

## Study on the Optimization of Cationic Ring Opening Polymerization of Silicone-Based Epoxy Monomers for Holographic Photopolymers

Daeheum Kim

*Chemical Engineering Department, Kwangwoon University, Seoul 139-701, Korea*

Dae-won Chung\*

*Department of Polymer Engineering, University of Suwon, Gyeonggi-do 445-743, Korea*

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**Abstract:** This study examined the optimum compositions of binder, photo-acid generator (PAG) and sensitizer for the cationic ring opening polymerization of 1,3-bis[2-(3-{7-oxabicyclo-[4.1.0]heptyl})]-tetramethyldisiloxane in the presence of polydimethylsiloxane with four epoxide moieties as a co-monomer. When diffractive efficiency (DE) values were compared quantitatively to analyze the effect of the binder on holographic photopolymerization, DE was affected by the viscosity of the binders and miscibility with the monomer mixture. Extremely low DE values were observed when the immiscible dimethyl silicone was used as a binder. Therefore, methylphenyl silicone, which is miscible with the monomer mixture, was used as the binder for further studies. The optimal conditions were a binder viscosity between 250 to 390 cP, and contents of the binder, PAG, and sensitizer were 75-125 wt%, > 6 wt% and 0.05 wt% to the total monomer mixture, respectively.

**Keywords:** photopolymer, cationic ring opening polymerization, polydimethylsiloxane, epoxide, hydrosilylation.

### Introduction

Many researches have been focused on photopolymers as holographic recording materials, especially for the application of holographic digital data storage.<sup>1</sup> These materials have the advantage of recording and reading holograms in real time with relatively large refractive index modulation, high sensitivity, and low cost, compared with inorganic photorefractive crystals and photorefractive polymers.<sup>2</sup>

Photopolymers, which generally consist of binder, monomer, photosensitizing dye and initiator, were first used as holographic recording materials in 1969.<sup>3</sup> The system consisted of a mixture of acrylamide and metal acrylate monomers and a photocatalyst such as methylene blue and *p*-toluene sodium salt. Since then numerous systems based on acrylic-type monomers have been examined.<sup>4-6</sup> Among them, the family of acrylate-based system known as Omnidex series<sup>7-9</sup> is 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.<sup>10</sup> 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.

Recently, new photopolymer systems based on the sol-gel process,<sup>11-13</sup> or azopolymers<sup>14,15</sup> have been extensively studied for holographic application. Many researches have also focused on the photopolymers including the dual functional monomers such as epoxide and acrylate<sup>16</sup> or methacrylate.<sup>17</sup>

Another approach based on the cationic ring opening polymerization (CROP) of various monomers including cyclohexyl epoxides has been extensively examined<sup>18,19</sup> since diaryliodonium salts were reported to initiate CROP of epoxide on irradiation with ultraviolet.<sup>20</sup> In particular, the system composed of silicone derivatives containing 1,3-bis[2-(3-{7-oxabicyclo[4.1.0]heptyl})]tetramethyldisiloxane (Di in Figure 1), as monomer and silicone oil as a binder has been extensively investigated.<sup>21-24</sup> According to the report<sup>25</sup> where multifunctional epoxy monomers used as co-monomer, holographic recording materials comprising Di and cyclic siloxane having four epoxy functionalities exhibited significantly decreased shrinkage, cracking and brittleness.

We have established holographic photorecording system<sup>26</sup> and the feasibility of new types of multi-functional epoxy monomer (Multi in Figure 2) for photopolymer system based on CROP of Di was examined.<sup>27</sup> As a result, Multi was found able to be applied for the cross-linking agent for holographic recording materials. In this study, the effects of the viscosity of binder on the holographic photopolymerization of Di in the presence of co-monomer (Multi) were

\*Corresponding Author. E-mail: dwchung@suwon.ac.kr

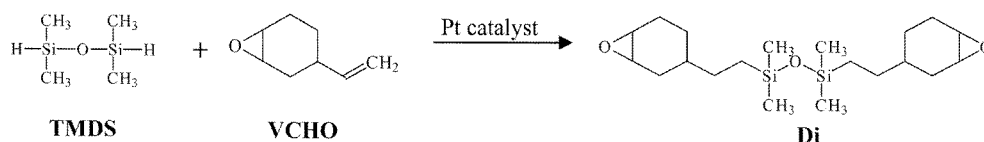


Figure 1. Synthesis of Di.

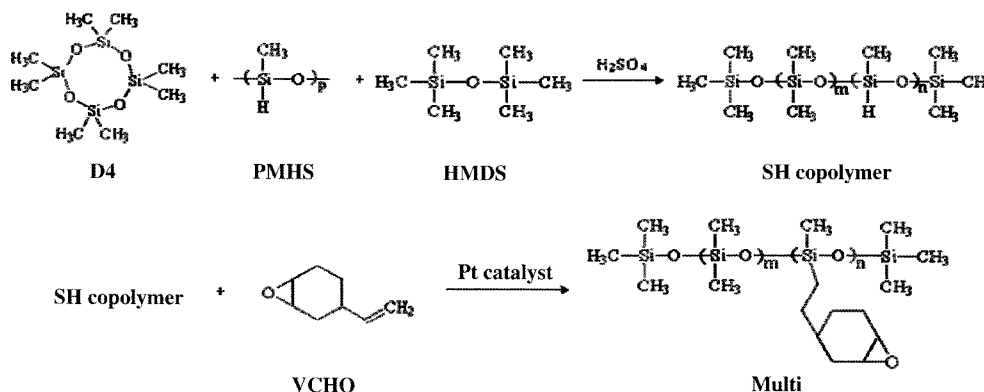


Figure 2. Synthesis of Multi.

investigated and the optimizations of the content of binder, photo-acid generator (PAG) and sensitizer were also carried out.

## Experimental

**Materials.** 1,1,3,3-Tetramethyldisiloxane (TMDS), 4-vinyl-1-cyclohexene 1,2-epoxide (VCHO), octamethylcyclotetrasiloxane (D4), poly(methylhydrosiloxane) (PMHS, average molecular weight, 1,700-3,200), hexamethyldisiloxane (HMDS) and hydrogen hexachloroplatinate (IV) hydrate, and 5,12-bis(phenylethynyl) were purchased from Aldrich and used without further purification. 4-Isopropyl-4-methyldiphenyliodonium tetrakis(pentafluorophenyl)borate was purchased from TCI Chemicals, and silicone oils such as methylphenyl silicone (MPS) and dimethyl silicone (DMS) were purchased from Shinetsu Co.

Speier catalyst was prepared by 5 mg of hydrogen hexachloroplatinate (IV) hydrate in 1 mL of isopropanol and kept in refrigerator before use.<sup>28</sup>

**Synthesis of Di and Multi.** Two silicone-based epoxy monomers (Di and Multi) were synthesized by hydrosilylation, which is most generally used for the coupling of organic molecules to silicones.<sup>29-32</sup>

Di was prepared according to the reported method<sup>27</sup> (Figure 1). Briefly, 2.4 moles of VCHO was hydrosilylated with 1.0 moles of TMDS in the presence of Speier catalyst at 65 °C. Characterization of the product was performed by the measurement of FTIR, <sup>1</sup>H NMR and <sup>29</sup>Si NMR.

Multi was synthesized by two step reactions as described in the earlier report<sup>27</sup> (Figure 2). The first step is the synthesis of SH-2004 copolymer composed of 20 units of dimethylsiloxane and 4 units of methylhydrogen (m=20 and n=4 in

Figure 2) and the characterization of SH copolymer was performed by the measurement of FTIR, <sup>1</sup>H NMR and <sup>29</sup>Si NMR.<sup>27</sup> The second step is the synthesis of Multi by the hydrosilylation reaction of SH copolymer with VCHO and the characterization of Multi was performed by the measurement of <sup>29</sup>Si NMR.

**Characterization.** Viscosity of a binder was measured using Brookfield viscometer (Synchro Electric, LVF-E) at room temperature. <sup>1</sup>H NMR and <sup>29</sup>Si NMR were obtained by Spectrometer FT-NMR (500 MHz) of Bruker using CDCl<sub>3</sub> as a solvent. Cr(acac)<sub>3</sub> was added to the solutions for <sup>29</sup>Si NMR measurements to decrease the relaxation time.<sup>33</sup>

**Photopolymerization.** All experiments were carried out in the dark room at room temperature. Monomer mixture was prepared by mixing Di and Multi with a mole ratio of 5 : 2 (3 : 7 with a weight ratio) and stirred to form a uniform and homogeneous liquid after adding binder. To this mixture were added photo acid generator (PAG) and sensitizer pre-dissolved in methylene chloride.

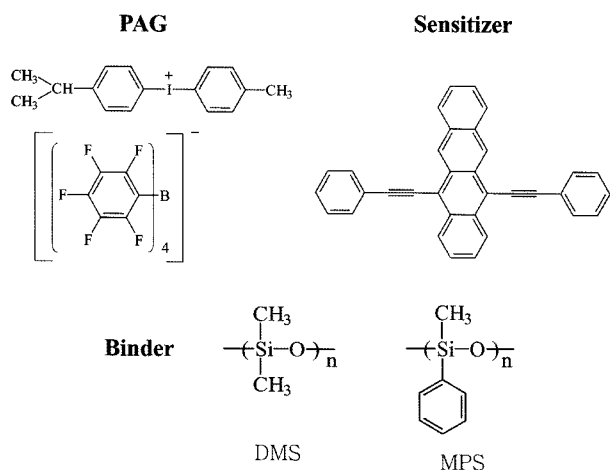
The chemical structure of each component is described in Figure 3 and the standard weight % to total monomer mixture is as followings;

Binder (silicone fluid): 100 wt%

PAG (4-isopropyl-4-methyldiphenyliodonium tetrakis(pentafluorophenyl)borate): 6.0 wt%

Sensitizer (5,12-bis(phenylethynyl)naphthacene): 0.05 wt%

Methylene chloride was removed by bubbling with nitrogen flowing for 2 h and a sample of resulting viscous recording medium was placed between two slide glasses (2×4 cm, 1 mm thickness) separated by a 100 μm poly(ethylene-terephthalate) spacer.



**Figure 3.** Chemical structure of PAG, sensitizer and binders.

Holographic photorecording is conducted by automatic photostoring system. Photorecording method adopted in this research is a typical technique used in the refractive index variation method, where laser beam is divided into two beams of same patterns by beam splitter.<sup>26</sup> The intensities of object beam and reference beam are same (1:1), and the angle between two beams is 40 degree. The intensity of the beam was controlled at 50% of the maximum intensity of the laser (532 nm green Ar-ion laser, 100 mW). Automated shutter control the illuminating time of object beam. Illuminating time is 3,000 ms and reading time is 500 ms.<sup>34</sup> DE's of each photopolymer films are calculated by division of diffracted beam from total beam (transferred beam + diffracted beam) as shown in eq. (1).

$$DE(\%) = \frac{\text{Diffraction Beam Intensity}}{\text{Total Beam Intensity}} \times 100 \quad (1)$$

DE's were obtained by manipulating the measuring system using MPAS operating program(S/W, prism tech. Co., Ltd). After exposing 3 sec, the shutter was closed, and the intensities of diffracted beams of reference beams were measured. The above sets of measurements were repeated up to 300 times to get DE value. The intensity of the beam was controlled at 50% of the maximum intensity of the laser (100 mW). More detailed configuration of the system is schematically described in our earlier report.<sup>26</sup>

## Results and Discussion

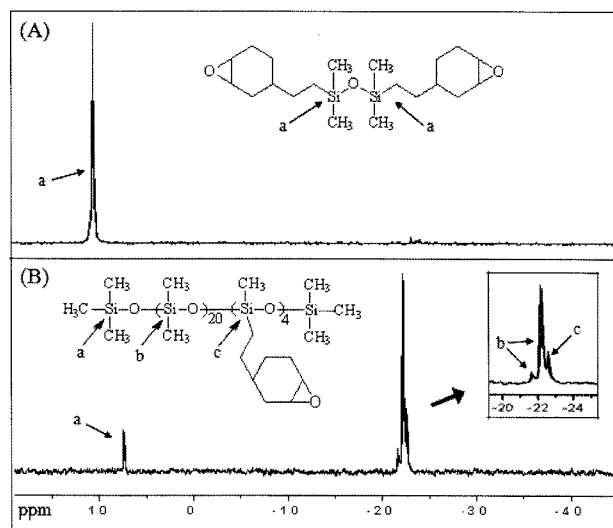
**Synthesis of Di and Multi.** The basic monomer (Di) and co-monomer (Multi) were synthesized by hydrosilylation reactions according to the reported method.<sup>27</sup> In this work, the hydrosilylation reactions were carried out at 65 °C using Speier catalyst. The characterization of both monomers was carried out by <sup>1</sup>H NMR<sup>27</sup> and the additional studies were performed by <sup>29</sup>Si NMR as described in Figure 4.

Only one signal at 8.0 ppm shown in <sup>29</sup>Si NMR spectrum

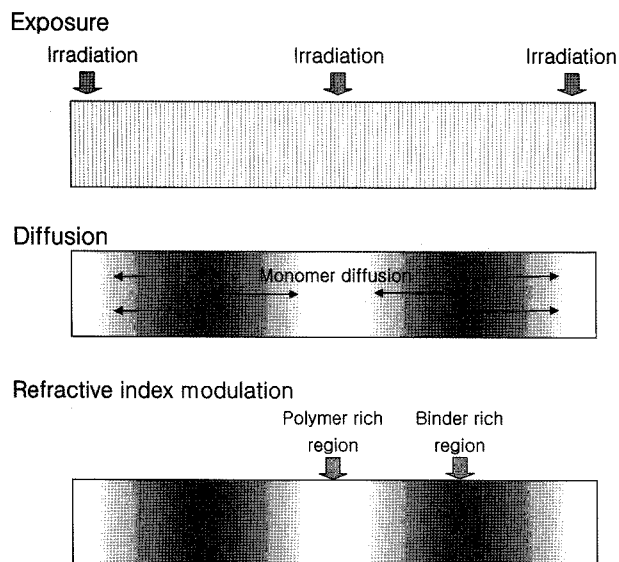
of Di (Figure 4(A)) demonstrate the absence of silicone hydride of unreacted VCHO or the possible side products (for example, a compound where only one VCHO coupled to one of two silicone hydrides of TMDS), which appears at -7.2 ppm if remained.

For Multi, two major peaks were observed and assigned as marked in Figure 4(B). A peak at around -22 ppm is very complicated and silicones assigned to "b" and "c" were duplicated. However, the enlarged spectrum as shown in the box indicates that "c" appeared at -22.6 ppm, and "b" is divided into two peaks. Of them, a minor peak at 21.7 ppm can be assigned as the silicones adjacent to terminal trimethylsiloxane. Exactly same spectrum was observed for polydimethylsiloxane grafted with polyoxyethylene, which was synthesized by the hydrosilylation reactions of SH copolymer and allyl-terminated polyoxyethylene.<sup>35</sup> In <sup>29</sup>Si NMR of Multi, the absence of a signal corresponding to silicone hydride of SH copolymer, which appears at -38 ppm if remained,<sup>27</sup> demonstrates complete hydrosilylation reaction.

**Effect of a Kind of Binder on Photopolymerization.** The holographic photopolymer system is composed of monomer, initiator, binder and, if necessary, sensitizer. Under the irradiation, the monomer undergoes polymerization to form a polymer that has a refractive index different from that of the binder. Diffusion of fresh monomer remained in non-illuminated regions into the illuminated regions provides higher density gradients that results in refractive index modulations needed, as schematically illustrated in Figure 5. In CROP, photopolymerization is initiated by acid generator capable of producing acid upon exposure to radiation. Thus, the term of "photo acid generator (PAG)" is generally used instead of initiator. Even if various types of Bronsted and Lewis acid are able to act as PAG, diaryliodonium salts are commonly used. In this work, the combination of 4-isopropyl-4-methyldiphenyliodonium tetrakis-(pentafluorophenyl)



**Figure 4.** <sup>29</sup>Si NMR of Di (A) and Multi (B).

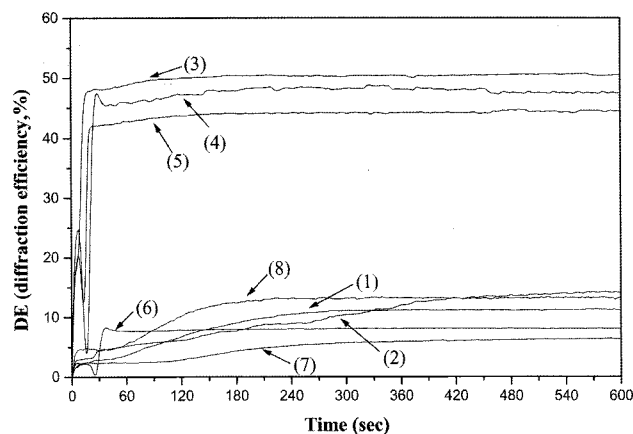


**Figure 5.** Diffraction gradient formation after exposure.

borate as PAG, 5,12-bis(phenylethynyl)naphthacene as sensitizer and 532 nm laser light as light source is used. As the binder, silicone fluid is usually used for CROP of Di.<sup>18-24</sup> In this work, the most common silicone oils such as DMS or MPS were applied as the binder.

DE, which is the basic index to evaluate the photopolymers system, depends on the many variations such as thickness of specimen, the light source characteristics and compositions of components (monomers, binder, PAG and sensitizer). In this work, the effects of binder, PAG and sensitizer on DE were investigated under the fixed thickness of specimen (100  $\mu\text{m}$ ), the light source (532 nm) and the molar ratio of monomer mixture ([Multi]:[Di]=2:5), which was found optimum in our previous research.<sup>27</sup>

Figure 6 shows the effect of a kind of binder on DE when 0.05 wt% of sensitizer, 6 wt% of PAG and 100 wt% of binder to monomer mixture were applied for holographic photo-recording. The viscosity and miscibility of monomer



**Figure 6.** DE traces of photopolymers with a kind of binder; (1) MPS080, (2) MPS130, (3) MPS250, (4) MPS340, (5) MPS390, (6) MPS550, (7) DMS250, (8) DMS390.

mixture with silicone oils used for the binder were summarized in Table I.

DE depends on the degree of diffracted laser light and the diffraction is caused by the density gradient due to photopolymerization of monomers initiated by PAG upon irradiation. The series using DMS as a binder showed extremely low DE values, which suggests that the photopolymerization was not sufficiently occurred or monomers in the unexposed area do not migrate to exposed area. DMSs are miscible with Di, but not with Multi, and the samples using DMS as a binder showed phase separation. The immiscibility of Multi with DMS is considered to induce the extremely low DE values.

When MPS miscible with both Di and Multi was used as the binder, strong dependence of the viscosity of the binder on DE was observed. As shown in Figure 6, MPSs with the viscosity range of 250-390 cP exhibited similar DE patterns, and the maximum DE value (48%) was achieved for MPS250. It is remarkable that response time, which is defined as a time taken until DE value reaches to a maximum after irradiation, is very short (about 10 sec).

**Table I. The Chemical Structure and Viscosity of Silicone Oils Used as Binder**

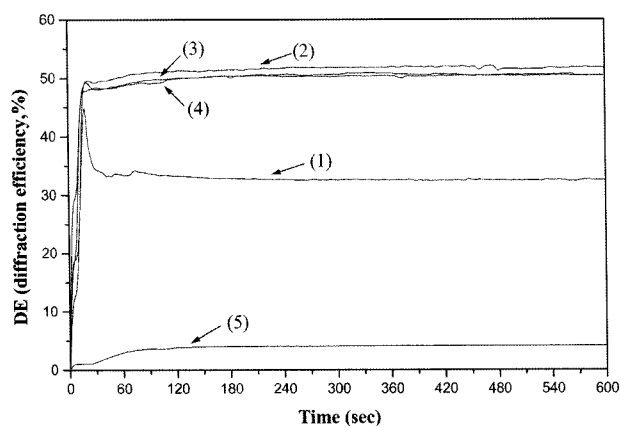
Chemical Type	Code	Trade Name	Viscosity (cP)	Miscibility <sup>c</sup> with Monomer Mixture
MPS <sup>a</sup>	MPS080	704	80	Miscible
	MPS130	704 + 705 (1:1 by weight)	130	
	MPS250	705	250	
	MPS340	705 + KF54 (1:1 by weight)	340	
	MPS390	705 + KF54 (1:2 by weight)	390	
	MPS550	KF54	550	
DMS <sup>b</sup>	DMS250	200 Fluid	250	Immiscible
	DMS390	400 Fluid	390	

<sup>a</sup>Methylphenyl silicone. <sup>b</sup>Dimethyl silicone. <sup>c</sup>Visually observed.

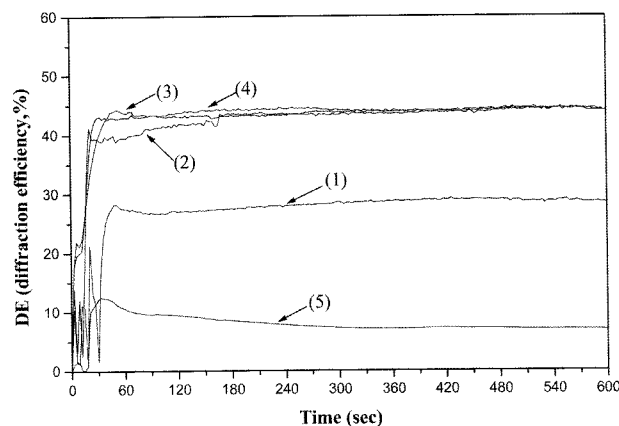
In our earlier study<sup>26</sup> for photopolymer systems based on the radical polymerization of acrylic monomers, response times were varied by many valuables, however, were at least more than 55 sec. The phenomena observed in this study are in accordance with CROP's fast reaction over radical polymerization, which is generally accepted as an advantage of CROP. On the other hand, DE values of the photopolymer systems using MPS080, MPS130 and MPS550 as a binder were less than 10%, and the response time is not clear.

The viscosity of binder should be a critical factor to decide the performance of holographic photopolymer systems because diffraction gradient is caused by the polymerization of monomers not only in the irradiated area, but also migrated from unexposed area to exposed area, as shown in Figure 5. However, among many researches where CROP is applied for the holographic photopolymer, only one study<sup>36</sup> describes viscosity value (250 cP) of a binder without any detailed studies on the effect of the viscosity of a binder. Considering the similarity of this value with the optimum viscosity obtained in our work, the appropriate viscosity of a binder for holographic photopolymer system is supposed in the range of 200-400 cP

**Effect of Amount of Binder.** Figure 7 shows the effect of an amount of binder (MPS250) on DE of photopolymer systems. When the content of MPS 250 in photopolymer system was in the range of 75-125 wt% to total monomer mixture, the similar DE patterns were observed and the final DE values reached to about 50%. On the other hand, for 50 wt% or 150 wt% of MPS250, final DE values reached to only 32% and 4%, respectively. In the case when MPS340 instead of MPS250 was used as the binder, almost same results were obtained, as described in Figure 8. The final DE values reached to about 42% in the range of 75-125 wt% of MPS340 to total monomer mixture, on the other hand, DE values were only 27% or 6% for 50 wt% or 150 wt%, respectively. Since the concentration of monomers decreases as the binder content increases, the polymerization has not



**Figure 7.** DE of photopolymers with various amount of MPS250; (1) 50 wt%, (2) 75 wt%, (3) 100 wt%, (4) 125 wt%, (5) 150 wt%.



**Figure 8.** DE of photopolymers with various amount of MPS340; (1) 50 wt%, (2) 75 wt%, (3) 100 wt%, (4) 125 wt%, (5) 150 wt%.

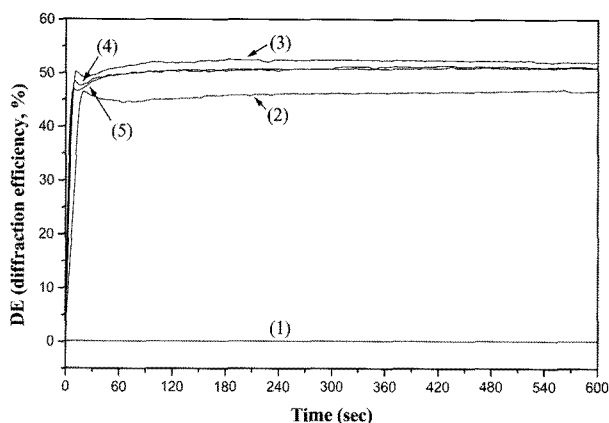
effectively occurred. Therefore, only 4% or 6% of DE are observed for 150 wt% of MPS250 or MPS340. On the other hand, when the binder content becomes lower, density gradient of monomers in the system is diminished and finally sufficient DE value has not been achieved for 50 wt% of binder.

In the previous research on photopolymers based on CROP<sup>23,25,37</sup> or radical polymerization,<sup>11,27,38</sup> the optimum compositions of PAG, sensitizer and binder to total monomer mixture were not clearly determined, and no studies on the effect of the content or the viscosity of a binder were carried out. However, 70-200 wt% of binder to monomer mixture were accepted as a general composition.<sup>11,36,38</sup> In this study, the optimum content of binder is also in the range of 100-125 wt% to total monomer mixture.

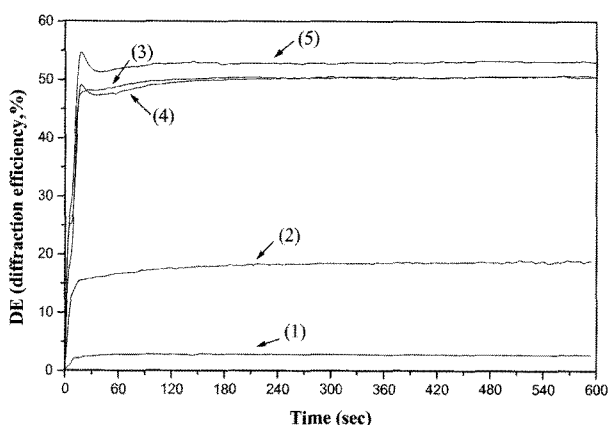
It is interesting that the DE values obtained from MPS 250 were slightly higher than those obtained from MPS340, which is more viscous than MPS250. Since the monomers in unexposed area are easily diffused as the viscosity of binder becomes lower, the density gradient is intensified. Therefore, MPS250 with lower viscosity is considered to exhibit slightly higher DE value.

**Effect of Amount of PAG.** Figure 9 shows DE of photopolymer systems where the amount of MPS250 is fixed with 100 wt% and the amount of PAG varies. Increase in DE suggests that laser light be diffracted by the density gradient due to photopolymerization of monomers initiated by PAG upon irradiation. As expected, no change in DE without PAG was observed in Figure 9(1). Photopolymers containing more than 6 wt% of PAG showed similar DE pattern and maximum DE values are 48-51%.

**Effect of Amount of Sensitizer.** As described earlier, CROP is initiated by PAG capable of producing acid upon exposure to radiation and activated by sensitizer. In this study, PAG produces iodonium salt upon irradiation and sensitizer makes iodonium salts sensitive to 532 nm. This combination is most commonly applied for CROP.



**Figure 9.** DE of photopolymers with various amount of PAG; (1) 0 wt%, (2) 3 wt%, (3) 6 wt%, (4) 9 wt%, (5) 12 wt%.



**Figure 10.** DE of photopolymers with various amount of sensitizer; (1) 0.025 wt%, (2) 0.0375 wt%, (3) 0.05 wt%, (4) 0.0625 wt%, (5) 0.075 wt%.

As described in Figure 10, no photopolymerization occurred when sensitizer was used in an amount of 0.025 wt% to total amount of monomers, and DE values increase as the amount of sensitizer increases. The lower DE values observed under 0.0375 wt% of sensitizer are considered due to insufficient photopolymerization in exposed area. The maximum DE values reached to about 50% when 0.05 wt% of sensitizer was applied and no further increase in DE value was observed as the content of sensitizer increased higher than 0.05 wt%.

## Conclusions

Optimum compositions of binder, PAG and sensitizer for the cationic ring opening polymerization of Di in the presence of Multi were investigated by quantitatively comparing DE values. The following results are drawn:

1) When two kinds of silicone oils were used as the binder, DE was found significantly affected by the viscosity of binders as well as the miscibility with monomer mixture.

Extremely low DE values were observed when the immiscible DMS was used as the binder. When MPS miscible with the monomer mixture was used as the binder, strong dependence of DE on the viscosity of a binder was observed. The maximum DE value (48%) was achieved for MPS250 and MPSs with the viscosity range of 250-390 cP exhibited similar DE patterns.

2) When the content of MPS250 in photopolymer system was in the range of 75-125 wt% to total monomer mixture, the similar DE patterns were observed and the final DE values reached to about 50%. On the other hand, for 50 wt% or 150 wt% of MPS250, final DE values reached to only 32% and 4%, respectively. The former can be explained by lower concentration of monomers in the system, and the latter by lower density gradient.

3) Photopolymers containing greater than 6 wt% of PAG showed similar DE pattern and maximum DE values are around 48-51%.

4) When sensitizer was used less than 0.025 wt% to total amount of monomers, no photopolymerization occurred. DE values increased as the amount of sensitizer increased. The maximum DE value reached to about 50% when 0.05 wt% of sensitizer was applied and no further increase in DE value was observed as the content of sensitizer increased higher than 0.05 wt%.

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