# Synthesis and Photopolymerization of Multifunctional Methacrylates Derived from Bis-GMA for Dental Applications

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ABSTRACT: Two multimethacrylates having three methacrylate groups (BPA-3M) and four methacrylate groups (BPA-4M) have been prepared by reacting hydroxyl groups of 2,2-bis[4-(2'-hydroxy-3'-methacryloyloxypropoxy)phenyl]propane (Bis-GMA) with methacryloyl chloride. BPA-3M and BPA-4M have much lower viscosities than the starting Bis-GMA, because they have only one or no hydroxyl group. Photopolymerizations of the multifunctional methacrylates were conducted by exposure to visible light using camphorquinone and 2-(N,N-dimethylamino) ethyl methacrylate as a photoinitiating system. High conversions >50% resulted from photopolymerization of BPA-3M, whereas Bis-GMA showed lower conversions under the same condition, implying better mechanical properties for the composite resins made from BPA-3M. BPA-4M showed much lower conversions in the photopolymerization condition. Water sorption of the photocured composite of BPA-3M containing 50 wt % of inorganic fillers was found to be 0.15%, which is only one-tenth of the commercial Bis-GMA composite. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2033–2037, 1999

**Key words:** multifunctional methacrylates; visible light curing; photopolymerization; water sorption; dental restorative composite; dental filling materials

## INTRODUCTION

Visible light-curable polymeric composites are now routinely used as filling materials for dental restorations.<sup>1,2</sup> These materials are based on difunctional methacrylate monomers and prepolymers along with silane-coated inorganic fillers. One major feature of the composites is the use of visible blue light (420-500 nm) for activating photopolymerization *in situ* in a tooth cavity. Polymeric dental composites generally consist of a multifunctional methacrylate prepolymer, a dimethacrylate diluent, a photoinitiator, or a photoinitiating system, as well as a large quantity of inorganic fillers. The polymeric composite is then photopolymerized intraorally by visible light to form strong network structures with adequate shaping. The polymeric dental restorative composites require such important properties as low shrinkage, low water uptake, low thermal expansion characteristics, good adhesion properties, and aesthetics closely matching with those of tooth structure along with acceptable biocompatibility.

2,2-Bis[4-(2'-hydroxy-3'-methacryloyloxypropoxy) phenyl]propane (Bis-GMA) is an essential component as a multifunctional methacrylate prepolymer in the light-curable polymeric dental composites. The rigid aromatic backbone structure of Bis-GMA based on bisphenol A (BPA) provides superior toughness and other desirable properties

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for the final applications.<sup>1,3</sup> However, two hydroxyl groups of the Bis-GMA molecule are considered to promote water sorption of the photocured composite in a mouth, resulting in gradual long-term deterioration of aesthetics and mechanical properties of the composites. Another drawback of Bis-GMA is its high viscosity owing to hydrogen bondings between the hydroxyl groups. These are the reasons why there have been some attempts to block the hydroxyl functional group of the Bis-GMA molecule by introducing appropriate groups.<sup>4-6</sup> Significant reduction in viscosity values of multimethacrylate prepolymers was reported in recent meetings by structural modification of the Bis-GMA molecule.<sup>4,7</sup> Fluorinated multimethacrylate prepolymers were also disclosed for enhancing composite durability by increasing hydrophobicity.8

In this article, two multifunctional methacrylates were prepared by blocking the hydroxyl groups in the Bis-GMA molecule with methacryloyl groups, and their photopolymerizations by visible light using camphorquinone and tertiary amine as a photoinitiator were studied. Water uptake of the photocured composites based on those multimethacrylates was also investigated.

#### **EXPERIMENTAL**

#### **Materials and Instruments**

Methacryloyl chloride, camphorquinone (CQ), 2-(N,N-dimethylamino)ethyl methacrylate (DMAEMA), triethylene glycol dimethacrylate (TEGDMA), and triethylamine were purchased from Aldrich Chemical Co. (Milwaukee, WI). Bis-GMA was purchased from Maruzen Chemical Co. or prepared by reacting diglycidyl ether of BPA and methacrylic acid according to a known method.<sup>3</sup> All of the chemicals were purified by conventional methods. The commercial dental composite sample (here named as Z) was purchased from a dealer. Bis-GMA was purified by passing silica gel columns twice using a mixture of hexane-ethyl acetate (3:1 and 1:1, v/v) as an eluent. Other methacrylates were also purified by passing silica gel columns.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were taken on a Varian Gemini 200-MHz spectrometer in deuteriochloroform using tetramethylsilane as an internal standard. Infrared (IR) spectra were recorded on an Polaris Fourier transform IR (FTIR) spectrophotometer (Mattson Instrument Co.). Exposure of the samples was made on a Curing Light XL1000 (3M Dental Products) with a range of 420–500 nm. The light intensity was  $\sim$  100 mW cm<sup>-2</sup> at a distance of 4 mm from the tip of the light guide. Viscosity of the prepolymer was measured with a plate-cone rheometer (HAAKE RV2 and PK100) at 20°C.

#### **Preparation of BPA-3M**

To a solution of Bis-GMA (5.12 g, 0.010 mol) and triethylamine (1.11 g, 0.011 mol) in chloroform (15 mL), methacryloyl chloride (1.15 g, 0.011 mol) was slowly added for 1 h. The mixture was stirred at room temperature for 24 h and filtered to remove a precipitated salt. The solution was washed with distilled water three times, and the solvent was stripped off. BPA-3M was obtained in a pale yellow oil from the crude product by column chromatography using a mixture of hexane-ethyl acetate (3:1, v/v) as an eluent; yield of BPA-3M 3.30 g (57%). IR (neat):  $\nu$  (cm<sup>-1</sup>) 3504 (—OH), 2964 (aliphatic C-H), 1721 (ester C=O), 1638 (methacryloyl C=C), 1609 (aromatic C=C), 1318 and 1175 (ester C-O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  (ppm) 1.62 [s, 6H, Ar<sub>2</sub>—C(CH<sub>3</sub>)<sub>2</sub>], 1.93 [s, 9H, 3C=C-CH<sub>3</sub>], 3.10-3.25 (b, 1H, OH), 4.01-4.19 [m, 4H, 2CH<sub>2</sub>—O—Ar], 4.24-4.60 [m, 6H, 2COO-CH<sub>2</sub>CH], 5.46-5.51 [m, 2H, CH<sub>2</sub>-OH (isomer)], 5.57 [s, 3H, 3H—C=C—COO (trans)], 6.11 and 6.14 [s, 3H, 3H-C=C-COO (cis)], 6.82 [d, 4H, aromatic C-H], 7.13 [d, 4H, aromatic, C—H]. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 17.82, 17.91, and 17.98 [CH<sub>2</sub>=C-CH<sub>3</sub>], 30.59 [Ar<sub>2</sub>-C-(CH<sub>3</sub>)<sub>2</sub>], 41.35 [Ar<sub>2</sub>—C—(CH<sub>3</sub>)<sub>2</sub>], 62.50, 65.35, 65.76, 68.09, 68.50, and 69.80 [Ar-O-CH<sub>2</sub>CHCH<sub>2</sub>-O], 125.94, 126.19, and 126.27 [CH2=C-CH3], 135.59 and 135.71 [CH<sub>2</sub>=C-CH<sub>3</sub>], 113.75, 127.54, 143.34, 143.55, 155.98, and 156.10 [aromatic], 166.34, 166.67, and 167.18 [carbonyl of methacrylate].

#### **Preparation of BPA-4M**

BPA-4M was prepared by a similar method of BPA-3M using a different methacryloyl chloride/ bis-GMA ratio (2.2/1). BPA-4M was obtained in a pale yellow oil from the crude product by column chromatography using a mixture of hexane-ethyl acetate (1 : 1, v/v) as an eluent; yield of BPA-4M 3.50 g (54%). IR (neat):  $\nu$  (cm<sup>-1</sup>) 2964 (aliphatic C—H), 1723 (ester C=O), 1638 (methacryloyl C=C), 1609 (aromatic C=C), 1318 and 1175 (ester C—O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  (ppm) 1.62 [s, 6H, Ar<sub>2</sub>—C(CH<sub>3</sub>)<sub>2</sub>], 1.93 [s, 12H, 4C=C—CH<sub>3</sub>], 4.17 [d, 4H, 2CH<sub>2</sub>—O—Ar], 4.39– 4.58 [m, 6H, 2COO—CH<sub>2</sub>CH], 5.57 [s, 4H, 4H—C=C—COO (trans)], 6.10 and 6.13 [s, 4H, 3H—C=C—COO (cis)], 6.83 [d, 4H, aromatic C—H], 7.13 [d, 4H, aromatic C—H]. <sup>13</sup>C NMR (50 MHz, in CDCl<sub>3</sub>):  $\delta$  17.80, 17.89 [CH<sub>2</sub>=C—CH<sub>3</sub>], 30.58 [Ar<sub>2</sub>—C—(CH<sub>3</sub>)<sub>2</sub>], 41.35 [Ar<sub>2</sub>—C—(CH<sub>3</sub>)<sub>2</sub>], 62.45, 65.77, and 69.78 [Ar—O—CH<sub>2</sub>CHCH<sub>2</sub>O<sub>2</sub>C], 125.87 and 126.07 [CH<sub>2</sub>=C—CH<sub>3</sub>], 135.62 [CH<sub>2</sub>=C—CH<sub>3</sub>], 113.82, 127.53, 143.48 and 156.01 [aromatic], 166.22 and 166.54 [carbonyl of methacrylate].

#### **Measurement of Photocuring**

The multimethacrylate BPA-3M or BPA-4M was mixed with 0.1–5.0 wt % of CQ and DMAEMA with respect to the prepolymer in acetone. The weight ratio of CQ and DMAEMA was kept unity. The sample mixture was coated on a NaCl plate and irradiated with the visible light apparatus with an intensity of 100 mW/cm<sup>2</sup>. Absorbance of the methacrylate C=C at 1638 cm<sup>-1</sup> was measured before and after exposure. The absorption band of the aromatic rings at 1609 cm<sup>-1</sup> was used as an internal standard. 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.

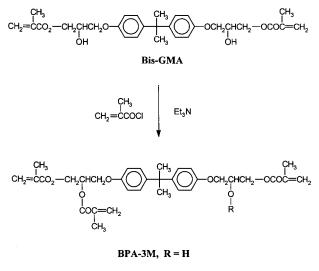
#### **Measurement of Water Sorption**

The inorganic filler consisting of zirconia/silica, with an average particle size of 0.7  $\mu$ m, was surface-treated by 3-(trimethoxysilyl)propyl methacrylate. The filler, a multimethacrylate prepolymer, CQ, and DMAEMA with a weight ratio of 50 : 50 : 0.5 : 0.5 were blended, and the composite was placed in a circular Teflon mold with 2.5 mm thickness and 10 mm radius. The composite sample was exposed to visible blue light (420–500 nm) through glass plates at both sides for 60 s. The photocured disk sample was immersed in a water bath controlled at 37°C. From time to time, up to 30 days, the sample was taken and weighed to determine water uptake after complete removal of water from the surface.

#### **RESULTS AND DISCUSSION**

#### Synthesis of BPA-3M and BPA-4M

Multifunctional methacrylates having three methacrylate groups (BPA-3M) and four methacrylate groups (BPA-4M) were prepared in the yields of 57% and 54%, respectively, by reacting



#### BPA-4M, R = methacryloyl

Figure 1 Synthesis of BPA-3M and BPA-4M from Bis-GMA.

hydroxyl groups of Bis-GMA with methacryloyl chloride as shown in Figure 1. BPA-3M shows a broad absorption band centered at  $3504 \text{ cm}^{-1}$  for the hydroxyl group in a FTIR spectrum, but BPA-4M does not. In a proton NMR spectrum BPA-3M also showed a broad peak at 3.1-3.4 ppm corresponding to the OH group. The commercial Bis-GMA has been identified as a mixture of three isomers of a similar chemical nature.<sup>3</sup> In this work, the starting Bis-GMA was found to contain  $\sim$  25–30% of the second and third isomers by analyzing <sup>1</sup>H NMR data. Therefore BPA-3M should have two isomers, and there is no isomeric form in BPA-4M. The isomer separation of BPA-3M was not attempted, because both isomeric methacrylates should have similar chemical nature in photocuring reactions.

#### **Viscosity Lowering**

The viscosities of three multimethacrylate prepolymers (Bis-GMA, BPA-3M, and BPA-4M) were measured using a plate-cone rheometer, and the values are listed in Table I. As expected, the viscosity of BPA-3M was greatly reduced by blocking the hydroxyl groups of the Bis-GMA molecule. More significant lowering of the viscosity was verified in the case of BPA-4M, which has no OH group. The viscosities of the prepolymers further decreased by adding a diluent, TEGDMA. Interestingly, Bis-GMA/TEGDMA (60/40) and BPA-3M/TEGDMA (80/20) showed an identical viscosity value. The result indicates that the amount of

Prepolymer	Diluent	Viscosity (Pa s)
Bis-GMA Bis-GMA	TEGDMA 40%	$2,700 \\ 0.65$
BPA-3M BPA-3M BPA-3M	 TEGDMA 10% TEGDMA 20%	$8.6 \\ 1.6 \\ 0.65$
BPA-4M	_	0.68

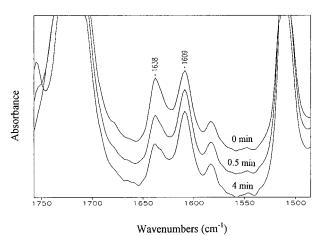
Table I Viscosities of Multimethacrylate **Prepolymers**<sup>a</sup>

<sup>a</sup> Measured by a plate-cone rheometer, HAAKE RV2, and PK100 at 20°C.

diluent can be reduced in formulation of the polymeric composites from BPA-3M or BPA-4M, and thus the mechanical properties of the composites could be enhanced.

#### Photocuring by Visible Light

Photocurable formulations comprising a prepolymer with a mixture of CQ and DMAEMA as a photoinitiating system were irradiated with visible light (420-500 nm), and their photoreactivities were investigated by FTIR spectral analysis. The absorption bands at 1638  $\text{cm}^{-1}$  representing the methacrylate C=C stretching vibration of the multimethacrylates gradually decreased with increasing exposure time, as depicted in Figure 2. The absorption band at 1609  $\rm cm^{-1}$  originating from the aromatic rings was used as an internal standard for evaluating the photopolymerization. The ratios of the calculated areas of the two absorption bands before and after exposure were



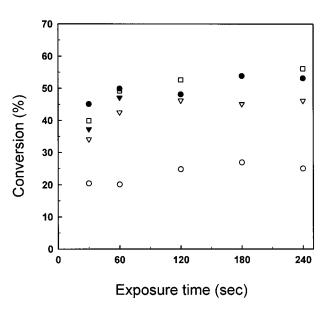


Figure 3 Plot of conversions of BPA-3M vs. exposure time with various amounts of the photoinitiator composed of equal weight of CQ and DMAEMA: ( $\bigcirc$ ) 0.2%, ( $\bigtriangledown$ ) 0.6%, (●) 1.0%, (▼) 1.3%, and (□) 5.0% for CQ in wt %.

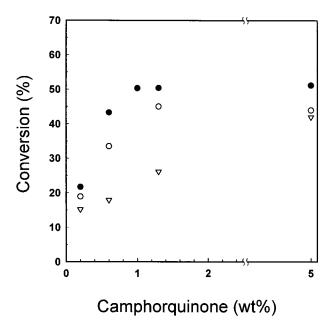
compared to determine the degree of conversion of the methacrylate C=C bonds. As shown in Figure 3, BPA-3M revealed saturated conversions  $\sim 50\%$ when irradiated for 60 s and no appreciable increase in conversion upon prolonged exposure.

The effect of the photoinitiating system composed of CQ and DMAEMA on the degree of conversions of the methacrylates in the formulations was investigated. The weight ratio of the photoinitiating compounds was kept unity in all the cases. When the sample from BPA-3M was exposed, the degree of conversion increased with increasing amounts of the photoinitiating compounds. A maximum conversion value was reached when 1.0 wt % CQ was used (hence 1.0 wt % DMAEMA), as shown in Figure 3 and Figure 4. However, further increase in the amount of CQ rendered no appreciable change in conversion. BPA-3M attained 50% conversion by photoirradiation for 60 s, whereas Bis-GMA showed 45% conversion under the same condition, implying superior mechanical properties for the composite formulations from BPA-3M. On the contrary, BPA-4M exhibited very low conversion below 30%, which might be attributable to a high autoacceleration effect.<sup>9</sup>

#### Low Water Uptake

The water uptake of the photocured composite formulations of Bis-GMA or BPA-3M was inves-

Figure 2 IR spectral change of BPA-3M before and after visible light exposure.

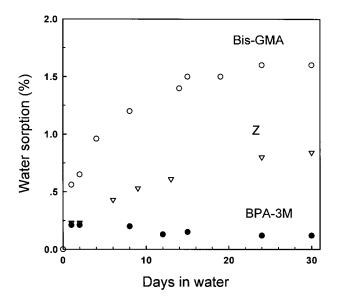


**Figure 4** Plot of conversions of three multimethacrylate prepolymers *vs.* amounts of CQ after being exposed for 60 s: ( $\bigcirc$ ) Bis-GMA; ( $\bullet$ ) BPA-3M; and ( $\bigtriangledown$ ) BPA-4M.

tigated and compared with a commercial dental composite Z, which is based on Bis-GMA. The photocurable composite samples were prepared by mixing a multimethacrylates, CQ, DMAEMA, and an inorganic filler, and the samples were then irradiated with visible blue light in a mold for 60 s. The cured samples were immersed in a water bath heated at 37°C, and their weight increases were measured from time to time for 1 month. The composite sample of BPA-3M rendered a much lower water uptake, compared with both the photocured sample of Bis-GMA and the commercial composite Z, as shown in Figure 5. The low water sorption of the BPA-3M composite could be attributed to the reduced hydrophilicity and higher conversions in comparison with both the Bis-GMA based composites.

#### **CONCLUSIONS**

Both the prepared multimethacrylates, BPA-3M and BPA-4M have much lower viscosities than Bis-GMA, thus providing an advantage of easier loading of inorganic fillers or reduction of the use of a diluent. BPA-3M showed a higher degree of conversion in photocuring than that of Bis-GMA. The photocured composites of BPA-3M exhibited a much lower water uptake, compared with the photocured samples based on Bis-GMA and the



**Figure 5** Water sorption of photocured dental composite samples from Bis-GMA and BPA-3M, and a commercial composite sample Z by immersion in 37°C water.

commercial dental composite. The trimethacrylate prepolymer, BPA-3M, having one hydroxyl group is very promising for dental applications with low water sorption, as well as low viscosity along with high photoreactivity.

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