Effect of Temperature on the Surface Relief Grating Formation caused by Rotation of Light-driven Molecular Motor

Shohei Ogino\textsuperscript{a}, Masuki Kawamoto\textsuperscript{b}, Kunihiko Okano\textsuperscript{c} and Takashi Yamashita\textsuperscript{a}

\textsuperscript{a) Department of Pure and Applied Chemistry, Tokyo University of Science, 2641 Yamazaki, Noda-shi, Chiba 278-8510, Japan.}  
\textsuperscript{b) RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan}  
\textsuperscript{c) Department of Applied Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku, Yokohama, Kanagawa, 351-0198, Japan}

Keywords: surface relief grating, molecular motor, mass migration

1. Introduction

Photochromism is the phenomena of color change of molecules caused by the structure change by photo-irradiation. Recently amplification of the photochemical reaction in the molecular scale to macroscopic mechanical change of materials is attracting much attention. For example, mass migration is induced by interference exposure on an azobenzene-containing polymer film to form surface relief gratings (SRGs) with micrometer scaled periodic pattern. Since the discovery of SRG formation on azobenzene-containing polymer films in 1995 \cite{1,2}, many reports have been published about the SRG, and design of photoresponsive materials for effective SRG formation has been attracting attentions. Several types of azobenzene containing films have been reported such as amorphous \cite{3}, liquid crystalline \cite{4}, and so on. In addition, other photochromic compounds such as spiropyran \cite{5} and diarylethene \cite{6} can give SRG structure through their photochromic reaction. Though there have been many reports on experimental and theoretical data on the SRG formation of the azobenzene-containing films until now, mechanism of the SRG formation is not sufficiently understood up to now. Novel material system forming SRG is expected to give information to clarify the SRG formation mechanism.

In this study, relationship between SRG formation and photo isomerization reaction is investigated using a light-driven molecular motor (9-(2-phenyl-2,3-dihydro-cyclopenta[a]naphthalen-1-ylidene)-9H-fluorene) as a novel photochromic molecules in SRG induction, which rotates in one direction through the processes of photochemical and thermal treatment \cite{7}. Mechanism of the molecular rotation is based on the photo induced inversion of central double bond followed by the thermal isomerization of the naphthyl group over the fluorenlyl group (Scheme 1).

Scheme 1 Rotational motion of the molecular motor by photoisomerization and thermal isomerization.
2. Experimental

The synthesis of molecular motor using in this study were performed with modified procedures reported previously [8].

Sample films were prepared by spin coating (1000 rpm) or casting from a toluene solution (3 wt%) of PMMA and molecular motor (weight ratio 50:50) on glass substrates. In order to investigate the photoisomerization of molecular motors in the film, UV and CD spectra were measured before and after the photoirradiation.

Photoirradiation to the sample films was performed by two-beam interference exposure of UV laser and exposure through a photomask. Experimental setup for the interfered UV laser exposure is shown in Fig. 1. Writing beam (Ar⁺ ion laser, 364 nm) is separated into two beams which are interfered on the film surface with incident angle of 7°. Intensity of the first-order diffracted beam of the probe (He-Ne laser, 633 nm) due to the SRG formation during the interference photoirradiation was recorded with a photodiode.

UV light irradiation (365 nm, 300 mW/cm², 100 min) was performed using an ultra-high pressure mercury lamp through a photomask (100 line/mm) for fabricating SRG.

3. Result and Discussion

Photoisomerization of molecular motor, (9-(2-phenyl-2, 3-dihydro-cycro-penta[a] naphthalene-1-ylidene)-9H-fluorene), in the solid state film was investigated based on the change in UV and CD spectra. Changes in the UV absorption at 390 nm and 440 nm show the stilbene-type photo-induced inversion of ethane group (Fig. 2a). Inversion in the CD spectra between the positive and negative peaks around 240 nm and 290 nm shows the movement of the naphthyl group over the fluorenyl group by the conformational change as to the cyclopentyl group with chirality change (Fig. 2b). This thermal isomerization process was promoted at higher temperature due to enhance of the conformation change, measuring the CD spectra at different temperatures in Fig. 3.
The sample film was exposed to two-beam interference of UV laser to give SRG probing the first-order diffracted beam intensity using He-Ne laser. Diffracted beam appeared after irradiation for 10 minutes, and the intensity of the diffracted beam became saturated after 25 minutes (Fig. 4). The diffracted light intensity change for azobenzene-containing film under interference photoirradiation is reported as the formation of gratings with a change in refractive index [8]. Therefore the formation of optical gratings for the present samples under the photoinduced rotation reaction of molecular motor could be induced by SRG formation. In fact, AFM measurement of the sample film after the interference photoirradiation showed SRG is generated on the film surface (Fig. 5). Regular surface modulation was obtained with a spatial period of 1.5 µm, and peak-to-trough modulation depth of about 10 nm. In addition, a similar pattern was also observed when using the (R)-isomer of molecular motors, meaning that SRG is induced by the rotation of the molecular motor itself, but it is not affected by the direction of the rotation.

Writing SRG on the molecular motor containing PMMA film was also investigated by the photo masked UV irradiation, which can conveniently form SRG under heated conditions. After UV light (365 nm, 300 mW/cm²) irradiation for 100 min through a photomask (100 line/mm), clear SRG was generated on the molecular motor-containing PMMA film. The SRG was also confirmed by measuring AFM to have about 20 nm depth (Fig. 6).

The width of the higher part of the topological profile in the AFM image in Fig. 7 is much wider than that of lower region though the width of the line and space of the photo mask is the same. This observation suggests us that mass transfer during the SRG formation occurs from dark area to bright area because the width of bright area on the film surface should be wider due to diffraction of the transmitted light through the mask, and so the higher region is regarded to correspond to dark area during exposure (Fig. 8).
Fig. 9 shows the temperature dependence on the SRG formation of the sample films photoirradiated on a hot stage at various temperatures (25, 50, 70, 90 and 110 °C). SRG depth becomes deeper as increase in temperature, because the mass transfer is amplified by the plasticization of PMMA at the higher temperature and the following promotion of rotation reaction of the molecular motors. The SRG disappeared, however, when the film was heated at 110 °C (Fig. 9) because of the structural relaxation of PMMA above Tg.

Fig. 10 shows the AFM image of the SRG on the sample film at mask edge region. Periodical grating is observed in the right hand side of blue line in the image, while higher part is observed in the left hand side of the blue line, where incident light is cut off by the mask edge. This picture clearly shows that the photoirradiated area is depressed meaning that the mass transfer occurs from dark area to bright area.

4 Conclusion
We have successfully induced surface relief grating on poly(methyl methacrylate) film containing a molecular motor by photoirradiation. The SRG is induced by mass transfer from unexposed area to the exposed area upon photoirradiation. This observation proves that the SRG can be generated not only by photochromic reactions but also photoinduced molecular rotation reactions.

References