams showed no regular structural periodicity. Therefore, it is clear that interfering polarized laser beams produced the surface relief structure. It is also evident that the cross-linkable functionality which was present in polymer PMDO3 was not a necessary condition for the creation of the surface relief structure. This is also consistent with the results of Rochon *et al.* whose acrylate-based polymer does not contain cross-linkable functionality.[12] The gratings could be erased by heating the polymer film above its T_g and were stable when kept below the T_g. The question to focus on is how such a large surface change is created. The intensity of the writing beam was much lower than the power required for the ablation of the polymer, and hence ablation as a mechanism responsible for this process is ruled out. As we have already confirmed, the azo groups can be oriented through local motions induced by the polarized light; however, it is not obvious that it can be the driving force leading to the large-scale molecular motions. Monitoring the diffraction efficiency during the writing process could provide useful information on the grating formation process.

Figure 5 shows the diffraction efficiency probed during the grating formation in the reflection mode when exposed to a p-polarized beam with 70 mW/cm^2. In this case, the grating spacing was about 1 μm. A diffraction efficiency of about 3% was obtained in the reflection mode. In the transmission mode, a diffraction efficiency as large as 15% could be achieved after long exposure. The grating formation process could be divided into three stages according to the slope of the diffraction efficiency vs exposure curve. In the first stage, which is the early stage continuing less than 3 min, the diffraction efficiency sharply increased. In the second stage, the diffraction efficiency increased almost linearly with a lower rate than the first stage. Finally, the rate became much lower and reached saturation. The distinction between the first and second stages was apparent when low-intensity light was used for the writing. Figure 6 shows the diffraction efficiency curve in the early stage when an Ar$^+$ laser beam at 488 nm with a relatively low intensity of 12 mW/cm^2 was used. When the writing beam was turned on, the diffraction efficiency increased rapidly and reached 0.04% in about 3 min. Then the diffraction efficiency decreased, which may indicate the presence of a transition stage, and again started increasing in the second stage. The diffraction efficiency of 0.04% was close to the value calculated from 10^{-2} of the birefringence.[19] No surface change at the first stage was observed during the AFM scan. Therefore it is apparent that the first stage of the grating formation is due to the well-established photoinduced birefringence of the azobenzene groups. The transition stage between the first and the second stages highly depended on the intensity of the writing beam. With low-intensity exposure, a slight decrease of the diffraction efficiency was observed as shown in Figure 6. One possible explanation is that migration of polymer chains, which causes the surface change, partially cancels the index modulation due to chromophore orientation. The development of the surface

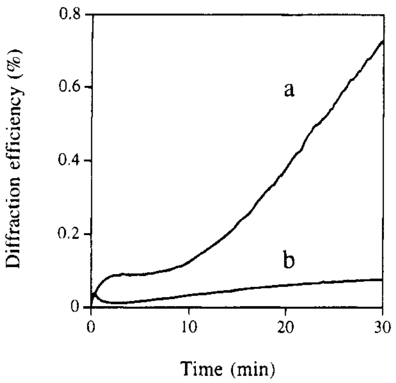

Figure 7. Diffraction efficiency of the polymer films exposed to (a) p-polarized beam and (b) s-polarized beam at 488 nm with 50 mW/cm^2.

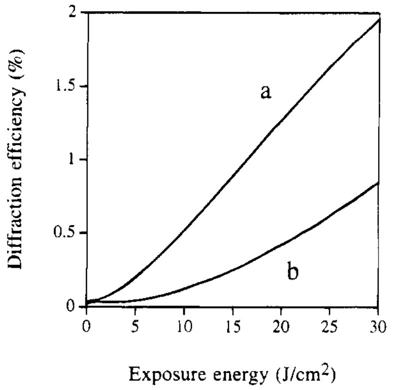

Figure 8. Effect of exposure intensity on the diffraction efficiency of the polymer films exposed with intensities of (a) 50 and (b) 5 mW/cm^2.

relief structure is responsible for the slow increase of the diffraction efficiency in the second stage.

The effect of the polarization of the writing beam on the process was significant. Figure 7 clearly shows the difference of the diffraction efficiency curves of the films when exposed under the same conditions except different polarization states of the writing beam. When the film was exposed to p-polarized beams, significantly larger diffraction efficiencies were observed than when the film was exposed to s-polarized beams. Although the light intensity absorbed by the polymer in both cases (correcting for reflections) is comparable, the surface modulation and consequently the diffraction efficiencies are considerably different. Since the polymer is isotropic before exposure, we believe that the p-polarized light cycles more azo moieties through a trans–cis–trans cycle than the s-polarized light, which has no component of the electric field normal to the plane of the polymer film.

Since the polymer films have a high absorption at the writing beam wavelength, any thermal effect due to absorption of light might contribute to the process. To study the thermal effects, polymer films were exposed to the writing beams with different intensities while keeping the same fluence of the total light energy. Figure 8 shows the effect of the writing intensity on the grating formation on the polymer films. One sample was exposed with an intensity of 50 mW/cm^2 for 600 s, and a second sample was exposed with 5 mW/cm^2 for 6000 s. Even though the total energy exposed was kept constant, the polymer film exposed to higher intensity light showed a larger surface deformation, leading to substantially higher diffraction efficiency than the sample exposed to lower intensity light. Therefore, a certain amount of thermal effect resulting from absorption of light seems to contribute to the surface deformation process or at least assist the process. A spatial variation of temperature resulting from the interference of the writing beams could make polymer molecules mobile and promote the macroscale molecular migration even though the T_g of the polymer is much higher than the ambient temperature. However, a thermal effect alone cannot explain the dependence of grating amplitude on the writing beam polarization. Although the thermal effect does play a significant assistive role, it is not the driving force for the grating formation process.

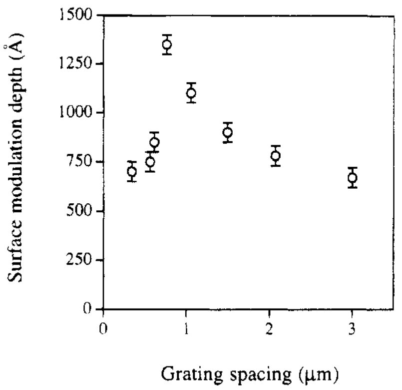

Figure 9. Effect of grating spacing on surface modulation depth on the samples exposed to beams at 488 nm with 50 mW/cm^2 for 30 min.

Diffraction efficiency depends on sample thickness. Higher diffraction efficiency was observed with thicker samples. However, when the thickness exceeded a certain limit, the efficiency difference was negligible, perhaps because the thickness was beyond the penetration depth. Thus, this process is considered as a volume effect rather than purely a surface effect.

The grating spacing could be readily adjusted by changing the angle between the two writing beams. The effect of the grating spacing on the surface modulation depth of the gratings is presented in Figure 9. The samples were exposed to the same fluence and intensity of light, and writing beams were turned off well before the grating efficiency saturated. The samples with grating spacing ranging from 3 to 0.35 μm were easily made. As the spacing became smaller from 3 to 0.8 μm, the amplitude of the surface modulation was increased to values as large as 1300 Å. However, the surface modulation heights dropped for samples with spacings shorter than about 0.8 μm. If we assume that material migration rate remains constant at a fixed incident intensity, we could explain the increase in the amplitude of the relief gratings when the period changes from 3 to 0.8 μm. However, the sharp drop in the diffraction efficiency at short periods clearly shows that the behavior is more complicated, perhaps involving thermal effects as discussed earlier. In addition, at small grating spacing (<0.8 μm), the incident angles of the writing beams were such that in the writing process part of these beams diffracted into the glass slides and possibly into the polymer films. Although the intensity of the diffracted beams is relatively small, additional complex interference patterns between these beams might result and make the analysis complicated.

The largest contribution to the diffraction is attributed to the surface gratings and the birefringence due to trans–cis isomerization has only a small contribution to the overall diffraction efficiency. The polymer used in this study contains azobenzene groups with electron donor–acceptor substituents which are known to undergo very fast cis–trans isomerization (less than a second). So immediately after the writing process has been carried out, there will be no cis isomer state. Therefore relaxation of the diffraction efficiency due to cis–trans isomerization is negligible and the diffraction efficiency is stable for more than 2 years at room temperature (about 80 °C below T_g of the polymer).

Conclusions

Holographic surface relief gratings with a large surface modulation depth (>1300 Å) were directly produced on polymer films containing azobenzene side groups. The grating formation process was found to consist of the optically induced orientation process of the azobenzene groups and the surface deformation process. The orientation was induced first in the polymer film and followed by the surface change. The surface deformation process highly depends on the polarization state of the writing beams. It was also demonstrated that a certain amount of thermal effects due to light absorption was involved in the process, although it is not the dominant factor. Although some question still remain to be answered, our study reported here implies a mechanism which involves both the orientation of the azobenzene groups and a localized thermal effect. The clear interpretation of this novel process will be possible after detailed examination of the role of each structural element—the polymer backbone, the spacer between the backbone and the side chain, and especially the structure of the side chain chromophores.

We are currently investigating these structural effects on the surface deformation process. Our current research indicates that neither index gratings nor surface relief gratings could be produced in the same epoxy-based polymer with biphenyl side groups, which are not able to undergo the trans–cis photoisomerization process characteristic of the azo dye based chromophores. This further establishes that the mechanism of the surface deformation process is not simply thermal diffusion resulting from local heating by photoabsorption. Photoinduced local reorientation and motion assisted by local heating induced by photoabsorption is responsible for the process. Detailed results from these studies will be reported in a subsequent report.

Acknowledgment. Financial support from ONR and NSF–DMR is gratefully acknowledged.

References and Notes

(1) Todorov, T.; Nikolova, L.; Tomova, N. *Appl. Opt.* **1984**, *23*, 4309.
(2) Eich, M.; Wendorff, J. H.; Reck, B.; Ringsdorf, H. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 59.
(3) Eich, M.; Wendorff, J. H. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 467.
(4) Eich, M.; Wendorff, J. H. *J. Opt. Soc. Am., B: Opt. Phys.* **1990**, *7*, 1428.
(5) Wiesner, U.; Antonietti, M.; Boeffel, C.; Spiess, H. W. *Makromol. Chem.* **1990**, *191*, 2133.
(6) Wiesner, U.; Reynolds, N.; Boeffel, C.; Spiess, H. W. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 457.
(7) Shi, Y.; Steier, W. H.; Yu, L.; Chen, M.; Dalton, L. R. *Appl. Phys. Lett.* **1991**, *59*, 2935.
(8) Rochon, P.; Gosselin, J.; Natansohn, A.; Xie, S. *Appl. Phys. Lett.* **1992**, *60*, 4.
(9) Natansohn, A.; Rochon, P.; Gosselin, J.; Xie, S. *Macromolecules* **1992**, *25*, 2268.
(10) Kim, D. Y.; Li, L.; Jeng, R. J.; Kumar, J.; Fiddy, M. A.; Tripathy, S. K. *SPIE Proc.* **1993**, *1853*, 23.
(11) Kim, D. Y.; Li, L.; Kumar, J.; Tripathy, S. K. *Appl. Phys. Lett.* **1995**, *66*, 1166.
(12) Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66*, 136.
(13) Johnson, L. F.; Kammlott, G. W.; Ingersoll, K. A. *Appl. Opt.* **1978**, *17*, 1165.
(14) Philips, H.; Callahan, D.; Sauerbrey, R.; Szabo, G.; Bor, Z. *Appl. Phys. Lett.* **1991**, *58*, 2761.
(15) Lee, T. C. *Appl. Opt.* **1974**, *13*, 888.
(16) Mandal, B. K.; Jeng, R. J.; Kumar, J.; Tripathy, S. K. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 607.
(17) Jeng, R. J.; Chen, Y. M.; Kumar, J.; Tripathy, S. K. *Pure Appl. Chem.* **1992**, *A29*, 1115.
(18) Marturunkakul, S.; Chen, J. I.; Li, L.; Jiang, X. L.; Jeng, R. J.; Sengupta, S. K.; Kumar, J.; Tripathy, S. K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 134.
(19) Smith, H. M. In *Holographic Recording Materials*; Smith, H. M., Ed.; Springer-Verlag: New York, 1977.

MA950481K