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Author(s)	He, Man; Cho, Yeong Hee; Kim, Nam; Kawakami, Yusuke
Citation	Proceedings of SPIE, 5636: 560-567
Issue Date	2005-02
Type	Journal Article
Text version	publisher
URL	<a href="http://hdl.handle.net/10119/4962">http://hdl.handle.net/10119/4962</a>
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Description	

# Formation and Characterization of Transmission Holographic Gratings Obtained Using a Novel Siloxane-containing Liquid Crystal

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## ABSTRACT

Liquid crystalline compounds with a siloxane component in the tail were found to be effective in the formation of holographic gratings of polymer dispersed liquid crystal systems over a wide concentration range from 3wt% to 30wt%. The structure of the siloxane chain had a big effect on the performance of the gratings. Fine gratings with a diffractive efficiency of 40wt% could be formed with a liquid crystalline compound containing 3wt% disiloxane

**Keywords:** Holographic Polymer Dispersed Liquid Crystals, Disiloxane, Phase Separation.

## 1. INTRODUCTION

Switchable holographic gratings-holographic polymer dispersed liquid crystals (HPDLCs) have been widely studied as promising new recording and display media. HPDLCs gratings are recognized as the most efficient materials for holographic storage, because they provide a simple, fast, and solvent-free recording process<sup>1</sup>. A fine grating with high diffraction efficiency, which diffracts light with a specific wavelength according to Bragg's law, can be created through the efficient modulation of the refractive index by taking advantage of the large difference in the refractive index between LC and polymer matrix. Very fine droplets with uniform size and dispersion are required to obtain high diffraction efficiency.

Current studies of HPDLCs have mainly focused on photo-reactive monomers<sup>2-3</sup> since the polymerization process determined the final character of the grating, but definite improvement has not been achieved due to unclear phase separation. Recently, siloxane-containing compounds have attracted interest due to their excellent performance in grating formation<sup>4</sup>. High contrast gratings with high diffractive efficiency have been created with such compounds, which indicated the long-term stability, and flexible and immiscible character of the siloxane chain might play an important role in creating fine gratings by a phase separation process. It was expected that the bulky, highly flexible siloxane tail would cause a reduction in the strength of the LC and polymer matrix due to increased chemical incompatibility, which might lead to a fast and distinct phase separation.

In our previous study, it was confirmed that the presence of a siloxane chain in diluent and monomer could give a clear phase separation. In this study, we have extended that work to siloxane-containing liquid crystals with the aim of creating more distinct phase separation and more efficient gratings.

## 2. EXPERIMENTAL

### 2.1 Materials used in holographic curing

The chemical structures of the components used in the syrup are given in (Fig. 1). *N*-vinylpyrrolidone(NVP) and trimethylolpropane triacrylate (TMPTA) were obtained from Aldrich Chemical and used as received.

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The photoinitiator, Rose Bengal (RB), and the co-initiator *N*-phenyl glycine (NPG) were obtained from Kanto Chemical and used without further purification.

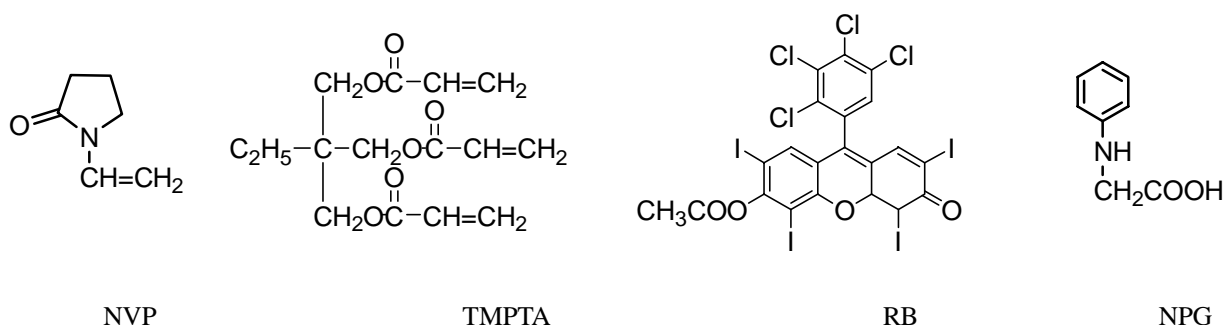


Figure 1. Chemical structures of the components in the holographic ingredient: *N*-vinylpyrrolidone (NVP), Trimethylolpropane triacrylate(TMPTA), photoinitiator Rose Bengal (RB), and the co-initiator *N*-phenyl glycine (NPG).

The control LC sample, E7, is a eutectic mixture of 4-cyanobiphenyl, 4-pentyl-4'-cyanobiphenyl, 4-heptyl-4'-cyanobiphenyl, 4-octoxy-4'-cyanobiphenyl and 4-pentyl-4'-cyano-*p*-terphenyl.

In order to study the effect of the siloxane chain on the formation of transmission gratings, a SLC (shown in Fig. 2) was chosen for present study, which was based on 4-methoxyphenyl 4-butenyloxybenzoate moiety, synthesized as reported <sup>5</sup>.

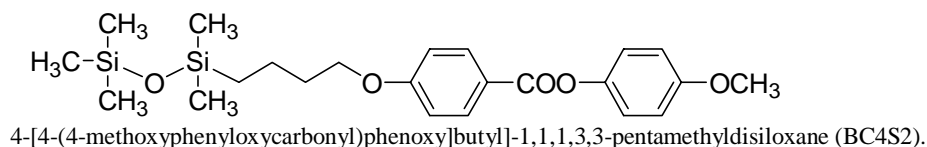
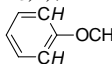
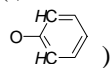
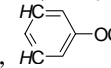
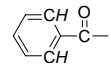


Figure 2. Chemical structure of siloxane-containing compound (BC4S2)

The crude product was purified by HPLC to yield the product in 90 % yield. The sample was characterized by <sup>1</sup>H-NMR and polarized optical microscopy (POM). <sup>1</sup>H-NMR chemical shifts (CDCl<sub>3</sub>, 500MHZ)

$\delta$  0.08 (s, 9H, OSi(CH<sub>3</sub>)<sub>3</sub>),  $\delta$  0.09 (s, 6H, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>),  $\delta$  0.64 (m, 2H, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>),  $\delta$  1.55(m, 2H, CH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>),  $\delta$  1.85(m, 2H, OCH<sub>2</sub>CH<sub>2</sub>),  $\delta$  4.00(t, J=6.8Hz, 2H, OCH<sub>2</sub>),  $\delta$  3.82 (s, 3H, CH<sub>3</sub>O),  $\delta$  6.92 (d, J=9.14Hz, 2H, ) ,  $\delta$  6.98 (d, J=8.92Hz, 2H, ) ,  $\delta$  7.12 (d, J=8.92Hz, 2H, ) ,  $\delta$  8.15 (d, J=8.69Hz, 2H, ) ).

## 2.2 Fabrication of holographic grating

The photopolymerizable mixture was prepared under diminished UV-free lights to eliminate any unexpected photopolymerization before holographic recording. The mixtures consisted of reactive monomer TMPTA, photoinitiator RB, co-initiator NPG and diluents solvent NVP with varying weight concentration ratio.

Typical weight percents of the mixtures are: TMPTA ranging from 72wt% to 9wt%, NVP ranging from 18wt% to 81wt%, and siloxane-containing compound was 10wt%. Each mixture was vigorously stirred for about 5 min to gain a clear homogeneous solution, and dropped into the space between two glass sliders separated by 14 $\mu$ m, to control the thickness of the sample.

Holographic transmission gratings were formed by two coherent beams of a Nd-YAG laser ( $\lambda = 532.6\text{nm}$ ) of equal intensity with a true power of 30mV. The angle between two illuminated beams was about  $32^\circ$ ; the recording time was 6min. After recording, all the glass cells were post-cured under a UV lamp for about 5 min to complete the photo-polymerization of the remaining functional groups.

### 2.3 Analysis of grating morphology and diffraction efficiency

Several analysis techniques were used to characterize the HPDLC gratings. AFM was used to examine the surface topology of the transmission grating. Samples used here were prepared by freeze-fracturing the HPDLC cells, using liquid nitrogen and extracting the SLC with reagent grade ethanol. Before analysis, all samples were again flushed with ethanol to remove the remaining SLC. Angle selectivity and real time efficiency studies were performed, to study the optical character of the gratings.

In the case of a simple transmission grating, the diffraction efficiency can be calculated as the ratio of diffraction intensity ( $I_d$ ) to the transmitted intensity ( $I_o$ ).

$$\eta (\%) = I_d / I_o \times 100$$

where  $I_d$  is the diffraction beam intensity,  $I_t$  is the transmitted beam intensity and  $I_o$  is the total transmitted beam intensities ( $I_d + I_t$ ) after recording.

## 3. RESULTS AND DISCUSSION

### 3.1 The effect of BC4S2 on grating morphology

By carefully controlling the concentrations of the matrix and siloxane-containing liquid crystal (BC4S2), we have successfully written HPDLC grating in samples. The resulting grating was examined in its original state in order to study the nature of the grating film and other optical performance measures. Fig. 3(a) shows the 3-D morphology and depth profile of the original grating sample fabricated from 90wt% matrix (TMPTA:NVP=4:6) and 10wt% BC4S2.

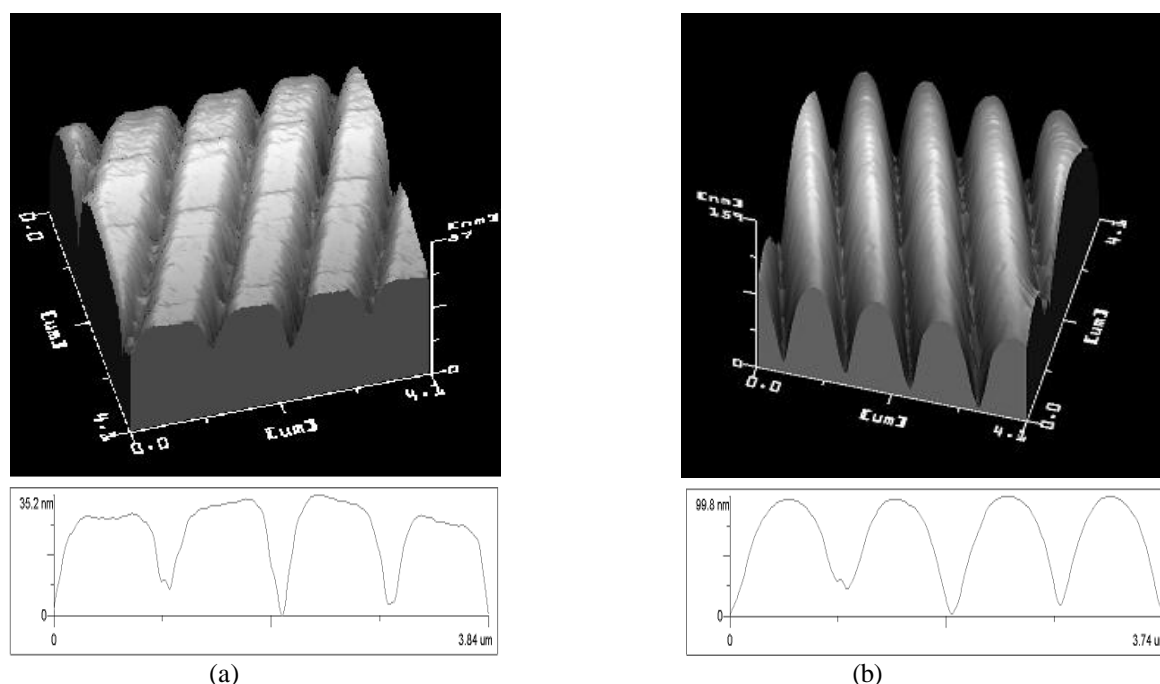


Figure 3. The AFM morphology and depth profile of the grating obtained with BC4S2 (a) before and (b) after washing with ethanol.

Fig. 3(b) shows the morphology of the grating after washing with ethanol to remove BC4S2. A clear grating morphology of a periodic interference fringe pattern can be observed. The evenly stratified composite film with periodic alternating layers is attributable to the effective phase separation of BC4S2 from matrix polymer. These pattern lead to the diffraction of light at a specific wavelength, in accordance with Bragg's law. The hilltop region is considered as the polymer region covered with some SLC. This flat and shallow morphology strongly suggests that after the gelation of the polymer, a part of the remaining SLC diffused out from the polymer matrix region and attached to the polymer surface, due to the mobility of the SLC and chemical incompatibility between the SLC and the polymer. In Figure 3 (a) and (b), similar spacing of grating is observed as  $0.96\mu\text{m}$  and  $0.93\mu\text{m}$  before and after removal of the SLC, and the depth of grating is much deeper ( $99\text{nm}$ ) after washing than that before washing ( $35\text{nm}$ ).

### 3.2 The effects of NVP concentration on diffraction efficiency with 10wt% liquid crystalline compound.

Diffraction efficiency is the most the important optical performance measure for gratings. It is controlled by the balance between phase separation through the diffusion of LC and the polymerization rate of multi-functional acrylate (TMPTA)<sup>6</sup>. Achieving a perfect phase separation to give a distinct grating requires a strong elastic driving force caused by cross-linking and fast diffusion of the LC. Increasing NVP concentration will reduce the high cross-linking density (NVP<45wt% in mixture) decreases phase separation by shortening the gelation time of the polymer; thus, though the elastic driving force is strong, most SLC had been retained in the polymer, hence, the index modulation is reduced. Under low NVP concentration (<45wt%), the diffraction efficiency was typically <13% (Fig. 4(a)). When NVP concentration is increased to 72wt % (Fig. 4(b)), the diffraction efficiency reached 38% and slightly increased if we prolonged curing time. This result seems to suggest that increasing NVP concentration will enhance the phase separation by increasing the diffusion rate of BC4S2. The slight increase of diffraction efficiency is caused by the slow polymerization of NVP, or by the diffusion of SLC from the gelled polymer. It was found that in the case of gratings made with E7 (10wt%) and with same concentration of NVP, the diffraction efficiency was no more than 10% and no visible increase of diffraction efficiency could be found. Thus, we concluded that under high NVP concentrations, SLC can be effectively separated from the polymer region to produce a high contrast grating, due to the high mobility of SLC, and the strong chemical incompatibility between SLC and polymer; the slightly increased diffraction efficiency is the result of the diffusion of SLC from the gelation polymer.

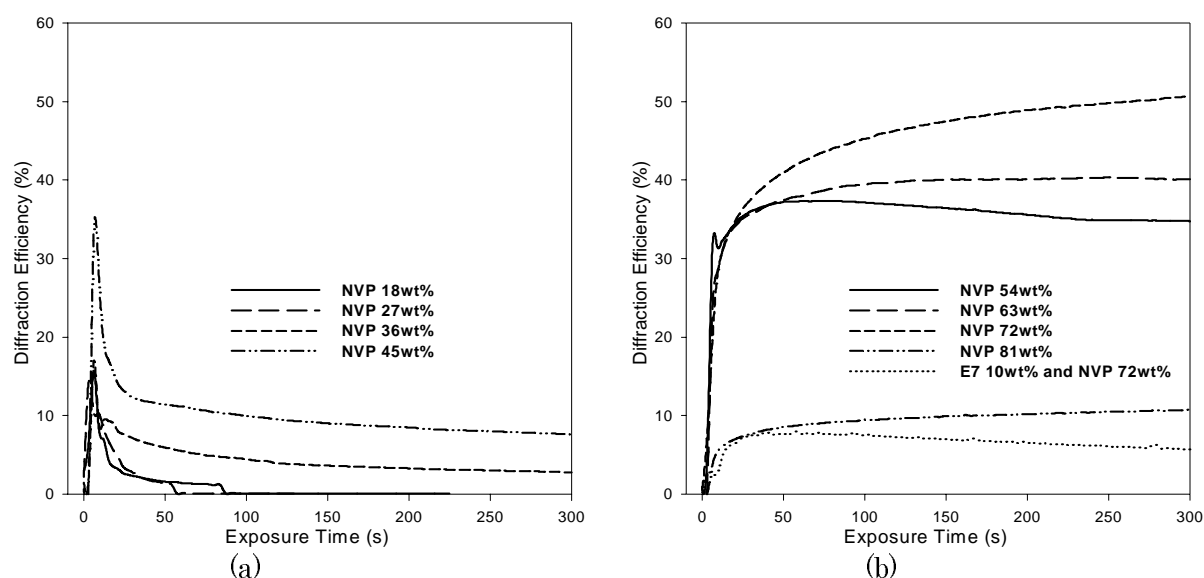


Figure 4. The real-time efficiency of grating made with BC4S2 and with (a) low NVP concentration, (b) high NVP concentration.

Typical AFM morphologies were shown in Fig. 5. In Fig. 5, a significant difference in surface morphology was observed. Compared with gratings made with E7 (Fig. 5(a)), a more even and smooth surface was observed in the gratings made with BC4S2 with the same concentration (Fig. 5(b)), which is considered to be caused by effective and distinct phase separation. Apparently more even and smooth morphology was observed for grating made with 45wt% NVP (Fig. 5(c)). Moreover, it was found by the precise analysis of the AFM profile of Fig. 5(b), the spacing of grating being approximately  $0.83\mu\text{m}$ , which is in excellent agreement with the calculated spacing of  $0.86\mu\text{m}$  by Bragg's equation. These facts indicated that the SLC are confined to the Bragg planes in the grating made with 72 % NVP. The consequent, result in efficient modulation of the refractive index, and the high diffraction efficiency could be obtained from grating made with 10wt% BC4S2 and 90wt% matrix (TMPTA:NVP=2:8, NVP 72 % in mixture). Although apparently smoother surface was observed in the grating of Fig. 5(c), the diffraction efficiency of the grating was much lower than the grating of Fig. 5(b).

Although the gratings formed with 72wt% NVP gave high diffraction efficiency, it was not stable for long-term storage. Those formed with 54 and 45% NVP were stable for a long time. The optimum concentration of NVP with 10% BC4S2 seems to be around 50%.

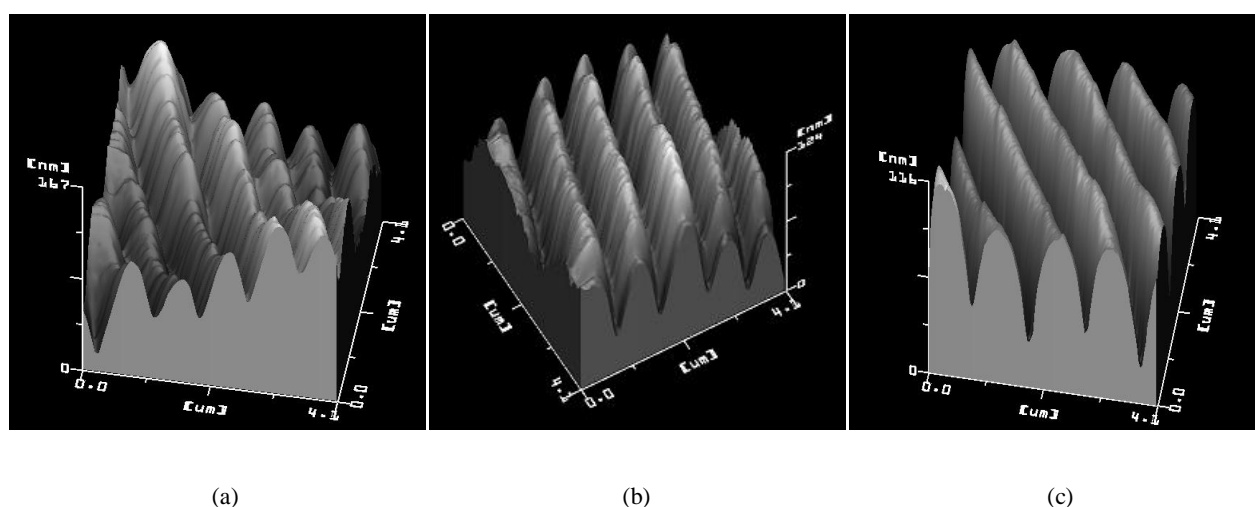


Figure 5. AFM morphology of grating made by (a) E7 10 wt%, NVP 72 wt%, (b) BC4S2 10 wt%, NVP 72 wt%, (c) BC4S2 10 wt%, NVP 45wt%, respectively.

### 3.3 The effect of SLC concentration on diffraction efficiency

Using the matrix (TMPTA:NVP=2:8), the effect of concentration of BC4S2 on the grating performance was studied. In order to create the alternating layers of LC and polymer, or produce the final modulation of the refractive index, sufficient amounts of separated LC is usually required. Generally, for grating formation, the LC loading is about 30wt%<sup>7</sup>, and never lower than 16wt%<sup>6</sup>. However, in our present study, it was observed that gratings could be formed with a wide SLC concentration range from 3wt% to 30wt%, and even the highest diffraction efficiency was observed with SLC ranging 3 to 10wt%. Moreover, as seen in Fig.6 no significant change in diffraction efficiency was observed when grating was made with low BC4S2 concentration (<20wt%). Only a little amounts of SLC could cause an effective modulation of the refractive index, which perhaps due to the high mobility and strong chemical incompatibility of SLC leading to a clear and effective phase separation. Interestingly, it was found that when the concentration of SLC was increased higher than 20wt%, the diffraction efficiency decreased. This might due to background scattering of the remaining SLC in the polymer matrix. The AFM morphology supported our hypothesis as well.

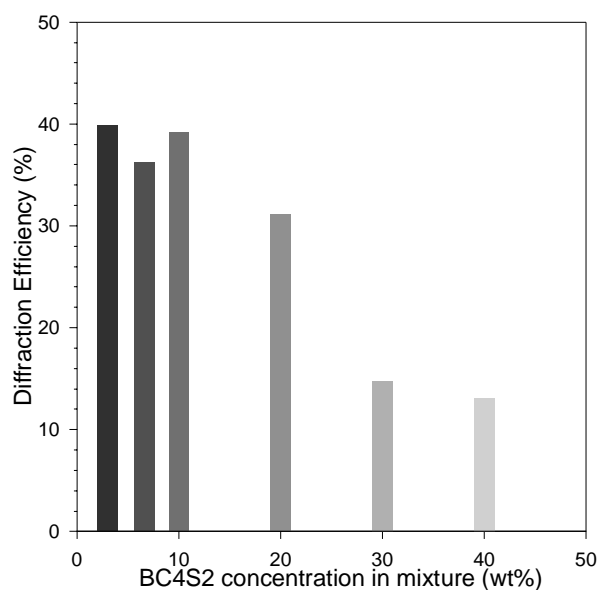
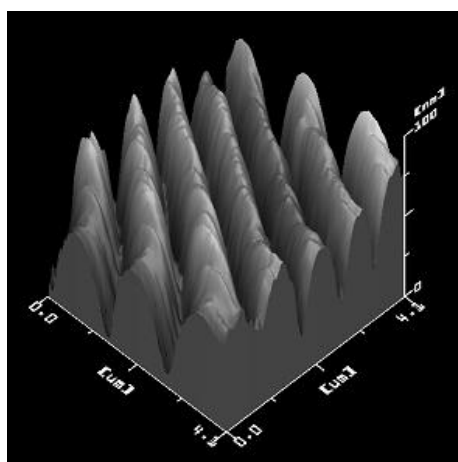
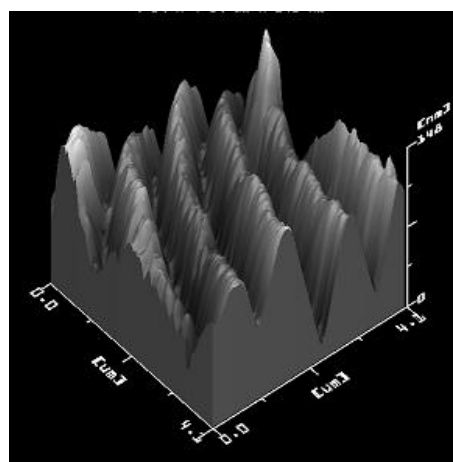


Figure 6. The effect of BC4S2 concentration on diffraction efficiency.

It was found that gratings made with BC4S2 in low and high concentration displayed a very similar morphology. As shown in Fig.7, the gratings made with 3 and 30wt% BC4S2 have quite similar morphology, but the irregular and coarse surface of the grating made with 30wt% BC4S2 (Fig. 7(b)) is somewhat rude. Much BC4S2 seemed to remain in the loosely cross-linked polymer matrix, which is easily removed by washing, is considered as the main reason of decreasing the diffraction efficiency by defective index modulation and background scattering. This situation seems also similar for the case of Figure 5(c), in which only excess BC4S2 existing on the surface of highly cross-linked polymer matrix were removed by washing keeping smooth morphology of the surface.



(a)



(b)

Figure 7. AFM morphology of gratings made with (a) 3wt% BC4S2, (b) 30wt% BC4S2.

### 3.4 The effect of irradiation power on the diffraction efficiency

According to Kogelnik's coupled wave theory, the diffraction efficiency will change as a sinusoidal pattern according to the different index modulation, which can be controlled by the polymerization rate. From Fig.8 we can see that with increasing the irradiation power, the diffraction efficiency changes approximately as the sinusoidal pattern. This slight change of diffraction efficiency was considered to occur periodically by changing the power by changing the polymerization rate and diffusion of SLC, simultaneously.

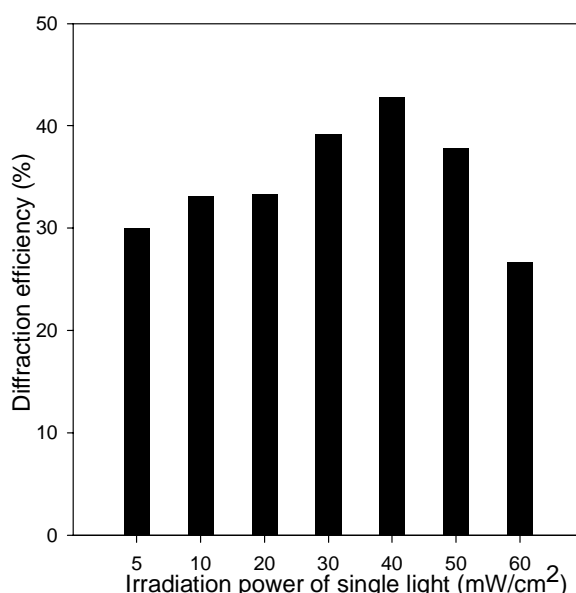


Figure 8. The effect of irradiation power on diffraction efficiency.

### 3.5 The angle selectivity of grating made with BC4S2

The (external) Bragg angle obtained from the grating made with BC4S2 is in good agreement with the experimental incident angle of about 16°. Moreover, the angle selectivity was found about 5 degree. All these results strongly suggest that the siloxane modified LC enhances the phase separation; the phase separated SLC was confined to the Bragg plane, which produce grating with high diffraction efficiency and angle selectivity.

## 4. CONCLUSION

This study has confirmed that the presence of a siloxane spacer at the polymer-SLC interface dramatically increases the diffraction efficiency of a holographic grating, due to the effective phase separation caused by the chemical incompatibility between the SLC and the polymer. Transmission gratings with a diffraction efficiency of 40% can be formed even with NVP 72wt% and SLC 10wt%. Moreover, it was found that gratings could be made with a wide SLC concentration range, from 3wt% to 30wt%, and no visible change in diffraction efficiency was observed in the case of low SLC loading. High NVP concentrations were found to significantly promote the diffraction efficiency. All results strongly indicated that by substituting E7 with SLC, the phase separation of the grating was greatly enhanced, which led to an increase in diffraction efficiency. Under high NVP concentration, the effective phase separation is considerable primarily caused by the soft, bulky, but incompatible siloxane chain structure.



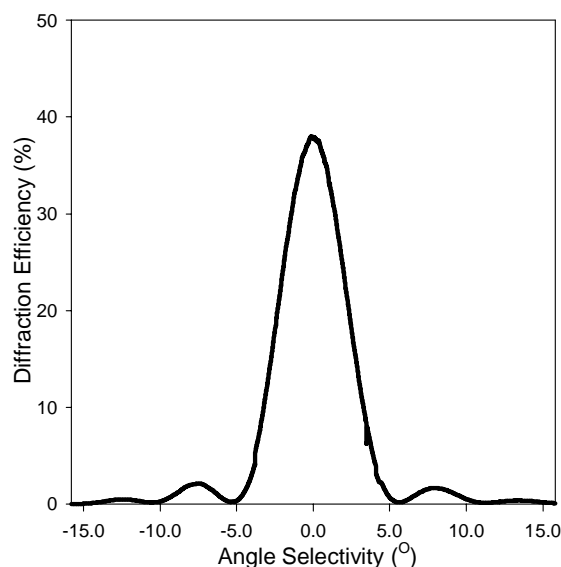


Figure 9. Angle selectivity of the grating made with BC4S2.

### ACKNOWLEDGEMENT

This work was partly supported by a Grant-in-Aid for Scientific Research (16205016) from the Ministry of Education, Science, Sports, Culture and Technology, Japan.

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