Improvement of holographic performance by novel photopolymer systems with siloxane-containing epoxides

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Abstract

Diffraction efficiency and morphology of holographic gratings were improved by combining ring-opening polymerizable epoxides with radical polymerizable conventional acrylate systems. By adding epoxide materials, the grating spacings were increased when compared with the case where only acrylate was used. The effects were especially notable for cyclohexane oxide derivatives. The diffraction efficiency was the highest, and nanoscale phase-separated liquid crystal domains were the most clearly formed using siloxane-containing cyclohexane oxide group, due to their incompatibility and fast curing.

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1. Introduction

Holographic technique as optical data storage has been extensively studied with a demand of vast and high-speed data storage. Holographic storage enables not only the increase of the information packing density by three-dimensional storage, but also the fast data transfer by simultaneous processing of writing and reading. Recently, photopolymers have been used as holographic recording materials because of their significant advantages of one step process, no post-treatment, and high flexible formulation over inorganic systems.

In holographic polymer dispersed liquid crystal (H-PDLC) systems, holographic gratings are usually constructed by anisotropic distribution of polymer and liquid crystal (LC)-rich lamellae formed by photo-polymerization of monomers or oligomers and following phase separation of LCs in the form of interference patterns by irradiation of two laser beams of different phase \cite{1}. Such system has been usually realized by using a vinyl monomer, which can polymerize very fast and produce optically transparent polymers. Actually, in the previous works, we succeeded in improvement of the diffraction efficiency and optical quality by polymerization of acrylate-endcapped polyurethanes \cite{2}. However, those films showed a serious volume shrinkage during the holographic grating formation even though the problem could be improved a little by modifying their chemical structures.

In this research, ring-opening polymerization (ROP) systems with increased excluded free-volume during the polymerization were combined with radical polymerization systems to further improve the volume shrinkage \cite{3}. Epoxide was chosen as a polymerizable functional group, which undergoes photo-initiated cationic ROP, just as used in photo-curing systems. Although various epoxide derivatives were used, cyclohexane oxide group should be more suitable to control the volume shrinkage in the polymerization due to their ring structure with more bulky group.

Meanwhile, siloxane components show high thermal stability, high optical clarity, and incompatibility with other components. Therefore, siloxane component will function to realize sharp phase separation derived from the incompatibility with carbon-based LC. Consequently, siloxane-containing cyclohexane oxide materials may give higher diffraction efficiency with a thermally stable low-volume shrinkage due to their clear and fast phase separation in ROP system.
2. Experimental

2.1. Materials

2.1.1. 1,3-Bis[2-(7-oxabicyclo[4.1.0]hept-4-yl)ethyl]-1,1,3,3-tetramethyldisiloxane

1,1,3,3-Tetramethyldisiloxane, 4-vinyl-7-oxabicyclo[4.1.0]heptane, and chlorotris(triphenylphosphine)rhomodium(I) [RhCl(PPh3)3] were purchased from Silar Laboratories, Aldrich Chemical Co., and KANTO Chemical Co., Inc., respectively.

Siloxane-containing bicyclic epoxide monomers were readily prepared by the direct hydrosilylation [4] in toluene at approximately 60–70 °C for 24 h as shown in the following Scheme 1. The solution was passed through a silica gel column, and desired monomer was obtained as low viscous colorless oil.

$^1$H NMR (CDCl3) δ (ppm): 3.1 (m, 4H, O–CH-epoxy), 2.19–0.89 (m, 18H, –CH2-cyclic), 0.46 (m, 4H, –CH2–Si), 0.01 (s, 12H, CH3–Si–O–).

2.1.2. Materials for used holographic systems

Ring-opening polymerizable materials used for holographic systems were listed in Fig. 1.

2.2. Composition of photosensitive solution and recording medium

Photosensitive system of photo-initiator (PI) and photosensitizer (PS) is required to have a sensitivity to visible light. In this study, PI and PS are prepared by the following structures (Scheme 2).

Fig. 1. Chemical structures of ring-opening polymerizable compounds used in holographic systems.
wavelength of Ar-ion laser to generate radical or cationic species. For this purpose, a diphenyliodonium hexafluorophosphate and a 3,3'-carbonylbis(7-diethylaminocoumarin) were selected as a PI and a PS, respectively, which function according to a chemically amplified mechanism [5]. A good point about this photosensitive system is in the insensitivity of cationic polymerization against oxygen. The concentrations of the PI and PS to the recording medium were 5, 0.3 wt%, respectively.

The formulation of the photopolymerizable system was composed of a ring-opening polymerizable compound (60 wt%), fast curing acrylate of dipentaerythritol penta/hexaacrylate (DPEPA; 30 wt%), and reactive diluent of benzyl glycidyl ether (10 wt%), respectively. LC with cyano bi-/terphenyl mixtures (E7, Merck) ($n_0 = 1.5216, n_e = 1.7462, n_{ave} = 1.3718$) of 35 wt% was used and added to the photopolymerizable recording medium.

Recording solution was injected into the glass cell with a gap of 20 µm controlled by bead spacer.

2.3. Fabrication of holographic gratings

Argon-ion laser with 514.5 nm wavelength was used as the irradiation source. The beams were splitted into two beams and collimated and expanded by using spatial filters and lens, respectively. The inter beam angle was set as 15° against the line perpendicular to the plane of the medium. Holographic gratings were fabricated under various experimental conditions changing laser intensity, irradiation time, and the optimum condition was established to obtain the high diffraction efficiency, high resolution, and excellent environmental stability after recording.

3. Results and discussion

3.1. Diffraction efficiency

By Kogelnik’s coupled wave theory [6], maximum diffraction efficiency for the unslanted transmission hologram is given [7,8]

$$\eta = \sin^2 \xi$$

$$\xi = n \pi \Delta n \frac{T}{\lambda (n^2 - \sin^2 \theta)^{1/2}}$$

where $\eta$ is the maximum diffraction efficiency, $n$ is average refractive index of the recording medium, $\Delta n$ is the modulation of refractive index, $\theta$ is an angle within the recording medium between the probe radiation and a line perpendicular to the plane of the medium, $T$ is the film thickness, and $\lambda$ is the recording wavelength.

In our experiment, $T$, $\theta$, $\lambda$ were fixed and $n$ is varied by chemical structure of recording materials. Therefore, diffraction efficiency was mainly affected by $n$ and $\Delta n$.

### Table 1

| Monomer | Refractive index (20°C, $n_0$) | Refractive index contrast with LC |
|---------|-----------------------------|----------------------------------|
| Structure A | ≈ 1.579 | 0.2072 |
| Structure B | 1.4570 | 0.0852 |
| Structure C | 1.4290 | 0.0572 |
| Structure D | 1.4980 | 0.1262 |
| Structure E | 1.4930 | 0.1212 |
| Structure F | ≈ 1.435 | 0.0632 |

Generally, $\eta$ values become large when refractive index contrast of photopolymerizable solution and LC is large if there is no chemical affinity between the polymer and LC. When the chemical affinity is large or rigidity of the cross-linked system is high to resist phase separation, the $\eta$ values will be small due to poor phase separation during the grating formation, even if their refractive index contrast was large. Therefore, it can be expected that a further enhancement of $\eta$ can be achieved by molecular design of photopolymerizable monomer or oligomer having high refractive index contrast and low chemical affinity leading to good phase separation. From this point of view, the various structures of epoxide materials with different refractive index were selected, and their diffraction efficiency was studied considering their refractive index contrast, chemical affinity, and polymerization rate.

The list of refractive index of materials used in this study was summarized in Table 1.

In Fig. 2, structure A has the smallest diffraction efficiency value even though their refractive index contrast is the largest. This can be understood by the largest chemical affinity lead by similar structure with LC of cyano bi- and terphenyl mixtures, or by the rigid structure of the cross-linked system. Better miscibility between polymer matrix and LC should give smaller extent of phase separation, leading to relatively blur gratings [9]. Rigidity of structure A may have also disturbed the coalescence of LC droplets.
during polymerization leading to grating formation and good phase separation.

Structure B has larger diffraction efficiency derived from larger refractive index contrast and its flexibility, which lead to more discrete phase separation than structure A with rigid structure also similar in chemical structure of LC.

In case of structure C, the diffraction efficiency value is the largest although its refractive index contrast is much lower than structure A or B. It may have more clearly phase-separated LC leaded by incompatibility of the siloxane component with LC and less cross-linked system. However, structure C is a mono-functional compound, and the grating cannot maintain stable structure after formation.

Fig. 3 shows the diffraction efficiency according to the chemical structures of bis(cyclohexane oxide). Diffraction efficiency increased in the order of structure E < D < F, with the order of refractive index contrast F < E < D. Structure D has more larger refractive index contrast than structure E, thus has more larger diffraction efficiency than structure E.

In case of structure F, diffraction efficiency was pronouncedly higher than those of structures D and E, although its refractive index contrast was the smallest among them. This can be considered that flexible and incompatible siloxane materials, has strongly influenced the phase separation of LC from the irradiated areas. The more coalescence of LC droplets was induced by the flexible chain of structure F resulting in good phase separation and effective grating formation.

3.2. SEM morphology

Holographic gratings with clearly phase-separated morphologies of periodic polymer rich layers (bright region) and LC rich layers (dark region) could be observed by SEM shown in Fig. 4.

The grating spacings of all ROP system (Fig. 4(b)–(d)) increased due to improved volume shrinkage than the case where only acrylate system was used. Especially, as shown in Fig. 4(c) and (d), grating spacings of structures D and F with cyclohexane oxide function were more larger than it of structure C (Fig. 4(b)) with glycidyl ether function. Steric requirement of more bulky cyclohexane oxide function seems to have caused less volume shrinkage than glycidyl ether function.

Compared with structure D, structure F with siloxane component had more clear phase separation of LC as shown in Fig. 4(c) and (d). LC drop sizes are also much larger for structure F. This is because of the incompatibility with LC and flexibility of siloxane component. This can also be discussed from the viewpoint of polymerization rate. Crivello reported that structure F is much more reactive than structure D in photo-initiated cationic polymerization despite the apparent closely related structures [10]. Generally, in holographic PDLC systems, there is an optimum polymerization rate to obtain good phase separation. It can be expected that higher reactivity will form

Fig. 3. Effects of spacer structures of bis(cyclohexane oxide) on the diffraction efficiency.
cross-linking fast, and cause more clear phase separation by pushing out LC fast from the polymerized system.

When compared the structure C with structure F with silicon component although their silicon number is different, the phase separation shown in Fig. 4(b) and (d) is quite different. Structure F has much larger LC drop sizes with discrete phase separation than structure B. The reason seems similar to the discussion already made.

4. Conclusion

By combining the ROP functional groups, such as glycidyl ether and cyclohexane oxide function, with ordinary vinyl polymerization system, volume shrinkage was improved. Especially, their effects were notable for cyclohexane oxide derivatives due to the more bulky ring structure. Siloxane component in such system induced the clearer phase separation of LC due to their incompatibility with carbon-based organic system and flexibility of the structure. Their diffraction efficiency was the highest although their refractive index contrast were the smallest.

Consequently, siloxane-containing cyclohexane oxide material gave gratings of a thermally stable low-volume shrinkage with the largest diffraction efficiency and clear and fast phase separation.

Further studies on the synthesis of siloxane-containing epoxide materials with more bulky group, such as dicyclopentadiene and more longer siloxane chain, and on their performance of holographic gratings are in progress.

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