*Pure Appl. Chem.*, Vol. 78, No. 10, pp. 1835–1842, 2006.
doi:10.1351/pac200678101835


# Design of high-performance holographic gratings using siloxane-containing mesogenic compounds*

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*Abstract*: Fine holographic gratings were fabricated using siloxane- and mesogen-containing compounds. A grating with 40 % diffraction efficiency was formed with 10 wt % non-liquid-crystalline 4-methoxyphenyl 4-[4-(pentamethyldisiloxanyl)butoxy]benzoate and trimethylolpropane triacrylate. 4-Methoxyphenyl 4-[4-(1,1,3,3,5,5,5-heptamethyltrisiloxan-1-yl)butoxy]-benzoate gave 50 % diffraction efficiency and angular selectivity of 5°.

Siloxane-containing liquid-crystalline compounds were also effective in fabricating fine gratings. These compounds induced distinct phase separation over a concentration range from 6 to 20 wt % in the formation of holographic gratings. The use of ring-opening polymerizable bifunctional epoxides as one of the reactive cross-linking matrix components, together with penta- or tetra-acrylate initiated by 3,3'-carbonylbis(7-diethylaminocoumarin)diphenyliodonium hexafluorophosphate, greatly improved the diffraction efficiency.

Fine gratings with 70 and 78 % diffraction efficiency and angular selectivity of 5° were formed with 10 wt % 4-cyano-4'-[(5-heptamethyltrisiloxan-1-yl)pentyloxy]-biphenyl and 4-cyanophenyl 4-[(5-heptamethyltrisiloxan-1-yl)pentyloxy]benzoate using pentaerythritol pentaacrylate-neopentylglycol diglycidyl ether-tripropylene glycol diacrylate (4:5:1) as the polymer matrix component.

*Keywords*: holography; siloxane; phase separation; atomic force microscopy; scanning electron microscopy.

Holographic techniques have generated much interest through the large digital storage capacity that results from utilization of multiplex storage techniques as the interference patterns. Since holographic storage also enables fast data transfer rates by simultaneous writing and reading, an upsurge of interest in optical holography has been noticed in the past decade. Many materials, including photochromic materials, photographic emulsions, photopolymers, polymer-dispersed liquid crystals (PDLCs) and photorefractive materials, have been investigated as holographic storage media [1].

In 1993, the holographic polymer-dispersed liquid crystal (HPDLC) system was introduced by R. L. Sutherland [2]. Gratings were produced via the phase separation of liquid crystal (LC) during irradiation by two coherent interfering laser beams as a refractive index-modulated interference fringe pattern of stratified alternating layers of LC and polymer. An important potential role of LC is the re-

*Paper based on a presentation at the 15th International Symposium on Fine Chemistry and Functional Polymers (FCFP-XV) and the 1st International Symposium on Novel Materials and their Synthesis (NMS-I), 17–20 October 2005, Shanghai, China. Other presentations are published in this issue, pp. 1803–1896.

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sponse against electric field in the formed gratings, which enables it to be applied as display devices [3], switchable lenses [4], and wave-guided switches [5].

In designing efficient holographic systems, attention has been focused mainly on the elucidation of the effects of functionality of photo-polymerizable monomers [6]. Little attention has been paid to the importance of the chemical structure of other components. The principal role of LC in PDLC is to phase-separate by the diffusion during the polymerization from polymer matrix formed by multi-functional monomer, and to give high modulation of the refractive index of the gratings.

Siloxane derivatives have many unique static and dynamic properties like low surface-free energy, incompatibility with other components, and bond flexibility leading to low viscosity, and are interesting in designing holographic materials with distinct phase-separation performance and high contrast of the refractive index against matrix components. We have been working on the use of siloxane-containing compounds as high-performance holographic recording materials [7].

## EXPERIMENTAL

### Materials used in holographic grating formation

Multifunctional compounds and mesogenic compounds used in this study are shown in Figs. 1 and 2.

Tripropylene glycol diacrylate (**2V**), trimethylolpropane triacrylate (**3V**), pentaerythritol tetraacrylate (**4V**), and dipentaerythritol pentaacrylate (**5V**) were used as multifunctional acrylates. Abbreviations **V** and **R** were used to indicate acrylate (**V**) and epoxide (**R**) monomer and the numerals indicate the functionality, for example, **5V** and **2R** indicate penta-functional acrylate and bifunctional epoxide, respectively. The combination of photosensitizer rose bengal (RB) and the initiator *N*-phenylglycine (NPG), and 3,3'-carbonylbis(7-diethylaminocoumarin) (KC)-diphenyliodonium hexafluorophosphate (DPI) initiator system were used.

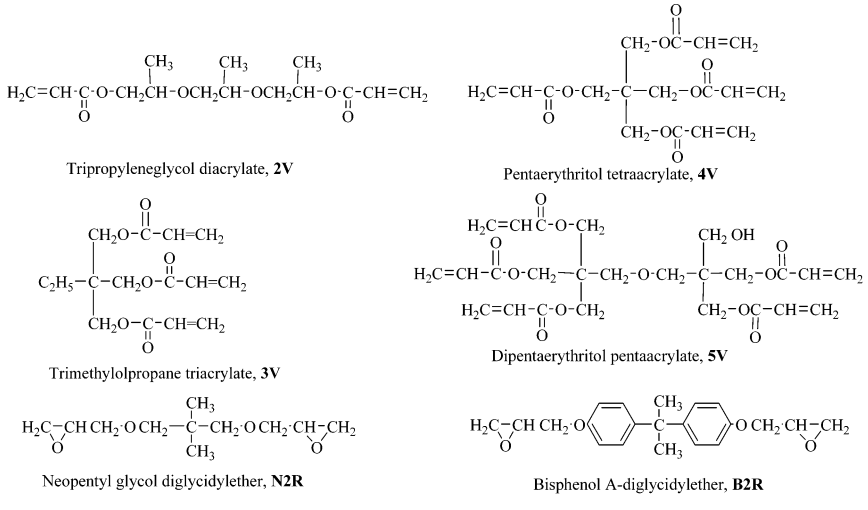



**Fig. 1** Chemical structures of multifunctional compounds.

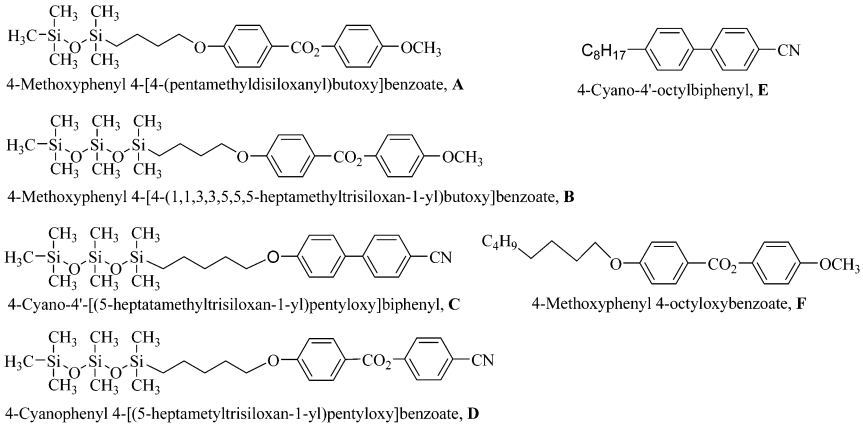



**Fig. 2** Chemical structures of mesogenic compounds.

## Fabrication and analysis of holographic grating

The recording solution was prepared under diminished white light to eliminate any unexpected photopolymerization before holographic recording. All recording solutions consisted of a multifunctional monomer, a photoinitiator system, and reactive diluent in varying weight concentration ratio. Just before irradiation, adequate amounts of initiator system were added, and the mixture was vigorously stirred for about 5 min to give a clear homogeneous solution, and dropped into a cell between the space of two glass slides to control the thickness of the sample.

Gratings were prepared by two coherent beams of Nd-YAG laser ($\lambda$ = 532 nm) (Coherent Inc., Verdi-V2) of equal intensity with a true power of 30 mW/cm$^2$.

The diffraction efficiency is defined as the ratio of diffraction intensity after recording ($I_d$) to transmitted beam intensities before recording ($I_t$), as illustrated in Fig. 3.

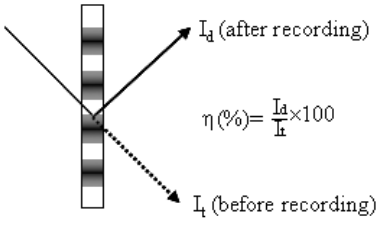



**Fig. 3** Definition of diffraction efficiency.

For a simple transmission grating, Kogelnik's coupled wave theory [8] gives the equation of diffraction efficiency,

$$\eta = \sin^2(\pi \Delta n\, T/\lambda)$$

where $\eta$ is the maximum diffraction efficiency, $\Delta n$ is the modulation of refractive index, $T$ is the film thickness, and $\lambda$ is the wavelength at Bragg's condition.

Real-time diffraction efficiency was measured by monitoring the intensity of diffracted beam simultaneously when the shutter was closed at a given time during the hologram recording with the interbeam angle set to 16°. After recording, all the samples were post-cured under a UV lamp to complete the photopolymerization, and the angular selectivity was determined by rotating the hologram precisely. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were mainly used to

characterize the morphology of gratings. Samples used for SEM were prepared by freeze-fracturing the cells using liquid nitrogen and extracting a mesogenic compound with ethanol.

## RESULTS AND DISCUSSION

### Diffraction efficiency of gratings

Mesogenic compounds with alkyl chains were crystalline, and scarcely gave homogeneous recording solution. Contrary, siloxane-containing mesogenic compounds gave completely homogeneous recording solution.

Changes in real-time diffraction efficiencies of the solution with 10 wt % **B**, not being LC, and various amounts of 1-vinyl-2-pyrrolidone, **NVP** as a reactive diluent and **3V** in [**3V**:**NVP**] (**3V** = 72 wt % and **NVP** 18 wt % gives the relative **NVP** weight of 20 %) are shown in Fig. 4.

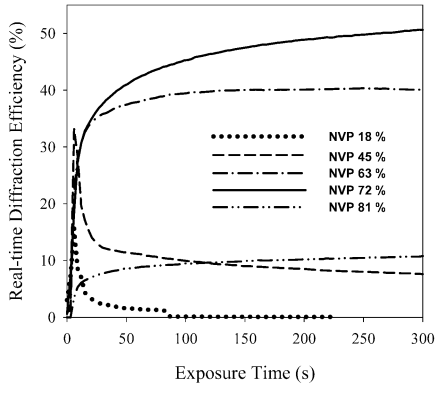



**Fig. 4** Real-time diffraction efficiency of gratings prepared with 10 wt % **B** and **3V** at various **NVP** concentrations.

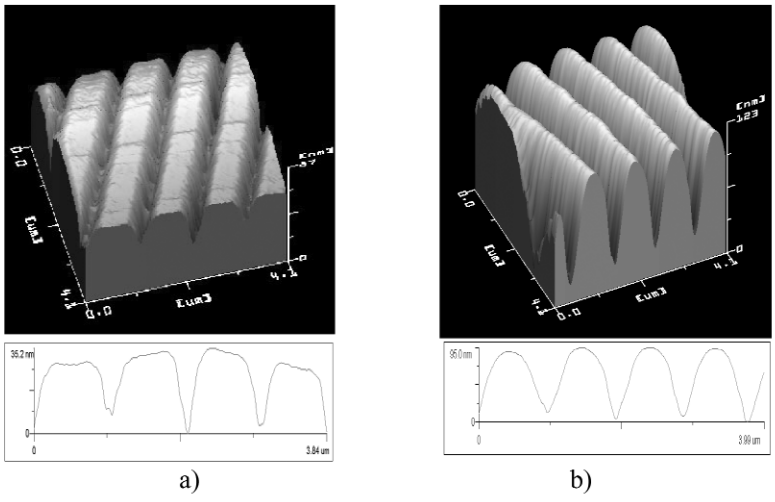
Gratings made with 4-methoxyphenyl 4-[4-(1,1,3,3,5,5,5-heptamethyltrisiloxa-1-yl)butoxy]benzoate, **B** gave better performance than that made with 4-methoxyphenyl 4-[4-(pentamethyldisiloxanyl)butoxy]benzoate, **A**.

A sharp increase of diffraction efficiency in the initial stage of the exposure with low **NVP** concentration indicated the rapid formation of cross-linking by a fast polymerization of **3V** followed by an equilibration by diffusion and relaxation of the components. Under low **NVP** concentration (<45 %), the final diffraction efficiency was typically less than 13 %. When **NVP** concentration was increased, the diffraction efficiency reached 38 % with 72 % **NVP**, and further slightly increased to 50 % with prolonged curing time. It was assumed that high cross-linking density (**NVP** < 45 % in mixture) decreased the phase separation by shortening the gelation time of the **3V**.

### Morphology of gratings

3-D morphology and depth profile, studied by AFM, of the gratings fabricated from 90 wt % matrix (**3V**:**NVP** = 4:6) and 10 wt % **B**, before and after washing with ethanol are shown in Fig. 5.

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 **B** from polymer matrix. The hilltop region is considered as the polymer region covered with some **B**. Spacing of grating is observed as 0.96 and 0.93 μm before and after removal of **B**, and the depth of grating is much deeper (99 nm) after washing than that before washing (35 nm). Such morphology seemed to be correlated to the high diffraction efficiency. Since these gratings are basically surface re-



a) b)

**Fig. 5** AFM morphology and depth profile of the grating prepared with 10 wt % **B**: (a) as produced, and (b) after washing with ethanol.

lief type, we should note that a high depth does not necessarily lead to a high diffraction efficiency, since the refractive index modulation determines the diffraction efficiency. Only an effective and distinct phase separation could apparently produce a clear and deep (e.g., >60 nm) grating with a high diffraction efficiency.

SEM observation clearly showed the formation of discrete grating as shown in Fig. 6.

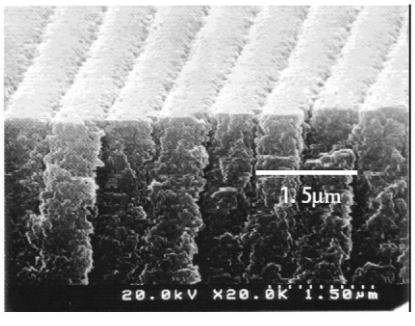



**Fig. 6** Top and edge views of the freeze-fractured grating prepared with 10 wt % **B** observed by SEM.

The formation of clear phase-separated layered structure in the grating was evidenced by the observation of the edge view of the cut sample after the removal of **B**. Each layer could be peeled off, which strongly suggested the well phase-separated layered structure of the grating. From these data, it was clearly shown that 10 wt % of **B** in recording solution is quite effective to cause the phase separation in grating, leading to high diffraction efficiency.

The grating prepared with 3 wt % **B** showed quite similar morphology with that prepared with 10 wt % of the compound, but the irregular surface for the grating made with 30 wt % **B**. Although reduced viscosity by increasing the concentration to 30 wt % made the diffusion of both **B** and monomers easier, it also made the polymer matrix easier to retain large amounts of **B** in the cross-linked matrix, which was considered the main reason of decreasing the diffraction efficiency by lowering the refractive index modulation.

### Angular selectivity of gratings

Narrow angular selectivity is very important for the optical performance of grating for high-density image storage. Angular selectivity of grating with 10 % **B** is shown in Fig. 7.

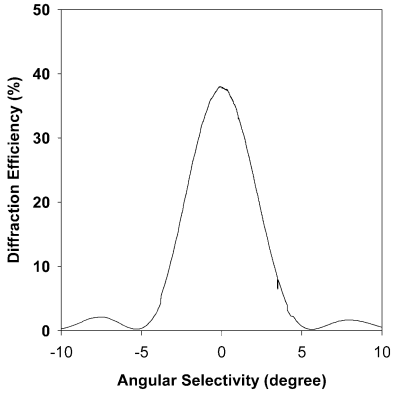



**Fig. 7** Angular selectivity of grating made with **B**.

The (external) Bragg angle obtained from grating is in excellent agreement with the experimental incident angle about 16°. Moreover, the angular selectivity of all samples was found to be about 5°. Narrow angular selectivity is related to high diffraction efficiency and a perfect phase separation. A significantly different angular selectivity was observed for the different chemical structure.

### Superiority of liquid crystals with trisiloxane tail in grating formation

Since trisiloxane derivative **B** gave better performance than disiloxane derivative **A** in grating formation with **3V**, LC compounds with a trisiloxane tail, **C** and **D**, were studied in the grating formation with multifunctional acrylates (**3V**–**5V**). The change in real-time diffraction efficiencies for the solution with 10 wt % 4-cyano-4'-{(5-heptatamethyltrisiloxan-1-yl)pentyloxy}biphenyl, **C** and various **NVP** wt % in [multifunctional acrylate:**NVP**] (e.g., **5V** = 40 wt % and **NVP** 60 wt % gives the relative **NVP** weight of 54 %) with initiator systems RB and NPG, or KC-DPI are shown in Table 1.

In the radically initiated systems, the systems with 36 wt % **5V** and **4V** with 10 wt % **C**, or cyanophenyl 4-[(5-heptamethyltrisiloxan-1-yl)pentyloxy]benzoate, **D** gave the highest diffraction efficiency. The system with the same concentration of **3V** gave relatively lower diffraction efficiency. LC compounds with alkyl spacer, typically 4-cyano-4'-octylbiphenyl, **E** gave low diffraction efficiency. When a part of **NVP** was replaced by a bifunctional **2V**, the diffraction efficiency was dramatically decreased.

**Table 1** Diffraction efficiency of gratings prepared under various conditions.

| No. | Matrix (90 wt %) | Initiator | LC (10 wt %) | DE (%) |
|---|---|---|---|---|
| 1 | **5V**:**NVP** = 4:6 | RB (0.4 %)-NPG (3 %) | **C** | 38 |
| 2 | **4V**:**NVP** = 4:6 | RB (0.4 %)-NPG (3 %) | **C** | 43 |
| 3 | **4V**:**NVP** = 4:6 | RB (0.4 %)-NPG (3 %) | **D** | 45 |
| 4 | **3V**:**NVP** = 4:6 | RB (0.4 %)-NPG (3 %) | **C** | 24 |
| 5 | **5V**:**2V**:**NVP** = 4:5:1 | RB (0.4 %)-NPG (3 %) | **C** | 1 |
| 6 | **5V**:**NVP** = 4:6 | RB (0.4 %)-NPG (3 %) | **E** | 3 |
| 7 | **5V**:**2V**:**NVP** = 4:5:1 | RB (0.4 %)-NPG (3 %) | **C** | 2 |
| 8 | **5V**:**2V**:**NVP** = 4:5:1 | KC (0.4 %)-DPI (3 %) | **C** | 2 |
| 9 | **5V**:**2V**:**BGE** = 4:5:1 | KC (0.4 %)-DPI (3 %) | **C** | 2 |
| 10 | **5V**:**N2R**:**BGE** = 4:5:1 | RB (0.4 %)-NPG (3 %) | **C** | 18 |
| 11 | **5V**:**N2R**:**BGE** = 4:5:1 | KC (0.4 %)-DPI (3 %) | **C** | 70 |
| 12 | **5V**:**N2R**:**BGE** = 4:5:1 | KC (0.4 %)-DPI (3 %) | **D** | 78 |

## Improvement of diffraction efficiency by the coexistence of radically and cationically polymerizable matrix components

The more important findings in this study are the influence of the bifunctional epoxide used together with multifunctional acrylates. The results are also shown in Table 1.

The diffraction efficiency was not improved when the initiator was simply changed from radical system RB-NPG to cationic system KC-DPI for the multifunctional acrylate recording solutions. The efficiency was not improved either, by simply changing **NVP** to **BGE**, when radical initiator system was used. The recording solution in which a major part of **NVP** was replaced by bifunctional epoxide, **N2R**, gave dramatic increase in diffraction efficiency when the initiator was changed from RB-NPG to KC-DPI, which could initiate cationic polymerization. The highest diffraction efficiency with **C** in radical system, namely 43 %, was improved to 70 % for the system **5V**-**N2R**-**BGE** [4:5:1]. The same recording system with **D** gave even higher diffraction efficiency of 78 %. Such an effect was considered to be caused by relatively fast initial cross-linking by **5V** followed by the slower cross-linking of the system by **N2R**. When the functionality of **5V** was diluted with **N2R**, the extent of initial cross-linking became slow, but the successive cross-linking by **N2R** pushed the LC out more effectively than the case of the too rapid cross-linking by **5V** alone. Thus, a gradual increase in diffraction efficiency was observed. When the functionality of radically polymerizable monomer was changed from 5 to 4 or 3, the diffraction efficiency was dropped to 30–40 % compared with 70 % for the pentaacrylate.

In SEM morphology of the grating, it was observed that the siloxane-containing **C** well phase-separated from the polymer matrix. The width of the liquid-crystalline layer is close to 10 % of spacing, which corresponds to the feed ratio of **C**. Clear phase-separated structure could not be observed by SEM for the sample prepared from **3V**:**N2R**:**BGE** = 4:5:1. 10 wt % **C** gave better phase-separated grating than that with 20 wt %.

The fact that there was no significant influence on the diffraction efficiency of the gratings made with these LCs of different mesogenic structure, seems to indicate that the siloxane-chain spacer played a more important role on the grating formation than the mesogenic group. It was also found that the diffraction efficiency did not change so much at small incident angles such as <30°, and reasonably narrow angular selectivity was also observed.

## CONCLUSION

Fine holographic gratings were fabricated using siloxane and mesogen-containing compounds. These compounds induced distinct phase separation over a concentration range from 6 to 20 wt % in the formation of holographic gratings. The use of ring-opening polymerizable bifunctional epoxides as one of the reactive cross-linking matrix components, together with penta- or tetra-acrylate initiated by 3,3'-carbonylbis(7-diethylaminocoumarin)diphenyliodoni-um hexafluorophosphate greatly improved the diffraction efficiency (>70 %).

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