

# Synthesis, Characterization, and Curing of a New Acrylate-Based Dental Restorative Resin

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**ABSTRACT:** The synthesis of monomer 1,3-bis [(2-hydroxy-3-acrylate) propoxy]2-hydroxy propane (BHAPP) is reported for the possible use in dental restoratives. The monomer was prepared by the reaction of acrylic acid with diglycerol diglycidyl ether (DGE) in the presence of triethyl amine as a catalyst. The progress of the reaction at 60°C followed by measuring the intensity of the epoxide absorption peak at 915 cm<sup>-1</sup> which has reached to its minimum value after 5 h. The structure of the monomer was characterized by FTIR and <sup>1</sup>H-NMR. The monomer was a moderately viscous light yellow color liquid having a refractive index of 1.544. Thermal curing

of the monomer in DSC in the presence of benzoyl peroxide showed exothermic peak with maximum temperature (*T<sub>p</sub>*) varied from 89 to 107°C depending on the heating rate and activation energy of 83 kJ/mol. Photopolymerization of the monomer by visible light in the presence of camphorquinone and *N,N*-dimethylaminoethyl methacrylate as the photoinitiating system showed maximum 60% conversion after 40 s exposure. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 983–987, 2008

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

## INTRODUCTION

Investigations into methacrylate-based monomers and oligomers for dental materials began in the 1940s. High polymerization shrinkage and low degree of monomer conversion made them of insufficient technical quality to replace fluoride-containing silicate ceramics in dental materials. It is well known that the remained uncured methacrylate monomers can be toxic, allergenic, and mutagenic, especially for the pulp.<sup>1–4</sup>

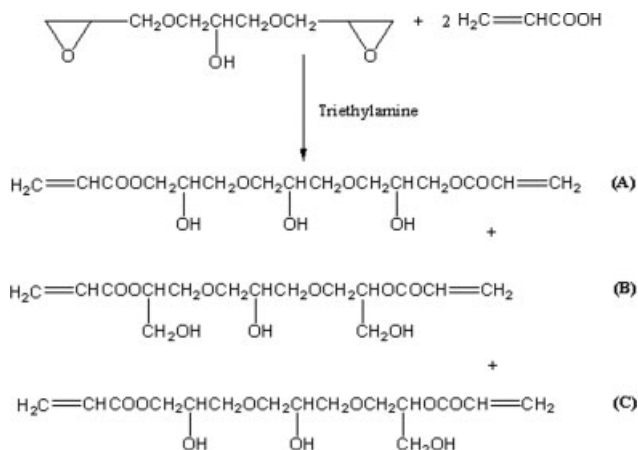
Bis-GMA, {[2,2-bis[4-(2-hydroxy-3-methacryloyloxy propoxy)] phenyl propane]}, a reaction product of methacrylic acid and diglycidyl ether of bisphenol A (DGEBA), has been used as a matrix material in most commercial dental restoratives. Bis-GMA has a rigid aromatic backbone and two hydroxyl groups in each molecule that causes the resin to have a very high viscosity but it also leads to satisfactory strength and lower polymerization shrinkage in the cured product. Therefore, it is difficult to formulate Bis-GMA into a homogeneous filled composite paste without the addition of a diluent comonomer.<sup>3–5</sup> The low viscosity dilution agents such as alkoxyalkyl dimethacrylate esters or/and to block the hydroxyl

functional groups of the Bis-GMA molecule by introducing appropriate groups can increase polymerization shrinkage and hydrophilicity.<sup>6–11</sup> High filler loadings (resulting in less monomer content) have been one strategy used to counteract polymerization volume change.

Free-radical polymerization of the matrix monomers results in a three-dimensional network. Monomer selection strongly influences resultant properties such as reactivity, water uptake, swelling, and strength.<sup>12–14</sup> The development of new monomers for restorative filling materials is predominantly motivated by the will to overcome the main shortcomings of resin composites, i.e., marginal leakage due to polymerization shrinkage and insufficient abrasion resistance. Crosslinking monomers are synthesized to improve the mechanical and processing properties of the composites, such composites demonstrate reduced water up-take, as well as self-adhesion to dentin or enamel. Informative reviews on new monomers for dental application are available.<sup>1,13,15</sup>

Following our previous work,<sup>16</sup> here we report the synthesis and characterization of a new multifunctional methacrylate based monomer. The monomeric product was prepared by a simple one step reaction between acrylic acid and diglycerol diglycidyl ether in the presence of tertiary amine *N,N*-dimethyl aniline as a catalyst. The progress of the reaction followed by measuring the absorption of the epoxide group using FTIR and the final structure of the

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**Scheme 1** Mechanism of the reaction between epoxide and carboxylic acid groups.

monomer was checked by  $^1\text{H-NMR}$ . Thermal and photopolymerization of the resultant monomer were investigated by using DSC in the presence of a free radical initiator and by visible light in the presence of a photo initiator, respectively.

## EXPERIMENTAL

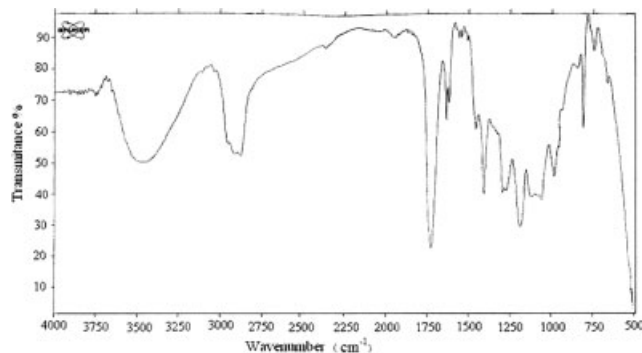
### Materials

Diglycerol diglycidyl ether was purchased from MERCK- Germany and used after analyzing its structure by FTIR spectrum:  $915\text{ cm}^{-1}$  terminal epoxide groups,  $1020\text{--}1040\text{ cm}^{-1}$  ether linkage, and  $3400\text{--}3500\text{ cm}^{-1}$ , hydroxyl group). Acrylic acid, triethyl amine, camphorquinone, and *N,N*-dimethylaminoethyl methacrylate were purchased also from MERCK- Germany.

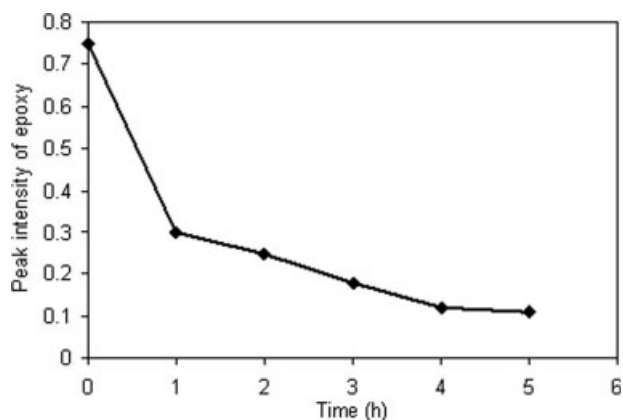
### Synthesis

Synthesis of 1,3-bis [(2-hydroxy-3-acrylate) propoxy]2-hydroxy propane (BHAPP)

A mixture of diglycerol diglycidyl ether (DGE) (2.45 g, 13 mmol) and acrylic acid (AA) (2 mL, 28 mmol)



**Figure 1** FTIR spectrum of BHAPP.



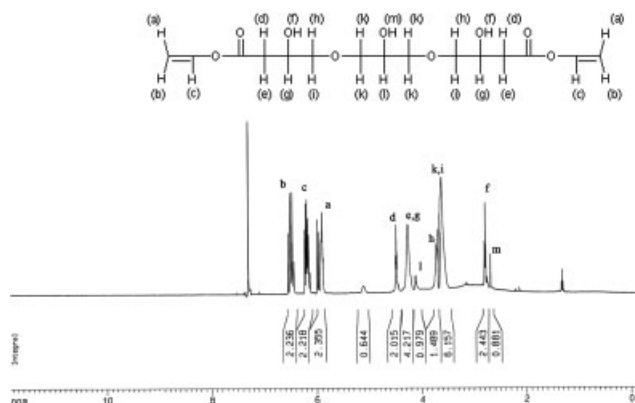
**Figure 2** Reduction of intensity of epoxy peak during reaction.

with a mole ratio of 2.15 (AA/DGE) was stirred in the presence of triethyl amine 2% w/w based on DGE as catalyst in argon atmosphere at  $60^\circ\text{C}$  without addition of solvent. Progress of the addition esterification reaction was monitored by following the disappearance of characteristic absorption peak of terminal epoxy group at  $915\text{ cm}^{-1}$ . After the reaction was complete, the mixture cooled slowly under argon atmosphere. The catalyst residue in the resulting clear liquid was neutralized with 5% solution of HCl. The solution was filtered and the filtrate extracted with distilled water several times. The organic phase was dried in a vacuumed desiccator for 24 h. The monomer was a moderately viscous light yellow color and the refractive index of 1.544 was measured at room temperature which is comparable with that of glass of 1.556 and with that of quartz of 1.446.

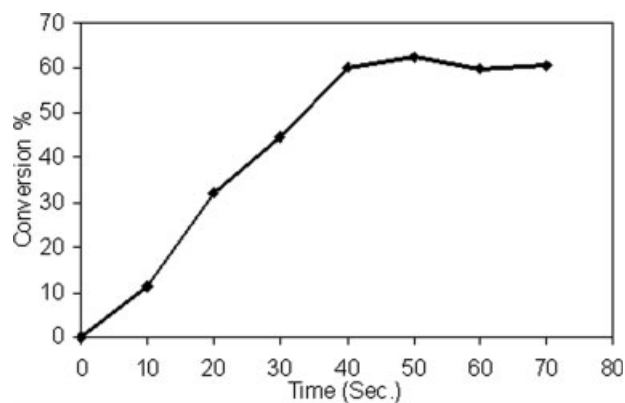
### Apparatuses

The following apparatuses were used for measurements.

FTIR: Bruker series Vector 22.  $^1\text{H-NMR}$ : Bruker AQS Advance 300 MHz. Refractive index: Eausch-



**Figure 3**  $^1\text{H-NMR}$  spectrum of BHAPP.



**Figure 4** Plot of conversion of acrylic C=C versus exposure time.

Lomb Abbe 3L. Thermal curing: Perkin-Elmer DSC-7. Photo curing: VCL OPTILUX 501.

## RESULTS AND DISCUSSION

The synthetic method to produce acrylate esters utilizing the reaction of acrylic acid with DGE introduces a flexible aliphatic chain containing three hydroxyl groups between the acrylate C=C double bonds in each molecule. The esterification reaction between epoxide and carboxylic acid groups usually takes place at high temperature leading to undesirable products and polymerization through olefinic double bonds can also occur. The esterification reaction of acrylic acid with DGE for the preparation of BHAPP was carried out in the presence of a base catalyst in an inert atmosphere for different times to check the end of reaction at 60°C. Generally, onium salts and tertiary amines are effective catalysts for the hydroxyl-epoxide reaction which proceeds at only moderately elevated temperatures.<sup>8</sup> The synthesis of BHAPP was also carried out in the presence of excess acrylic acid to ensure that all DGE underwent additional esterification reaction. With difunctional reagents there is the possibility of three isomers being formed that is shown in Scheme 1 (linear (A), branched (C) and double branched (B)), although it was not a feasible proposition to attempt to separate these isomers. <sup>1</sup>H-NMR spectra obtained from a number of reactions indicate that the major product is the linear, in favor of the derivative derived from attack at the least substituted carbon atom. The mix-

ture of reaction was very sensitive to the air presence at the high temperature leading to a solid insoluble product, probably by undesirable polymerization through olefinic double bonds. Solidification of the reaction mixture made determination of the end of reaction through measurements of terminal epoxy group disappearance impossible. Therefore, separate reactions were carried out for different periods of time (1, 2, 3, 4, and 5 h) for determination of the end of reaction. The reaction mixture was cooled to room temperature under argon atmosphere before to be exposed to the air. HCl (5% solution) was added to the reaction mixture to neutralize the amine. The product is soluble in chloroform and the remained monomer and the catalyst were extracted by water. The time required to complete the reaction at 60°C was determined by measuring the disappearance of absorption peak of the epoxy group at 915 cm<sup>-1</sup>. An optimum temperature of 60°C for almost 4 h ensured a complete disappearance of the characteristic absorption peak of the epoxy group, thereby confirming total conversion of DGE and acrylic acid into BHAPP. Important peaks observed in the FTIR spectra of BHAPP, Figure 1, were those corresponding to the carbonyl group at 1725 cm<sup>-1</sup>, bending vibration of the -C=CH<sub>2</sub> peak at 947 cm<sup>-1</sup>, stretching vibration of the same group at 1636 cm<sup>-1</sup>, -C-H stretching at 2959 cm<sup>-1</sup>, and -O-H stretching vibration around 3500 cm<sup>-1</sup>.

The relative absorption intensity of epoxy group was calculated by using eq. (1) and plotted versus time of reaction as shown in Figure 2.

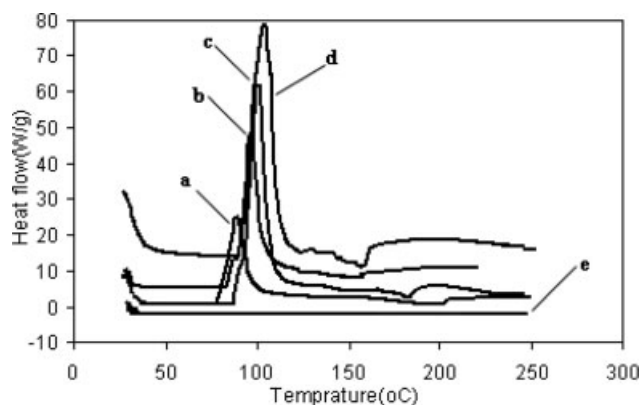
$$\text{Relative peak intensity of epoxy} = A_t/B_t \quad (1)$$

where  $A_t$  is the height of absorption peak of epoxy at 915 cm<sup>-1</sup> and  $B_t$  the height of absorption peak of carbonyl at 1719 cm<sup>-1</sup> for different reaction times. As can be seen in Figure 1, the epoxide groups show high reactivity in the first 1 h of the reaction and then followed by a gradual decrease in rate which can be due to decrease in the concentration of epoxide groups and also to the raise of viscosity of the reaction media.

The mechanism of the reaction between epoxide and carboxylic acid groups is complicated and has been suggested<sup>17,18</sup> that the initiation step in the presence of a tertiary amine involves a proton

**TABLE I**  
DSC Data for Thermal Curing of BHAPP

$\beta$ (°C/min)	$T_p$ (K)	$1/T_p \times 10^3$ (K <sup>-1</sup> )	$\ln \beta$	$-\ln (\beta/T_p^2)$	Exo. heat (J/g)
5	362	2.76	1.61	10.17	259.03
10	370	2.70	2.30	9.53	274.49
15	374	2.66	2.71	9.14	272.22
20	380	2.63	2.99	8.88	245.19



**Figure 5** DSC thermograms of BHAPP cured with 1 wt % of benzoyl peroxide at different heating rates: (a) 5 Co/min, (b) 10 Co/min, (c) 15 Co/min, (d) 20 Co/min.

transfer from the carboxyl group and formation of the carbonyl-amine adduct. The characteristic signals in the  $^1\text{H}$ NMR spectrum of the monomer BHAPP was shown in Figure 3.

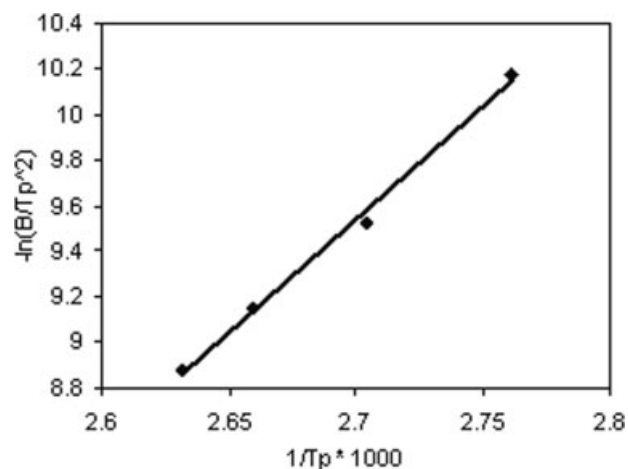
### Light curing

Curing of BHAPP monomer was found to be very easy and fast under irradiation of visible light with irradiance of  $700 \text{ mW/cm}^2$ . The monomer was mixed with 0.5 wt % comphorquinone as light initiator and 0.5 w% *N,N*-dimethyl amino ethyl methacrylate as accelerator. A drop of mixture was placed between thin films of polyethylene and exposed to visible light. The progress of photo curing reaction followed by measuring the absorption intensity of  $\text{C}=\text{C}$  in the region of  $1636 \text{ cm}^{-1}$  after exposure to the light for different periods of time (10 up to 70 s). A small exposure time of 40 s was enough to reach the maximum conversion. The absorption band of carbonyl group at  $1719 \text{ cm}^{-1}$  was used as reference peak for evaluating the photopolymerization of BHAPP monomer. The ratio of the absorbance intensities of two bands before and after photo polymerization was compared to determine the degree of conversion of the acrylate  $\text{C}=\text{C}$  bonds by using eq. (2)<sup>8</sup>

$$\text{DC}\% = (1 - A_t/B_{t0}) \times 100 \quad (2)$$

where  $A_t$  is the ratio of absorption peak of the acrylate ( $>\text{C}=\text{C}<$ ,  $1636 \text{ cm}^{-1}$ ) to the reference ( $>\text{C}=\text{O}$ ,  $1719 \text{ cm}^{-1}$ ) for different times of curing and  $B_{t0}$  the ratio of the initial absorption peaks of acrylate ( $>\text{C}=\text{C}<$ ) and the reference ( $>\text{C}=\text{O}$ ).

Three samples were used for each exposure time and the average values of conversion versus time of light exposure were used to plot Figure 4. When light falls on the mixture, the photoinitiator undergoes dissociation in the presence of tertiary amine-



**Figure 6** Plot for determination of  $E_a$  using Kissinger method.

initiating polymerization reaction that results in the hardening of the paste into a solid mass. The general mechanism of the initiation step of photo polymerization is given in the literature.<sup>19</sup>

### Thermal curing

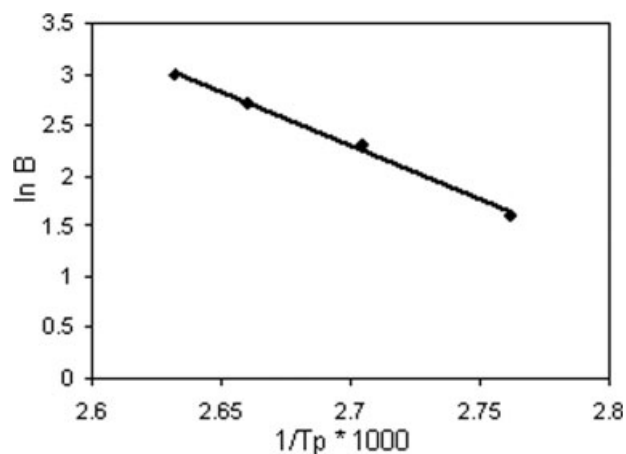
The monomer BHAPP was thoroughly mixed with 1 wt % of benzoyl peroxide as thermal initiator. Ten milligram of the mixture was placed in the sample pan and DSC (Table I) was scanned from 30 to  $300^\circ\text{C}$  at four different heating rates (5, 10, 15, and  $20^\circ\text{C}/\text{min}$ ). As shown in Figure 5(a–d), DSC thermograms showed large exothermic peak with maximum temperature ( $T_p$ ) varied from 89 to  $107^\circ\text{C}$  depending on the heating rate. The second scan curve at  $10^\circ\text{C}/\text{min}$  in Figure 5(e) shows disappearance of the exothermic peak indicating the complete of the cure during the first scan. DSC thermograms of all samples have shown a transition step at temperatures much higher than the  $T_p$ . The transition step varied from 170 to  $205^\circ\text{C}$  as the heating rate decreased from  $20^\circ\text{C}/\text{min}$  to  $5^\circ\text{C}/\text{min}$ . As time of thermal curing increased by decreasing the heating rate, the transition step shifted toward higher temperatures. This transition can probably be taken as the glass transition temperature ( $T_g$ ) of the cured sample and its shift to higher temperature can be an indication of formation of higher degree of crosslinks.

According to the method of Kissinger,<sup>20</sup> the activation energy is obtained from the maximum reaction

**TABLE II**  
Values of Kinetic Parameters

$E_a$ (kJ/mol)	$E_b$ (kJ/mol)	$A$ ( $\text{min}^{-1}$ )	$K$ ( $\text{min}^{-1}$ )
82.03	83.83	$2.64 \times 10^8$	$8 \times 10^{-4}$

$E_a$ , Kissinger method;  $E_b$ , Ozawa Method;  $T = 372$  (K).



**Figure 7** Plot for determination of  $E_a$  using Ozawa method.

rate where  $d(d\alpha/dt)/dt$  is zero under a constant heating rate condition. The resulting relation, for the analysis of DSC data, has been expressed as

$$-\ln(\beta/T_p^2) = E_a/R T_p - \ln(AR/E_a) \quad (3)$$

where  $T_p$  is the temperature at which the instant conversion rate was maximum,  $\beta$  constant heating rate,  $A$  frequency factor,  $R$  gas constant, and  $E_a$  activation energy. The  $E_a$  value was calculated from the slope of the linear plot of  $-\ln(\beta/T_p^2)$  against  $(1/T_p)$ , as shown in Figure 6. The  $E_a$  value was given in Table II.

The Ozawa-Flynn-Wall method based on Doyle's approximation<sup>21</sup> is an alternative method for the calculation of  $E_a$  and has been expressed as

$$\ln(\beta) = \text{Const.} - 1.05E_a/RT_p \quad (4)$$

Plot of  $\ln(\beta)$  versus  $(1/T_p)$  gave a straight line with a slope of  $1.05E_a/R$  as shown in Figure 7. The  $E_a$  value was given in Table II.

## CONCLUSIONS

<sup>1</sup>H-NMR spectra obtained from a number of reactions of monomer preparation indicated the major product as a linear derivative. Four hours of reaction

time at 60°C ensured complete disappearance of the characteristic absorption peak of the epoxy group confirming total conversion of DGE and acrylic acid into monomer.

The prepared diacrylate monomer showed maximum 60% conversion during 40 s exposure to the visible light. Heat cured polymerization of the monomer recorded by using DSC at different heating rates showed large single exothermic peak with the maximum temperature varied from 89 to 107°C depending on the heating rate.  $T_g$  of the cured samples appeared from 170 to 205°C depending on the heating rate. The activation energy of thermal curing of the monomer by analyzing DSC data and using two kinetic methods were similar of 83 kJ/mol.

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