

PHOTOPOLYMER FOR RECORDING HOLOGRAMS



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ABSTRACT

The photopolymerizable materials for recording holograms were composed of higher-index polymers, lower-index monomers, and photoinitiators. The materials have sensitivity from UV to green light(514.5nm). The diffraction efficiencies of the transmission holograms recorded by two beams from a laser were more than 80%. These holograms have good physical and chemical stability. The mechanisms of the formation of holograms was discussed.

1. INTRODUCTION

In recent years, a number of photopolymers¹⁻⁵⁾ have been proposed for recording high-resolution and high-diffraction efficiency phase holograms. They are useful for applications as optical elements, 3D-displays, security, and optical devices. We have developed the photopolymerizable materials consisting of higher-index polymers, lower-index monomers, and photoinitiators. In this paper, experimental results for transmission holograms are reported and the mechanisms of refractive index modulation in photopolymerization of the materials are discussed.

2. EXPERIMENTAL

2.1 Preparation of photosensitive layer

The photopolymerizable materials used in this work were prepared by mixing higher-index polymers with lower-index (metha)acrylic monomers and photoinitiators as benzil or coumarin and so on. A small amount of organic solvents was added to improve the viscosity and solubility. The solution of the materials was coated on a glass plate and dried at room temperature under vacuum, then sandwiched with another glass plate. The thickness of the samples was prepared using PET film as spacer.

2.2 Record of transmission holograms

He-Cd laser(441.6nm) and Ar ion laser(488nm, 514.5nm) were used for recording the transmission holograms with usual recording optical arrangement. After recording the interference pattern, no treating to fix such as heat processing or postexposure of UV needed.

3. MECHANISM OF REFRACTIVE INDEX MODULATION

Figure 1 shows the mechanism of refractive index modulation during hologram formation. The mixture of polymers and monomers on glass plate was exposed to interference pattern of light. Then, the highly photopolymerizable material, such as (metha)acrylic monomer, begins to polymerize in the bright regions of interference pattern. This result produces concentration gradients of monomer between the bright and the dark regions. This gradients lead to move the mobile unreacted monomers from the dark regions into the bright regions where they polymerize further. As a result, the mixture separates into polymers in the dark regions and polymeric monomers in the bright regions. On exposure to white light diffusion ceases and a phase hologram is formed with refractive index modulation.

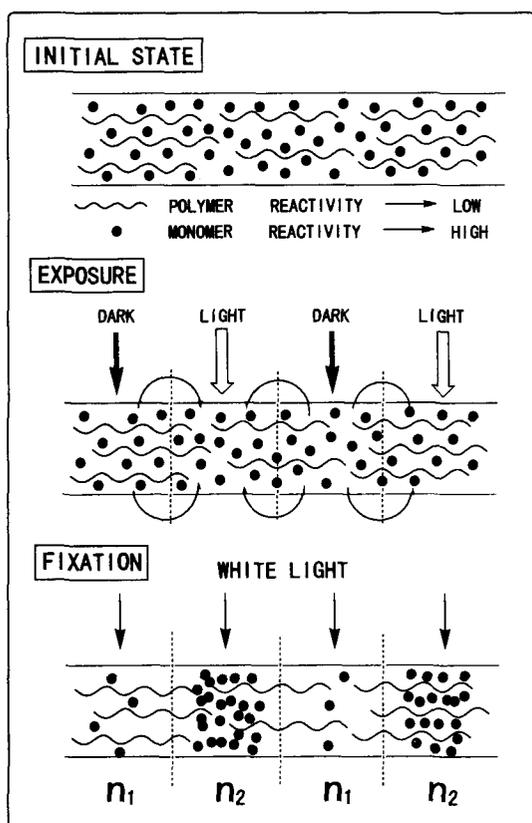


Fig. 1 The mechanism of refractive index modulation during hologram recording.

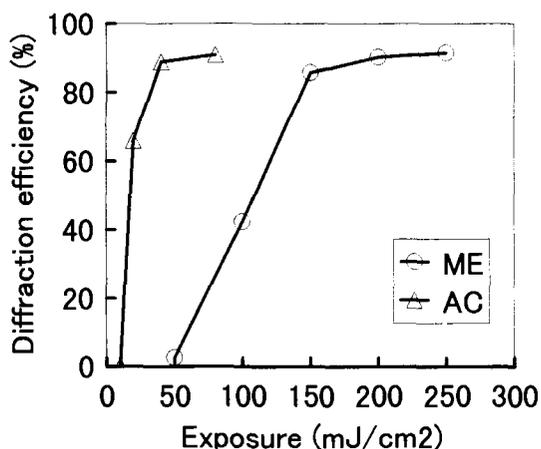


Fig. 2 Diffraction efficiency - exposure curves for the transmission holograms at 441.6nm. Circular and triangular marks are ME and AC monomers, respectively.

4. RESULTS AND DISCUSSION

4.1 The influence of type of monomers on transmission hologram recording

Figure 2 shows the diffraction efficiency - exposure curves for the transmission holograms produced using the materials consisting of higher-index polymers, lower-index monomers, benzil, and Michler's ketone. Acrylic and methacrylic monomers were used. The holograms were recorded by two beams of He-Cd laser at 18° angle. The spatial frequencies investigated correspond to 708 lines/mm. The light intensity of each beam was adjusted to $1.3\text{mW}/\text{cm}^2$. The peak values of the diffraction efficiency are 91.6% at $250\text{ mJ}/\text{cm}^2$ for methacrylic monomers (ME) and 90.6% at $80\text{mJ}/\text{cm}^2$ for acrylic monomers (AC), respectively. Thus, these peak values of diffraction efficiencies in both monomers are same level, but exposure value at the peak value of AC is quite promoted as compared with that of ME. These results may be due to the difference of photopolymerization rate because the polymerization rate of AC are faster than that of ME.

4.2 The record of interference pattern by Ar ion laser

Next, we investigated the ability of record of interference pattern by two beams of Ar ion laser(488nm). Figure 3 shows the diffraction efficiency - exposure curve for the transmission holograms produced using the materials consisting of higher-index polymers, lower-index acrylic monomers, and coumarin type initiators. The holograms were recorded by two beams of Ar ion laser at 34° angle. The spatial frequencies investigated correspond to 1200 lines/mm. The light intensity of each beam was adjusted to $3.1\text{mW}/\text{cm}^2$. The peak value of the diffraction efficiency is 89.3% at $100\text{mJ}/\text{cm}^2$. The shape of this curve shows a steep rise in efficiency until $10\text{mJ}/\text{cm}^2$ and the ability of record is comparable to that of the system recorded by He-Cd laser.

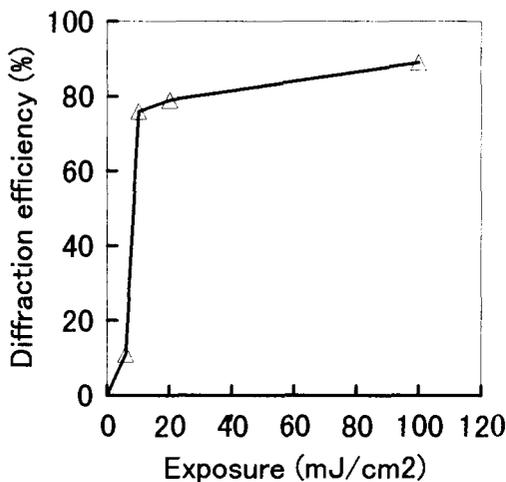


Fig. 3 Diffraction efficiency - exposure curve for the transmission holograms at 488nm.

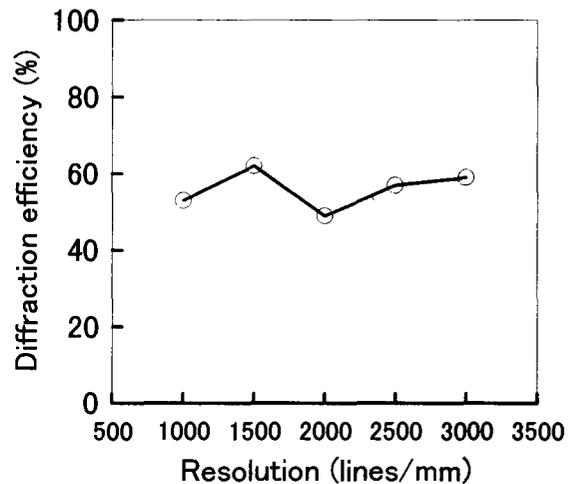


Fig. 4 Diffraction efficiency - resolution curve for the transmission holograms at 488nm.

4.3 The influence of resolution on record of grating pattern

The influence of resolution on transmission hologram recording was examined by using Ar ion laser with above same compositional materials. The result was showed in Figure 4. The diffraction efficiencies are kept approximately constant at $50\sim 60\%$ in wide range of resolutions from 1000 lines/mm to 3000 lines/mm. Thus, good performance for resolution was observed.

4.4 The observation by TEM

The grating pattern recorded in a hologram was observed by means of TEM. The sample was recorded by Ar ion laser(488nm) and was of 73% diffraction efficiency and $16 \mu\text{m}$ thickness. Figure 5 shows a vertical sectional view of the sample colored by lutonium acid. There was stripe pattern in the film thickness direction, and it was proven that the period was the about $0.7 \mu\text{m}$. Thus, the grating pattern based on the difference of refractive indexes was clearly observed. In general, it is considered that the coloring agent is linked with residue unsaturated groups of the monomer rich region than polymer region. We have previously revealed that the different of the molecular structure exist in the bright regions and the dark regions by infrared spectral analysis⁶⁾. The result of TEM are consistent with this one.

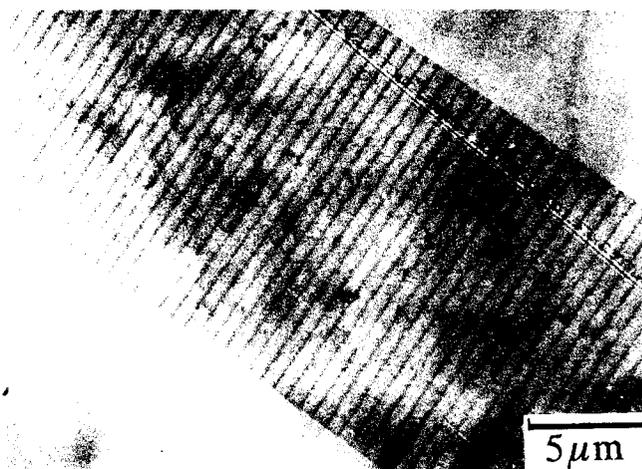


Fig. 5 TEM photograph of the transmission hologram recorded using 488nm Ar ion laser.

5. CONCLUSION

The photopolymerizable materials for recording holograms were described. These materials were found to be high-sensitivity, high-diffraction efficiency, high-resolution and high-transparency. The recording systems are self-developing and white light is sufficient for fixing. The obtained films were stable for solvents such as acetone, toluene, and THF. These results indicate that the three-dimensional network is formed in this hologram formation system.

References

1. R. T. Ingwall, H. L. Fielding, *Opt. Eng.*, 24, 808(1985).
2. A. M. Weber, W. K. Smothers, T. J. Troul, D. J. Mickish, *Proc. SPIE*, 1212, 30(1990).
3. M. Kawabata, A. Sato, I. Sumiyoshi, T. Kubota, *Appl. Opt.*, 33, 2152(1994).
4. T. Kumayama, N. Taniguchi, Y. Kuwae, N. Kusibiki, *Appl. Opt.*, 28, 2455(1989).
5. H. Tanigawa, T. Ichihashi, A. Nagata, *Kougaku*, 20, 227(1991).
6. T. Ichihashi, H. Tanigawa, K. Adachi, A. Nagata, *Chemistry Express*, 8, 633(1993).