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Photoinitiator-Free Photopolymerization of Silicon-Containing Maleimides Based on Electron-Donor-Acceptor Systems

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Summary: Photocured coatings promise enhanced performance, higher productivity and an improved environmental impact on the favorable reduction or near elimination of volatile organic compounds. Increasing interest in the photocuring industry has been imposed on the "photoinitiator-free photopolymerization [PIFP]" system based on the electron-donor-acceptor [EDA] concept, which commonly employs a mixture of a vinyl ether monomer (donor) and an *N*-substituted maleimide or bismaleimide monomer (acceptor). The PIFP systems employing silicon-containing maleimides together with vinyl ether monomers were firstly investigated and their photoreactions resulted in quite fast curing comparable to the conventional acrylate-based photocurable systems.

Keywords: electron-donor-acceptor polymerisation; photoinitiator; photopolymerization; silicon-maleimides; vinyl ethers

Introduction

Photocuring has found over the years an increasing number of industrial applications and will continuously find new application areas to meet the required properties in advanced technologies. The major reasons for this increase are its unique benefits, including solvent-free formulations, high-cure speed and low-temperature processing.[1] Photo- or UV-curing technology is becoming the process of choice in many industries as engineers are developing processes for new products. Photocured coatings promise enhanced performance, higher productivity, and considerable economic and ecological advantages, in particular, adaptable environmental effects by no use of organic solvents. Acrylate-based photocurable formulations with various photoinitiators [PI] are currently used in most photocuring formulations because of their superior reactivity.[1,2] As the unreacted PI residues may affect the long term properties of photocured polymer coatings, growing attention has been given to photoinitiator-free formulations undergoing fast polymerization upon UV exposure. Increasing interest in the photocuring industry for alternatives to the commonly used acrylate monomers and prepolymers has recently focused on the photoinitiator-free photopolymerization of electron-donor-acceptor [EDA] type monomers upon UV exposure in the absence of any added photoinitiator [PI].[3] Hall *et al.*[4–6] have investigated the alternating copolymerizations of various functional EDA monomer systems undergoing spontaneously without using a radical initiator and concluded that electron-donor-acceptor olefins could, in certain cases, lead to photoinduced copolymerization by a free radical process via EDA complexation.

Upon selective combination of a moderate electron-donor and a strong electron-acceptor or the reverse, self-initiated

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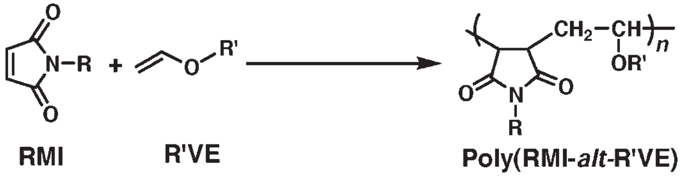

Figure 1.
Radical copolymerizations of RMI and R'VE based on the electron-donor-acceptor concept usually produce alternating copolymers poly(RMI-*alt*-R'VE).

photo-polymerizations are realized even in the absence of externally added PIs. A series of such photocuring systems employing photoinduced polymerization of EDA monomer pairs has been studied in the past decade by C. Decker, S. Jonsson, C. E. Hoyle *et al*. In particular, as such non-acrylate photocurable resins, the vinyl ether-maleimide combination has exhibited the distinct advantage of undergoing a rapid photopolymerization upon UV exposure in the absence of any added photoinitiator.[7–13] Mixtures of a vinyl ether (R'VE) (donor) and an *N*-substituted maleimide (RMI) (acceptor) are a well-known EDA monomer pair and their radical copolymerizations are extensively studied to give alternating copolymers as described in Figure 1.

The mostly studied "photoinitiator-free photopolymerization [PIFP]" system is known to consist of a mixture of R'VE and RMI or bismaleimide (BisRMI) monomers and it undergoes a photocuring reaction as described in Figure 2. The photoreactivities of some R'VE/RMI based systems were found to be as high as those of widely used photocurable acrylate resins containing a radical-type PI. These photoinitiator-free formulations were found to be less sensitive to oxygen inhibition than typical photocurable acrylate resins.

Certain RMI monomers undergo homopolymerization even when they are exposed to UV-radiation, provided that the RMI monomer contains easily abstractable hydrogens.[9–12] To initiate the chain reaction, either one of the two monomers needs to contain labile hydrogen atoms, in order to produce free radicals through hydrogen abstraction by the excited maleimide (RMI*) molecule as shown in Figure 3.[6,12–14] The labile hydrogen atoms on either one of the monomers and donor (DH) molecules was shown to be essential in order to achieve a rapid polymerization upon UV exposure.

There has been a practical interest in such photoinitiator-free photocuring systems that polymerize readily upon UV-irradiation because, in conventional photocurable systems, the unreacted residual

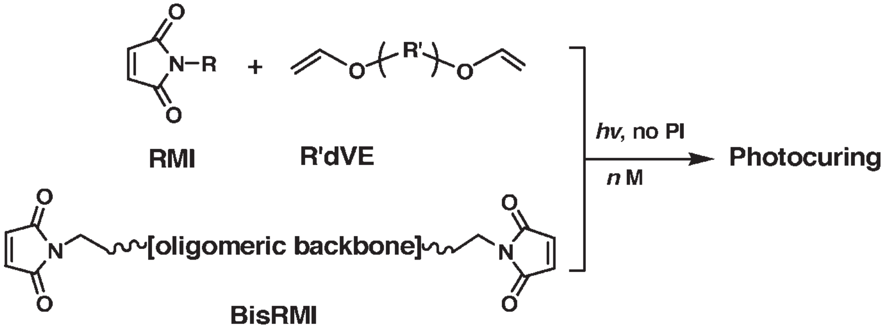

Figure 2.
Photoinitiator-free photopolymerization (PIFP) of RMI and R'VE based on the electron-donor-acceptor concept.

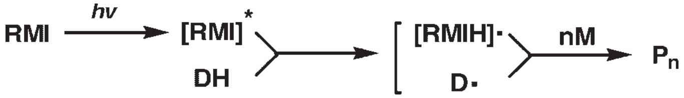

Figure 3.
The photopolymeriztion mechanism initiated by excited RMI (as RMI*) through the hydrogen abstraction which plays a key role in the photocuring efficiency.

photoinitiator and its photoproducts may have some detrimental effects on the final properties of the photocured coating materials causing for color, odor, extractables etc. As described in Figure 2, upon UV-irradiation, difunctional *N*-substituted BisRMIs association with difunctional vinyl ethers (R'dVE) lead to the build-up of photocured polymer networks by PIFP and there are known some commercial combination of these monomers for photoinitiator-free photocurable systems.[15]

In our previous reports, variously *N*-substituted functional maleimides have been prepared and copolymerized for application in lithographic photopatterning.[16–19] Photocurable resin formulations having efficient photoinitiating systems have been also investigated for application as photocurable dental materials.[16,20,21] In this report, several silicon-containing RMIs have been prepared and combined with commercial R'VEs to be applied as the efficient PIFP system. The PIFP systems employing silicon-containing maleimides along with vinyl ether monomers were investigated and their photoreactions were evaluated by virtue of FTIR and UV spectroscopy and DPC analysis to compare them with the conventional acrylate-based photocurable systems.

Experimental Part

Materials and Instruments

Maleimide (MI), *N*-ethylmaleimide (EMI), 1,7-dichlorooctamethyltetrasiloxane, various chlorosilanes, benzoin methyl ether (BME), benzoin, and other benzoin alkyl ethers were purchased from Aldrich Chemical Co. and used in the reactions as received. Two kind of ester type divinyl ethers, bis{[4-(vinyloxymethyl)cyclohexyl]-methyl} glutarate (BCHGVE) and bis[4-(vinyloxy)butyl] adipate (BBAVE) were purchased from Aldrich Chemical Co. Triethyleneglycol divinyl ether (TEGDVE), 4-hydroxybutyl vinyl ether (HOBVE), and other alkyl vinyl ethers were kindly donated from ISP-Korea (Seoul). Trimethylolpropane triacrylate (TMPTA), various multifunctional acrylates, and commercially known aromatic carbonyl photoinitiators were kindly donated from Miwon Commercial Co. (Korea). An oligomeric polyether bismaleimide (MIA200, light-yellowish viscous liquid), poly(oxybutylene)-di(2-maleimidoacetate), was commercially available as LUMICURE MIA-200 and kindly donated from Dainippon Ink & Chemical, Inc. (Japan). Those various vinyl ether and acrylate monomers and photoinitiators were used as received or purified by fractional distillation if necessary.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer of Perkin-Elmer using deuteriochloroform as internal standard. Infrared spectra were recorded on a Polaris FT-IR spectrophotometer of Mattson Instrument Co. Thermal properties of polymers were analyzed by Model DSC 910 and Model 951 TGA of TA Instruments, Inc. UV spectra were recorded on a JASCO Model V530 UV-Vis spectrophotometer. Photocuring was performed by using a UI-501 C/Q Exposure System equipped with a 500 W high pressure Hg-lamp of Ushio Co. (Japan). The light intensity was 8.0 mW/cm^2 measured at 365 nm wavelength. A Differential Photocalorimeter (DPC 930) equipped with a 250 W Hg-lamp (light intensity of 2.5 mW/cm^2) in conjunction with Model DSC 2910 of

TA Instruments (USA) was used to evaluate the photoreactivity.

Syntheses of Silicon-Containing Maleimides (RSiMI)

Variously *N*-substituted functional maleimides have been prepared by reactions of maleimide (MI) and corresponding chlorosilanes according to the procedure previously reported.[22,23,24] *N*-(Trimethylsilyl)-maleimide (TMSMI) was prepared by a reaction of MI and chlorotrimethylsilane in 70% yield as liquid.[23]

Synthesis of N-(Dimethylvinylsilyl)maleimide (VSiMI)

In a 500 ml-three neck-flask MI (5.00 g, 0.052 mol) was dissolved in anhydrous 200 ml benzene and triethylamine (NEt_3) (5.00 g. 0.052 mol) was added, and stirred under nitrogen flow for 1 hr. To the solution was added dropwisely chlorodimethylvinylsilane (9.05 g, 0.075 mol) while cooling in an ice-water bath and then the solution was refluxed for 5 hr in a heated oil bath. The salt precipitate was removed by filtration and passing through an alumina column, and then benzene was removed from the resulting solution under reduced pressure. The crude product was purified by column chromatography in silica gel (ethyl acetate/hexane, 3:7 by vol) to obtain white crystals of VSiIMI in a yield of 40.4% (3.82 g), mp 36–38 °C. ^1H NMR (200 MHz, $CDCl_3$): 0.55 (s, 6H), 5.8-6.3 (m, 3H), 6.7 (s, 2H).

Synthesis of N-(Trimethylsiloxyethyl)maleimide (TMSiOEMI)

Firstly, *N*-(2-hydroxyethyl)maleimide (HEMI) was prepared by thermolysis for a retro-Diels-Alder reaction of a maleic anhydride and HEMI adduct in a short distillation apparatus at 140 °C under high vacuum condition in a yield of 58.6%, mp 65 °C. ^1H NMR (200 MHz, $CDCl_3$): 2.67 (s, 1H, OH), 3.80 (m, 4H, CH_2CH_2), 6.68 (s, 2H, $CH{=}CH$). The Diels-Alder adduct of maleic anhydride and furan in 60 ml ethanol was reacted with ethanolamine to obtain a maleic anhydride and HEMI adduct (mp 128 °C) in a yield of 78% according to a modified procedure.[25,26]

Into a 250 ml-three neck-flask HEMI (5.00 g, 0.035 mol) was charged and dissolved in anhydrous 100 ml benzene, and NEt_3 (3.55 g, 0.035 mol) was added while stirring under nitrogen flow for 1 hr. Chlorotrimethylsilane (5.79 g, 0.053 mol) was added to the solution while cooling in an ice-water bath and then the same reaction procedure as above for VSiMI was followed. After column chromatography in silica gel (ethyl acetate/hexane, 1:1 by vol) obtained was white crystals of TMSiOEMI in a yield of 75.3% (5.72 g), mp 50–52 °C. ^1H NMR (200 MHz, $CDCl_3$): 0.10 (br s, 9H), 3.7 (s, 4H), 6.7 (s, 2H).

Synthesis of N-(Dimethylvinylsilyloxyethyl)maleimide (VSiOEMI)

The reaction of HEMI (5.00 g, 0.035 mol) and chlorodimethylvinylsilane (6.86 g, 0.053 mol) was performed following the above procedures for TMSiOEMI. After column chromatography in silica gel (ethyl acetate/hexane, 1:5 by vol) obtained was white plate crystals of VSiOEMI in a yield of 71.9% (5.75 g), mp 28–30 °C. ^1H NMR (200 MHz, $CDCl_3$): 0.55 (s, 6H), 3.7 (br s, 4H), 5.8–6.3 (m, 3H), 6.7 (s, 2H).

Synthesis of 1,7-Bis(2-maleimidoethoxy)octamethyltetrasiloxane (TSiOBMI)

The reaction of HEMI (10.00 g, 0.071 mol) and 1,7-dichlorooctamethyltetrasiloxane (14.93 g, 0.043 mol) was the same as above and followed by column chromatography in silica gel (ethyl acetate/hexane, 1:2 by vol) to obtain colorless viscous liquid of TSiOBMI in a yield of 64.8% (12.90 g) solidified less than 0 °C. ^1H NMR (200 MHz, $CDCl_3$): 0.1 (s, 24H), 3.8 (dm, 8H), 6.7 (s, 4H).

Photopolymerization and Analysis

The chosen RMI monomer was well mixed with a viscous R'VE monomer in equimolar amounts to prepare the given photocurable sample. In some cases, a minimum amount of methanol was used to make a homogenous liquid sample when an RMI is solid and sparingly soluble in the chosen R'VE. The viscous samples were coated on a quartz plate for the UV absorption spectral analysis. For photopolymerization study, he viscous liquid samples were covered with a laminating polypropylene (PP) film to protect it from the diffusion of atmospheric oxygen during the UV irradiation. The liquid samples were placed in between the PP films for the FT-IR spectral analysis and the thickness of the photocured films was about 2–3 μm. The decrease in absorption spectral intensities of the C=C double bonds of the both monomers during the photopolymerization was measured to analyze the photoreactivity. The photocuring efficiency was also evaluated with a differential photocalorimeter (DPC) using 2-5 mg of the samples.

Results and Discussion

Various silicon containing maleimides (RMI), bismaleimides (BisRMI), vinyl ethers (R'VE), and divinyl ethers (R'dVE) used in this study are listed in Figure 4 and they were applied for photoinitiator-free photocurable systems. All the prepared silicon-containing maleimides are low temperature melting solids except TSiOBMI which is viscous liquid in room temperature and they were prepared in good yields with taking appropriate methods.[22–24] The

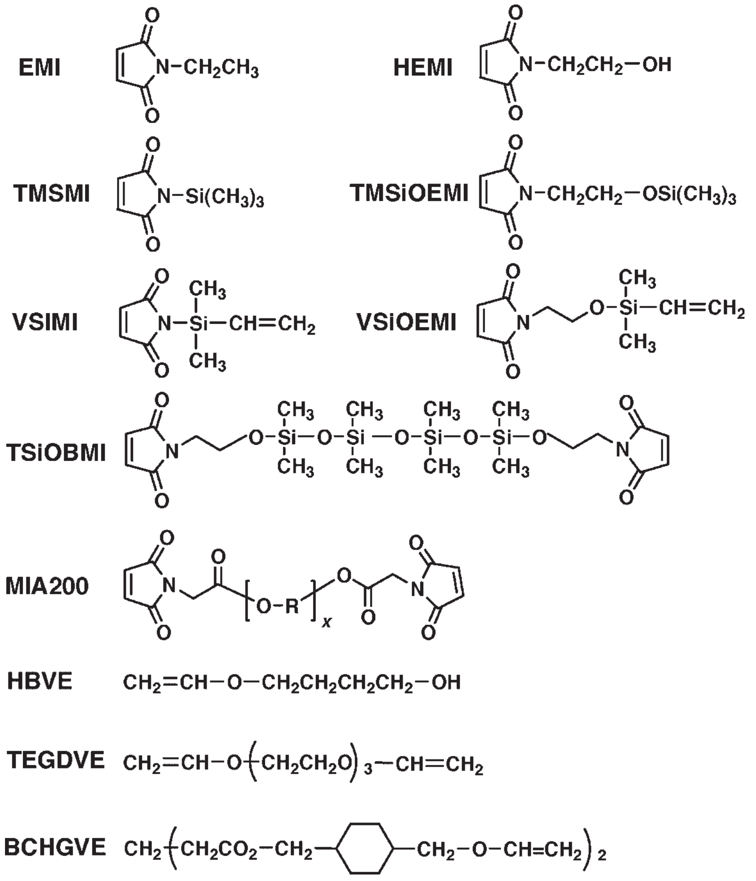

Figure 4.
Various silicon containing maleimides (RMI), bismaleimides (BisRMI), vinyl ethers (R'VE), and divinyl ethers (R'dVE) were used for PIFP in this study.

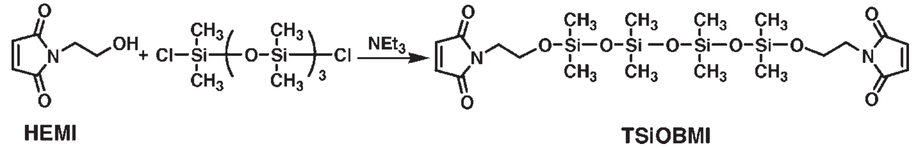

Figure 5.
Synthesis of TSiOBMI by a reaction of dichlorosiloxane and HEMI.

oligomeric siloxane- BisRMI, TSiOBMI, was prepared by a reaction of 1,7-dichloro-octamethyltetrasiloxane and HEMI in 65% yield as shown in Figure 5. Polymerizable PIs such as alpha-methylol-benzoin methyl ether methacrylate (BMEMA) and benzoin methacrylate (BzMA) were prepared according to our previous report.[27] The commercially available BisRMI (MIA200) as light-yellowish viscous liquid, poly(oxy-butylene)-di(2-maleimidoacetate), was made of oligomeric poly(butylene ether) having mol. wt. of about 1,000 and known to have high solubility and photoreactivity.[15]

There have been reported many silicon-containing RMIs as specific functional monomers as well as numerous photo-polymerization results using various silicon-containing multifunctional acrylates to improve required properties for specific applications.[24,28,29] The photocurable monomer pairs consisted of equimolar amounts of each RMI and R'VE, and then photocuring reactions without using PI were analyzed by DPC, FT-IR and UV absorption spectroscopy during the UV exposure. The silicon-containing RMIs, TMSiOEMI or TSiOBMI, combined with a commercial divinyl ether, BCHGVE, were photopolymerized in 50:50 mol% and their photocuring tendency was monitored by measuring IR spectral intensity

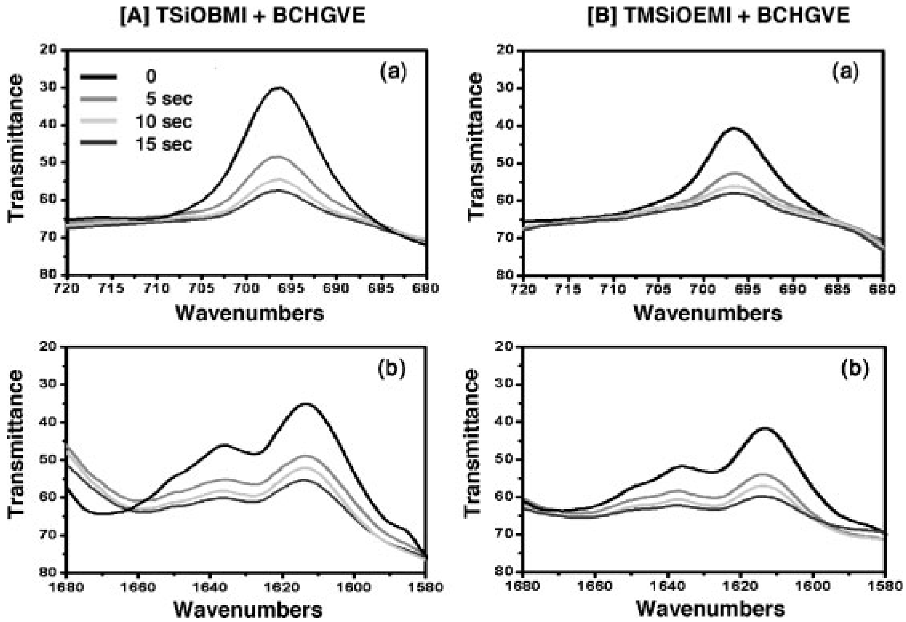

Figure 6.
FT-IR spectral changes in C=C double bond absorption intensities of (a) maleimide at 698 cm^{-1} and (b) vinyl ether 1615 at cm^{-1} before and after UV exposure for various irradiation time of 0, 5, 10, 15 sec.

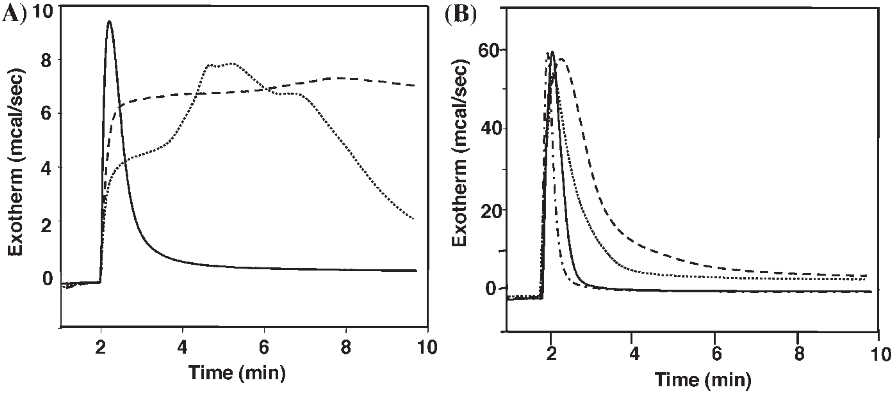

Figure 7.

DPC thermograms for the samples containing various RMIs and TEGDVE by PIFP and with 0.5% BME. Left figure (**A**) by PIFP: solid line, TEGDVE + TSiOBMI; dotted line, TEGDVE + EMI; dashed line, TEGDVE + VSiOEMI. Right figure (**B**) with 0.5% BME: solid line, TEGDVE + TSiOBMI; dotted line, TEGDVE + EMI; dashed line, TEGDVE + VSiOEMI; dot-dashed line, TEGDVE + TSiOBMI + 0.5% BMEMA.

changes. The C=C double bond absorption intensities at 698 cm^{-1} and 1615 cm^{-1} owing to maleimide of RMI and vinyl ether of BCHGVE, respectively, decreased as increasing the irradiation time as compared in Figure 6. No further spectral change confirming to have reached complete photocuring was observed after irradiation of 15 sec and the resulting 3-μm thick cured film was non-sticky, transparent solidified state. The photocuring of TSiOBMI combined with BCHGVE rendered a clear, hard and flexible film within 10 sec and the sample of TMSiOEMI and BCHGVE underwent solid film formation within 15 sec. So, the photocuring tendency for the solid film formation under the conditions is summarized by FT-IR analysis as follows: TSiOBMI+HBVE (4 sec) > TSiOBMI+BCHGVE (10 sec) > TMSiOEMI+BCHGVE (15 sec), TMSiMI + BCHGVE (15 sec) > VSiOEMI+ HBVE (30 sec), EMI + HBVE (30 sec). In the case of a commercial bismaleimide MIA200, the photocuring underwent within short exposure time comparable to TSiOBMI combined with R'VE to form cured films in the laminated PP films.

Such photocuring tendency of the photocurable systems was also confirmed by photobleaching and analyses of UV absorption spectral changes and DPC thermograms. The weak absorption band intensity at 300 nm owing to the C=C double bond of maleimides was decreased during the UV exposure since the maleimide groups took part in the photopolymerization with vinyl ethers. To the contrary of a general concept on photoreactions, the photocuring was rather sluggish when the maleimides contain a vinyl group directly attached to the silicon atom such as VSiMI and VSiOMI. In Figure 7 DPC thermograms revealed the photocuring tendency for the samples containing various RMIs and TEGDVE by PIFP and in the presence of 0.5 wt% BME. They are interpreted such as the mixture of TSiOBMI and TEGDVE has very high photoreactivity by PIFP but that of EMI and VSiOEMI is very low as expected. In the presence of a PI, photocuring was much improved comparable to the conventional systems and even much faster photocuring was observed by the use of a polymerizable PI, BMEMA.[27] It was also observed that the PIFP system rendered the photoreactivity order depending on the type of R'VE such as TEGDVE > HBVE > BCHGVE. The photocuring tendency of the PIFP system is apparently depending on the H-abstraction ability of RMI and R'VE monomers.

Conclusions

The "photoinitiator-free photopolymerization [PIFP]" systems advantageously employing silicon-containing maleimides together with commercial vinyl ether monomers were firstly reported and their photocuring tendency was found to be quite fast comparable to the conventional acrylate-based photocurable systems. In particular, the oligo-siloxane type bismaleimide, TSiOBMI is the only viscous liquid state among the prepared silicon maleimides and underwent fast photopolymerization with vinyl ethers in the absence of photoinitiators. The PIFP systems using BisRMI and R'dVE are quite promising for applications to photocuring without using any detrimental aromatic carbonyl photoinitiator.

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