Synthesis of Multifunctional Epoxy Monomers and their Potential Application in the Production of Holographic Photopolymers

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Abstract: Polydimethylsiloxanes having four epoxide functionalities (Multi) were synthesized through hydrosilylation of polydimethylsiloxane-co-polydimethylhydrogensiloxane with 4-vinyl-1-cyclohexene 1,2-epoxide and were characterized using FT-IR, 1H-NMR, and 29Si-NMR spectroscopy. Diffraction efficiency studies on the use of Multi as a co-monomer for holographic photopolymerization of 1,3-bis[2-(3-{7-oxabicyclo[4.1.0]heptyl]-tetramethyldisiloxane, based on cationic ring opening polymerization, were undertaken; a fast response time (3 sec) was observed. The effects of the amount of photo-acid generator and chain length of Multi are described.

Keywords: photopolymer, cationic polymerization, polydimethylsiloxane, epoxide, hydrosilylation

Introduction

In recent years, great effort has been exerted into the research of photopolymers as holographic recording materials, especially for the application of holographic digital data storage. These materials have the advantage of recording and reading holograms in real time with high diffraction efficiencies, compared with those of inorganic photorefractive crystals and photorefractive polymers. Photorefractive polymer systems are based on the techniques of photo-detachment or photo-attachment reactions of binding polymers without polymerization of monomers. On the other hand, photopolymer systems consist of binding polymer, monomer, photosensitizing dye, and initiator. Holographic exposure produces spatial diffraction patterns as a result of photo-initiated polymerization. Concentration gradient of unreacted monomers between exposed and unexposed areas induces diffusion of the species from the unexposed zone to the exposed zone. Diffusion produces a compositional gradient, establishing refractive index grating, which makes it possible to record digital data.

Photopolymers were first used as holographic recording materials in 1969 [1]. The system consisted of a mixture of acrylamide and metal acrylate monomers and a photoinitiator, such as methylene blue and p-toluene sulfonic acid sodium salt. Since then, numerous systems based on acrylic-type monomers have been examined [2-4]. As a result of earlier research, two commercially available materials were developed by the Polaroid Corporation and E.I. DuPont Nemours and Co.. The former consists of a mixture of methylenebisacrylamide and lithium acrylate as the monomer and a poly-N-vinylpyrrolidone as a binder [5]. Although it is more sensitive than the DuPont materials, the necessity for incubation in a 50 % humidity environment prior to use and post-recording treatment has prevented its widespread applications. The latter is part of the family of acrylate-based systems, known as the Omnidex series [6-8], which are generally considered to be the best commercially available materials for holographic recording at this time because of their high diffraction efficiency (DE), high sensitivity, and good resolution [9]. However, the change in Bragg detuning caused by volume reduction, which is accompanied by the polymerization of acrylic monomers upon exposure, has not been prevented.

To reduce the volume reduction upon photopolymerization, cationic ring opening polymerization (CROP) of various monomers, including epoxides, has been examined extensively [10,11] since diaryliodonium salts were reported to initiate the CROP of epoxides on...
irradiation with ultraviolet light [12]. In particular, the system composed of silicone derivatives containing the epoxycyclohexyl ring as the monomer and silicone oil as the binder has been investigated extensively [13-16]. For the photopolymer system composed of 1,3-bis[2-(3-{7-oxabicyclo[4.1.0] heptyl} tetramethyldisiloxane (Di in Figure 1) as the monomer, iodonium salts as the initiator, and silicone oil as the binder, volume reductions lower than 0.05 % were achieved [17,18]. Recently, the brittleness of the above system was reported to be improved by adding a co-monomer, such as a multi-functional epoxy monomer, which is able to act as a cross-linking agent [18,19]. However, research into such photopolymers for holographic recording materials has been limited to only a few research groups. Recently, we established a holographic photorecording system and reported the effects of the addition of SeO₂ inorganic crystals with semiconducting properties on the acrylate-based photopolymer systems [20].

In this study, new types of multi-functional epoxy monomer (Multi in Figure 2), which are able to be applied as the cross-linking agent for holographic recording materials based on CROP of Di, were synthesized through two-step reactions (Figure 2) and characterized using FT-IR, ¹H-NMR, and ²⁹Si-NMR spectroscopy. The feasibility of using Multi as the cross-linking agent in the holographic photopolymer system composed of Di was also investigated.

**Experiments**

**Materials**

1,1,3,3-Tetramethyldisiloxane (TMDS), 4-vinyl-1-cyclohexene 1,2-epoxide (VCHO), octamethycycloketetrasiloxane (D₄), poly(methylhydrosiloxane) (PMHS; average molecular weight: 1700 – 3200), hexamethyldisiloxane (HMDS), and hydrogen hexachloroplatinate(IV) hydrate were purchased from Aldrich and used without further purification.

Speier’s catalyst was prepared by dissolving 5 mg of hydrogen hexachloroplatinate(IV) hydrate in 1 mL of isopropanol; it was kept in a refrigerator until needed [21].

**Synthesis of Di**

A solution of 19.5 g (158 mmol) of VCHO in 15 mL of hexane was placed in a three-neck round-bottom flask equipped with a thermometer, dropping funnel, and reflux condenser; the temperature was maintained at 65 °C. To this solution, 0.36 mL of Speier’s catalyst was added and then 10 g (75 mmol) of TMDS was added dropwise using a dropping funnel. During the course of the reaction, samples were removed periodically, and the conversions were monitored by GC. After confirming the completion of the reaction, 0.58 g of charcoal was added to remove the catalyst at room temperature and the solution was stirred for 2 h. After filtration, the solvent and excess VCHO were removed by evaporation under vacuum at 50 °C. 24.1 g (88 % yield) of product (Di) was obtained. Characterization of the product was performed through the measurement of FT-IR and ¹H-NMR spectra.
Synthesis of SH Copolymer

An SH-1204 copolymer composed of 12 units of dimethylsiloxane and 4 units of methylhydrogen (m=12 and n=4 in Figure 2) was synthesized according to the general procedure [22,23] described below; other SH copolymers (2004 and 2804) were prepared by adjusting the mole ratios of the reagents.

D4 (44 g), PMHS (12.5 g), and HMDS (7.6 g) (end-capper) were added to a 250-mL four-necked reactor. After raising the temperature to 45 °C, 3 g of sulfuric acid was added and stirred under a nitrogen atmosphere for 48 h. Sodium hydrogen carbonate was added to neutralize the acid in the reaction mixture. The precipitate was filtered out and the cyclic monomers the remained at equilibrium were removed by vacuum stripping at 100 °C for at least 2 h.

Synthesis of Multi

A solution of 2.1 g (1.6 mmol, 6.4 milli-equivalents based on Si-H) of SH-1204 copolymer in 8 mL of hexane was placed in three-neck round-bottom flask equipped with a thermometer, dropping funnel, and reflux condenser; the temperature was maintained at 65 °C. To this solution, 0.04 mL of Speier’s catalyst was added and then a solution of 1 g (8 mmol) of VCHO in 4 mL of hexane was added dropwise using a dropping funnel. During the course of the reaction, samples were removed periodically and the conversions monitored by FT-IR spectroscopy. The reaction was considered complete (4 h) when the band at 2156 cm⁻¹ (assigned to Si-H bonds) had completely disappeared. Charcoal (65 mg) was added at room temperature to remove the catalyst and the solution was stirred for 2 h. After filtration, the solvent and excess VCHO were removed by evaporation under vacuum at 50 °C. 2.4 g (83 % yield) of product (Multi) was obtained. Characterization of the product was performed through the measurement of FT-IR and ¹H-NMR spectra.

Characterization

Gas chromatograms were measured with a capillary column [HP-1 (30 m × 0.25 mm i.d. × 0.25 µm)] using M600D (Young-Lin Instrument Co., Ltd). FT-IR spectroscopy was performed using a NEXUS apparatus (Nicolet Instrument Corp. U.S.A). The neat samples were cast directly onto sodium chloride plates. GPC was conducted on a Waters 2690 instrument equipped with a microstyrage column (HR1) and a refractive index detector. Chloroform was used as the solvent at a flow rate of 1 mL/min. ¹H-NMR and ²³Si-NMR spectra were obtained using a Bruker FT-NMR spectrometer (500 MHz) and CDCl₃ as the solvent. Cr(acac)₃ was added to the solutions for ²³Si-NMR spectroscopic measurements to decrease the relaxation time [24].

Photopolymerization

All experiments were performed in a dark room at room temperature.

The monomer mixture was prepared by mixing Di and Multi at a mole ratio of 1.0:0.37 and stirring to form a uniform and homogeneous liquid after adding the binder. To this mixture were added the photoacid generator (PAG) and sensitizer pre-dissolved in methylene chloride. The weight percentages of each component of the total monomer mixture were as follows:

- Binder (Dow Corning 705 silicone fluid): 100 wt%
- PAG (4-isopropyl-4-methylphenyldiphenildionium tetraakis(pentafluorophenyl)borate): 6.0 wt%
- Sensitizer [5,12-bis(phenylethynyl)naphthacene]: 0.05 wt%

Methylene chloide was removed by bubbling with nitrogen for 2 h; a sample of the resulting viscous recording medium was placed between two slide glasses (2 × 4 cm, 1 mm thickness) separated by a 100 µm poly(ethyleneterephthalate) spacer.

Holographic photorecording was conducted using an automatic photostoring system. The photorecording method adopted in this research was a typical technique used in the refractive index variation method, where a laser beam is divided into two beams of the same patterns by a beam splitter [20]. The intensities of the object and reference beams were same (1:1), the intensity of light was 50 mJ/cm², and the angle between the two beams was 40°. An automated shutter controlled the illuminating time of the object beam. The illuminating time was 3000 ms and the reading time was 500 ms [25]. Values of DE of each photopolymer film were calculated by division of the diffracted beam from the total beam (transferred beam + diffracted beam) as shown in equation (1).

\[
\text{DE (\%) = } \frac{\text{Diffraction Beam Intensity}}{\text{Diffraction Beam Intensity} + \text{Transmission Beam Intensity}} \times 100
\]

Results and Discussion

Synthesis of Di

Platinum is well known to catalyze hydrosilylation reactions and several types of stable platinum-containing catalyst, such as Lamoreaux [26], Speier, and Karstedt [27], have been applied for the synthesis of various silicone-type epoxy monomers, including Di. Activities of all these catalyst systems are generally known to be best at temperatures between 60 and 70 °C. In this work, the hydrosilylation reactions were performed at 65 °C using Speier’s catalyst.
Progress of the reaction was monitored by GC (Figure 3) and the intermediate (Mono), synthesized by coupling TMDS with one molecule of VCHO, was observed during the reactions. The progress of the reaction was also monitored by FT-IR to observe the disappearance of the strong Si-H stretching band at 2156 cm⁻¹ of TMDS and a band at 1666 cm⁻¹ assigned to vinyl groups of VCHO (Figure 4).

Di, purified by removal of the catalyst and evaporation, is a colorless high-boiling, low-viscosity liquid that is a mixture of stereo and geometric isomers. The presence of isomers resulted in extremely complicated signals in the region 0.9 ~ 2.2 ppm of the ¹H-NMR spectrum (Figure 5B). Compared to the ¹H-NMR spectrum of VCHO (Figure 5A), the shifts of protons “d” from 5.7 to 1.1 ppm and “e” from 4.9 to 0.4 ppm are direct evidence that the hydrosilylation reactions had occurred; the integration ratio of peaks “a”, “e’”, and “f’” corresponds to the ideal ratio (1:1:3).

Synthesis of SH Copolymer

SH copolymers were synthesized by the equilibrium polymerization of D4 and PMHS using HMDS as the end-capping reagent to control the molecular weight. Incorporation of HMDS in the feed led to the copolymer containing methylhydrosiloxy units; the ratio of methylhydrosiloxy units to dimethylsiloxy units in the copolymer can be regulated by the equivalent HMDS/D4 ratio in the feed.

The structure of the SH-1204 copolymer synthesized was analyzed using ¹H-NMR and ²⁹Si-NMR spectros-
Table 1. Compositions of the SH Copolymers and Their Average Molecular Weights

<table>
<thead>
<tr>
<th>D4/Si-H equivalent ratio in feed</th>
<th>Expected $M_n$ (g/mol)</th>
<th>Molar ratio of methylhydro/dimethylsiloxyl units in SH copolymera</th>
<th>$M_n^a$ (g/mol)</th>
<th>Polydispersity indexb</th>
</tr>
</thead>
<tbody>
<tr>
<td>12/4</td>
<td>1290</td>
<td>12.8/3.8</td>
<td>1337</td>
<td>1.30</td>
</tr>
<tr>
<td>20/4</td>
<td>1882</td>
<td>21.1/3.6</td>
<td>1939</td>
<td>1.35</td>
</tr>
<tr>
<td>28/4</td>
<td>2474</td>
<td>29.6/3.6</td>
<td>2568</td>
<td>1.42</td>
</tr>
</tbody>
</table>

a Based on $^{29}$Si-NMR spectra.

b Based on GPC.

Figure 7. IR spectra of the reaction mixture for the synthesis of Multi at reaction times of (A) 0 and (B) 4 h.

Figure 8. $^1$H-NMR spectrum of Multi.

Table 1. The ratios of methylhydrosiloxyl to dimethylsiloxyl units were almost the same as the targeted ratios, whereas the observed molecular weights were slightly higher than the targeted molecular weight, which we believe is due to the loss of low molecular weight species during vacuum stripping at 100 °C after the reaction. The PDI values of the SH copolymers were between 1.30 and 1.42, which are slightly higher than the values (1.24 ~ 1.32) reported previously for SH copolymers prepared using the same procedure [23].

Synthesis of Multi

The pendant silicone hydride units of the SH copolymer were used to hydrosilylate the vinyl groups of VCHO in the presence of a platinum-based catalyst to produce a systematic series of multifunctional epoxy silicones. A slight excess of VCHO (1.25 moles per mole of silicone hydride in copolymer) was introduced to react all of the silicone hydride groups. The progress of the reaction was monitored by FT-IR spectroscopy to observe the disappearance of the strong Si-H stretching band at 2156 cm$^{-1}$ (Figure 7). The completion of the reaction was confirmed by the complete disappearance of a peak (4.7 ppm) assigned to Si-H units in the $^1$H-NMR spectrum of Multi (Figure 8) and the absence of protons attached to the vinyl groups of VCHO, which would appear at 4.8 and 5.7 ppm if any unreacted VCHO remained.
Photopolymerization

In CROP, photopolymerization is initiated by an acid generator that is capable of producing an acid upon exposure to radiation. Thus, the acronym PAG is generally used instead of the word photo-initiator. Even though various types of Bronsted and Lewis acids are able to act as PAGs, diaryliodonium salts are commonly used. In the absence of a sensitizer, iodonium salts are typically sensitive only to radiation in the far-ultraviolet region, but such radiation is inconvenient for the production of hologram because ultraviolet lasers are substantially more expensive than are visible lasers. It is well known, however, that sensitizers, such as aromatic hydrocarbons substituted with at least two alkynyl groups or two alkenyl groups, can make iodonium salts sensitive to 514.5 nm radiation from an argon ion laser and 532 nm radiation from a YAG laser, both of which are convenient sources for the production of holograms. In this work, we used the most commonly used combination of 4-isopropyl-4-methyldiphenyliodonium tetrakis(pentafluorophenyl)borate as the PAG, 5,12-bis(phenylethynyl) naphthacene as the sensitizer, and 532 nm laser light as the light source.

DE, which is a basic index used to evaluate photopolymers system, depends on the many factors, such as the thickness of the specimen, the light source characteristics, and the compositions of its components (monomers, binder, PAG, and sensitizer). In previous research [15,18,19] on CROP photopolymers, the optimum compositions of PAG, sensitizer, and binder with respect to the total monomer mixture were not clearly determined. However, 0.05 wt% of the sensitizer and 100 wt% of the binder relative to the monomer mixture have been generally accepted compositions. In our efforts to evaluate the feasibility of using Multi as a co-monomer, the same compositions of the sensitizer and the binder, which were prepared by adding Multi with 0.4 mole% of Di, were applied for holographic photorecording in the presence of various amounts of PAG.

Figure 9 shows DE traces of photopolymer systems containing Multi-2004 (Multi prepared from SH-2004 copolymer) in the presence of various amounts of PAG. The increase in DE suggests that laser light was diffracted by the density gradient due to photopolymerization of monomers initiated by PAG upon irradiation. As expected, no change was observed in DE in the absence of PAG in (1) of Figure 9, which confirms that PAG initiates the photopolymerization. Photopolymers containing more than 6 wt% of PAG showed similar DE patterns; the maximum DE values are between 48 and 50 %. It is remarkable that the response time (the time required for the DE value to reach a maximum after irradiation) was very short, i.e., 3 sec. In our earlier study [20] of photopolymer systems based on the radical polymerization of acrylic monomers, the response times varied according to many factors, but they all were at least 55 sec. Considering CROP’s fast rate of reaction relative to radical polymerization, we believe that the phenomena observed in this study are due to CROP. The maximum DE (44 %) was reached 6 sec after irradiation for the photopolymer with 3 wt% of PAG. This significant delay in the response time is probably due to the decrease in the amount of PAG, which acts as an initiator in CROP.

Figure 10 presents DE traces of the photopolymers Multi-1204, 2004, 2804, and that containing only Di without Multi; in these systems the amount of PAG was fixed at 6 wt% with respect to the total monomer mixture. In the absence of Multi, the response time (3 sec) was the same as those for the photopolymers containing Multi, but only 14 % DE was obtained; this lower value of DE strongly suggests that the addition of Multi into Di is necessary for generating an effective photopolymer system. Among Multi-1204, -2004, and -2804,
no differences in response times were observed. The maximum DE values for Multi-2004 and -1204 were almost same, and slightly higher than that of Multi-2804. The lowest DE for Multi-2804 is considered due to its high viscosity. Diffraction of photopolymers is caused by the polymerization of monomers in the irradiated area as well as by monomers migrating from unexposed areas to exposed areas. Therefore, the intensity of diffraction can be affected by the viscosity of the monomers and binders. Further studies using Multi with higher molecular weight are needed in order to more clearly explain these phenomena.

Conclusions

Application of Multi as a co-monomer for the holographic photopolymerization of Di was studied. The following results are drawn:

1) Multis having different chain lengths were successfully synthesized through the hydrosilylation of SH copolymer with VCHO in the presence of a platinum-based catalyst.

2) The photopolymerization of Multi and Di was initiated by H⁺ produced from PAG upon irradiation.

3) Although the response time of the photopolymerization and DE depended on the amount of PAG, no further change was observed when more than 6 wt% of PAG relative to the total monomer mixture was used.

4) The characteristics of cationic polymerization in this system were manifested as a fast response time (ca. 3 sec), much faster than those of photopolymer systems based on the radical polymerization of acrylic monomers.

5) A monomer system combining both Multi and Di produced higher DE values than did the monomer composed of Di only.

6) No significant difference in the response time or DE was observed for Multis having different chain lengths, although the DE of Multi-2804 was slightly lower than those of Multi-1204 and -2004.

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References


