

# Synthesis and Characterization of a Dimethacrylates Monomer with Low Shrinkage and Water Sorption for Dental Application

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**ABSTRACT:** In this study, a dimethacrylates monomer 1,3-bis[2-(4-(2'-hydroxy-3'-methacryloyloxy-propoxy)phenyl)-2propyl]benzene (BMPB) was synthesized to replace 2,2-bis[4-(2'-hydroxy-3'-methacryloyloxy-propoxy)phenyl]propane (Bis-GMA) as one component of dental restorative material with the aim of reducing polymerization shrinkage and water sorption. The structure of BMPB was confirmed by FTIR, <sup>1</sup>H-NMR, and elemental analysis. Double bond conversion, polymerization shrinkage, contact angle, water sorption, solubility, flexural strength, and flexural modulus of BMPB/tri(ethylene glycol) dimethacrylate (TEGDMA) based resin were measured. Bis-GMA/TEGDMA based resin was used as reference. The results

illustrated that double bond conversion, polymerization shrinkage, water sorption, and solubility of BMPB/TEGDMA were lower than that of Bis-GMA/TEGDMA ( $P < 0.05$ ). BMPB/TEGDMA had the same flexural strength with Bis-GMA/TEGDMA ( $P > 0.05$ ), but higher flexural modulus ( $P < 0.05$ ). Therefore, BMPB could possibly replace Bis-GMA as one component of dental restorative materials with the advantages of similar mechanical properties, being slightly more hydrophobic but presenting less shrinkage. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 114–120, 2012

**Key words:** dental polymers; photopolymerization; FTIR

## INTRODUCTION

Visible light-curable composites are now extensively used as dental restorative materials. These materials are always consisted of dimethacrylate-based resin matrix and inorganic fillers.<sup>1</sup> Compared with dental amalgams and dental ceramics, dimethacrylate-based dental restorative materials possess several advantages, such as excellent esthetic quality and the ability to bond to enamel surface. However, disadvantages like polymerization shrinkage and water sorption of dimethacrylate-based dental restorative materials limit their application in clinic to some extent.

Polymerization shrinkage is the major drawback of methacrylate-based dental restorative materials which may bring on marginal gaps between the tooth and the material leading to recurrent caries.<sup>2,3</sup> It was reported that polymerization shrinkage is induced by the change of distance between molecules before and after polymerization,<sup>4</sup> and is dependent on conversion and initial reactive group concentration.<sup>5</sup> Another draw-

back of methacrylate-based dental restorative materials is water sorption. Water sorption represents the amount of water adsorbed on the surface and into the material. The water intrusion in the dental materials can cause adverse effects to the materials, such as impairing mechanical properties,<sup>6</sup> elution of unreacted monomers,<sup>7,8</sup> hydrolysis,<sup>9</sup> and reducing thermal stability.<sup>10</sup> It is revealed that the water sorption is mostly affected by the hydrophilicity and structure of the resin monomer,<sup>11–13</sup> filler composition,<sup>14</sup> crosslinking,<sup>15</sup> and environment temperature.<sup>16,17</sup>

To improve the properties of methacrylate-based dental restorative materials, many researches have been taken to reduce polymerization shrinkage and water sorption of dental materials which have focused on the synthesis of new methacrylate monomers with reduced shrinkage and water sorption.<sup>2,3,18–21</sup> But in spite of the extensive studies, polymerization shrinkage and water sorption are still two major drawbacks in methacrylate-based dental restorative materials.

In this study, a dimethacrylates monomer 1,3-bis[2-(4-(2'-hydroxy-3'-methacryloyloxy-propoxy)phenyl)-2propyl]benzene (BMPB) was synthesized and used as base monomer of dental restorative material with the aim of decreasing polymerization shrinkage and water sorption. Therefore, the objective of this investigation was to evaluate the polymerization shrinkage, contact angle, water sorption, and solubility of the monomer as well as the commercially available

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dimethacrylates monomer, 2,2-bis[4-(2'-hydroxy-3'-methacryloyloxy-propoxy)-phenyl]propane (Bis-GMA). Double bond conversion and flexural strength were investigated additionally.

## MATERIALS AND METHODS

### Materials and instrument

1,3-Bis(2-(4-hydroxyphenyl)-2-propyl)benzene (BPB), Bis-GMA, and tri(ethylene glycol) dimethacrylate (TEGDMA) were purchased from Aldrich Chemical Co., St. Louis, USA. Epichlorohydrin and anhydrous magnesium sulfate were obtained from Shanghai No.1 Chemical Reagent Co. Ltd., China. Methacrylic acid was purchased from Guangzhou Chemical Reagent Co. Ltd., China. *N,N*-dimethylbenzylamine was purchased from Shanghai No.3 Chemical Reagent Co. Ltd., China. Sodium hydroxide, dichloromethane, and hydroquinone were purchased from Tianjin Chemical Reagent Co. Ltd., China. Hydrochloric acid was purchased from Guangzhou Donghong Chemical Co. Ltd., China. Camphorquinone (CQ) was purchased from Alfa Aesar Co., Ward Hill, USA. 2-(*N,N*-Dimethylamino)ethylmethacrylate (DMAEMA) was purchased from Acros Organic Co., New Jersey, USA. FTIR spectra were measured on a Vector33 Model Fourier Transform Infrared Instrument (Bruker Co., Germany). The samples were in the form of KBr pellets, and were scanned from 4000 to 400  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  spectra were recorded on an Avance AV 400MHz Instrument (Bruker Co., Switzerland). The chemical shifts were reported in ppm on the  $\delta$  scale with tetramethylsilane as the internal reference and  $\text{CDCl}_3$  as the solvent. Elemental analysis was done with a Vario EL CHNS Elemental Analyzer (Element AR Co., Germany). Exposure of samples was made with a Curing Light 2500 ( $\lambda = 400\text{--}520$  nm,  $I \approx 550$   $\text{mW cm}^2$ , 3M, USA).

### Method

#### Synthesis of monomer

BMPB was synthesized via a two steps reaction (Fig. 1). BPB reacted with epichlorohydrin to afford 1,3-bis[2-(4-(oxiranylmethoxy)phenyl)-2-propyl]benzene (BOPB), and then BOPB was converted to BMPB by the reaction with methacrylic acid.

**Preparation of 1,3-bis[2-(4-(oxiranylmethoxy)phenyl)-2-propyl]benzene.** A mixture of BPB (6.93 g, 0.02 mol) and epichlorohydrin (22.20 g, 0.24 mol) was stirred until a clear solution was obtained. Aqueous NaOH solution (40 wt %, 8.00 g) was added and the mixture was stirred for 4 h at  $(110 \pm 2)^\circ\text{C}$ . To hydrolyze residual epichlorohydrin, an additional aqueous NaOH solution (40 wt %, 10.00 g) was added and the mixture was stirred at  $90^\circ\text{C}$  for 4 h. Dichlorome-

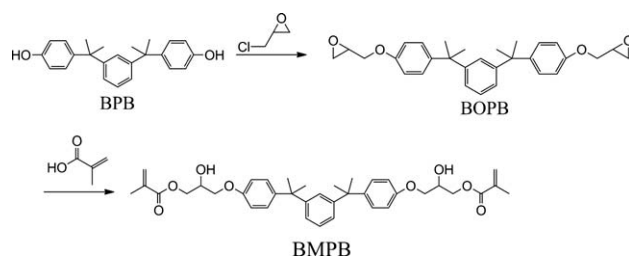


Figure 1 Synthesis of BMPB.

thane (100 mL) was added to the reaction mixture, and the resultant solution was washed with brine and dried over night with anhydrous sodium sulfate. After filtration to remove the drying agent, the solvent was stripped off and BOPB was obtained as a yellow viscose liquid (7.13 g, 77.9%). The results of spectroscopic studies for BOPB are as follows: IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) 3055, 2968, 2930, 2873, 1615, 1596, 1512, 1463, 914.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz):  $\delta$  1.69[s, 12H, 4Ar-C- $\text{CH}_3$ ], 2.81–2.83, 2.94–2.97[m, 4H, 2Ar-O- $\text{CH}_2\text{CHCH}_2$ ], 3.39–3.44[m, 2H, 2Ar-O- $\text{CH}_2\text{CHCH}_2$ ], 3.99–4.03, 4.25–4.29[m, 4H, 2Ar-O- $\text{CH}_2\text{CHCH}_2$ ], 6.87–6.89, 7.19[m, 8H, 2-O-Ar-C( $\text{CH}_3$ ) $_2$ -], 7.10–7.12, 7.17, 7.21–7.25[m, 4H, -C( $\text{CH}_3$ ) $_2$ -Ar-C( $\text{CH}_3$ ) $_2$ -]. Elemental analysis: calculated for BOPB (whose formulation is  $\text{C}_{30}\text{H}_{34}\text{O}_4$ ), C 78.60%, H 7.42%, O 13.98%; found, C 77.16%, H 7.43%, O 15.41%.

**Preparation of 1,3-bis[2-(4-(2'-hydroxy-3'-methacryloyloxy-propoxy)phenyl)-2-propyl]benzene (BMPB).** A mixture of BOPB (9.16 g, 0.02 mol), methacrylic acid (6.88, 0.08 mol), *N,N*-dimethylbenzylamine (66.8 mg) and hydroquinone (66.8 g) was stirred at  $90^\circ\text{C}$  for 9 h. Dichloromethane (100 mL) was then added to the reaction mixture. The resulting solution was washed successively with 0.5 mol/L aqueous HCl and 10 wt % aqueous NaOH solution. The organic layer was then dried overnight with anhydrous magnesium sulfate. After removing the drying agent by filtration, the dichloromethane was removed by distillation under vacuum and BMPB was obtained as a brown viscose liquid (9.36 g, 74.3%). The results of spectroscopic studies for BMPB are as follows: IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) 3429, 3100, 3060, 2968, 2931, 2867, 1719, 1634, 1615, 1596, 1512, 1463.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz):  $\delta$  1.61[s, 12H, 4Ar-C- $\text{CH}_3$ ], 1.95[s, 6H, 2C=C- $\text{CH}_3$ ], 4.00–4.38[m, 12, 2Ar-O- $\text{CH}_2\text{CHOHCH}_2\text{-COO}$ ], 5.59[s, 2H, 2H-C=C-COO (*trans*)], 6.16[s, 2H, 2H-C=C-COO (*cis*)], 6.77–6.80, 7.09[m, 8H, 2-O-Ar-C( $\text{CH}_3$ ) $_2$ -], 7.03–7.05, 7.07, 7.15–7.19[m, 4H, -C( $\text{CH}_3$ ) $_2$ -Ar-C( $\text{CH}_3$ ) $_2$ -]. Elemental analysis: calculated for BMPB (whose formulation is  $\text{C}_{38}\text{H}_{46}\text{O}_8$ ), C 72.38%, H 7.30%, O 20.32%; found, C 71.38%, H 7.29%, O 21.33%.

#### Preparation of resin formulations

Photo-cured resin formulation was a mixture of BMPB (or Bis-GMA), TEGDMA, CQ, and DMAEMA.

CQ and DMAEMA were used as photoinitiator system. Their mass ratio was 50 : 50 : 2.0 : 4.0 of BMPB (or Bis-GMA)/TEGDMA/CQ/DMAEMA. All of resin formulations were stored in the dark before used.

#### Measurement of double bond conversion

The double bond conversion (DC) of each formulation was measured by the FTIR spectroscopy. Each sample was coated on a KBr plate and covered with a polyethylene film, and irradiated with visible light. DC was determined from the ratio of the calculated areas of two absorption bands ( $1635\text{ cm}^{-1}$  for C=C and  $1608\text{ cm}^{-1}$  for aromatic rings as an internal standard) before and after exposure. The DC was then calculated as following equation:

$$C(t) = \frac{(A_{C=C}/A_{Ph})_0 - (A_{C=C}/A_{Ph})_t}{(A_{C=C}/A_{Ph})_0} \quad (1)$$

where  $A_{C=C}$  and  $A_{Ph}$  are the absorbance peak area of methacrylate C=C at  $1636\text{ cm}^{-1}$  and phenyl ring at  $1608\text{ cm}^{-1}$ , respectively;  $(A_{C=C}/A_{Ph})_0$  and  $(A_{C=C}/A_{Ph})_t$  are the normalized absorbance of functional group at the radiation time 0 and  $t$ , respectively;  $C(t)$  is the conversion of methacrylate C=C as a function of radiation time.

#### Measurement of polymerization shrinkage

Polymerization shrinkage was determined by density change of resin before and after curing. First, density of uncured resin was determined. A 10-mL density bottle was massed, filled with uncured resin, and massed again. The same bottle was then emptied, thoroughly washed and dried, filled with distilled water and massed again. This procedure was repeated five times. The density of resin before curing ( $D_r$ ) was then calculated as:

$$D_r = (M_r/M_w) \times D(T) \quad (2)$$

where  $D(T)$  is the density of water at the room temperature,  $M_r$  is the mass of uncured resin,  $M_w$  is the mass of water.

Second, density of cured resin was determined. Resins were poured into a Teflon mold sized  $25\text{ mm} \times 2\text{ mm} \times 2\text{ mm}$ , then light-cured for 5 min using a dental light source at room temperature and about 5 mm of distance between the light tip and the radiometer face. Five specimens for each resin were prepared. The cured resin specimen was removed and massed to obtain the mass of cured resin ( $M_s$ ). A 10-mL density bottle was filled with distilled water and massed to obtain the mass of water ( $M_w$ ). Cured resin was put into the bottle, spilled water was gently wiped with a soft absorbent paper, and then the bottle with water and cured resin was massed to obtain  $M_{sw}$ . The density of resin after curing ( $D_s$ ) was calculated as:

$$D_s = \frac{M_s \times D(T)}{M_w + M_s - M_{sw}} \quad (3)$$

Hence, the polymerization shrinkage ( $S$ ) was calculated as:

$$S = \frac{D_s - D_r}{D_s} \times 100\% \quad (4)$$

#### Measurement of contact angle

Contact angle was measured on disc-shaped specimens ( $15 \pm 0.1\text{ mm} \times 1.0 \pm 0.1\text{ mm}$ ) of every resin formulation ( $n = 5$ ). Specimens were photopolymerized on each side for 300 s. Three 2- $\mu\text{L}$  droplets of double-distilled water were placed on predetermined areas (polished with 1200 grit silica carbide paper) of every disc specimen for a total of 15 readings per tested resin material. The contact angle was then measured 20 s after drop placement utilizing a DSA100 optical contact angle measuring instrument (Kruss Co., German) at room temperature.

#### Measurement of water sorption, solubility

Resins were added into a cylindrical Teflon mold with an internal diameter of 15 mm and a height of 1.0 mm, then light-cured for 5 min using a dental light source. Three specimens of each sample were prepared. The specimens were placed in a desiccator at room temperature under normal pressure and massed every 24 h until a constant mass ( $M_1$ ) was obtained (i.e., variation was less than 0.001 g in any 24 h period). Following, the specimens were immersed in distilled water. At fixed time intervals they were removed, blotted dry to remove excess water, massed and returned to the water. Equilibrium mass ( $M_2$ ) was obtained until there was no significant change in mass. The specimens were then dried at  $40^\circ\text{C}$  until their mass was constant, and the result was recorded as  $M_3$ . Water sorption (WS) and solubility (SL) were then calculated using the following formulae:

$$WS = \frac{M_2 - M_3}{V} \quad (5)$$

$$SL = \frac{M_1 - M_3}{V} \quad (6)$$

where  $V$  is the volume of the specimen.

#### Three point bending test

The samples were prepared by injecting the resins into Teflon molds, covering the open sides with polyethylene films, and irradiating each side for 300 s. The sample average dimensions were  $20\text{ mm} \times 4\text{ mm} \times 2\text{ mm}$ , and five specimens were prepared

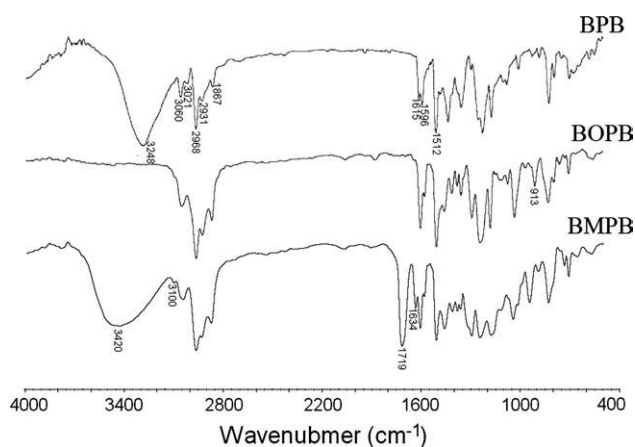


Figure 2 FTIR spectra of BPB, BOPB, and BMPB.

for each formulation. A three-point bending test was carried out to evaluate the flexural strength of the cured resin with a GT-TCS-2000 universal testing machine (Dongguan Gao Tie Co. Ltd., China) at a cross-head speed of 1.00 mm/min.

#### Statistical analysis

The results were analyzed and compared using one-way ANOVA and the Tukey's test at the significance level of 0.05.

## RESULTS AND DISCUSSION

### Synthesis of BMPB

The yields of the intermediate BOPB and the target monomer BMPB were 77.9% and 74.3%, respectively. The chemical structures of BOPB and BMPB were characterized with FTIR,  $^1\text{H-NMR}$ , and elemental analysis. As shown in Figure 2, one typical absorption peaks was observed at  $914\text{ cm}^{-1}$  (epoxy group) in BOPB, while the absorption peak at  $3248\text{ cm}^{-1}$  (-OH) of BPB disappeared. This indicated that the hydroxyl group in BPB had reacted with epichlorohydrin completely. The  $^1\text{H-NMR}$  spectrum (Fig. 3) and elemental analysis of BOPB could confirm the structure of BOPB.

Compared with the FTIR spectrum of BOPB, the absorption peak at  $914\text{ cm}^{-1}$  disappeared and three new absorption peaks at  $3429\text{ cm}^{-1}$  (-OH),  $1719\text{ cm}^{-1}$  (C=O), and  $1634\text{ cm}^{-1}$  (C=C) appeared in the FTIR spectrum of BMPB. Meanwhile, in  $^1\text{H-NMR}$  spectrum of BMPB (Fig. 4), distinctive signals assigned to C=C-CH<sub>3</sub> (1.95 ppm), Ar-O-CH<sub>2</sub>CHOHCH<sub>2</sub>-COO (4.00–4.38 ppm), H-C=C-COO (5.59 ppm *trans*), H-C=C-COO (6.16 ppm *cis*) were observed, and the signals between 2.81 and 4.29 ppm corresponding to the epoxide CH and CH<sub>2</sub> groups of BOPB disappeared. This suggests that the epoxy groups in BOPB

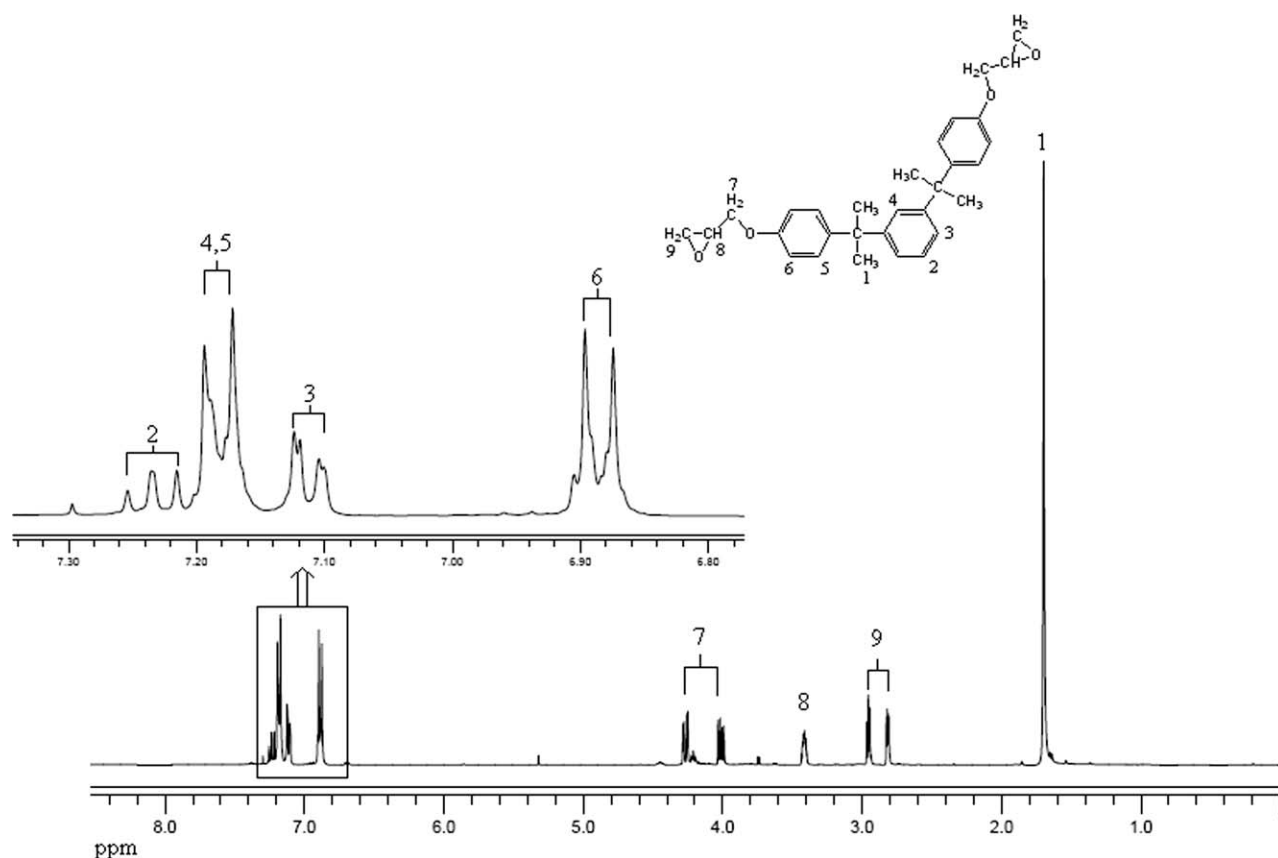


Figure 3  $^1\text{H-NMR}$  spectra of BOPB.



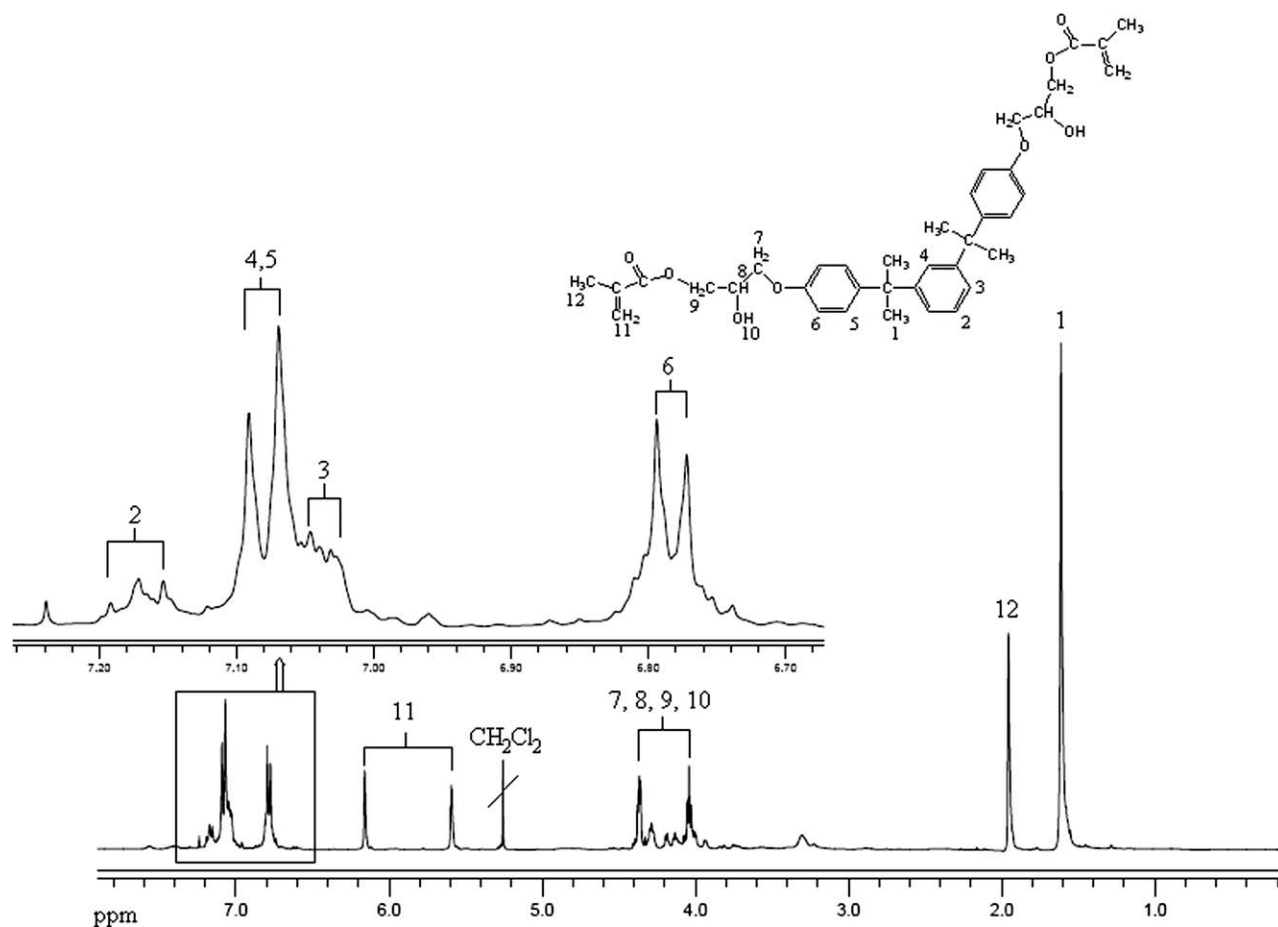


Figure 4  $^1\text{H-NMR}$  spectra of BMPB.

reacted completely with methacrylic acid and methacrylate groups were introduced successfully.

### Photopolymerization behavior

Figure 5 shows the curves of double bond conversion versus irradiation time of BMPB/TEGDMA formulation and Bis-GMA/TEGDMA formulation. As shown in Figure 5, double bond conversion increased significantly with increasing radiation time, and got a maximum at 60 s of radiation time, then did not obviously increase with prolonging radiation time. From Figure 5, double bond conversion of BMPB/TEGDMA formulation was lower than Bis-GMA/TEGDMA formulation. This might be attributed to the difference between the structure of BMPB and Bis-GMA. There are more phenyl groups in BMPB than that in Bis-GMA. The bulkiness of BMPB may reduce the mobility of growing radical chains and induce an earlier time to vitrification,<sup>22</sup> which lead more unreacted monomers and macroradicals to being trapped in the network at early time, and reduce the double bond conversion of BMPB based resin.

### Polymerization shrinkage

Polymerization shrinkage of each formulation was shown in Table I. As shown in Table I, polymerization shrinkage of BMPB/TEGDMA system was lower than that of Bis-GMA/TEGDMA system. It

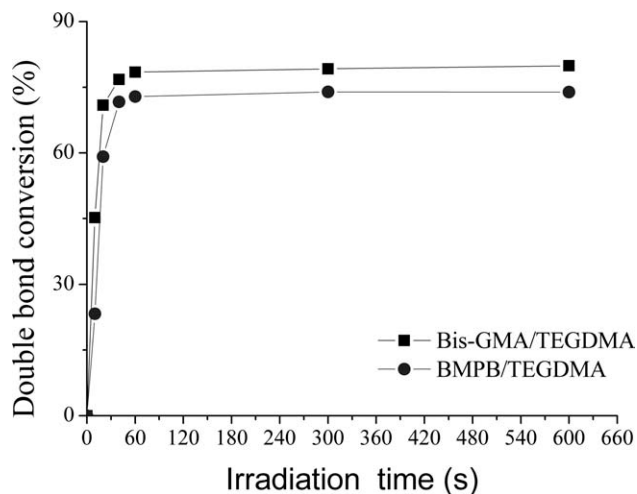


Figure 5 Double bond conversion of BMPB/TEGDMA system and Bis-GMA/TEGDMA system.

**TABLE I**  
**Properties of Bis-GMA/TEGDMA Based Resin and BMPB/TEGDMA Based Resin**

System	Properties <sup>a</sup>					
	Polymerization shrinkage (%)	Contact angle (°)	Water sorption ( $\mu\text{g}/\text{mm}^3$ )	Water solubility ( $\mu\text{g}/\text{mm}^3$ )	Flexural strength (MPa)	Flexural modulus (GPa)
Bis-GMA/TEGDMA	8.73	$79.2 \pm 1.1^a$	$57.3 \pm 1.3^a$	$33.8 \pm 2.3^a$	$64.6 \pm 5.5^a$	$0.94 \pm 0.03^a$
BMPB/TEGDMA	4.00	$82.5 \pm 2.1^b$	$47.0 \pm 0.8^b$	$28.0 \pm 1.8^b$	$63.5 \pm 1.9^a$	$1.05 \pm 0.04^b$

<sup>a</sup> Lower case letters indicate statistical differences within a column (Tukey's test,  $P = 0.05$ )

was reported that polymerization shrinkage was directly influenced by concentration and conversion of double bond.<sup>4,21,23</sup> Comparing monomers of the same functionality, polymerization shrinkage increases when initial molecular weight decreases,<sup>21</sup> and lower double bond conversion generates less polymerization shrinkage.<sup>4,23</sup> In this study, molecular weight of BMPB (630) was higher than that of Bis-GMA (512) and double bond conversion of BMPB-based resin was lower than that of Bis-GMA based resin. Therefore, the polymerization shrinkage of BMPB based formulation was lower than that of Bis-GMA based formulation.

#### Contact angle, water sorption, and solubility

Contact angle, water sorption, and water solubility were summarized in Table I. From Table I, contact angle of BMPB/TEGDMA copolymer was higher than that of Bis-GMA/TEGDMA copolymer ( $P < 0.05$ ), water sorption and solubility of BMPB/TEGDMA copolymer were lower than that of Bis-GMA/TEGDMA copolymer ( $P < 0.05$ ).

It was reported that the water sorption of the copolymer was influenced by the hydrophilicity<sup>24</sup> and crosslinking density of copolymer.<sup>25</sup> Decreased hydrophilicity and increased crosslinking density of copolymer could reduce the water sorption of the copolymer. In this work, the relative hydrophilicity of the copolymers can be investigated by comparing the contact angles made when droplets of distilled water are placed on the polymerized resin surface.<sup>26–28</sup> From the result of contact angle, we can see that hydrophilicity of BMPB/TEGDMA copolymer was less than that of Bis-GMA/TEGDMA copolymer, because there are more hydrophobic groups, such as phenyl groups and methyl groups, in the structure of BMPB than that of Bis-GMA, and it could make water sorption of BMPB/TEGDMA copolymer lower than that of Bis-GMA/TEGDMA copolymer. However, the lower double bond conversion of BMPB/TEGDMA copolymer, on the other hand, should decrease crosslinking density of it, and induce higher water sorption. The final water sorption of BMPB/TEGDMA copolymer was lower than that of Bis-GMA/TEGDMA, this was mainly attrib-

uted to the less hydrophilicity of BMPB/TEGDMA copolymer.

Water solubility of the copolymers is related to the amount of the unreacted monomers in the crosslinking network,<sup>29</sup> and the characteristics of the network and monomer. In this research, double bond conversion of BMPB/TEGDMA formulation was lower than that of Bis-GMA/TEGDMA formulation, so there might be more unreacted monomers in its copolymer. However, water solubility of BMPB/TEGDMA copolymer was lower than that of Bis-GMA/TEGDMA copolymer, this might be attributed to the bulky structure of BMPB, which made it difficult to leach out of the crosslinking network.

#### Flexural strength and modulus

Flexural strength and modulus of Bis-GMA/TEGDMA copolymer and BMPB/TEGDMA copolymer were shown in Table I. As can be seen from Table I, BMPB/TEGDMA copolymer and Bis-GMA/TEGDMA copolymer had comparable flexural strength ( $P > 0.05$ ), and BMPB/TEGDMA copolymer had higher flexural modulus than Bis-GMA/TEGDMA copolymer ( $P < 0.05$ ). The additional phenyl group in BMPB would make the network of BMPB/TEGDMA copolymer more rigid than that of Bis-GMA/TEGDMA copolymer, so the modulus of BMPB/TEGDMA copolymer was higher than that of Bis-GMA/TEGDMA copolymer. Though there were more phenyl groups in the network of BMPB/TEGDMA copolymer, which would strengthen the mechanical properties of it, there was no obvious difference between the flexural strength of BMPB/TEGDMA copolymer and Bis-GMA/TEGDMA copolymer. This result might be attributed to the lower double bond conversion of BMPB/TEGDMA formulation.

#### CONCLUSIONS

In this study, a dimethacrylate monomer BMPB with a molecular weight of 630 and a large molecular volume was synthesized in two steps utilizing BPB, epichlorohydrin and methacrylic acid as raw materials. The structures of the intermediate BOPB and target monomer BMPB were fully characterized by FTIR, <sup>1</sup>H-NMR, and elemental analysis. The properties of

BMPB based resin, such as lower shrinkage, lower water sorption and solubility, and similar flexural strength, render it with potential to replace Bis-GMA based resin as resin matrix in dental restorative materials.

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