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PHOTOPOLYMERIZATION OF BIFUNCTIONAL MALEIMIDES BASED ON ELECTRON-DONOR/ACCEPTOR SYSTEMS

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ABSTRACT

Photopolymerization of three bifunctional *N*-phenylmaleimide derivatives consisting of a maleimide and a methacrylate or a styryl moiety within the same molecule such as *N*-[4-(2-hydroxy-3-methacryloyloxypropyl)oxyphenyl]maleimide (GMAPMI), *N*-(4-methacryloyloxyphenyl)maleimide (MAPMI) and 4-(4-maleimidobenzoyloxy)styrene (MIBOSt) has been studied based on electron-donor/acceptor (EDA) polymerization. The photoinduced homo- and copolymerizations of GMAPMI with *N*-vi-nyl-2-pyrrolinone (NVP) and styrene (St) as an electron-donor or maleic anhydride (MAh) as an electron-acceptor were carried out with or without using photoinitiators. Self-photopolymer-izations were possible even without photoinitiators but higher polymerization yields were obtained using benzoin methyl ether (BME) as a photoinitiaor. The copolymerization of GMAPMI

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with NVP or styrene was mainly undergone with participation of the maleimide moiety to give higher yields. The reactivity for photoinduced homopolymerization of MIBOSt is superior to GMAPMI and MAPMI since it has an electron-rich styryl moiety. All of the obtained polymers were insoluble in organic solvents due to crosslinking between different functional groups. The progress of photopolymerization was monitored by differential photocalorimetry and IR spectral analysis, and the results were compared with thermal free radical polymerizations. The mixtures of GMAPMI and commercial dimethacrylates revealed the acceptable photopolymerization tendency in the preliminary evaluation for application as photocurable dental materials.

INTRODUCTION

In recent years, self-initiation of radical photopolymerizations in the absence of photoinitiators has gained much attention. Hall *et al.* [1, 2] have investigated the alternating copolymerizations of various monofunctional electron-donor/acceptor (EDA) systems 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 photopolymerizations are realized even in the absence of externally added photoinitiators [3]. As a pertinent example, a combination of maleic anhydride or *N*-carbethoxymaleimide (a strong electron-acceptor) and *p*-*tert*-butylstyrene (a moderate electron-donor) resulted in photoinduced self-polymerization [4]. Photopolymerizations mediated by the EDA systems without use of an initiator have emerged as a new photocuring process with prominent advantages over a conventional process using acrylate monomers and photoinitiators [5]. Hult and coworkers [6] reported a unique photopolymerization system based on bifunctional liquid-crystalline monomers containing both the vinyl ether moiety as an electron-donor and the maleimide moiety as an electron-acceptor within the same molecule, thereby revealing noteworthy results on successful self-photopolymerization in the bulk state without photoinitiators.

Recently, Jönsson and Hoyle [7-10] have published a few of reports dealing with photoinduced EDA polymerization of various maleimides and electron-donor monomers. They suggested the formation of an excited state EDA complex between the pair of the monomers followed by decay reactions leading to polymerization. In the previous report, we have described synthesis and free radical polymerizations of bifunctional *N*-phenylmaleimide derivatives containing both the maleimide (MI) moiety and the methacrylate (MA) or the styryl moiety within the same molecule [11]. They were homo- and copolymerized with comonomers such as *N*-vinyl-2-pyrrolidinone (NVP), styrene (St) and methyl methacrylate (MMA) in high yields by EDA polymerization.

In this laboratory, variously *N*-substituted functional maleimides have been prepared and copolymerized for studying their polymers as lithographic photoresist materials [12]. In addition, photocurable resin formulations along with efficient photoinitiation systems have been investigated for applications as photocurable dental materials [13]. In this regard, the combination of the functional maleimides and multimethacrylate monomers led us to the study on a photopolymerization system based on the bifunctional maleimides containing a methacrylate moiety within the same molecules.

This paper presents the results of the studies on photopolymerizations of three bifunctional *N*-phenylmaleimide derivatives, *N*-[4-(2-hydroxy-3-methacryloyloxypropyl)-oxyphenyl]maleimide (GMAPMI), *N*-(4-methacryloyoxyphenyl)maleimide (MAPMI), and 4-(4-maleimidobenzoyloxy)styrene (MIBOSt) which possess two polymerizable C=C double bonds with different reactivities within the same molecule. Photochemically induced homo- and co-polymerization with NVP, St and MAh were investigated to study self-initiation as well as electronic effects of the bifunctional maleimide monomer system. The potential applicability of GMAPMI as photocurable dental materials was also studied.

EXPERIMENTAL

Materials and Instruments

Three bifunctional *N*-phenylmaleimide derivatives, GMAPMI, MAPMI, and MIBOSt, were prepared as described in the previous paper [11]. *N*-Vinyl-2-pyrrolidinone (NVP) and benzoin methyl ether (BME) were purchased from Aldrich Chemical Co. Vinyl monomers, maleic anhydride (MAh), and solvents such as 1,2-dichloroethane and 1,4-dioxane were purified by fractional distillation or recrystallization before use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer of Perkin-Elmer using deuteriochloroform. Infrared spectra were recorded on a Polaris FT-IR spectr-pho-tometer 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. Photopolymerizations were performed under a 500 W high pressure Hg-lamp of Ushio Co. (Japan). A Differential Photocalorimeter (DPC) in conjunction with the above mentioned DSC of TA Instruments was used to evaluate the photopolymerization tendency.

Photopolymerization of GMAPMI without a Photoinitiator

GMAPMI (200 mg, 0.56 mmol) was photopolymerized in 0.56 ml of 1,2-dichloethane or dioxane solvent without a photoinitiator. The solution of 1M concentration was placed in a pyrex petri dish and covered with a quartz plate. Then, the petri dish was placed on an ice-water bath and the solution was exposed to UV (55 mW/cm^2 at 260 nm) through the quartz cover for 2 hours. The precipitated polymer was collected and dried under vacuum to give 105 mg (53% yield, in 1,2-dichloroethane) and 80 mg (40% yield, in dioxane). IR (KBr) of poly(GMAPMI), ν (cm^{-1}): 3500 (OH), 2980 and 2900 (C-H), 1720 (C=O), 1635 (C=C), 1300 and 1050 (C-O), 830 (C=C of maleimide).

Photopolymerization of GMAPMI Using BME as a Photoinitiator

GMAPMI (200 mg, 0.56 mmol) in 0.56 ml of 1,2-dichloroethane or dioxane and a photoinitiator BME (2.5 mg, 2 mol%) were placed in a petri dish covered with a quartz plate and the solution was exposed to UV (55 mW/cm^2 at 260 nm) through a quartz cover for 2 hours at 0°C. The precipitated polymers were collected and dried under reduced pressure to give 140 mg (70% yield in 1,2-dichloroethane) and 110 mg (55% yield in dioxane). Photoinduced co-polymerizations of GMAPMI (0.56 mmol) were performed with equimolar amounts of comonomers such as St, NVP and MAh using BME (2 mol%) in dioxane. All of the obtained copolymers were insoluble in organic solvents. IR (KBr) of Poly(GMAPMI-co-St), ν (cm^{-1}): 3500 (OH stretching), 1720 (C=O of imide and ester stretching), 1635 (weak, C=CH$_2$ stretching), 1608 (C=C of aromatic stretching), 1290 and 1100 (C-O bending), 830 (weak, CH=CH of maleimide). IR (KBr) of Poly(GMAPMI-co-NVP), ν (cm^{-1}): 3500 (OH stretching), 1720 (broad and strong, C=O of imide and ester stretching), 1610 (C=C of aromatic stretching, 1300 and 1100 (C-O bending), 830 (weak, CH=CH of maleimide). IR (KBr) of Poly (GMAPMI-co-MAh), ν (cm^{-1}): 3500 (OH stretching), 1780, 1750 and 1720 (C=O of imide and ester stretching), 1608 (C=C of aromatic stretchin), 1290 and 1100 (C-O bending), 830 (weak, CH=CH of maleimide).

Photopolymerization of MAPMI and MIBOSt

MAPMI (200 mg, 0.78 mmol) and MIBOSt (230 mg, 0.78 mmol) in 0.78 ml dioxane with or without a photoinitiator BME (2 mol%) were placed in a petri dish covered with a quartz plate and the solutions were exposed to UV (55 mW/cm^2 at 260 nm) through a quartz cover for 2 hours at 0°C. The precipitated polymers were collected and dried under reduced pressure to give 60 mg (30% yield without BME) and 100 mg (50% yield with BME) of poly(MAPMI), and 120 mg (52% yield without BME) and 170 mg (74% with BME) of poly(MIBOSt). All of the obtained polymers were insoluble in organic solvents. IR (KBr) of poly(MAPMI), ν (cm^{-1}): 1720 (C=O of imide and ester stretching), 1608 (C=C of aromatic stretching), 1300 and 1100 (C-O bending), 830 (CH=CH of maleimide). IR (KBr) of Poly(MIBOSt), ν (cm^{-1}): 1720 (C=O of imide and ester stretching), 1610 (C=C of aromatic stretching), 1300 and 1100 (C-O bending), 830 (weak, CH=CH of maleimide).

Evaluation of Photopolymerization in Cast Films

A solution of GMAPMI (100 mg, 0.28 mmol) with or without a photoinitiator BME in small amounts of dioxane was applied on a salt IR plate and the solvent was removed under reduced pressure to make a uniform waxy film. The 10 (μm-thick films were exposed to UV (55 mW/cm^2 at 260 nm) for 3 minutes. After the exposure the cast films became a soft polymer films. The photoreaction progress was monitored by observing the decrease of absorption intensities of the methacrylate and maleimide moieties by FT-IR spectroscopy. The progress of photoinduced copolymerizations of GMAPMI with equimolar amounts of NVP, St and MAh was also analyzed according to the same method.

Photopolymerization in Dental Photocurable Formulations

Dental formulations were made using GMAPMI and commercially available ingredients such as a prepolymer Bis-GMA and a diluent triethylene glycol dimethacrylate (TEGDMA) with a commercial photoinitiating system consisting of camphorquinone (CQ) and ethyl *p*-(*N*,*N*-dimethylamino)benzoate (EDMAB) (Figure 3) [13, 14]. The formulations were applied on a salt IR plate to make a waxy film and covered with another salt plate to avoid air inhibition during the photopolymerization. Photopolymerizations were conducted by the exposure to visible blue light of a 75 W tungsten/halogen lamp (Curing Light XL 100, 3M Dental Products). The films were irradiated both sides of the plate with the periods of 30 s to 150 s. The extent of photoreaction in the thin-film specimens was calculated by comparing the absorption intensity changes owing to reaction of C=C double bonds at 1635 cm^{-1} according to a known procedure [13, 14]. The heat evolution of photoreactions in the dental photocurable samples were analyzed with DPC measurements by irradiation with a 250 W Hg-lamp.

RESULTS AND DISCUSSION

Monomer Synthesis

Three bifunctional *N*-phenylmaleimide monomers were prepared by the methods previously reported [11] and the chemical structures are shown in Figure 1. UV spectra showed their absorption maxima: *N*-[4-(2-hydroxy-3-methacryloyloxypropyloxy carbonyl)phenyl]maleimide (GMAPMI, λ_{max} = 249 nm); *N*-(4-methacryloyloxyphenyl) maleimide (MAPMI, λ_{max} = 263 nm) and 4-(4-maleimidobenzoyloxy)styrene (MIBOSt, λ_{max} = 261 nm) measured with 1.94x10^{-6} M in chloroform.

Photopolymerizations

The monomers were photopolymerized in solution with benzoin methyl ether (BME) as a photoinitiator or without the photoinitiator, and the results are summarized in Table 1. The monomers gave higher photopolymerization yields when the photoinitiator was used. To investigate the solvent effect, photopoly-

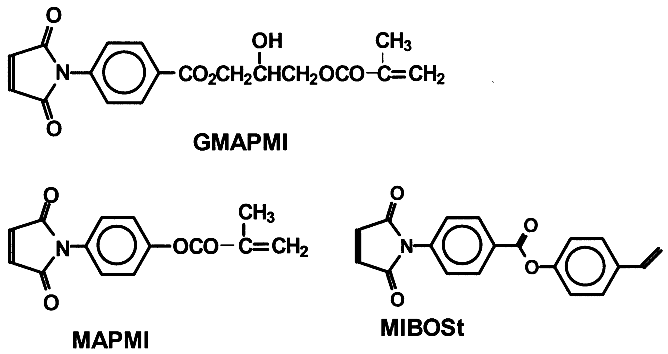

Figure 1. Chemical structures of bifunctional maleimide monomers.

TABLE 1. Photopolymerizations of Bifunctional Maleimides[a]

Monomer/ Comonomer	Solvent (mol/L)	BME[b] (mol %)	Yield (%)
GMAPMI	dichloroethane (1)	-	53
GMAPMI	dichloroethane (1)	2	70
GMAPMI	dichloroethane (0.1)	-	25
GMAPMI	dioxane (1)	-	40
GMAPMI	dioxane (1)	2	55
GMAPMI	dioxane (0.1)	-	18
GMAPMI / NVP	dioxane (1)	2	75
GMAPMI / St	dioxane (1)	2	65
GMAPMI / MAh	dioxane (1)	2	50
MAPMI	dioxane (1)	-	30
MAPMI	dioxane (1)	2	50
MIBOSt	dioxane (1)	-	52
MIBOSt	dioxane (1)	2	74

[a] UV irradiation with 55 mW/cm^2 for 2 hours in 1M or 0.1 M solution; equimolar comonomers fed in copolymerization of GMAPMI.
[b] Benzoin methyl ether (BME) as a photoinitiator.

merizations of GMAPMI were carried out in 1,2-dichloroethane or dioxane under the same conditions. Dissociation of excited complex to a solvated free ion is known to be favored in polar solvents. By careful choice of nonpolar solvents which should not interfere with the electron-donor/acceptor interaction of the monomers, formation of a radical intermediate is favored as well as avoiding formation of free ion radicals [4]. Cyclic ethers as a polar solvent are known to compete with other donors [16]. In this regard, the photopolymerization behaviors employing 1,2-dichloroethane or dioxane were supposed to prove the above explanation. Thus, when the photopolymerizations of GMAPMI were performed in 1 M solution of 1,2-dichloroethane as a nonpolar solvent, the yields were higher compared with the reactions in dioxane as a polar solvent. MIBOSt resulted in higher photopolymerization yields because its styryl moiety acts as an electron-donor but the methacrylate moiety of GMAPMI and MAPMI do not. These results are consistent with those of the thermal radical polymerizations observed in the previous study [11]. All of the obtained polymers in the photopolymerizations of the bifunctional maleimides were cross-linked.

The IR spectra of the obtained polymers exhibited all the corresponding absorption bands of the functional groups comprised in the polymers as mentioned previously [11]. In addition, the IR spectra of the polymers prepared with or without using BME were nearly identical compared with the polymers obtained by thermal polymerizations. The copolymers of GMAPMI with MAh showed characteristic absorption bands of anhydride at 1780 and 1750 cm^{-1} and appreciable disappearance of maleimide absorption at 830 cm^{-1} owing to [2+2] photocycloaddition between maleic anhydride and maleimide groups. However, the comonomer MAh as an electron-acceptor was variously reacted with GMAPMI since MAh was considered to react with a maleimide moiety by [2+2] cycloaddition and also copolymerized with the methacrylate moiety in a relatively low yield. Therefore, the yield of copolymerization of GMAPMI and MAh with the photoinitiator BME was lower than that of the homopolymerization of GMAPMI under the same conditions. GMAPMI was readily copolymerized with NVP and styrene to give higher yields. These pronounced copolymerizabilities of GMAPMI could be explained by higher reactivities of styrene or NVP with the maleimide moiety than that of the methacrylate moiety [17]. Thus, styrene and NVP as an electron-donor easily formed EDA complexes with the maleimide moiety of GMAPMI giving high polymerizability.

Evaluation of Photopolymerization in Cast Films

The cast films of GMAPMI on salt IR plates were exposed to UV (55 mW/cm^2 at 260 nm) and the progress of the photopolymerization was analyzed by measuring the changes in IR absorption intensities due to the reactions of C=C double bonds in the methacrylate and maleimide moieties. The obtained polymers as a cured film appreciably revealed the same characteristic absorption bands of the poly(GMAPMI) prepared in dioxane with or without BME. The progress of photopolymerization of GMAPMI with 2 mol% BME was monitored by IR spectral changes of the maleimide and methacrylate moieties as shown in Figure 2. Upon UV exposure for 3 minutes, the absorption intensity of methacrylate moieties at 1635cm^{-1} was significantly decreased owing to photopolymerization in comparison with invariable aromatic C=C absorption at 1610 cm^{-1}. The absorption intensities of the maleimide moieties at 830 cm^{-1} were also equally decreased with those of methacrylates, contrary to the thermal radical polymerization behavior. The equal decrease in maleimide absorption is partly ascribable to [2+2] photocycloaddition between two maleimide moieties.

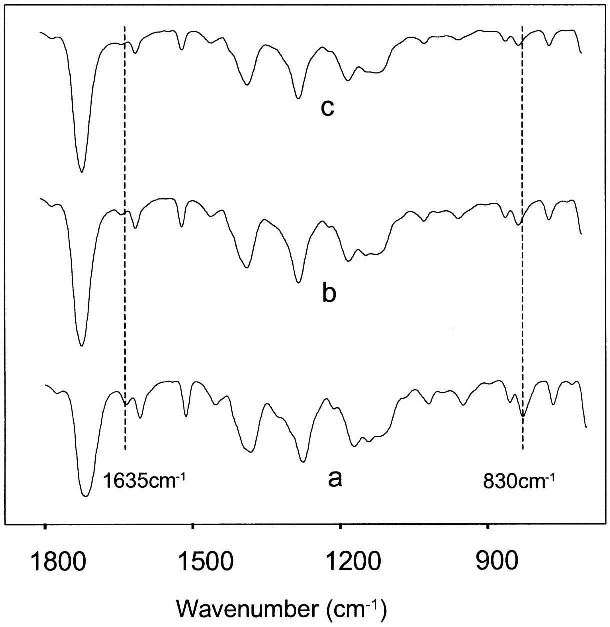

Figure 2. IR spectral changes for photopolymerization of GMAPMI with 2 mol% BME in a cast film: (a) before exposure, (b) 1 minute exposure and; (c) 3 minutes exposure.

The photoinduced copolymerizations of GMAPMI with NVP or styrene were also analyzed in cast films on salt IR plates. The preferential reaction of the maleimide moieties over methacrylates was initially observed and, then the methacrylate groups appeared to react with NVP or St in the later stages [17]. The copolymerization of GMAPMI with NVP is considered to proceed by two reaction steps in thermal radical initiation as well as in photoinitiation. Thus, initially formed EDA complexes between the maleimide and NVP moieties undergo alternating copolymerization followed by random copolymerization of methacrylates with NVP or maleimide moieties, thereby resulting in crosslinked copolymers, poly (GMAPMI-co-NVP).

Formulations as Photocurable Dental Materials

In order to investigate the potential applicability of GMAPMI as visible light-curable dental materials, photopolymerizable compositions were formulat-

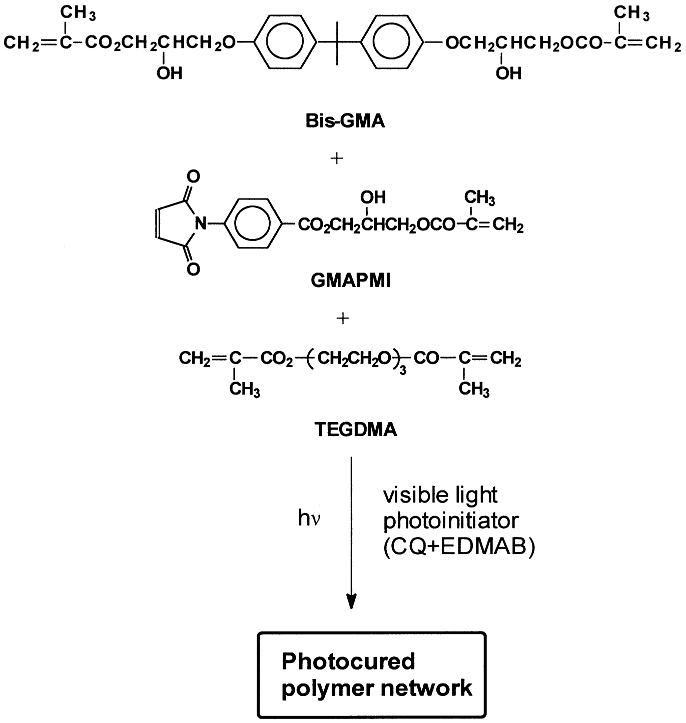

Figure 3. Photocuring of Bis-GMA and TEGDMA with GMAPMI for application as photocurable dental materials.

ed using commercial dental ingredients as shown in Figure 3 [18, 19]. A prepolymer Bis-GMA, a diluent TEGDMA, and GMAPMI were mixed with a commercial photoinitiator consisting of EDMAB and CQ, and the formulations were applied on a salt IR plate to make a waxy film [13, 14]. The extent of photopolymerizations by visible light exposure was calculated by the changes in absorption intensities at 1635 cm^{-1} due to the reactions of methacrylates and the results are summarized in Table 2 [13, 15]. In the presence of GMAPMI (10 wt%) and TEGDMA (10 wt%), the degree of conversion for the methacrylate groups was found to be over 50%, similar values observed without GMAPMI. Thus, the bifunctional monomer GMAPMI could be applicable as a new monomer for photocurable dental materials. The photocurable samples were also prepared by mixing a photoinitiator (CQ and EDMAB) and GMAPMI in a liquid prepolymer Bis-GMA using a diluent TEGDMA. The samples were sub-

TABLE 2. The Degree of Conversion in Photopolymerization of Photocurable Dental Formulations[a]

Ingredient	Composition[b]			
Bis-GMA	90	90	80	70
GMAPMI	-	10	10	10
TEGDMA	10	-	10	20
EDMAB	1.2	1.2	1.2	1.2
CQ	1	1	1	1
Conversion (%)[c]	49	48	52	25

[a]Photopolymerization in film by visible blue light for 120 seconds on salt plates; [b]Composition in parts by weight; [c]Conversion for the methacrylates calculated by changes in IR spectral intensities.

jected to DPC analysis in order to evaluate photopolymerizability of the new monomer GMAPMI under the photopolymerization conditions. Upon UV-irradiation, heat evolution of the photocurable dental samples was analyzed by DPC measurements [8]. The photothermograms revealed higher exotherm when GMAPMI was used as shown in Figure 4. The results imply that two kinds of the C=C double bonds of GMAPMI take part in the photopolymerization to render highly crosslinked polymers, similar to photocurable dental formulations (Figure 3). However, further study is required to verify its usefulness in dental applications.

CONCLUSION

Three bifunctional maleimides were photopolymerized in high yields with a photoinitiator and also moderate yields even without photoinitiators. By selective combination of electron donor-acceptor monomers having a malemide moiety, an efficient self-photopolymerization system can be realized [5, 10, 20]. The comonomers with a good electron-donor character can readily copolymerize with the maleimide moiety as an electron-acceptor. The photopolymerization behaviors of the bifunctional maleimides are consistent with the thermal radical

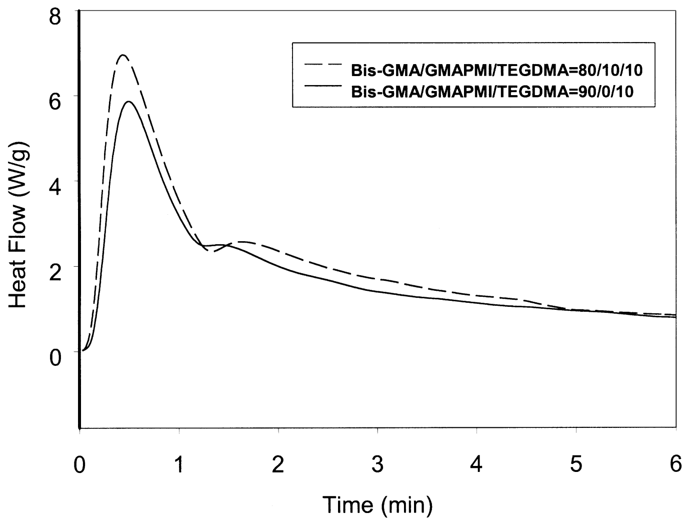

Figure 4. Photoinduced DPC thermograms of two dental formulations using as CQ and EDMAB photoinitiating system (formulations described in Table 2).

polymerizations because both the systems are based on the EDA radical polymerization with or without using initiators. The highly crosslinking photopolymerization of the bifunctional maleimides is promising for applications in new UV curing systems. The preliminary results on photocuring of GMAPMI in combination with commercial ingredients revealed the potential applicability as photocurable dental materials.

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REFERENCES

[1] H. K. Hall, Jr. and A. B. Padias, *Acc. Chem. Res.*, *23*, 3 (1990) and *30*, 322 (1997).

[2] H. K. Hall, Jr. and A. B. Padias, *Aldrichimica Acta*, *28 (2),* 37 (1995).
[3] H. Wang, A. B. Padias, and H. K. Hall, Jr., *Macromolecules*, *31,* 3247 (1998).
[4] C. Lee and H. K. Hall, Jr., *Macromolecules, 22*, 21 (1989).
[5] P. Kohli, A. B. Scranton, and G. J. Blanchard, *Macromolecules, 31*, 5681 (1998).
[6] H. Andersson, U. W. Gedde, and A. Hult, *Macromolecules*, *29*, 1649 (1996).
[7] S. Jönsson, P.-E. Sundell, M. Shimose, J. Owens, and C. E. Hoyle, *ACS Proc. PMSE*, *72*, 470 (1995).
[8] C. E. Hoyle, C. Clark, S. Jönsson, and M. Shimose, *Polymer*, *38*, 5695 (1997).
[9] C. W. Miller, M. Shimose, C. E. Hoyle, and S. Jönsson, *Polym. Preprints*, *38 (2)*, 454 (1997).
[10] F. Morel, C. Decker, S. Jönsson, S. C. Clark, and C. E. Hoyle, *Polymer, 40*, 2447 (1999).
[11] K.-D. Ahn, J.-M. Kim, C.-W. Lee, D. K. Han, D.-Y. Lee, and Y.-M. Lee, *Journ. Mac. Sci.-Pure & Appl. Chem*., submitted.
[12] (a) K.-D. Ahn, in *Polymeric Materials Encyclopedia*; Vol. 4, Salamone, J. C., Ed., CRC Press, Boca Raton, FL, 1996, p. 2621; (b) C.-M. Chung and K.-D. Ahn, *Macromol. Symp*., *118*, 485 (1997).
[13] K.-D. Ahn, C.-M. Chung, and Y.-H. Kim, *J. Appl. Polym. Sci.*, *71*, 2033 (1999).
[14] K. M. Choi and J. W. Stansbury, *Chem. Mater*., *8,* 2704 (1996).
[15] F. A. Rueggeberg, D. T. Hashinger, and C. W. Fairhurst, *Dent. Mater*., *6,* 241 (1996).
[16] A. Ledwith and M. Sambhi, *J. Chem. Soc. B*, 670 (1966).
[17] Y.-C. Lai, *J. Polym. Sci., Polym. Chem. Edn*, *35*, 1039 (1997).
[18] B. M. Culberston, Q. Wan, and Y. Tong, *J. Macromol. Sci., Pure & Appl. Chem., A34*, 2405 (1997).
[19] K. S. Anseth, S. M. Newman, and C. N. Bowman, *Biopolymers II,, Adv. Polym. Sci*., *122*, 177 (1997).
[20] S. Jönsson, G. Doucet, G. Mattson, S. Clark, C. Miller, C. E. Hoyle, F. Morel, and C. Decker, *RadTech Asia '97, Conference Proc*.; Nov. 4-7, Yokohama, Japan, 1997, p. 216 and p. 255.

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