

Title	Optimization of Holographic Polymer-Dispersed Liquid Crystals Using Siloxane-containing Materials
Author(s)	CHO, Yeong Hee; KIM, Nam; KAWAKAMI, Yusuke
Citation	Proceedings of SPIE, 5636: 475-482
Issue Date	2005-02
Type	Journal Article
Text version	publisher
URL	<a href="http://hdl.handle.net/10119/4961">http://hdl.handle.net/10119/4961</a>
Rights	Copyright 2005 Society of Photo-Optical Instrumentation Engineers. This paper was published in Yeong Hee CHO, Nam KIM, and Yusuke KAWAKAMI, Proceedings of SPIE, 5636, 2005, 475-482 and is made available as an electronic reprint with permission of SPIE. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper are prohibited.
Description	

# Optimization of Holographic Polymer Dispersed Liquid Crystals Using Siloxane-containing Materials

Yeong Hee CHO<sup>a</sup>, Nam KIM<sup>b</sup>, and Yusuke KAWAKAMI\*<sup>a</sup>

<sup>a</sup>School of Materials Science, Japan Advanced Institute of Science and Technology  
1-1 Asahidai, Tsurunokuchi, Ishikawa, Japan

<sup>b</sup>Dept. of Computer & Communication Eng., Chungbuk Nat'l Univ., 48 Gaeshin-dong, Heungduk-gu,  
Cheongju, Chungbuk 361-763, South of Korea

## ABSTRACT

Optimization of performance of holographic gratings was investigated by changing the chemical structures of photopolymerizable monomers, the LC content, and recording beam intensity, which strongly related to the control of kinetics of polymerization and phase separation of LCs.

High diffraction efficiency was obtained using 3-acryloxypropyltrimethoxysilane (APTMS) and 2-[(3,4-epoxycyclohexyl)ethyl]trimethoxysilane (ECTMS) as siloxane-containing reactive diluent by inducing a fast and good phase separation originated from the incompatible and flexible properties of siloxane chain even at a very low LC concentration (10~25wt%), in contrast to the case using diluent without siloxane component, like *N*-vinylpyrrolidinone.

The phase-separated morphologies of gratings, such as spacing and surface topology, were observed by atomic force microscopy (AFM). Very regular and smooth morphologies were observed for the formed holographic gratings with APTMS and various amounts of LC.

**Keywords:** Holographic polymer dispersed liquid crystal, phase separation, diffraction efficiency, siloxane-containing epoxides, ring-opening polymerization, volume shrinkage

## 1. INTRODUCTION

Polymer dispersed liquid crystals (PDLCs) are potential systems for a number of applications in electrooptical devices such as optical switches, reflective displays without polarizers, switchable windows, optical logic gates<sup>1-4</sup>. Recently, holographic techniques have been applied to these systems, in which liquid crystal (LC) domains are dispersed randomly in a polymer matrix, to give rise to switching and high diffraction efficiency<sup>5-6</sup>. These systems are known as holographic polymer dispersed liquid crystal (HPDLC) systems, consisted of periodic polymer rich layers and LC rich layers formed by interference of two laser beams, have drawn the attention by many physical chemists owing to their potential applications in graphic arts, security, and photonics<sup>7-8</sup>.

Generally, in HPDLC systems, it is very important to control the kinetics of polymerization, diffusion, and phase separation of LC to achieve high diffraction efficiency. Many research groups<sup>9-11</sup> have studied the mechanics of formation of holographic gratings by controlling the LC domain size, distribution, and shapes, and chemical structures of polymerizable materials.

In our previous study, siloxane-containing epoxides were found effective to induce clear phase separation during the formation of gratings, and to realize high diffraction efficiency and low volume shrinkage in HPDLC systems<sup>12</sup>. We have pointed out the importance of the chemical structures of photopolymerizable materials, and showed that siloxane-containing epoxides materials gave rise to the much clear phase separation derived from the incompatibility of the siloxane component with organic matrix materials.

In this research, efforts were focused on the optimization of performance of holographic gratings by varying the chemical structure of photopolymerizable materials with siloxane component, the LC content, and experimental conditions such as recording beam intensity.

## 2. EXPERIMENTAL

\*Correspondence: E-mail: kawakami@jaist.ac.jp; phone 0081 0761 51-1630; fax 0081 0761 51-1635

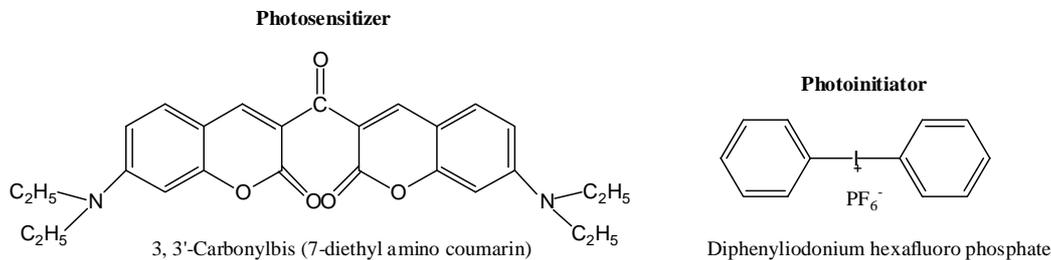
## 2.1 Materials for holographic recording

To tune the reaction rate and cross-linking density, multi-functional acrylate of trimethylolpropane triacrylate (TMPTA) was used as cross-linking monomer. As a reactive diluent, *N*-vinylpyrrolidone (NVP) and 3-acryloxypropyltrimethoxysilane (APTMS) capable of radical polymerization, benzyl glycidyl ether (BGE) and 2-[(3,4-epoxycyclohexyl)ethyl]trimethoxysilane (ECTMS) capable of ring-opening polymerization were used.

A commercial liquid crystal of E7 with cyano bi-terphenyl mixtures with high birefringence and adequate  $T_{NI}$  (nematic-isotropic transition temperature), which plays an important part in making the reaction solution, was used. LC contents in recording medium (photo-polymerizable compounds) were varied from 10wt% to 40wt%. Recording solution was injected into the glass cell with a gap of 14 $\mu$ m controlled by bead spacer.

## 2.2 Photosensitive solution

Photosensitive system of photo-initiator (PI) and photo-sensitizer (PS) is required to have a sensitivity to visible wavelength of Nd-YAG laser ( $\lambda=532$ nm) to generate the radical or cationic species. The following two diphenyliodonium hexafluorophosphate (AVOCADO research chemicals Ltd.) and 3, 3'-carbonylbis(7-diethylaminocoumarin) (Kodak) were selected as PI and PS, respectively<sup>13</sup>. Good points about this photosensitive system are the insensitivity of cationic polymerization against oxygen and the reaction according to a chemically amplified mechanism. The concentrations of the PI and PS to the recording medium were 0.5~3wt%, 0.1~1wt%, respectively.



## 2.3 Optical setup for hologram

Nd-YAG solid-state continuous wave laser with 532nm wavelength (Coherent Co. Verdi-V2) was used as the irradiation source as shown in Figure 1. The beams were collimated and expanded by spatial filters and lens, respectively. The inter beam angle was set to 16° against to the line perpendicular to the plane of the medium. Real-time diffraction efficiency was measured by monitoring the intensity of diffracted beam with the shutter closed at constant time interval during the hologram recording. After the hologram was recorded, diffraction efficiency was measured by rotating the hologram precisely by constant angle using motor-driven controller, with the shutter closed to cut-off the reference light, to determine the angular selectivity.

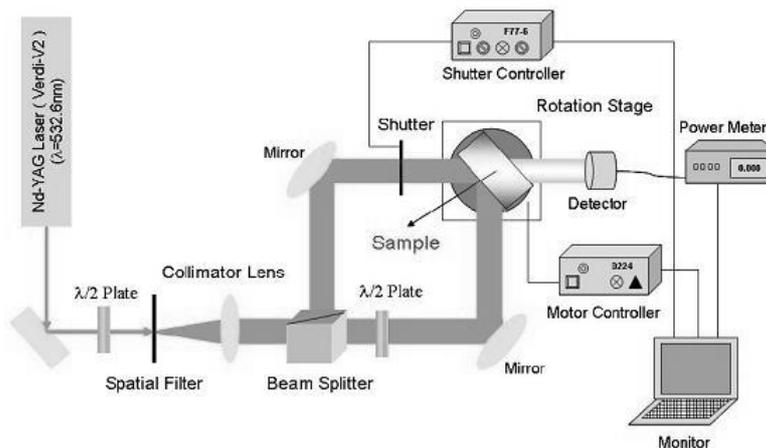


Figure 1. Experimental setup of the holographic recording and real-time reading.

Holographic gratings were fabricated under various experimental conditions, by changing laser intensity, irradiation time, and the optimum condition to obtain the high diffraction efficiency, high resolution, and excellent long-term stability after recording was established.

### 3. RESULTS AND DISCUSSION

#### 3.1 Effects of siloxane-containing materials as reactive diluents on real-time diffraction efficiency

Changes in real-time diffraction efficiency were measured to observe the diffraction efficiency, saturation time, and stability of holographic gratings. The diffraction efficiency was calculated as the ratio of the diffracted intensity by the holographic gratings to the transmitted intensity of glass substrate without gratings and plotted against to exposure times. Figure 2 shows the change in diffraction efficiency with exposing time in holographic gratings made from syrups with NVP as a reactive diluent by varying the LC contents (TMPTA : NVP= 30: 70 wt%). With this monomer diluent ratio, all samples had very low diffraction efficiency below 10%, their stability was not good, and holographic gratings showed irregular line. It should be noted that the cross-linking density is too low due to high loading of NVP, and results in the decrease of the driving force to push out LCs toward low intensity fringes and in the disruption of the support ability of gratings.

As increasing the LC contents from 10 wt% to 35 wt%, diffraction efficiency increased slightly due to more phase-separated LCs by the presence of more LCs, and at 40 wt% LC, the value was started to decrease. It means that syrups with more LC loadings have less reactive monomers, thus polymerization may not be accomplished to form the gratings. Much higher diffraction efficiency can be obtained by varying the ratio between TMPTA as cross-linkable monomer and NVP as reactive diluent, which related to the kinetics of polymerization and diffusion.

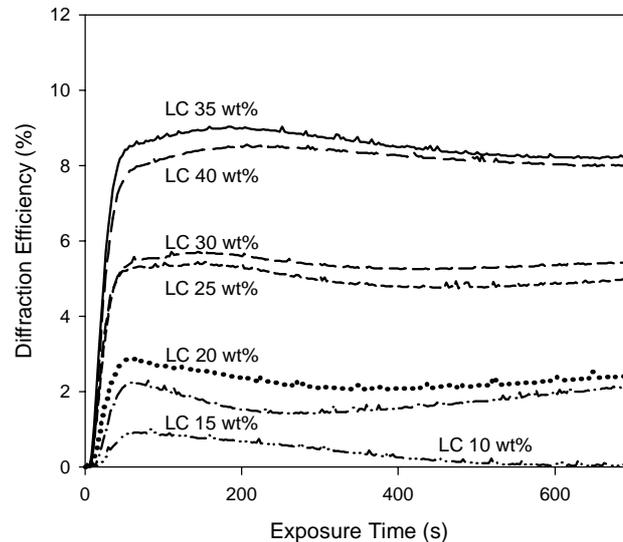


Figure 2. Dependence of diffraction efficiency on exposure time for holographic gratings prepared from NVP as a reactive diluent at various LC contents.

Figure 3 shows the evolution of holographic gratings of syrups with APTMS as a reactive diluent by varying the LC contents (TMPTA : APTMS= 30: 70 wt%). As mentioned above, by using the siloxane component in photopolymerizable syrups, phase separation should be induced between the LC and carbon based polymer matrix which now contained siloxane chain. A remarkable effect was observed in diffraction efficiency with over 80% APTMS, although very low cross-linking density caused the decrease in driving force for phase separation by elastic force of cross-linked system. It seems that siloxane component very strongly contributed to the phase separation of LCs. Of course, one can assume that difference of phase separation should be caused by difference of polymerization rate due to their different chemical structures. However, their difference should not be large because they have the same functional group. Therefore, siloxane component was considered to affect effectively on phase separation of LCs leading to high diffraction efficiency.

In Figure 2(a), as increasing the LC contents, diffraction efficiency was pronouncedly increased due to the generation of high modulation caused by good phase separation. In Figure 2(b), LC contents from 25 wt% to 40 wt%, diffraction efficiency had very high values and slowly decreased with the prolonged exposure time. With increasing the LC contents, maximum diffraction efficiency were shown at shorter exposure times, and decreased abruptly and pronouncedly. These results may be considered that with too much excess of phase separated LCs by too high loadings, collapse of the gratings occurred because the cross-linked polymer capable to support the gratings decreased, and refractive index modulation was also decreased by the presence of excess LC in polymer matrix as described above. The effects increased with increasing the LC contents.

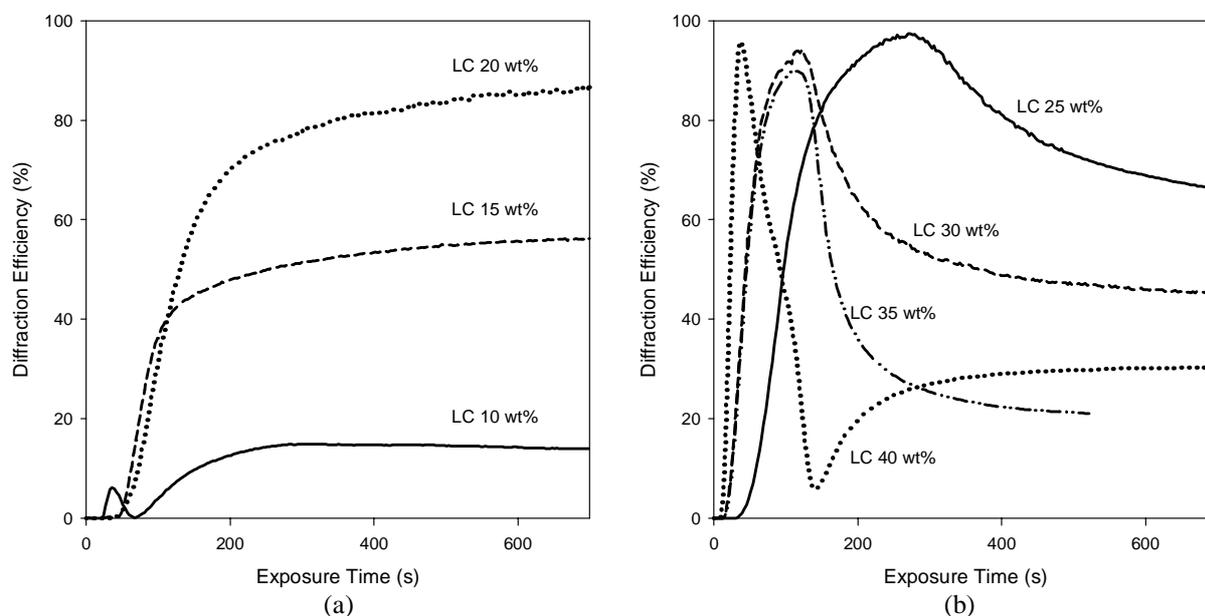


Figure 3. Dependence of diffraction efficiency on exposure time for holographic gratings prepared from APTMS at various LC contents; (a) low LC contents (10 wt% ~ 20 wt%) and (b) high LC contents (25wt% ~ 40 wt%).

Figure 4 shows the evolution of holographic gratings formed from epoxy functional materials capable of ring-opening polymerization as reactive diluents. To investigate the volume shrinkage caused by photopolymerization, epoxy function group was used as reactive diluents. When the BGE and ECTMS were used in fabrication of holographic gratings, their diffraction efficiencies were lower than that of NVP or APTMS capable of radical polymerization, respectively. It may be understood that in this photopolymerization system, cationic polymerization rate is slower than radical polymerization rate, thus pushing force the LCs toward low intensity fringes should be reduced that result in poor phase separation of LCs.

By using the ECTMS with siloxane component, diffraction efficiency became higher than BGE without siloxane component. As increasing the LC contents, diffraction efficiency was increased as shown in Figure 4(a), and was decreased in Figure 4(b). It means that in case of using BGE, phase separation may not be good, thus much more LCs should be needed in generation of modulation, but in case of ECTMS, good phase separation may be occurred due to its flexibility and incompatibility of siloxane chain, thus less LC (with more cross-linkable monomer) seem to be efficient on formation of holographic gratings. All formed gratings were stable against the laser light during the holographic recording. Therefore these results confirmed that addition of ECTMS with siloxane component as a diluent gave better phase separation. However ultimate diffraction efficiency was not as high as APTMS.

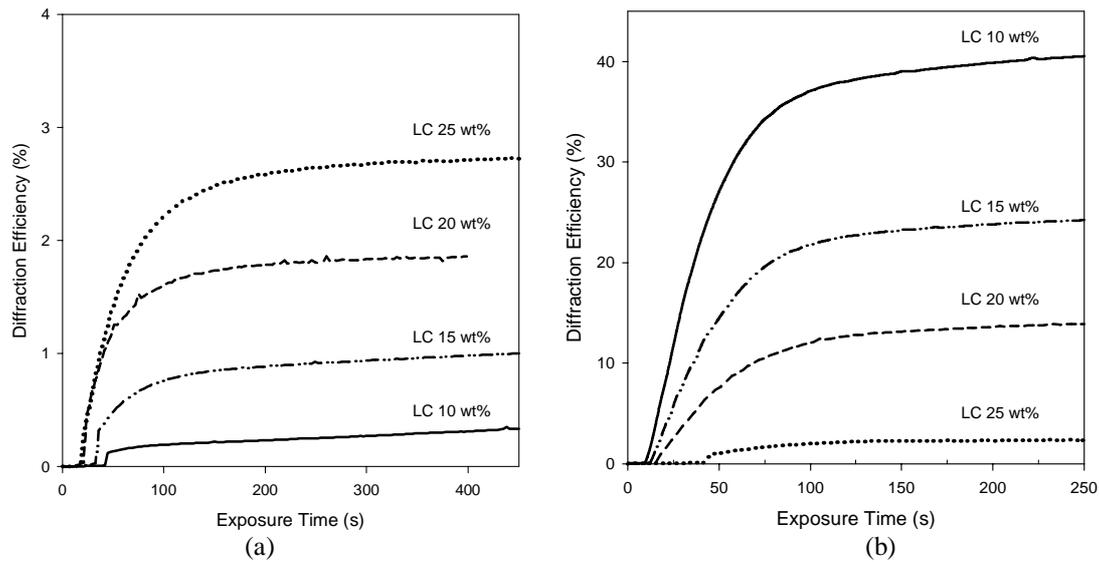


Figure 4. Dependence of diffraction efficiency on exposure time for holographic gratings prepared from epoxy function materials as a reactive diluents at various LC contents; (a) BGE and (b) ECTMS.

### 3.2 Angular Selectivity

When the multiplex hologram is recorded it is necessary to know the angular selectivity width. The smaller the value the more multiplex data or gratings can be recorded.

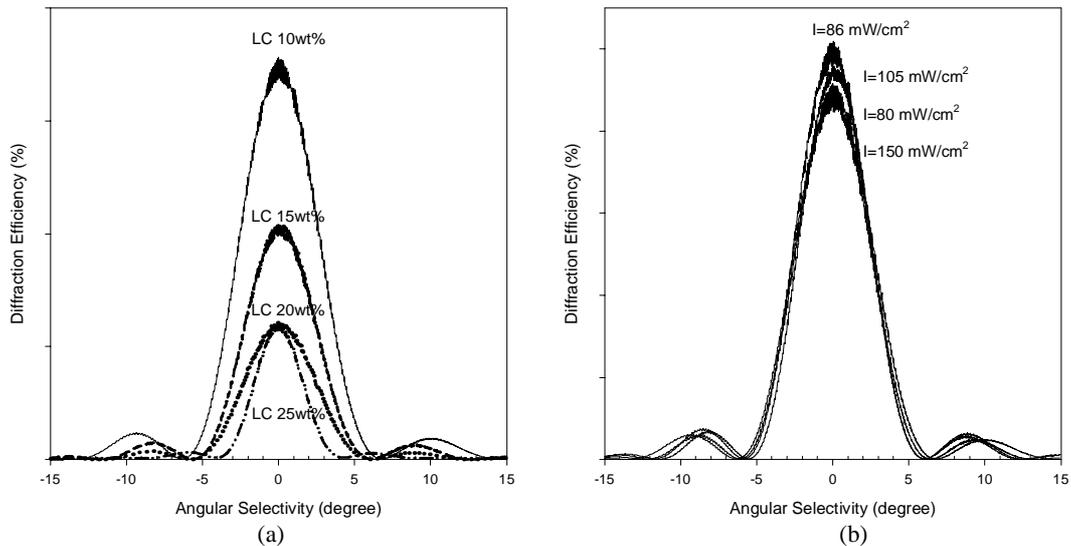


Figure 5. Angular selectivity for holographic gratings prepared from ECTMS in (a) various LC contents and (b) various exposure intensity.

As shown in Figure 5 angular selectivity widths were decreased with increasing the LC contents (about 5°~6°). According to the Kogelnik's coupled wave theory<sup>14</sup>, modulation of refractive index is dependent on the contrast of refractive index and the thickness of the sample. LCs enhance the contrast of refractive index but diffraction efficiency decreased. Adjustment of sample thickness is needed to enhance the efficiency of the sample with 25wt% LC, which showed the sharpest angular selectivity. In Figure 5(b), there is almost no difference of angular selectivity according to

exposure intensity due to similar of refractive index modulation.

### 3.3 Morphology

3D topologies and profiles of AFM of holographic gratings formed from APTMS and ECTMS with siloxane component as reactive diluents were observed as shown in Figure 6. Well-fabricated holographic gratings were observed and in case of using APTMS very regular and clean morphologies were observed at every LC contents.

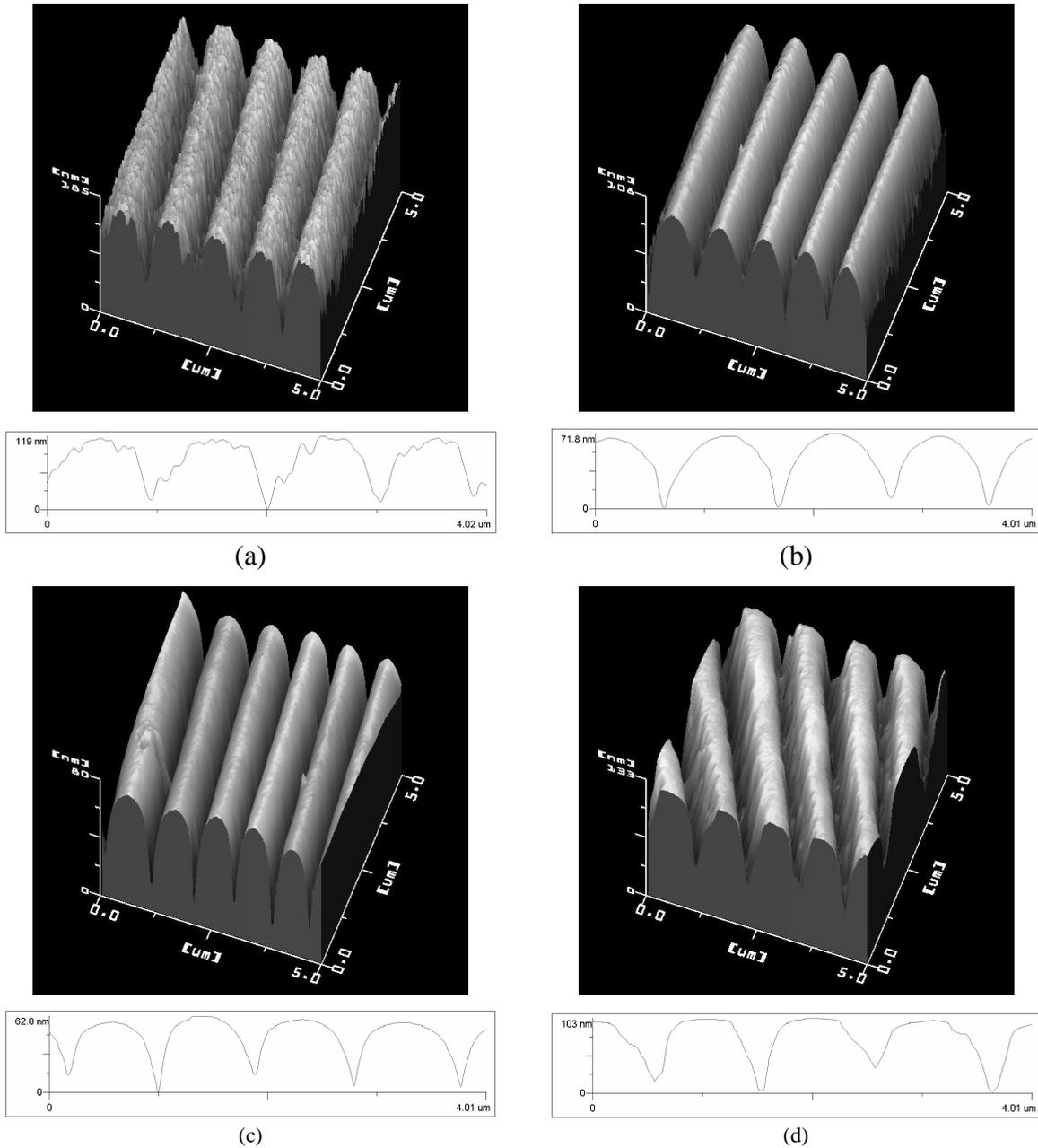


Figure 6. 3D topologies and profiles of AFM of holographic gratings prepared from (a) ECTMS with LC content of 15wt%, (b) APTMS with LC content of 15wt%, (c) APTMS with LC content of 20wt%, and (d) APTMS with LC content of 30wt% (all samples were taken without LC extraction).

To improve the volume shrinkage, epoxy materials capable of ring-opening polymerization were introduced, but there is no difference in grating spacing relating volume shrinkage between Figure 6(a) and Figure 6(b), indicating that reactive diluent effects scarcely in volume shrinkage due to its mono-function group. In both case, grating spacings were about 1.0  $\mu\text{m}$ , this value is a good agreement of theoretical value of 0.965  $\mu\text{m}$  according to Bragg's law ( grating spacing,  $\Lambda = \lambda / 2\sin\theta$ , in this experiment,  $\lambda$  is 532 nm and  $\theta$  is 16 degree).

By varying the LC contents with APTMS ( Figure 6(b)~Figure 6(d) ), surface topologies like sinusoidal patterns were changed very interestingly. As increasing the LC contents, the crests of periodic pattern became smooth as shown in their profiles due to more LCs phase-separated by much loading of LCs. According to diffraction efficiency in Figure 3, the finest morphology of holographic gratings having highest diffraction efficiency in final gratings was observed in LC content of 20wt%, and in LC content of 30 wt%, its morphology was not good owing to low diffraction efficiency caused to low modulation of refractive index.

To observe the behavior and degree of phase separation of LCs, and polymer film formation from reaction monomers, AFM topologies were observed before and after the extraction of LCs with methanol as shown in Figure 7. Holographic gratings with regularly phase-separated morphologies between the high intensity fringe regions and the low intensity fringe regions according to interference light pattern were observed. In morphology removed the LCs (Figure 7(b)), polymer film was also formed very clearly. We assume that the difference of profile volume of sinusoidal pattern means the degree of phase separation of LCs on surface of holographic samples.

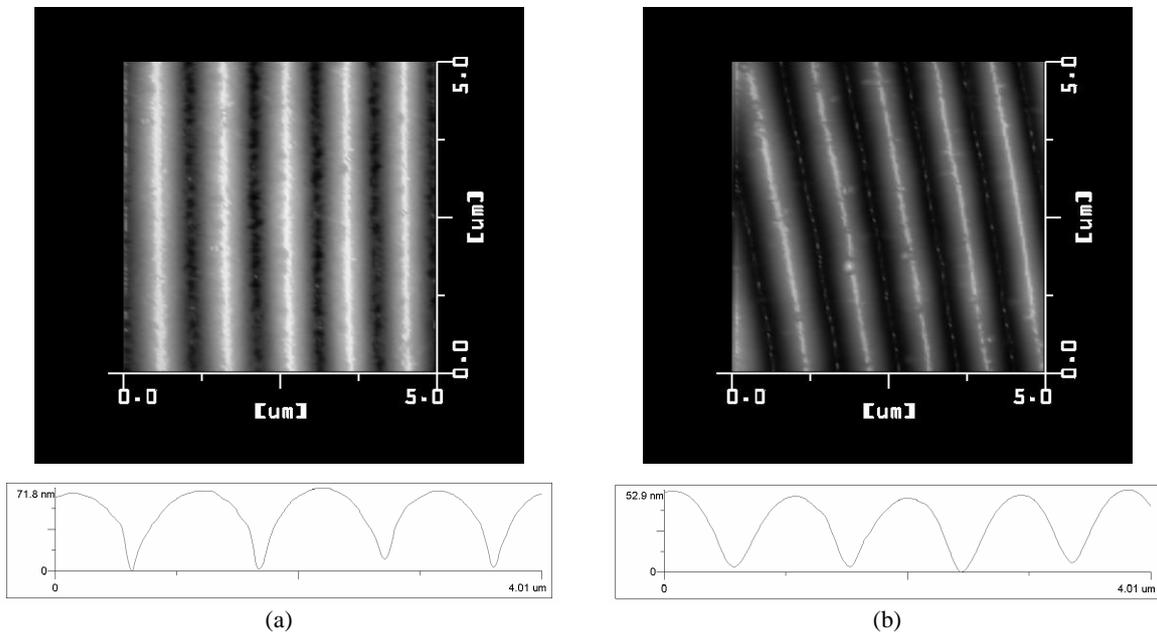


Figure 7. Surface topologies and profiles of AFM of holographic gratings prepared from structure D with LC content of 15wt%; (a) before extraction of LC and (b) after extraction of LC.

#### 4. CONCLUSION

We have demonstrated the effects of siloxane component in photopolymerizable materials as reactive diluents on performance of holographic gratings at various LC contents.

By controlling the reaction rate and degree of phase separation of LC, optimum condition with high diffraction efficiencies, angle selectivity widths of  $<6^\circ$ , and good morphologies were developed.

High diffraction efficiency was obtained in case of using 3-acryloxypropyltrimethoxysilane (APTMS) and 2-[(3,4-epoxycyclohexyl)ethyl]trimethoxysilane (ECTMS) with siloxane component as reactive diluents by inducing a fast and good phase separation due to their incompatibility and flexibility properties of siloxane chain even though at a very low LC concentration (10~25wt%) in contrast with without siloxane component materials.

Very regular and clean morphologies of holographic gratings formed from APTMS were observed at most of LC contents.

## REFERENCES

1. H.M.J. Boots, J.G. Kloosterboer, C.Serbutoviez, and F.J. Touwslager, "Polymerization-Induced Phase Separation. 1. Conversion-Phase Diagrams", *Macromolecules*, **29**, 7683-7689, 1996.
2. B.J. Luther, G.H. Springer, and D.A. Higgins, "Templated Droplets and Ordered Arrays in Polymer-Dispersed Liquid-Crystal Films", *Chem. Mater.*, **13(7)**, 2281-2287, 2001.
3. T. Kyu and D. Nwabunma, " Simulations of Microlens Arrays Formed by Pattern-Photopolymerization-Induced Phase Separation of Liquid Crystal/Monomer Mixtures", *Macromolecules*, **34(26)**, 9168-9172, 2001.
4. S. Kubo, Z.Z. Gu, K. Takahashi, Y. Ohko, O. Sato, and A. Fujishima, "Control of the Optical Band Structure of Liquid Crystal Infiltrated Inverse Opal by a Photoinduced Nematic-isotropic Phase Transition", *J. Am. Chem. Soc.*, **124(37)**, 10950-10951, 2002.
5. M.S. Park, Y.H. Cho, B.K. Kim, and J.S. Jang, "Fabrication of Reflective Holographic Gratings with Polyurethane Acrylates (PUA)", *Curr. Appl. Phys.*, **2(3)**, 249-252, 2002.
6. M.S. Park, B.K. Kim, and J.C. Kim, "Reflective Mode of HPDLC with Various Structures of Polyurethane Acrylates", *Polymer*, **44(5)**, 1595-1602, 2003.
7. J. Zhang, C.R. Carlen, S. Palmer, and M.B. Sponsler, "Dynamic Holographic Gratings Recorded by Photopolymerization of Liquid Crystalline Monomers", *J. Am. Chem. Soc.*, **116**, 7055-7063, 1994.
8. T.J. Bunning, L.V. Natarajan, V.P. Tondiglia, and R.L. Sutherland, "Holographic Polymer-Dispersed Liquid Crystals (H-PDLCs)", *Annu. Rev. Mater. Sci.*, **30**, 83-115, 2000.
9. R.T. Pogue, L.V. Natarajan, S.A. Siwecki, V.P. Tondiglia, R.L. Sutherland, and T.J. Bunning, "Monomer Functionality Effects in the Anisotropic Phase Separation of Liquid Crystals", *Polymer*, **41**, 733-741, 2000.
10. C.R. Fernandez-Pousa, R. Mallavia, and S. Blaya, "Holographic Determination of the Irradiance Dependence of Linear-chain Polymerization Rates in Photopolymer Dry Films", *Appl. Phys. B*, **70**, 537-542, 2000.
11. C.F. van Nostrum, R.J.M. Nolte, D.J. Broer, T. Fuhrman, and J.H. Wendorff, "Photoinduced Opposite Diffusion of Nematic and Isotropic Monomers during Patterned Photopolymerization", *Chem. Mater.*, **10(1)**, 135-145, 1998.
12. Y.H. Cho, M. He, B.K. Kim, and Y. Kawakami, "Improvement of Holographic Performance of by Novel Photopolymer Systems with Siloxane-containing Epoxides", *Science and Technology of Advanced Materials*, **5**, 319-323, 2004.
13. Jean Pierre Fouassier and Fabrice Morlet-Savary, "Photopolymers for Laser Imaging and Holographic Recording: Design and Reactivity of Photosensitizers", *Optical Engineering*, **35**, 304-312, 1996.
14. H. Kogelnik, *Bell Syst. Tech. J.*, **48**, 2909-2947, 1969.