Control of morphology and diffraction efficiency of holographic gratings using siloxane-containing reactive diluent

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Abstract

Performance of holographic gratings, prepared by using epoxy-functionalized siloxane compound as a reactive diluent, was compared with that using N-vinylpyrrolidinone as a diluent in the presence of various contents of liquid crystal under different exposure beam intensity. Siloxane component strongly influenced the kinetics of polymerization, diffusion, and phase separation of the liquid crystalline compound, and high diffraction efficiency was obtained when 3-acryloxypropyltrimethoxysilane or 2-[(3,4-epoxycyclohexyl)ethyl]trimethoxysilane was used as a reactive diluent even at a very low concentration (10–25 wt%) of commercial liquid crystal mixture, E7 (Merk), in contrast to the case with N-vinylpyrrolidinone or benzyl glycidyl ether as the diluent without siloxane component.

The phase-separated morphologies of gratings, such as spacing and surface topology, observed by SEM and AFM, were well controlled, and very regular and smooth morphologies were observed for the holographic gratings prepared with 3-acryloxypropyltrimethoxysilane and various contents of the liquid crystal.

Keywords: Holographic polymer dispersed liquid crystal; Submicron size LC droplets; Phase separation; Holographic gratings; Diffraction efficiency; Siloxane component; Incompatibility

1. Introduction

Much attention has been devoted to the polymer dispersed liquid crystal (PDLC) systems due to their potential applications in electro-optic technology, such as optical switches, reflective displays without polarizer, switchable windows, and many other display devices [1–4]. One of the useful methods of formation of these systems is photopolymerization-induced phase separation of liquid crystal (LC) from polymer matrix, using the mixture of photoreactive multi-functional monomers and LCs [5]. Recently, holographic techniques have been applied to the systems known as holographic polymer dispersed liquid crystal (HPDLC), in which gratings are formed as the periodic polymer rich layers and LC rich layers by interference of two incident laser beams [6–8].

Generally, in HPDLC systems, LCs are phase-separated into submicrometer size, in contrast to PDLC systems having micrometer size LC droplets. The performance of holographic gratings strongly depends on the final morphologies, sizes, distribution, and shapes of phase-separated LC domains. The size can be controlled by adjusting the kinetics of polymerization and phase separation of LCs during the polymerization, which depends on (1) experimental conditions such as exposure beam intensity, interbeam angle, and exposure time, and (2) concentration, and physical properties such as viscosity of LCs, and the chemical structures of reactive diluents.

Boots et al. [9] have described the behavior of phase separation during photopolymerization of multi-functional vinyl monomers. They estimated three factors to determine the polymerization-induced phase separation of a LC from the system. The first factor is the increase in the fraction of large molecules during polymerization (size-induced phase separation). Second is the difference in the interaction parameters between monomer and polymer. When cross-linking is formed during polymerization, the elasticity of
the formed network is the third driving force for phase separation. This effect becomes strong by the increase of gel fraction and the number of cross-links.

Many research groups [10–12] have studied the mechanism of formation of holographic gratings by controlling the LC domain size, distribution, and shapes, and chemical structures of polymerizable materials [10–12]. Actually, in our previous study, we reported the clear phase-separated morphology, low volume shrinkage, and high diffraction efficiency for the systems with siloxane-containing epoxides as diluents or bifunctional monomers [13], and pointed out the importance of incompatibility of reactive diluents against reactive multi-functional monomers and LC’s.

In this research, performance of holographic gratings was optimized by using reactive diluent with siloxane moiety under the conditions of various contents of LC and exposure beam intensity.

2. Experimental

2.1. Materials for holographic recording

To tune the reaction rate and cross-linking density, multi-functional acrylates of trimethylolpropane triacrylate (TMPTA) and dipentaerythritol penta-/hexaacrylate (DPEPA) were used as cross-linking monomers. Two types of reactive diluents were used, namely, radically polymerizable N-vinylpyrrolidinone (NVP) and 3-acryloxypropyltrimethoxysilane (APTMS), and ring-opening polymerizable benzyl glycidyl ether (BGE), 2-[(3,4-epoxycyclohexyl)ethyl]trimethoxysilane (ECTMS), and 1,3-bis[2-(3,4-epoxycyclohexyl)ethyl]-1,1,3,3-tetramethyldisiloxane (BEC-TMDS). Their chemical structures are illustrated in Scheme 1.

A commercial LC, E7, was used. E7 is the mixture of cyano bi-/terphenyls with high birefringence and adequate \( T_{NI} \) (nematic–isotropic transition temperature), and plays an important role in the preparation of the recording solution. LC contents in recording solution (photopolymerizable compounds) were varied from 10 to 40 wt%. Recording solution was injected into the glass cell with a gap of 14 \( \mu \)m controlled by bead spacers.

2.2. Photosensitive system

Photosensitive system consisting of photoinitiator (PI) and photosensitizer (PS) is required to be sensitive to Nd-YAG laser to generate the radical or cationic species. Diphenyliodonium hexafluorophosphate (AVOCADO Research Chemicals Ltd) and 3,3’-carbonylbis(7-diethylaminocoumarin) (Kodak) were selected as PI and PS, respectively [14]. Good point about this photosensitive system is the insensitivity of cationic polymerization against oxygen according to a chemically amplified mechanism. The concentrations of the PI and PS to the recording medium were 0.5–3 and 0.1–1 wt%, respectively.

2.3. Optical setup for hologram

Nd-YAG solid-state continuous wave laser apparatus with 532.6 nm wavelength (Coherent Co. Verdi-V2) was used as the irradiation source as shown in Fig. 1. The beams were collimated and expanded by the spatial filters and lens. The inter-beam angle was set to 16 °C against the line perpendicular to the plane of the recording cell. 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 a motor-driven controller, with the shutter closed to cut-off the reference light, to determine the angular selectivity. Holographic gratings were fabricated by changing laser intensity and exposure time.

3. Results and discussion

3.1. Effects of siloxane-containing reactive diluent 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 time.

Fig. 2 shows the change in diffraction efficiency with exposure time in holographic gratings made from recording
solutions consisting of NVP and various amounts of the LC’s using trimethylolpropane triacrylate (TMPTA) as a multi-functional acrylate (TMPTA:NVP = 30:70 wt%). With this ratio, all samples showed very low diffraction efficiency even below 10%, and the formed holographic gratings showed irregular line and their stability was not good. It should be noted that the cross-linking density was too low due to high loading of NVP, which resulted in the decrease of the driving force to push out LCs toward low intensity fringes, and resulted in the disruption of the supporting ability of gratings.

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

Fig. 3 shows the diffraction efficiency in fabrication of holographic gratings with APTMS as a reactive diluent (TMPTA:APTMS = 30:70 wt%). As mentioned above, by
using the siloxane component in photopolymerizable solutions, phase separation should be induced between the LC and polymer matrix, which now contained siloxane components. A remarkably high diffraction efficiency was observed in diffraction efficiency even with over 80% mono-functional APTMS. Presumably very low cross-linking density of the system would cause the decrease in driving force for phase separation by elastic force of cross-linked system. It seemed that the incompatibility of siloxane component very strongly contributed to the phase separation of LC in the system. Of course, one can assume that difference of phase separation should be caused by difference of polymerization rates between TMPTA and APTMS. However, their difference should not be large because they have the same functional group. Therefore, siloxane component was considered to effectively affect the phase separation of LC from the polymer matrix leading to high diffraction efficiency.

With increasing the LC content from 10 to 20 wt%, diffraction efficiency was pronouncedly increased as shown in Fig. 3(a), probably due to the generation of high modulation caused by good phase separation. When LC content increased from 25 to 40 wt%, diffraction efficiency became very high, and gradually decreased with the prolonged exposure time, as shown in Fig. 3(b). With increasing the LC content, maximum diffraction efficiency was shown at shorter exposure time, and decreased abruptly and pronouncedly after passing the maximum. These results may be considered to be related to that with too much excess of phase-separated LCs caused 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. The decreases became more notable with increasing the LC contents.

Fig. 4 shows the diffraction efficiency in fabrication of holographic gratings formed from epoxy-functional reactive diluents capable of ring-opening polymerization. When BGE and ECTMS without siloxane component were used in fabrication of holographic gratings, their diffraction efficiencies were lower than those of radically polymerizable NVP or APTMS. It may be understood that in this photopolymerization system, cationic polymerization is slower than radical polymerization, thus elastic force to push out the LC towards low intensity fringes is also reduced to result in poor phase separation of the LC.

By using the ECTMS with a siloxane component, diffraction efficiency became higher than BGE. By increasing the LC contents, diffraction efficiency increased for BGE, although the absolute value was small, as shown in Fig. 4(a), and the moderate efficiency decreased for ECTMS as shown in Fig. 4(b). In the case of grating formation using BGE, phase separation might not be good enough, and much more LC was needed to generate the modulation. Contrary, in the case of ECTMS, good phase separation might have occurred due to the flexibility and incompatibility of the siloxane component, thus less LC (more cross-linkable monomer in the solution) seems to be sufficient to form holographic gratings. All the formed gratings were stable against the laser light during the holographic recording. These results confirmed that addition of ECTMS to a siloxane component as a reactive diluent gave better phase separation. However, ultimate diffraction efficiency in the formed grating was not as high as in the case of the grating with APTMS.

3.2. Angular selectivity

When the multiplex hologram recording is required, it is necessary to know the angular selectivity. The smaller the value the more multiplex data can be recorded.
Fig. 4. Dependence of diffraction efficiency on exposure time for holographic gratings prepared with epoxy-functional reactive diluents at various LC contents: (a) BGE and (b) ECTMS.

Fig. 5. Angular selectivity of holographic gratings prepared with ECTMS by changing (a) E7 contents and (b) exposure intensity.

Fig. 6. SEM images of holographic gratings prepared with BEC-TMDS and E7: (a) 15 wt% and (b) 35 wt%.
As shown in Fig. 5 angular selectivity decreased with increasing LC contents (about 5–6°). According to the Kogelnik’s coupled wave theory [15], modulation of refractive index is dependent on the contrast of refractive index and the thickness of the sample. LC enhances the contrast of refractive index but decreases the diffraction efficiency. To actually use this system as a recording material, adjustment of the thickness of the sample with 25 wt% LC, which showed the highest angular selectivity, is desirable. There was almost no difference of angular selectivity according to exposure intensity due to similarity of the refractive index modulation, as shown in Fig. 5(b).

3.3. SEM morphology

Clearly phase-separated morphologies of periodic polymer rich layers (bright region) and LC rich layers (dark region) could be observed by SEM observation for
the formed holographic gratings. In Fig. 6, SEM pictures of the samples fabricated with polymerizable mixture [DPEPA, NVP, and BEC-TMDS in 30:10:60 wt% ratio] (85 and 65 wt%) and the LC (15 and 35 wt%) were shown. The difference of phase-separated morphology depending on the LC content was noticed. With 15 wt% LC, the grating was more clearly fabricated than the case with 35 wt% LC. The grating fabricated with 35 wt% LC collapsed a little due to too much phase-separated LC component. The morphology of holographic gratings could be controlled by LC content.

3.4. AFM topology

The 3D topologies and depth profiles of holographic gratings formed with mono-functional reactive diluent APTMS and ECTMS with siloxane component evaluated by AFM were shown in Fig. 7. Well-fabricated holographic grating patterns were observed for all the gratings. Especially, in the gratings formed with APTMS showed very regular and clean morphologies with any LC contents.

Original intention to introduce ring-opening polymerizable epoxy diluent was to improve the volume shrinkage, but there was apparently no difference in grating spacing, which strongly related to the volume shrinkage, between the gratings with APTMS and ECTMS, as shown in Fig. 7(a) and (b). Although detailed study is needed, this might be due to the use of mono-functional ECTMS as the reactive diluent. In both cases, the grating spacing were about 1.0 μm, which was in good agreement with the theoretical value of 0.965 μm according to Bragg’s law (grating spacing \(A = \lambda/2 \sin \theta\), \(\lambda\) is 532 nm and \(\theta\) is 16° in this experiment). By varying the LC contents in the recording solution with APTMS (Fig. 7(b)–(d)), surface topology like sinusoidal pattern was changed in a very interesting manner. As LC contents increases, the crests of the periodic pattern became smooth as shown in the depth profiles, probably due to the presence of more phase-separated LC caused by too much loading.

Together with the data on diffraction efficiency shown in Fig. 3, the finest morphology of holographic gratings having the highest diffraction efficiency in final gratings was formed with 20 wt % LC. Grating fabricated with 30 wt% LC did not show smooth morphology separated LC owing to too much loading, and showed a low diffraction efficiency caused by low modulation of refractive index.

Topologies observed by AFM before and after the treatment with methanol were shown in Fig. 8. The depth profile was slightly changed and became sharper to approach sinusoidal pattern even for the grating fabricated with 15 wt% LC after the treatment, probably because of the removal of LC. Holographic gratings with regularly phase-separated morphologies between high- and low-intensity fringe regions were observed. Morphology of the polymer film, after removal of LC, was also very clear (Fig. 8(b)), which meant that the small amounts of phase-separated E7 was located only on the surface of well-fabricated holographic grating.

4. Conclusion

We have demonstrated the effectiveness of siloxane-containing reactive diluent on the performance of holographic gratings. High diffraction efficiency was obtained
by using 3-acryloxypropyltrimethoxysilane and 2-[(3,4-epoxycyclohexyl)ethyl]trimethoxysilane as reactive diluents, by inducing a fast and good phase separation due to their flexible and incompatible properties even at low LC concentration (10–25 wt%) in contrast to the diluents without siloxane component. Very regular and clean morphologies were also observed for the holographic gratings formed with siloxane-containing reactive diluents.

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

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