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Self-Organized Striped Pattern in Photopolymer and the Resulting Angular Dependence in the Transmittance

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The photopolymerization by uniform irradiation from rod-shaped UV source produced the self-organized striped pattern of refractive indices in the polymer plate. The photopolymer has interesting optical properties due to the microstructure, that is, the angular dependence in the transmittance. The monomer mixture was prepared by mixing bifunctional methacrylate monomer (BM), cyanoethylmethacrylate (CNMA), and 2,4,6-trimethyl benzoyl phosphine oxide (TBDP) as photoinitiator, and the monomer mixture placed in a space between two glass plates. A self-organized striped pattern was observed by optical microscopy in the polymer plate obtained by uniform UV irradiation. Electron probe X-ray microanalysis of the cross section of the polymer plate revealed the elements contained in the photopolymer were distributed almost homogeneously. The result suggests that the striped pattern observed in an optical microscope is not due to the compositional modulation but due to crosslink density modulation.
Key words: photopolymerization, self-organization, transmittance, crosslink density modulation

1. INTRODUCTION

Microstructure is significant for getting a sophisticated function and several studies have been carried out on various fields.[1-8] Moreover, self-organization has been scientifically and technologically noticed as useful process for microstructure formation.[5-8]

Here we report on a self-organized microstructure of photopolymer, and the microstructure is striped pattern of refractive indices. The photopolymer has interesting optical properties due to the striped pattern, that is, the angular dependence in the transmittance.[9] The photopolymerization with uniform irradiation of UV light produced the striped pattern of the refractive indices in the polymer plate. The periodicity of the stripes was varied from several microns to dozens of microns by the intensity of the UV light. The transmittance of the polymer plate dramatically changes according to the angle of the incident light. If one can control both the microstructure of refractive indices and the resulting optical properties, this self-organized polymer plate would be used as an optical transmission filter,[10] a polarizing plate,[11,12] and an optical waveguide.[13]

A similar phenomenon has been reported.[14-17] In the previous reports, the striped pattern is attributed to phase separation of two kind of monomer.[17] However, our result of Electron probe microanalysis on the cross section of the photopolymer plate revealed the compositional inhomogeneity was quite small. This result suggests that the striped pattern of the refractive indices is attributed to the crosslink density modulation in our system. It is also explained that the self-organization is due to the light intensity distribution produced by microgel in the previous studies. However, the reason of the stripe direction parallel to the rod-shaped UV light source is unclear.

To design a three-dimensional microstructure and the resulting optical properties, it is necessary to understand the self-organization mechanism during photopolymerization. The purpose of this study is to clarify the mechanism of self-organization.

2. EXPERIMENTAL

Bifunctional methacrylate monomer (BM) (see ref. 9), cyanoethylmethacrylate (CNMA) (Mitsubishi Chemical), and 2,4,6-trimethylbenzoyl diphenyl phosphine oxide (TBDP) (Ciba-Geigy) as the photoinitiator were mixed. The concentration of each component was maintained at the same weight ratio throughout the experiment (BM: CNMA:TBDP = 5:5:0.01).

The monomer mixture was injected into the space between two circular glass plates supported by silicon rubber. The thickness of the space was 2 mm and the diameter was 75 mm as shown in

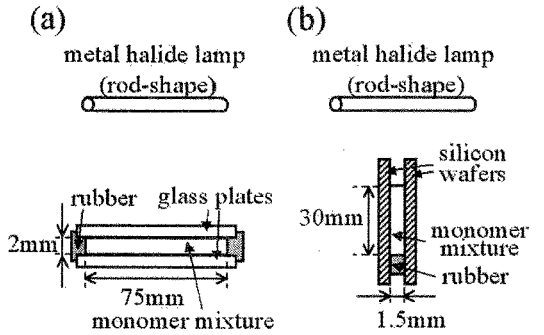

Fig. 1 Schematic illustrations of the experimental setup. (a) The reactor to obtain the circular plate. (b) The reactor for cuboid plate.

Fig. 1a. The photopolymerization was carried out by a uniform irradiation of UV light (peak wavelength 365 nm) using a rod-shaped metal halide lamp. The irradiation period was fixed at 150 s for all samples unless otherwise stated. Irradiation intensity was varied within a range 2.4–7.2 mW/cm^2. After the photo-crosslinking reaction, the colorless crosslinked polymer plates were obtained.

To observe the cross-section of the polymer plate, the space of the monomer mixture was changed as shown in Fig. 1b. The walls perpendicular to the longitudinal direction of rod-shaped UV lamp were silicon wafers and the other walls and bottom side was silicon rubber. The upper side was free surface.

The optical microscope images were captured by a digital camera (Epson CP-800S) and subsequently transformed into gray scale by an image processing software. The transmittance was measured by UV/vis spectrophotometer (Jasco ART-25C) and the 550 nm wavelength monochromatic light was used as an incident light. The sample was cut perpendicular to the stripes by using a microtome and the elemental analysis of the cross section of the sample was carried out by using electron probe microanalyzer (EPMA) (JEOL JXA-8600).

3. RESULTS AND DISCUSSION

Optical microscope images of the polymer plates photopolymerized at different UV irradiation intensities were shown in Fig. 2. All images were taken from the upper surface of the polymer plate, i.e. from the irradiated surface. Although the monomer mixture was uniformly irradiated, the striped pattern was created. The direction of the stripes was parallel to the longitudinal direction of rod-shaped lamp in all samples. The average inter-stripe distance of the sample polymerized at 7.2 mW/cm^2 UV irradiation intensity (Fig. 2a) was 20-30 μm measured from the optical microscope image, and almost all stripes ran to the same direction (parallel to the longitudinal direction of rod-shaped UV lamp). In

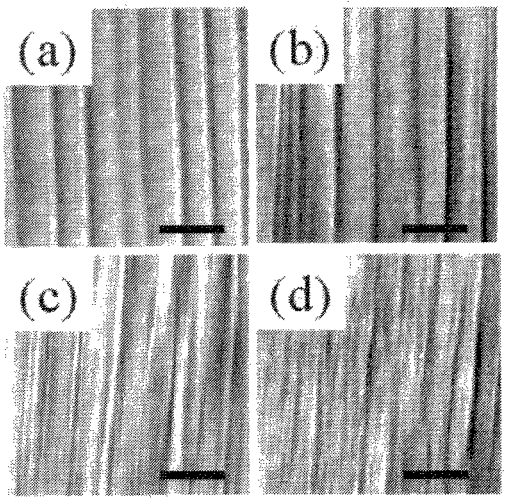

Fig. 2 Optical microscope images of the polymer plates obtained by the experiment of Fig. 1a. Each sample was photopolymerized by the UV irradiation of intensities (a) 7.2 mW/cm^2, (b) 4.8 mW/cm^2, (c) 3.7 mW/cm^2, and (d) 2.4 mW/cm^2. The scale bars in all images correspond to 50 μm.

the image of the sample polymerized at 4.8 mW/cm^2, smaller inter-stripe distance was locally observed (left side in Fig. 2b). Further smaller distance was noticeable in the sample polymerized at lower irradiation intensity (Fig. 2c). In the sample polymerized at 2.4 mW/cm^2, under 10μm inter-stripe distance was observed in whole area of the sample (Fig. 2d).

The striped pattern was also observed from the cross section obtained by cutting the above-mentioned sample (not shown). The striped pattern on the cross section ran vertically (i.e. from the upper surface to the bottom surface). Considering the striped pattern in the horizontal plane (Fig. 2), a sheet-shaped structure existed side by side inside the polymer plate. It is difficult, however, to accurately observe the structure on the cross section, especially close region to the upper surface because the cutting defects could not be eliminated completely. To investigate the detail structure of the cross section, vertically thin photopolymer plate was obtained by the experiment as shown in Fig. 1b. It was possible to non-destructively observe the flat cross section that was reflected the silicon wafer wall. Two layers were observed in the cross section as shown in Fig. 3a. One layer was about 200 μm thick following the upper surface (irradiated surface, that was revealed as the border between the black and gray color in the upper side of the image). No structure was observed in the optical microscope image in this layer. Down below the layer, there was the other layer, which had periodic structure. Although the effects of changing the sample size on the structure formation were not clear, these two layers were similarly observed in samples obtained by the experiment

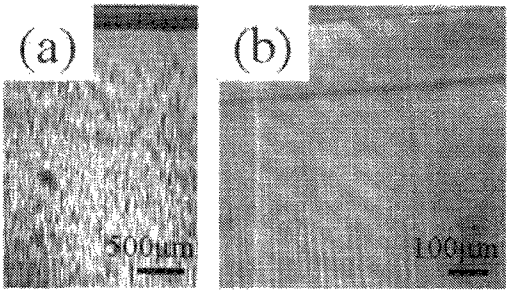

Fig. 3 Optical microscope images of the cross section of the polymer plate (near the upper surface) obtained by the experiment of Fig. 1b. Magnification of lens was (a) 40 and (b) 100.

as Fig. 1a, and the inter-stripe distance on the each sample was approximately same (dozens of microns). In more detail, the interface between the two layers was relatively irregular, i.e. the periodic structure was generated at various depths from the surface as shown in Fig. 3b. Two horizontal lines in the Fig. 3b would be reflected the upper surface of the sample that had tilt on the stage of the optical microscopy.

Fig. 4 shows the angular dependence in the transmittance of the 550 nm wavelength monochromatic light for samples photopolymerized at 7.2, 4.8, and 2.4 mW/cm^2 UV irradiation intensities. An incident angle θ is defined as the angle between the direction of the incident light and the normal of the polymer surface. The angular dependence in the transmittance as shown in Fig. 4 can be only observed in the perpendicular direction of the stripes in the sample (i.e. the direction of the rod-shaped UV lamp source). The average transmittance at a wider incident angle ($|\theta| \geq 20°$) is about 90% for all samples. The transmittance dramatically decreases below the threshold angle. The value of the transmittance change increased with decreasing the UV irradiation intensities, but the threshold angle was almost constant for all samples (about ±7°). The large transmittance change at the weakly irradiated sample was related to the total reflection and/or the diffraction due to the microstructure with the small inter-stripe distance (Fig. 2d).[9]

The formation of the striped pattern during the photopolymerization was investigated. Figures 5a and 5b show the optical microscope image of the polymer plates photopolymerized by UV irradiation for 10 s and 20 s. The UV irradiation intensity was 2.4 mW/cm^2. The images were captured under a UV-shielded environment after the UV irradiation was stopped. However, the effects of dark reaction would exist because it took a few seconds to capture the image. Few stripes were partially observed as shown in Fig. 5a, and the stripes were observed in all over the sample as shown in Fig. 5b. The sample photopolymerized for 5 s was still liquid. These results lead that the gelation occurred around 5-10 s and that the striped pattern observed by optical microscopy was generated during several seconds after the gelation. However, the mechanism of the self-organization of the striped pattern was still under investigation. The sample photopolymerized for 20 s had the angular dependence in the transmittance (not shown) although the value of the transmittance change was weak. On the other hand, the sample photopolymerized for 10 s revealed the constant transmittance at all incident angles. The result suggests that the angular dependence in the transmittance was attributed to the striped pattern inside the polymer plate.

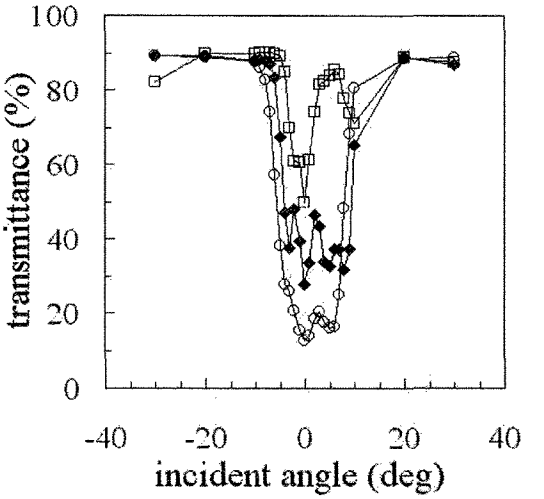

Fig. 4 Angular dependence in the transmittance. Open squares, closed diamonds, and open circles represent the spectra of the sample photopolymerized by the UV irradiation of intensities 7.2 mW/cm^2, 4.8 mW/cm^2, and 2.4 mW/cm^2, respectively.

Elemental analysis by EPMA was carried out to determinate quantity of the microstructure observed by optical microscopy. The polymer plate photopolymerized at 7.2 mW/cm^2 UV irradiation intensity was cut perpendicular to both the striped pattern and the surface of the sample by a

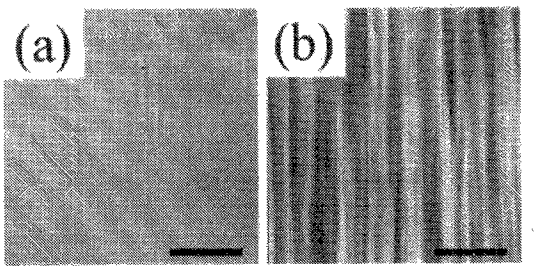

Fig. 5 Optical microscope images of the polymer plates. Each sample was photopolymerized by 2.4 mW/cm^2 UV irradiation intensity for (a) 10 s and (b) 20 s. The scale bars in both images correspond to 50 μm.

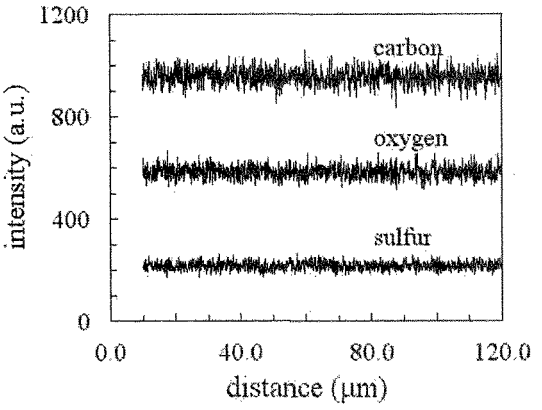

Fig. 6 Distribution of carbon, oxygen, and sulfur contents on the cross section of the photopolymer. The signals of all elements below 10 μm were cut because of the lack of the sensitivity of EPMA.

microtome. Then the flat cross section was obtained. Line scanning of EPMA was carried out parallel to the original surface, that is, perpendicular to the stripes observed on the cross section by optical microscopy. Fig. 6 shows the distribution of carbon, oxygen, and sulfur on the line. The data below 10 μm was eliminated because of the noise due to the lack of the sensitivity of EPMA. The signals of three elements revealed almost constant throughout the line. The result suggests that there is little compositional modulation and/or density modulation through the diffusion of monomers. The optically observed striped pattern is thought to be attributable to the crosslink density modulation and the resulting refractive-index modulation, but the detail investigation such as the confocal laser Raman spectroscopy on the flat surface is necessary to conclude the origin of the striped pattern.

4. CONCLUSION

Self-organized striped pattern of refractive indices in photopolymer and the resulting angular dependence in the transmittance have been reported. The inter-stripe distance increased with an increase in UV irradiation intensity. Considering the striped pattern on the cross section of the polymer plate, there were side by side sheets structure inside the polymer plate, though there was an optically uniform layer near the upper surface (the thickness of the layer was about 200 μm). The value of the transmittance change with the incident angle was decreased with an increase in UV irradiation intensity. The optical microscope images of the samples photopolymerized for different irradiation time revealed that the striped pattern was generated following the gelation. Almost homogeneous distribution of all elements measured by EPMA suggests that the optically observed striped pattern was due to the crosslink density modulation. Further studies are necessary to clarify the self-organization mechanism of the striped pattern.

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