

# Synthesis, Characterization, and Cure Reaction of Methacrylate-Based Multifunctional Monomers for Dental Composites

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**ABSTRACT:** The synthesis of 2,2-bis[4-(2-hydroxy-3-methacryloxyethoxy)phenyl]propane (BHEP) and (1-methacryloxy-3-ethoxymethacryloxy-2-hydroxy)propane (MEHP) for use as the monomer phase in dental composites are reported. The monomers were prepared by the reaction of 2-hydroxyethyl methacrylate (HEMA) with diglycidyl-ether of bisphenol A (DGEBA) and with glycidyl methacrylate (GMA), respectively. The progress of the reaction was followed by measuring the disappearance of the epoxide group peak using FTIR and the structure of the monomers was characterized by <sup>1</sup>H-NMR. BHEP and MEHP have lower viscosity because of the presence of long ali-

phatic spacer on both sides of the aromatic ring in BHEP and the absence of aromatic rings and the presence of only one hydroxyl group in each molecule of MEHP. Thermal curing of the monomers was conducted in a DSC using benzoyl peroxide as an initiator. Photopolymerization of the monomers was also conducted with the visible light using camphorquinone and *N,N*-dimethylaminoethyl methacrylate as the photoinitiating system. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1917–1923, 2007

**Key words:** synthesis; dental materials; dimethacrylates; photo-polymerization; DSC; FTIR

## INTRODUCTION

In general, methacrylate-based monomers and oligomers are used extensively in dental composites, bonding resins, sealants, and dental-adhesive systems. Investigations into this class of compounds began in the 1940s with methyl methacrylate. The initial filling materials had several serious defects because of high polymerization shrinkage and low degree of monomer conversion. Residual uncured monomers can leach from the restorative. It is well known that methacrylates can be toxic, allergenic, and mutagenic, especially for the pulp.<sup>1–4</sup>

Ever since Bowen developed Bis-GMA, [2,2-bis[4-(2-hydroxy-3-methacryloxy propoxy)]phenyl propane], in 1962, it has been used as a matrix material in most commercial dental restoratives. Bis-GMA is a reaction product of methacrylic acid and the diglycidyl ether of bisphenol A (DGEBA). Free-radical polymerization of the matrix monomers results in a three-dimensional network. Monomer selection strongly influences resultant properties, such as reactivity, water uptake, and swelling, and strength.<sup>5–7</sup> Informative reviews on dental monomer systems are available.<sup>6,8</sup> Bis-GMA has a rigid aromatic backbone that leads to lower polymerization shrinkage than other methacrylates and superior toughness. A composite that contains Bis-GMA pos-

sesses a satisfactory strength owing to the existence of an aromatic segment and good adhesion to the adjacent enamel. Bis-GMA also has some disadvantages. It is difficult to purify by crystallization or distillation, and has a very high viscosity. It is difficult to formulate into a homogeneous filled composite paste without the addition of a diluent comonomer.<sup>3,4,9</sup> To reduce the viscosity sufficiently and to allow adequate filler loading and suitable handling characteristics, low viscosity alkoxyalkyl dimethacrylate esters are used as dilution agents.<sup>9</sup> Dilution with such monomers, however, increases water uptake and also polymerization shrinkage.<sup>10</sup> Also, there have been attempts to solve the problem by incorporating low molecular weight aliphatic dimethacrylate diluents such as triethylene glycol dimethacrylate (TEGDMA), ethylene glycol dimethacrylate (EDMA), etc., or/and to block the hydroxyl functional group of the Bis-GMA molecule by introducing appropriate groups.<sup>11–15</sup> Sometimes the diluent comonomers can increase polymerization shrinkage and hydrophilicity. High filler loadings (resulting in less monomer content that can shrink during curing) has been one strategy used to counteract polymerization volume change. Shrinkage results in stresses that can cause the adhesive between the restorative and the tooth wall to fail and microcracks in the composite itself to the detriment of restorative longevity.

Here we report, synthesis and characterization of two novel multifunctional methacrylate-based monomers. The monomeric products were prepared by a simple one step reaction between 2-hydroxy ethyl

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methacrylate with diglycidyl-ether of bisphenol A (DGEBA) and glycidyl methacrylate, respectively, in the presence of a tertiary amine as a catalyst. The progress of the reaction was followed by measuring the absorption of the epoxide group using FTIR and the final structure of the monomers was checked by  $^1\text{H-NMR}$ . Thermal polymerization of the resultant monomers by DSC using peroxide as the free radical initiator, and photopolymerization by irradiation with visible light using camphorquinone and a tertiary amine as a photoinitiating system were studied.

## EXPERIMENTAL

### Materials

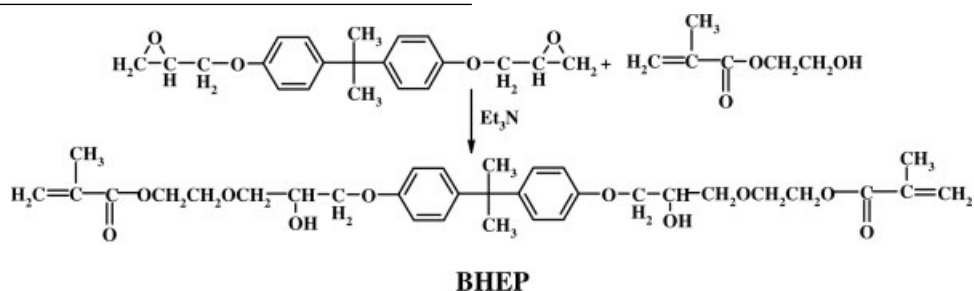
Diglycidyl ether of bisphenol A (DGEBA), Epon 828 (Ciba Geigy, India) was used after analyzing its structure by FTIR spectrum and checking its purity by various analyses such as epoxy equivalent of 182 eq/100 g and hydroxyl value of 0.149 eq/100 g. Camphorquinone, 2-hydroxyethyl methacrylate (HEMA), *N,N*-dimethylanilin, triethylamine, and *N,N*-dimethylaminoethyl methacrylate were purchased from MERCK-Schuchardt. Glycidyl methacrylate (GMA) also from MERCK-Schuchardt was used after analyzing its

structure by FTIR spectrum;  $907\text{ cm}^{-1}$  terminal epoxy and  $1020\text{--}1040\text{ cm}^{-1}$  aliphatic ether.

### Methods

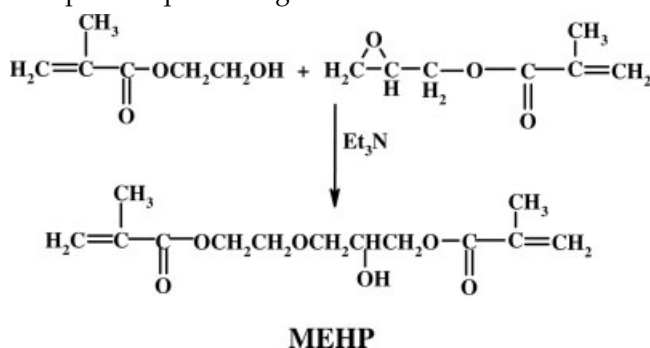
Synthesis of 2,2-bis[(4-(2-hydroxy-3-ethoxy methacrylate)propyloxy phenyl] propane (BHEP)

A mixture of DGEBA (10 mmol, 3.4 g) and HEMA (22 mmol, 2.6 mL) with a weight ratio of 1:2.1, without addition of solvent was stirred in the presence of nitrogen atmosphere at  $70^\circ\text{C}$ . Various amounts of triethyl amine (1%, 2 and 3% w/w, based on DGEBA) as catalyst were used in the absence of solvent to complete the reaction. Progress of the addition etherification reaction was monitored by following the disappearance of absorption peak at  $914\text{ cm}^{-1}$  characteristic of terminal epoxy group using FTIR. After the reaction was complete, the catalyst residue in the resulting clear liquid was neutralized with 5% solution of HCl. The solution was filtered and the filtrate was extracted with distilled water several times. The organic phase was dried in a vacuum oven at  $60^\circ\text{C}$  for 24 h. The monomer was a moderately viscous transparent liquid having a refractive index of 1.544, which is comparable with that of glass of 1.556 and with that of quartz of 1.446. The main component of the organic part is BHEP.



### Synthesis of 1-methacryloxy 3-ethoxy methacrylate 2-hydroxy propane (MEHP)

A mixture of GMA (10 mmol, 1.6 mL) and HEMA (12 mmol, 1.2 mL) was stirred in nitrogen atmosphere at  $70^\circ\text{C}$ . Triethyl amine was used as catalyst and the reaction was carried out in the absence of solvent to complete. The procedure was exactly the same as given earlier for the preparation of BHEP. The monomer was a moderately viscous transparent liquid having a refractive index of 1.472.



### FTIR spectra

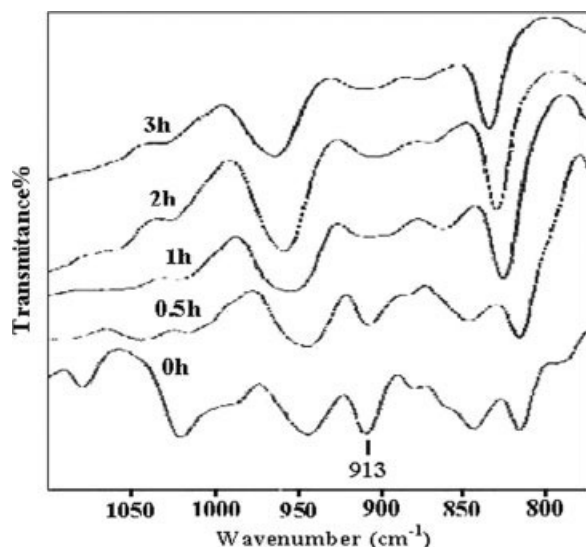
FTIR spectra of monomers were obtained as a thin film of one drop reaction solution on NaCl disc using a Bruker series Vector 22. The progress of the reaction was followed by measuring the absorption peak of epoxide group at  $914\text{ cm}^{-1}$ . The epoxide concentration and the degree of conversion were obtained by the following equations:

$$\text{Relative Ratio of Epoxide} = \frac{\text{Absorbance Intensity of Epoxide}}{\text{Absorbance Intensity of Reference Peak}}$$

$$\text{Epoxide Concentration (\%)} = 100 \times \frac{\text{Relative Ratio of Epoxide at Time } t}{\text{Relative Ratio of Epoxide at Zero Time}}$$

$$\text{Degree of Conversion (\%)} = \text{Epoxide Concentration (\%)}$$

The relative ratio of epoxide was obtained by dividing the intensity of absorption peak of epoxide group at



**Figure 1** FTIR monitoring of product (MEHP) as a function of time.

914  $\text{cm}^{-1}$  to the intensity of absorption of a reference peak (at 1607  $\text{cm}^{-1}$  of aromatic double bond for BHEP or at 1719  $\text{cm}^{-1}$  of carbonyl group for MEHP) at different periods of time.

#### $^1\text{H}$ -NMR spectra

Proton spectra were obtained by dissolving sample in  $\text{CDCl}_3$  using Bruker AQS Advance 300 and 90 MHz.

#### Refractive index

Refractive index measurements were obtained using Eausch-Lomb Abbe 3L at room temperature.

#### Thermal curing

Thermal curing of the monomers was carried out by scanning from room temperature to 300°C using Perkin-Elmer DSC series Pyris 1 at a heating rate of 10°C/min under nitrogen atmosphere.

#### Photo curing

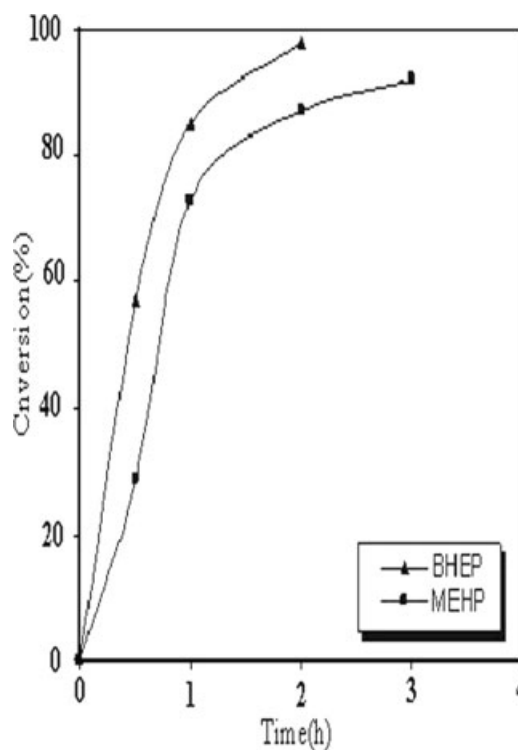
Photo curing of each monomer in mixture with the camphorquinone was carried out by a light cure, model VCL OPTILUX 501, and irradiated with the visible light with an irradiance of 700  $\text{mW}/\text{cm}^2$  for 40 s (distance between sample and the light source was 1 cm) and followed by measuring the intensity of disappearance peak of aliphatic carbon-carbon double bond ( $\text{C}=\text{C}$ ) at 1635  $\text{cm}^{-1}$ . The degree of conversion of methacrylate  $\text{C}=\text{C}$  bond during photocuring was

calculated by using the following equation:

$$\text{DC}\% = \left( 1 - \frac{\text{peak area after curing}}{\text{peak area before curing}} \right) \times 100$$

## RESULTS AND DISCUSSION

The synthetic method to produce dimethacrylate esters utilizing the reaction of HEMA with DGEBA introduces a flexible aliphatic spacer between the methacrylate  $\text{C}=\text{C}$  and hydroxyl group. This effectively isolates the olefinic double bond from steric or electronic effects, which may be introduced by the aromatic rings. The etherification reaction between epoxide and hydroxyl groups usually takes place at temperature above 200°C in the absence of catalyst. At this temperature side reactions leading to undesirable products and polymerization through olefinic double bonds can occur. The etherification reactions of HEMA with DGEBA for the preparation of BHEP and with GMA for the preparation of MEHP were carried out in the presence of a base catalyst in an inert atmosphere for the required time to complete the reaction at 70°C. Generally, onium salts and tertiary amines are effective catalysts for the hydroxyl-epoxide reaction, which proceeds at only moderately elevated tempera-



**Figure 2** Conversion (%) against time of reaction.



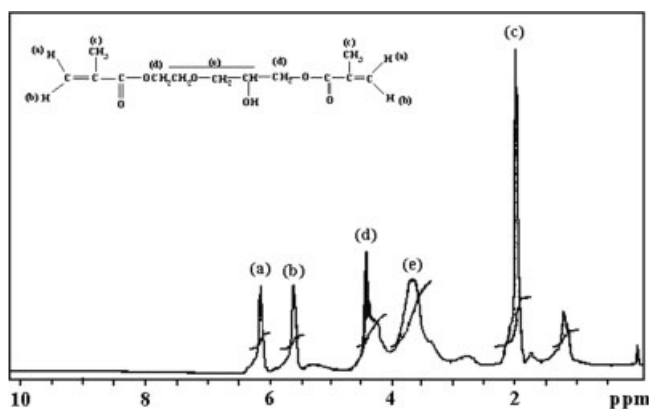


Figure 4  $^1\text{H-NMR}$  spectra of MEHP monomer.

tion of the same group at  $1637\text{ cm}^{-1}$ , and  $-\text{C}-\text{H}$  stretching at  $2959\text{ cm}^{-1}$ . Hydroxyl (OH) stretching vibration around  $3300\text{ cm}^{-1}$  for BHEP is present as a broad band and for MEHP is present around  $3650\text{ cm}^{-1}$  as a less broad absorption band in a thin film on NaCl disc, Figure 3. The absorption because of hydrogen bonding is barely visible in dilute solution and is replaced by a sharp absorption band at higher frequencies around  $3600\text{ cm}^{-1}$ , which is associated with the OH stretch of free hydroxyl groups.<sup>16</sup>

The band associated with free hydroxyl for MEHP appears as a small shoulder near  $3600\text{ cm}^{-1}$  on the more intense hydrogen bonded absorption band, indicative of strong intramolecular hydrogen bonding that strongly influences the viscosity of the monomers. However, there is a much more flexible spacer between hydroxyl group and methacrylate  $\text{C}=\text{C}$  bond in BHEP monomer.  $^1\text{H-NMR}$  spectra of the monomers MEHP and BHEP are shown in Figures 4 and 5, respectively, and the major peaks have been characterized and the data are shown in Table I.

### Light curing

Curing reaction of the synthesized monomers was carried out under irradiation of visible light with irradi-

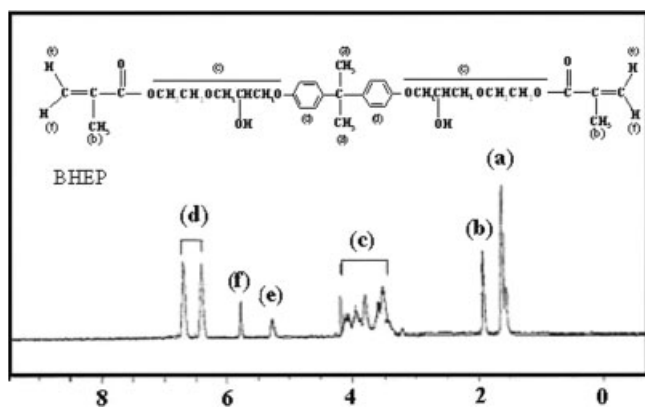


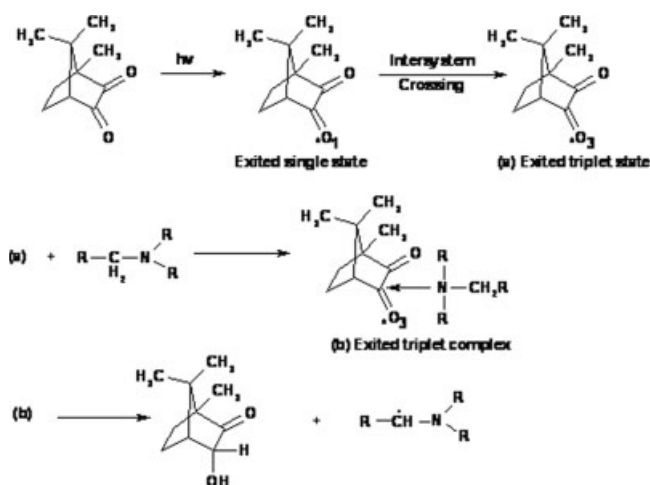
Figure 5  $^1\text{H-NMR}$  spectra of BHEP monomer.

TABLE I  
Important  $^1\text{H-NMR}$  Spectral Peaks Indicating Specific Protons

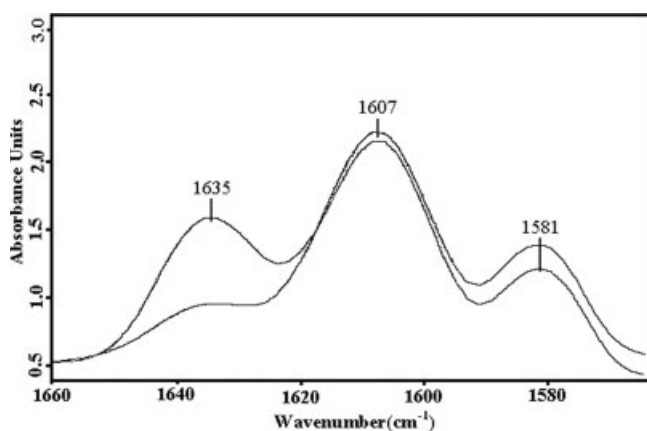
Monomer	Peak	$\delta$
MEHP	a	6.1(d, q)(2H)
	b	5.6(d, q)(2H)
	d	4.1–4.5(m)(4H)
	e	3.1–3.9(m)(6H)
	c	2(d) and 1.2(d)(6H)
BHEP	d	6.3–6.8(d)(8H)
	f	5.75(d, q)(2H)
	e	5.25(d, q)(2H)
	c	3.3–4.1(m)(20H)
	a	1.8(s)(6H)
	b	1.6(d) and 1.2(d)(6H)

ance of  $700\text{ mW/cm}^2$  and found to be very easy and fast. A small exposure time (40 s) was enough to harden the paste. The monomer was mixed with 0.5 wt % comphorquinone as light initiator and 0.5 wt % *N,N* dimethylamino ethyl methacrylate as accelerator. A drop of mixture was placed between thin films of polyethylene to be exposed by the visible light. When light falls on the paste, the photoinitiator undergoes dissociation in the presence of tertiary amine-initiating polymerization reaction that results in the hardening of the paste into a solid mass. The mechanism<sup>17</sup> of the initiation step of polymerization is given in Scheme 2.

The progress of photocuring reaction was followed by measuring the intensity of absorption peak of the methacrylate  $\text{C}=\text{C}$  in the region of  $1636\text{ cm}^{-1}$  before and after exposure. The decrease of IR absorption of  $\text{C}=\text{C}$  bond of BHEP during light exposure is shown in Figure 6. The absorption bands at  $1719\text{ cm}^{-1}$  and  $1607\text{ cm}^{-1}$  originating from the carbonyl groups and the aromatic rings were used as reference peaks for evaluat-



Scheme 2 Mechanism of initiation step of photopolymerization.



**Figure 6** FTIR spectra changes of BEEP during 40 s visible light exposure.

ing the photopolymerization of MEHP and BHEP pastes, respectively. The ratio of the absorbance intensities of two bands before and after photopolymerization was compared to determine the degree of conversion of the methacrylate C=C bonds.

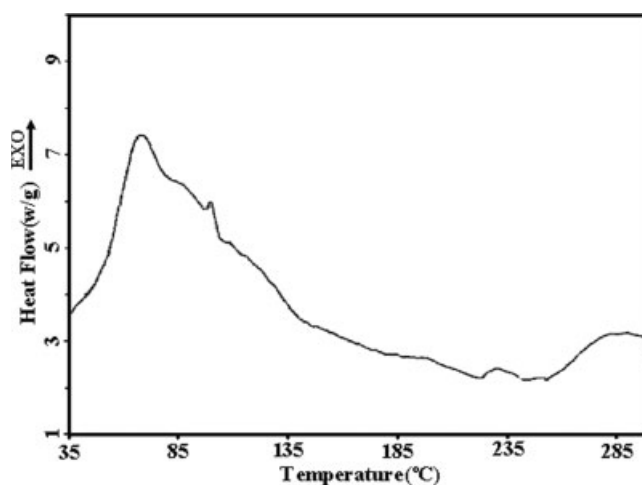
Table II shows the degree of conversion of IR absorption of methacrylate C=C bond in polymerization reaction during 40 s exposure to the visible light. As seen in Table II, MEHP showed a lower degree of conversion in photocuring than that of BHEP. This is probably suggesting that the presence of a flexible spacer between hydroxyl group and methacrylate C=C bond in BHEP lower the viscosity of the paste and as a result of that the aliphatic C=C double bond shows higher reactivity.

### Thermal curing

Thermal curing of the synthesized monomers was carried out in dynamic mode of DSC. Monomer was mixed with 1 wt % benzoyl peroxide as thermal initiator and 9 mg of the mixture was placed in the sample pan and scanned from 30 to 300°C at the heating rate of 10°C/min. DSC thermograms of samples of MEHP and BHEP are shown in Figures 7 and 8, respectively. Both pastes showed a large exothermic peak with a maximum temperature ( $T_p$ ) at 66°C during thermal curing and also showed shoulder peaks at the higher temperatures indicating progress of polymerization reaction above 100°C. This reaction is probably carried out through the unreacted methacrylate C=C groups trapped inside the formed network.

**TABLE II**  
Conversion (%) of Monomers After 40 s Photocuring

Paste	Conversion% sample 1	Conversion sample 2	Conversion sample 3	Average
MEHP	59.90	58.84	57.19	58.64
BHEP	78.74	71.32	75.63	75.23

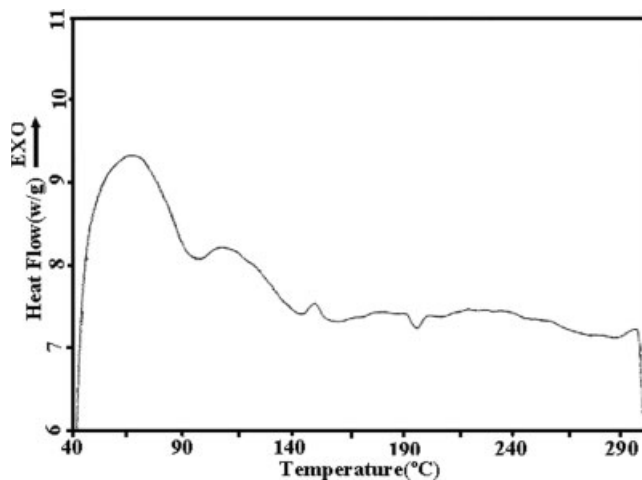


**Figure 7** DSC thermogram of thermal cure reaction of MEHP.

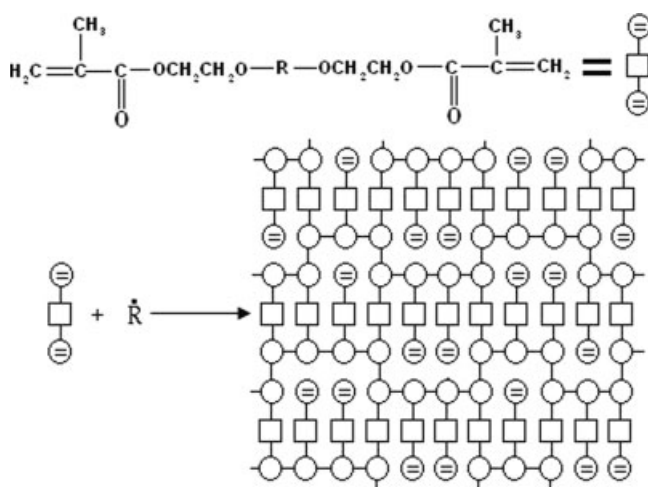
A model of network formation with the remained methacrylate C=C bonds trapped inside is shown in Scheme 3.

### CONCLUSIONS

Aromatic and aliphatic dimethacrylate esters, BHEP and MEHP were synthesized by the reaction of 2-hydroxyethyl methacrylate (HEMA) with diglycidyl-ether of bisphenol A (DGEBA) and with glycidyl methacrylate (GMA), respectively. The progress of the reactions was followed by measuring the disappearance of the epoxide ring at 916  $\text{cm}^{-1}$  by using FTIR. The monomers were characterized by FTIR and  $^1\text{H-NMR}$  spectra. The monomers were cured thermally in the presence of benzoyl peroxide and by irradiation with visible light using camphorquinone and N,N dimethylamino ethyl methacrylate as the initiation catalyst. The prepared dimethacrylate monomers showed degree of conversion of 75 and 58%, respec-



**Figure 8** DSC thermogram of thermal cure reaction of BHEP.



**Scheme 3** A model for network formation.

tively, in photocuring. Heat cured polymerization of these monomers was carried out in DSC at 10°C/min with large exothermic peaks and with the maximum temperature at 66°C. The presence of the remaining methacrylate C=C bonds in the network was suggested to be responsible for the longer continuation of curing reaction after  $T_p$ .

## References

1. Moszner, R. *Macromol Symp* 2004, 217, 63.
2. Tamareselvy, K.; Rueggeberg, F. A. *J Appl Polym Sci* 1995, 57, 705.
3. Bogdal, D.; Pielichowski, J.; Boron, A. *J Appl Polym Sci* 1997, 66, 2333.
4. Kwang-duk, A.; Chan-moon, C.; Young, K. *J Appl Polym Sci* 1999, 71, 2033.
5. Linden, L. A. *Proc Indian Acad Sci* 1993, 105, 405.
6. Moszner, N.; Salz, U. *Prog Polym Sci* 2001, 26, 535.
7. Bowen, R. L. *J Dental Res* 1979, 58, 1493.
8. Peutzfeldt, A. *Eur J Oral Sci* 1997, 105, 97.
9. Kalliyana, K. V.; Lizymol, P. P.; Sindhu, P. N. *J Appl Polym Sci* 1999, 74, 735.
10. Kalachandra, S.; Turner, D. T. *J Biomed Mater Res* 1987, 21, 329.
11. Anseth, K. S.; Newman, S. M.; Bowman, C. N. *Biopolymers II Adv Polym Sci* 1995, 122, 177.
12. Sheela, M. S.; Selvy, K. T.; Krishnan, V. K.; Pal, S. N. *J Appl Polym Sci* 1991, 42, 561.
13. Holter, D.; Frey, H.; Mulhaupt, R.; Klee, J. E. *ACS Polym Prepr* 1997, 38, 84.
14. Culbertson, B. M.; Wan, Q.; Tong, Y. *J Macromol Sci Pure Appl Chem* 1997, A34, 2405.
15. Kalachandra, S.; Taylor, D. F.; McGrath, J. E.; Sankarapandian, M.; Shobha, H. K. *ACS Polym Prepr* 1997, 38, 94.
16. Vogel, A. I. In *Textbook of Practical Organic Chemistry*, 5th ed.; Furniss, B. S., Hannaford, A. J., Smith, P. W. G., Tatchell, A. R., Eds; G. B. Longman Scientific and Technical: Essex, England, 1989; pp 283-286.
17. Fouassier, K. P.; Allonas, X. *Prog Org Coat* 2003, 47, 16.