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Photo-Induced Formation of the Surface Relief Grating on Azobenzene Polymers: Analysis Based on the Fluid Mechanics

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Photofabrication of surface relief grating (SRG) on azobenzene functionalized polymers was investigated in order to elucidate the dynamics of this phenomenon. The systematic study examined the influence of experimental and geometrical parameters such as the film thickness, the irradiating light intensity and the spacing of the interference light pattern. Experimental results were discussed within the framework of existing fluid mechanics model. The cubic dependence of SRG inscription rate on the film thickness (h) in the small h region and an asymptotic tendency in the large h region were well characterized by the model. We established that the writing behavior of photofabricated SRG depends on the irradiated light intensity. The effective critical intensity of the irradiating light was found to be independent of the spacing of the interference light pattern. It was discussed in terms of the viscosity change of the polymer film caused by light irradiation and viscous fluid nature of the system during the SRG photofabrication was suggested.

Keywords: Surface Relief Grating; Azobenzene Polymers; Fluid Mechanics Model; Formation Dynamics

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INTRODUCTION

Azobenzene molecules under irradiation with polarized light show photoinduced reorientation through the *trans-cis-trans* photo-isomerization cycles. This is well known as optically induced birefringence and dichroism. A holographic phase grating can be formed on azobenzene containing films by irradiating an interference pattern of coherent light, though this phase grating is easily eliminated by thermal relaxation.

In recent years, unique photofabrication of surface relief gratings (SRG) on azobenzene functionalized polymer films has been reported [1,2] and has attracted great attention [3-7]. The photofablicated SRGs are very stable unless the film is heated up to their glass transition temperature (T_g). This phenomenon is quite different from other conventional microscopic processing techniques such as laser ablation and chemical etching. Because the SRGs are not formed by any physical removal of the molecules from the film surface but as a result of large-scale photodriven mass transport process in thin solid films at a temperature much below the T_g of the polymer.

Although several models were recently proposed to account for the photofabrication mechanism of SRG [8-10], the problem is still controversial. In order to discuss the dynamics of photo-induced SRG formation more precisely, we proposed a viscous fluid model [11] in which distribution of the SRG driving force and the experimental geometry are taken into account.

In this paper, a systematic study of the deformation process on azobenzene functionalized polymers has been examined in order to investigate the influence of experimental and geometrical parameters such as the film thickness, the irradiating light intensity and the spacing of the interference light pattern. Experimental results are analyzed by proposed fluid mechanics model [11] and the SRG photofabrication dynamics are discussed.

EXPERIMENTAL

An azobenzene polymer (PMD) shown in figure 1 was obtained by copolymerization of 4-(N-(2-Methacryloyloxyethyl)-N-ethylamino)-4'-nitroazobenzene and methyl methacrylate. Detailes of this synthesis will be reported in the literature [7]. Typical surface profile of the SRG fabricated on a PMD film is also shown in the figure. The number averaged molecular weight (M_n) and the glass transition temperature (T_g) of the polymer were 5.9×10^3 and 128 °C, respectively.

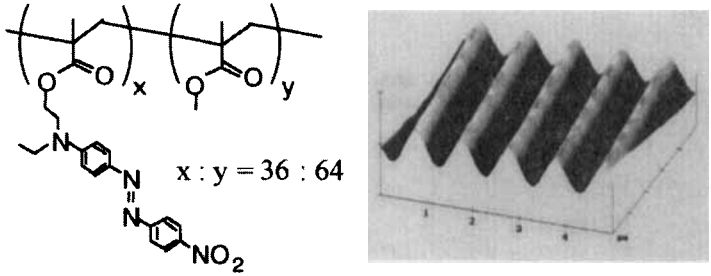

FIGURE 1 Chemical structures of PMD and typical atomic force microscope (AFM) image of SRG.

Amorphous thin films with good optical quality were prepared on glass substrates by spin coating. The thickness of the films was measured by using a mechanical stylus profiler.

The SRG was recorded by exposing the polymer thin film to an interference pattern. It was produced by the two coherent beams at 488 nm from an Ar^+ laser with intensities ranging from 0.1 to 50 mW/cm^2. The details of the optical measurement were previously reported [2,7].

The surface structure was measured by AFM (Nanoscope IIIa, Digital Instruments Co.) in the tapping mode under ambient condition.

RESULTS AND DISCUSSION

A schematic illustration of the proposed fluid mechanics model is shown in the figure 2 (a). The system was assumed to satisfy the laminar flow condition, i.e., viscosity of the polymer is large enough and surface modulation is small. Oridinating in the irradiating interference light pattern, a driving force has a sinusoidal profile in the x-direction resulting in the sinusoidal distribution of the velocity of mass transport along x-axis (v_x). The driving force decays in the y-direction due to the light absorption, that causes exponential distribution of v_y as shown in the figure.

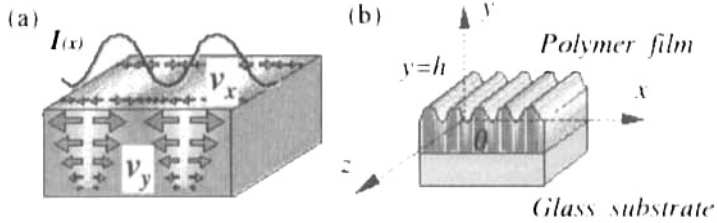

FIGURE 2 (a) Schematic of the model and (b) the coordinate system.

According some physical assumptions above, the simplified Navier-Stokes equation can be expressed as follows:

$$0 = \frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{1}{\mu} F_x(x,y), \qquad (1)$$

where μ and $F_x(x, y)$ are the viscosity and the body force acting on the polymer as a viscous fluid.

Applying appropriate boundary conditions, final formulation of the SRG inscription rate ($\partial h/\partial t$) can be obtained as follows:

$$\frac{\partial h}{\partial t} = v_y\Big|_{y=h} = \frac{-F_0 k \cos kx}{\mu(k^2-\alpha^2)}\left[\frac{1}{\alpha} - \frac{\alpha}{k^2} - \frac{1}{\alpha}e^{-\alpha h} + \frac{2\alpha + ke^{-\alpha h}(e^{-kh} - e^{kh})}{k^2(e^{-kh} + e^{kh})}\right] \qquad (2)$$

where α, h and k are an absorption coefficient of the polymer, the thickness of the film and the wave number of the grating, respectively.

Figure 3 shows the influence of experimental and geometrical parameters on the SRG photofabrication: (a) dependence on the h, and (b) dependence on the irradiating light intensity (I) and the k, which is related to the grating spacing (Λ) as $k = 2\pi/\Lambda$.

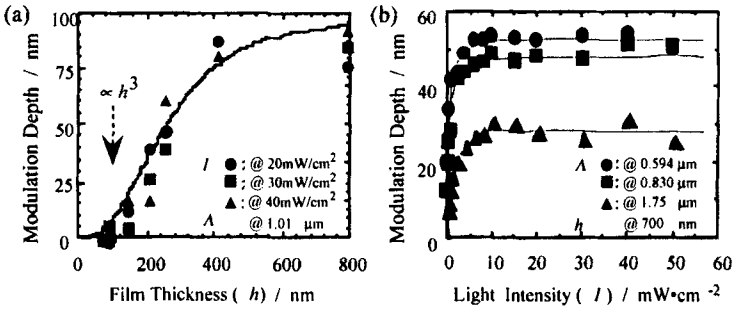

FIGURE 3 The SRG inscription rate dependence as a function of (a) the h, and (b) the I and the Λ. Irradiated total photon energy was fixed at 14 and 7.2 J/cm^2 for each experiment, respectively.

The cubic dependence of SRG inscription rate in the small h region and an asymptotic tendency in the large h region were well characterized by the theoretical curve obtained from eq. (2). On the other hand, the effective critical light intensity (~5mW/cm^2) was observed on the I dependence measurement regardless of the k (or Λ). This behavior cannot be explained by eq. (2) so far as the viscosity is constant upon the light irradiation. However, if we assume the successive diminution of the viscosity of the azobenzene polymer film against the light intensity, this result can be described. This assumption could be allowed by the photo-plasticization of the azo polymer through

the *trans-cis-trans* photoisomerization and the photoinduced molecular reorientation.

CONCLUSION

The systematic study was performed on the SRG photofabrication. According to the existing fluid mechanics model, the thickness dependence of the SRG inscription rate was well described. Strong dependence of the SRG formation on the light intensity in the small intensity region was established. It was suggested that this might be explained by the viscosity change of the azobenzene film upon the light irradiation. As a result, viscous fluid nature of the system and validity of the model was confirmed.

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