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## PREPARATION AND EVALUATION OF VISIBLE LIGHT-CURED MULTI-METHACRYLATES FOR DENTAL COMPOSITES

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**Key Words:** Dental Composites; Visible Light-curing; Multi-methacrylates; Water Sorption

### ABSTRACT

To explore new VLC oligomers exhibiting low shrinkage, low water sorption, and improved mechanical properties, a family of multi-methacrylates, based on poly(isopropylidenediphenol) resin (BPA), was synthesized, characterized, and evaluated. The BPA resin, having an average of eight phenolic hydroxyl groups per molecule, was treated with ethylene carbonate and the resultant product esterified at four different grafted levels, using methacryloyl chloride. Structures of these EEBPA oligomers, were confirmed by FT-IR and  $^{13}\text{C}$  NMR. The EEBPA oligomer/TEGDMA (50/50, w/w) blends were combined with 0.5 wt% camphoroquinone (CQ) and 1.0 wt% N,N-dimethylaminoethyl methacrylate (DMAEM). The control was BisGMA/TEGDMA (50/50, w/w) blends having the same levels of CQ/DMAEM. Differential photocalorimetry (DPC) and differential scanning calorimetry (DSC) showed the multi-methacrylate/TEGDMA (neat resin) blends have polymerization characteristics comparable to the BisGMA/TEGDMA control. These multi-functional oligomers have lower polymerization shrinkage and lower uptake of water and other liquids. In addition, two experimental oligomers EEBPA #2

and #3 have higher compressive strength than the BisGMA and comparable diametral tensile strength to the BisGMA control. These results suggest that the new type of multi-functional methacrylate oligomers (EEBPA) have potential application in formulating dental composites with improved properties.

## INTRODUCTION

Dental composite formulations, which mainly contain an organic matrix combined with inorganic fillers, have been widely used as restorative and prosthetic dental materials since the 1960's [1, 2]. Many commercial BisGMA (2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl] propane) based composites exhibit satisfactory clinical performance, especially for anterior restorations. However, there are some deficiencies associated with using the BisGMA resin matrix. In the past, many efforts have been made to develop new resin systems. One approach focuses on preparing BisGMA type analogues, containing fluorine or other fluorinated multi-functional methacrylates [3, 4]. In other studies, aromatic multi-methacrylates or dimethacrylates without hydroxy group, which would be structurally more rigid and more hydrophobic, were explored for providing resin materials with improved creep resistance, reduced water sorption, and increased glass transition temperature in the wet environment [5-13]. Another approach is to incorporate nonshrinking monomers and oligomers into the formulations with conventional dimethacrylate dental monomers in order to minimize the extent of polymerization shrinkage. Several polyfunctional monomers and oligomers that expand during cyclopolymerization or ring-opening polymerization reaction have also been prepared and evaluated [14-16]. The resulting expansion can be applied to counter the polymerization shrinkage of the conventional methacrylate monomers and thereby provide formulations with drastically reduced degrees of shrinkage. However, the potential of these kinds of monomers as candidate resins for formulating photopolymerizable composites has not been utilized.

The objectives of this study were to develop a new family of multi-methacrylates, which have higher molecular weights and hydrophobicity than the BisGMA based systems, and to evaluate their potential for formulating improved dental composites. The visible light-curing (VLC) polymerization characteristics for the new resins were tested by DPC, DSC, and FT-IR. The polymerization shrinkage, water sorption, and mechanical properties were examined and compared with the BisGMA control.

## Materials and Methods

### *Syntheses of EEBPA #1-#4 Oligomers*

The starting material, poly(isopropylidenediphenol) resin (trade name Enzo\*BPA1300) was provided by Enzymol International, Inc. (Columbus, OH). Enzymol claims Enzo\*BPA1300 has a number average molecular weight (Mn) of 1300. Ethylene carbonate, from Aldrich Chemical Co. (Milwaukee, WI), was used as received. Methacryloyl chloride (Aldrich Chemical) was distilled (bp=95-96°C) before use.

The syntheses of EEBPA oligomers involved two steps: ethoxylation of BPA and esterification of ethoxylated BPA. The BPA resin was ethoxylated by using ethylene carbonate with  $N(n\text{-Bu})_3$  as a catalyst at temperatures from 160 to 180°C. After reaction for 4-5 hours, the crude product was purified by precipitation using methanol-water solvent. The hydroxyl groups on the EBPA oligomer were partially esterified by a condensation reaction with methacryloyl chloride. The extent of esterification was adjusted by the addition of controlled amounts of methacryloyl chloride. Four EEBPA oligomers (EEBPA #1-#4) were obtained and purified by using column chromatography (silica gel: 200 mesh; eluent: hexane/ethyl acetate). The EBPA and EEBPA oligomers were identified by FT-IR and  $^{13}\text{C}$  NMR spectroscopy. The degree of esterification was determined by measuring the percentage of unreacted hydroxyl groups on the EEBPA oligomers, according to the quantitative analyses of organic compounds [17].

### *IR and NMR Characteristics*

The IR spectra were obtained by using a MIDAC FT-IR Spectrophotometer (MIDAC Corp., Costa Mesa, CA). The  $^{13}\text{C}$  NMR method employed deuterated chloroform ( $\text{CDCl}_3$ ) as a solvent and tetramethylsilane (TMS) as a reference.

### *Measurement of Viscosity*

The Carri-Med CSL<sup>2</sup> Controlled Stress Rheometer was used to determine the viscosity of each sample. A 2-cm, 0.5° cone with 15-micron truncation was the measuring system. All samples were run in duplicate; additional runs were made if the viscosities from the first two runs were different by more than 2%. All viscosities were determined at 25°C. The analysis program of the rheometer was then used to determine the viscosity of each sample using the best model fit to the data.

### *Photopolymerization*

The VLC characteristics of the experimental oligomer blends were evaluated by differential photocalorimetry (DPC). The VLC oligomer systems

were formulated as follows: Oligomer (50 g), triethylene glycol dimethacrylate (TEGDMA) (50 g), camphoroquinone (CQ, 0.5 g), and N,N-dimethylaminoethyl methacrylate (DMAEMA, 1.0 g). The control was BisGMA/TEGDMA (50/50, w/w) blends having the same levels of CQ/DMAEM. The mixtures (about 5 mg) were weighed into a small aluminum pan and exposed to visible light (argon lamp) for 1 and 3 minutes under nitrogen gas at 25°C, using a TA Instruments 930 DPC unit (TA Company, Wilmington, DE). The heat of reaction ( $\Delta H$ ) was calculated by employing the TA data analysis DPC 4.1A program.

In order to examine the postcuring polymerization behavior and remaining double bonds of the VLC resins available for further thermal polymerization, the samples, which had been previously light-cured for three minutes, were further examined by DSC.

#### *Preparation of VLC Resin Specimens*

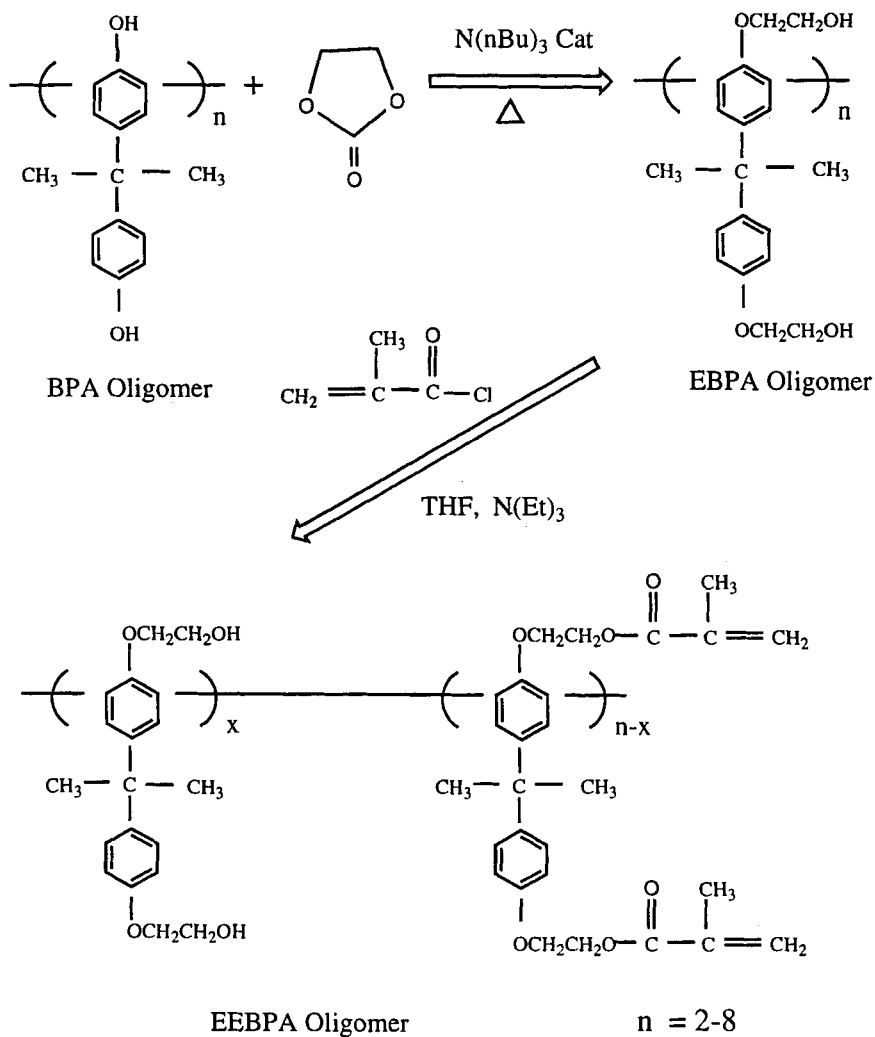
The neat resin samples for mechanical properties and water sorption were prepared as follows. The cylindrical resin specimens (3.3 x 6.6 mm) were made by putting the VLC oligomer blends into transparent glass molds, followed by photocuring with an Elipar Light source (ESPE, Seefeld, Germany) for a total of 5 minutes. After removal from the glass mold, the sample surface was polished by using silicon carbide paper (FEPA P# 400). All specimens were conditioned in distilled water at 37°C for one week prior to property tests.

#### *Compressive and Diametral Compression Tests*

The compressive (CS) and diametral compression tests were carried out using a screw-driven mechanical testing machine (Model 4204, Instron Corp., Canton, MA), with a constant crosshead speed of 0.5 mm/min. For each resin, five samples were tested.

#### *Water Sorption*

For each resin, five VLC cylindrical specimens were conditioned to a constant weight in a desiccator and then immersed in distilled water at 37°C. At different time intervals, the specimens were removed from the water, lightly blotted with a paper tissue, and weighed. After immersion in water for six months, the specimens were removed and reconditioned to a constant weight in a desiccator. The water sorption for each specimen was determined from the difference in weight between the specimen immersed for the predetermined time intervals and the reconditioned specimen.

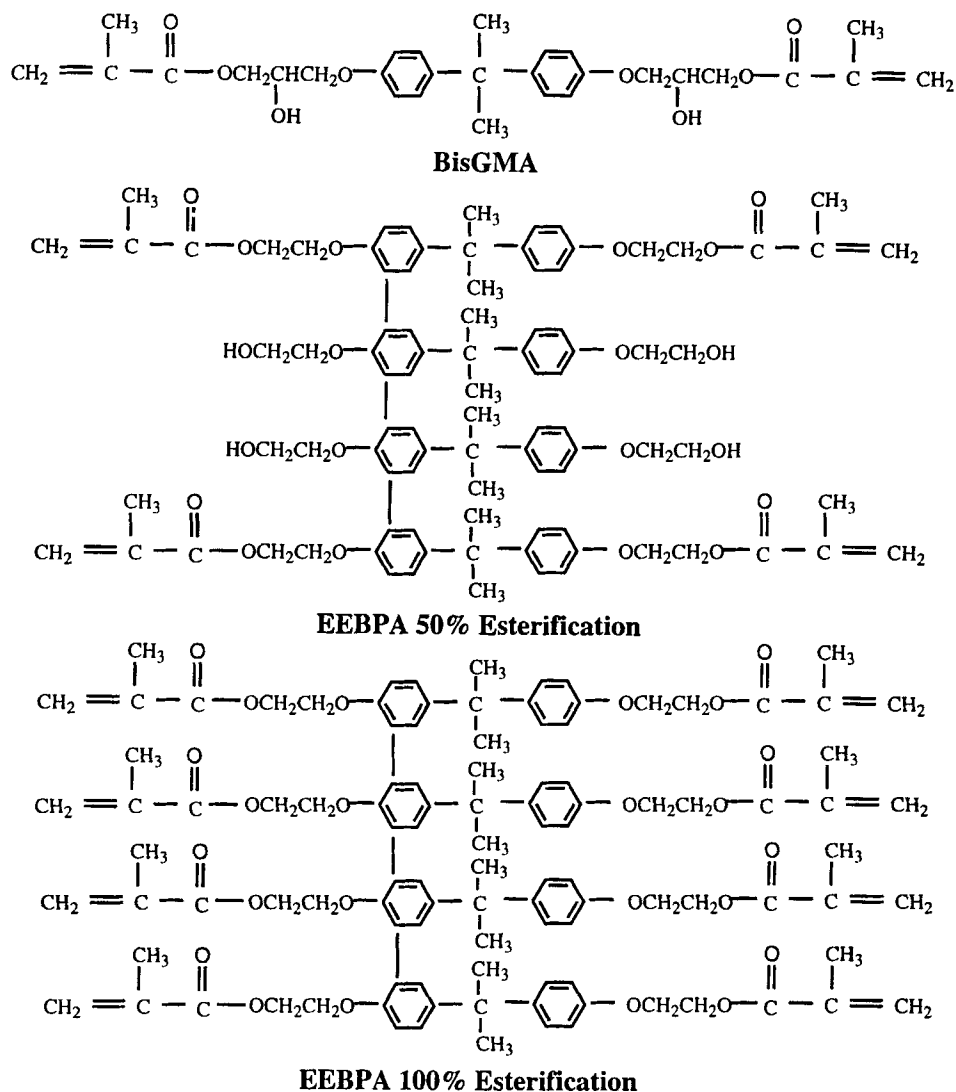


**Figure 1.** Synthesis Route for Ethoxylated BPA Polyols and Multi-methacrylate Oligomers

*Determination of Polymerization Shrinkage*

The polymerization shrinkage was obtained by measuring the density differences between uncured and cured resin test specimens. The volumetric shrinkage was calculated using the following relationship:

$$\text{Shrinkage (\%)} = \left( \frac{d_{\text{uncured}}}{d_{\text{cured}}} - 1 \right) \times 100\%$$



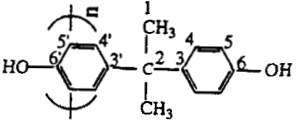
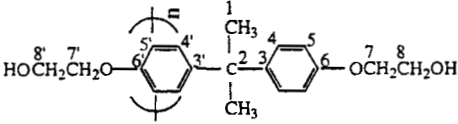
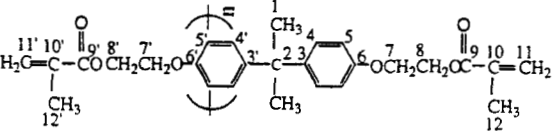
**Figure 2.** Structures of BisGMA, EEBPA 50% Esterification, and EEBPA 100% Esterification Oligomers

Monomer density was measured by weighing the liquid injected from a calibrated syringe. The VLC-cured resins were made in a cylindrical shape and polished and their density obtained by the calculation of weight divided by volume.

#### *Statistical Analyses*

All the statistical analyses were performed by using analysis of variance

TABLE 1.  $^{13}\text{C}$  NMR Chemical Shifts of BPA, EBPA Polyol, and EEBPA Multi-methacrylate.

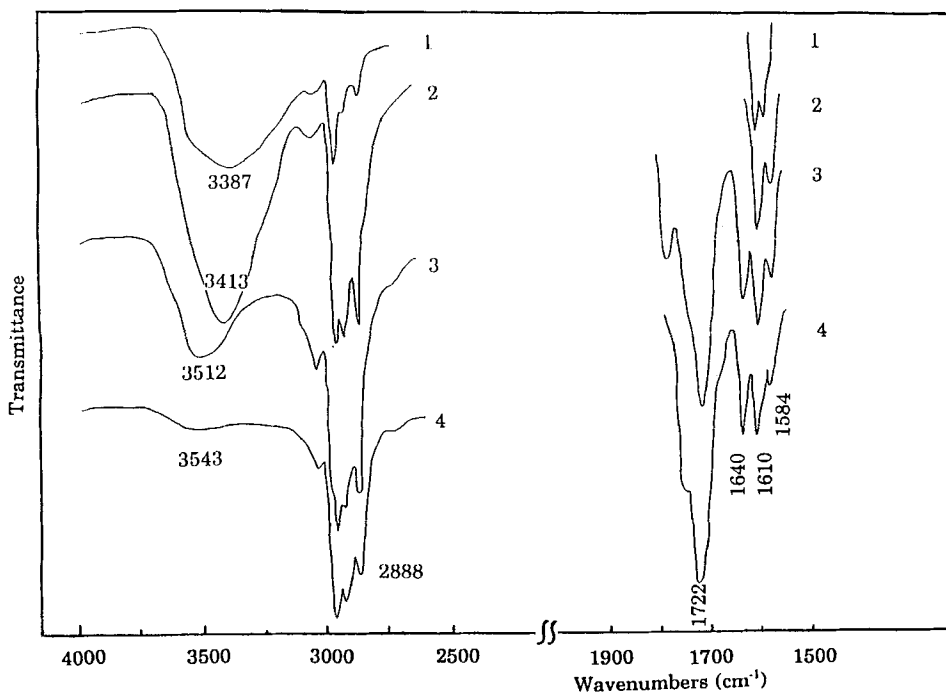
Compound / Structure	$^{13}\text{C}$ NMR Chemical Shift (ppm)
BPA 	$\text{C}_1$ (31.2); $\text{C}_3$ (146.6); $\text{C}_4$ (127.1); $\text{C}_2$ (41.9); $\text{C}_3$ (142.2); $\text{C}_4$ (120.9); $\text{C}_5$ (115.2); $\text{C}_6$ (155.7); $\text{C}_5$ (125.8); $\text{C}_6$ (154.3)
EBPA 	$\text{C}_1$ (31.1); $\text{C}_3$ (143.2); $\text{C}_4$ (127.7); $\text{C}_2$ (41.7); $\text{C}_3$ (139.2); $\text{C}_4$ (126.2); $\text{C}_5$ (113.9); $\text{C}_6$ (156.4); $\text{C}_7$ (69.2); $\text{C}_5$ (128.1); $\text{C}_6$ (141.2); $\text{C}_7$ (70.2); $\text{C}_8, \text{C}_8'$ (61.5)
EEBPA #4 	$\text{C}_1$ (31.1); $\text{C}_3$ (143.2); $\text{C}_4$ (126.1); $\text{C}_2$ (41.7); $\text{C}_3$ (136.2); $\text{C}_4$ (115.5); $\text{C}_5$ (113.9); $\text{C}_6$ (156.6); $\text{C}_7$ (65.8); $\text{C}_5$ (127.7); $\text{C}_6$ (156.3); $\text{C}_7$ (67.8); $\text{C}_8$ (63.7); $\text{C}_9$ (172.3); $\text{C}_{10}$ (143.2); $\text{C}_8$ (62.9); $\text{C}_9$ (167.3); $\text{C}_{10}$ (135.9); $\text{C}_{11}$ (115.5); $\text{C}_{12}$ (24.3); $\text{C}_{11'}$ (125.7); $\text{C}_{12'}$ (18.2)

(ANOVA) with the subsequent Tukey multiple comparisons test at a level of  $\alpha = 0.05$  [18].

## RESULTS AND DISCUSSION

The synthesis scheme for the EEBPA oligomers is shown in Figure 1. The structures of BisGMA and EEBPA with 50% and 100% esterification ( $n=4$ ) are illustrated in Figure 2. The  $^{13}\text{C}$  NMR chemical shifts of BPA, EBPA and EEBPA #4 are shown in Table 1. The typical absorption bands of the IR spectra over the wavenumber ranges of 3500-2800, and 1800-1500  $\text{cm}^{-1}$  are plotted in Figure 3.





**Figure 3.** Partial IR Spectra of 1: BPA; 2: EBPA; 3: EEBPA #2; 4: EEBPA #4.

For BPA, there is a strong, wide absorption peak for phenolic OH at  $3387\text{ cm}^{-1}$ . After ethoxylation, this peak shifts to  $3413\text{ cm}^{-1}$ , representing an OH absorption, and there also appear strong bands at  $2877$  and  $2990\text{ cm}^{-1}$ , indicating addition of the ethylene ( $-\text{CH}_2\text{CH}_2-$ ) group. With increasing levels of esterification, the OH absorption peak gradually decreased and shifted to higher wavenumbers. As for the absorption around  $1800\text{--}1500\text{ cm}^{-1}$ , BPA and EBPA resins did not have peaks at  $1720$  ( $\text{C}=\text{O}$ ) and  $1640$  ( $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ , since they lacked  $\text{C}=\text{O}$  and  $\text{C}=\text{C}$  functional groups. As the extent of esterification increased, the latter two peaks also become stronger. The FT-IR and NMR data were consistent with the structures shown in Figure 1.

The average molecular weight (MW), degree of esterification, and hydroxyl group content are shown in Table 2. The experimental multi-methacrylates EEBPA have significantly higher molecular weights and more rigid molecular chains than the BisGMA. The viscosity of the EEBPA oligomers decreased with an increase in

TABLE 2. Monomer and Oligomer Characteristics

Oligomers	W % of - OH Group	Number of OH	Number of C=C	P (%)*	MW**
TEGDMA			2		286
BisGMA	6.64	2	2		512
EEBPA #1	5.03	4.5	3.5	44	1512
EEBPA #2	3.68	3.5	4.5	57	1589
EEBPA #3	1.92	2	6.0	76	1670
EEBPA #4	0.7	0.7	7.3	91	1787

\* P: Degree of Esterification;

\*\* The EEBPA MW is a calculated value, based on the starting material having Mn of 1300.

extent of esterification, i.e., the order of viscosity was EBPA (0% esterification) (Solid) > EEBPA #1 (44% esterification, 598 cp) > EEBPA #2 (57% esterification, 259 cp), EEBPA #3 (76% esterification, 267 cp), EEBPA #4 (91% esterification, 268 cp) > BisGMA (198 cp).

The enthalpy values ( $\Delta H$ ) of the DPC results for the dimethacrylate resins, subjected to visible light-curing for a total of 1 and 3 minutes, are shown in Table 3. The  $\Delta H$  for the BisGMA control was significantly higher than that of each experimental oligomer system. The  $\Delta H$  values of the experimental oligomers, with different levels of esterification, are not significantly different after light-curing for 1 minute. However, after light-curing for 3 minutes, the experimental EEBPA oligomers with higher levels of methacryloyl esterification have somewhat higher  $\Delta H$  values.

TABLE 3. Heat of Reaction ( $\Delta H$ ) of Oligomer/TEGDMA Mixtures Light-cured 1 and 3 minutes\*

Oligomer/TEGDMA Mixtures**	Light-cured 1 min.		Light-cured 3 min.	
	$\Delta H$ (J/g) (SD)	Degree of Cure (%)	$\Delta H$ (J/g) (SD)	Degree of cure (%)
BisGMA	150.8 (4.8) A	50.3 (1.6) A	251.0 (14.4) A	83.8 (4.8) A
EEBPA #1	44.1 (8.5) B	19.1 (3.6) B	165.6 (10.5) B	67.0 (7.7) B
EEBPA #2	53.6 (11.8) B	20.3 (4.4) B	153.9 (23.3) B	58.3 (8.8) B
EEBPA #3	55.2 (9.9) B	18.9 (3.4) B	189.3 (12.7) BC	64.9 (4.4) B
EEBPA #4	57.8 (9.7) B	18.4 (3.1) B	202.8 (19.3) C	64.6 (6.2) B

\*The  $\Delta H$  values, as determined by DPC, using TA Instruments 930 DPC fitted with an argon lamp for VLC, employed a sample size range of 5-6 mg.

Each entry is the mean value (standard deviation) for a group of three specimens (N = 3). Means with the same letter for  $\Delta H$  and Degree of cure are not significantly different at the  $\alpha = 0.05$  level (P > 0.05).

\*\*Oligomer/TEGDMA 50/50 (w/w) with 0.5 wt.% initiator (CQ) and 1.0 wt.% coinitiator (DMAEM).

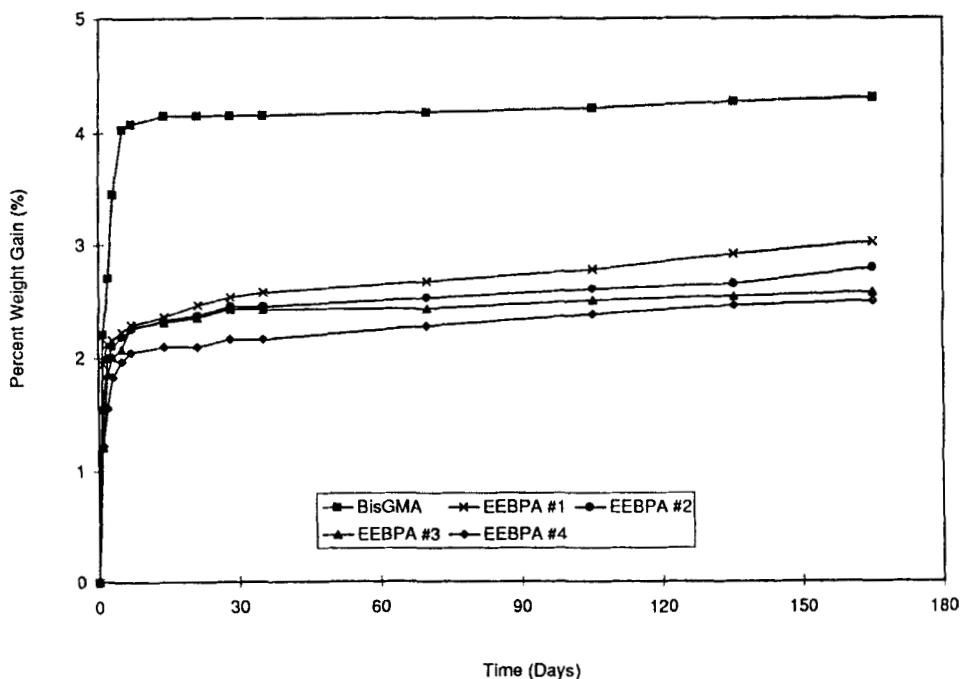
TABLE 4. Polymerization Characteristics of BisGMA and Oligomer/TEGDMA Blends\*

Oligomer/TEGDMA	Degree of postcure (%) (DSC) (SD)	Percentage of RDB(%) (FT-IR) (SD)	Shrinkage (%) (SD)
Mixtures**			
BisGMA	8.5 (2.0) A	17.8 ((2.3) A	-10.3 (0.4) A
EEBPA #1	13.6 (1.2) B	24.8 (4.2) B	-9.7 (0.5) AB
EEBPA #2	15.5 (2.0) B	22.9 (1.8) AB	-9.5 (0.7) B
EEBPA #3	15.0 (0.6) B	20.8 (3.8) AB	-9.1 (0.5) B
EEBPA #4	14.0 (1.2) B	20.2 (4.8) AB	-9.2 (0.3) B

\* Each entry is the mean value (standard deviation) for degree of postcure (N = 3); percentage of RDB (N = 5); polymerization shrinkage (N = 6). Means with the same letter for each characteristic are not significantly different at the  $\alpha = 0.05$  level (P > 0.05).

\*\*Oligomer/TEGDMA 50/50 (w/w) with 0.5 wt.% initiator (CQ) and 1.0 wt.% coinitiator (DMAEM).

The photo-polymerization properties can be further characterized by DSC and FT-IR to test the postcuring behavior and the amount of remaining double bond after photo-curing. The samples, which had been previously light-cured for three minutes, were further examined by DSC. The results are given in Table 4. The percentage of remaining double bonds (RDB %) available for further heat polymerization in the VLC BisGMA is significantly lower than that in each experimental oligomer statistically.



**Figure 4.** Water Sorption of the VLC Experimental and BisGMA Neat Resins at 37°C, using distilled Water.

The RDB % of dental composite resins can also be quantitatively estimated by using FT-IR [19]. In this method, the transmission IR spectra of starting monomer mixture and cured resin were recorded. The areas of the aliphatic C=C absorption at 1640 and aromatic C=C absorption at 1610  $\text{cm}^{-1}$  were determined for both monomer ( $A_{m1640}$ ,  $A_{m1610}$ ) and resulting resin ( $A_{r1640}$ ,  $A_{r1610}$ ). The ratio between  $A_{r1640}/A_{r1610}$  and  $A_{m1640}/A_{m1610}$  was then taken as the fraction of unreacted double bonds in the resin. The data of remaining double bonds of experimental oligomers and BisGMA are also listed in Table 4. Except that of EEBPA #1, the remaining double bonds of the experimental oligomers are not statistically significant from that of the BisGMA system.

Table 4 also gives the results of the polymerization shrinkage for the experimental oligomer and BisGMA neat resins. The experimental oligomer neat resins EEBPA #2-4 have significantly lower polymerization shrinkage statistically.

As explained earlier, EEBPA oligomers have higher viscosity at room temperature and more rigid molecular chains than the BisGMA control. It is not

TABLE 5. The Percent Weight Increase of VLC Neat Resins after 30-day Immersion

Oligomer/TEGDMA Mixtures**	Weight Gain (%) (SD)		
	Water	Acetone	75% Ethanol
BisGMA	4.1 (0.1) A	13.6 (0.2) A	11.1 (0.2) A
EEBPA #2	2.4 (0.3) B	11.6 (0.1) B	7.4 (0.7) B
EEBPA #3	2.3 (0.4) B	10.9 (0.3) C	6.1 (0.6) C

\*Each entry is the mean value (standard deviation) for a group of five specimens ( $N = 5$ ); Means with the same letter for weight gain are not significantly different at the  $\alpha = 0.05$  level ( $P > 0.05$ ).

\*\*Oligomer/TEGDMA 50/50 (w/w) with 0.5 wt.% initiator (CQ) and 1.0 wt.% coinitiator (DMAEM).

surprising that these experimental oligomer blends have relatively lower photopolymerization activities and a higher level of remaining double bonds after photocuring, compared to the BisGMA control. However, since they contain multifunctional (carbon-carbon double bonds) groups in a single molecule, the photocured neat resins, with even somewhat lower double bond conversion, can still function well.

Figure 4 shows the water sorption values of VLC experimental oligomers and BisGMA control systems. For a period of six-month immersion in 37°C water, the water sorption for the BisGMA control was significantly higher than each of the experimental resins. Although the water sorption decreases for the higher esterification degree of EEBPA oligomers, the differences are not statistically significant. The percent weight increases for the neat resins after 30 day-immersion in acetone, ethanol, and water are shown in Table 5. As expected, the

TABLE 6. Compressive Strength and Diametral Tensile Strength of the Wet VLC Experimental and BisGMA Neat Resin\*

Oligomer/TEGDMA Resin**	Compressive strength (S.D.) (MPa)	Diametral Tensile Strength (S.D.) (MPa)
BisGMA	375.6 (34.3) A	32.8 (5.8) A
EEBPA #1	452.3 (20.9) B	23.3 (0.9) B
EEBPA #2	477.6 (41.5) B	26.4 (2.9) A
EEBPA #3	473.2 (36.6) B	25.3 (3.6) A
EEBPA #4	362.9 (23.6) A	22.0 (2.2) B

\* Resin specimens ( $3.3 \times 6.6$  mm) were conditioned in distilled water at 37 °C for one week prior to test.

Each entry is the mean value (standard deviation) for a group of five specimens ( $N = 5$ ); Means with the same letter for a specific mechanical property are not significantly different at the  $\alpha = 0.05$  level ( $P > 0.05$ ).

\*\* Oligomer/TEGDMA 50/50 (w/w) with 0.5 wt.% initiator (CQ) and 1.0 wt.% coinitiator (DMAEM).

VLC neat resins tend to absorb more solvents, such as acetone and ethanol, than water. Again, the percent weight increase of BisGMA control is significantly higher than that of either EEBPA #2 or EEBPA #3 in the above three liquids. The liquid uptake in the neat resins is a diffusion-controlled process determined by the chemical composition and structure of each resin, the affinity of the polymer matrix

with the exposed liquid, the extent of cure, and the sample size and shape. Here, for each resin, the composition, the sample size and shape, and the extent of cure were almost kept the same. Since the neat resins had the largest weight increases in acetone, as shown in Table 5, it seems that acetone has the best affinity with BisGMA and its analogous resins, followed by ethanol and water [20].

Aliphatic hydroxyl groups are usually considered to increase the water sorption of the cured resin due to enhanced hydrophilicity. This partially accounts for the high water sorption of the BisGMA based neat resin. In fact, our experimental oligomers EEBPA also contain hydroxyl groups, but the weight percent ratios of hydroxyl group in the molecules are significantly lower than the BisGMA control. In addition, the experimental resins contain more double bonds in a single molecule (Table 2). Thus, these multi-methacrylate oligomers form highly dense, crosslinked structures when cured, along with formation of rigid molecular chains. Presumably, the hydroxyl group may be restrained in such a network. All these factors contribute to the lower water sorption for the experimental resins.

Compressive strength (CS) and diametral tensile strength (DTS) are important properties for restorative dental materials. The CS is considered relevant because the restorative materials must withstand biting forces under *in vivo* conditions. Because the resins fail by crack propagation, the material is generally much weaker in tension than in compression, which may contribute to failure of the material in service. Therefore, some measurement of tensile strength is considered necessary. For relatively brittle dental resins, the DTS is generally measured, rather than using the uniaxial tension test, because it is difficult to prepare samples and to obtain uniform results. However, if the specimen deforms before failure or fractures into more than two equal pieces, the data may not be valid. In this study, the neat resins failed with somewhat permanent deformation under the diametral compressive test. Hence, the DTS data were only used for relative comparison. The measured values of CS and DTS for the water saturated or wet VLC experimental and BisGMA neat resins are shown in Table 6. Experimental neat resins with esterification degrees of 76%, 57%, and 44% have higher compressive strength than experimental neat resin EEBPA #4 and the BisGMA control. The diametral tensile strength of BisGMA is significantly higher than those of EEBPA #1 and #4, but not significantly different from those of EEBPA #2 and #3. These results show that at least two experimental neat resins EEBPA #2 and #3 have comparable mechanical properties to the BisGMA control.



## CONCLUSIONS

A family of multi-methacrylates, based on enzyme oligomerized Bis-phenol A resins, was synthesized, characterized, and evaluated. These multi-methacrylates are miscible with TEGDMA, a common diluent used in dental composites, and able to form photopolymerizable and thermal-polymerizable monomer mixtures. Results show that these multi-functional oligomers possess comparable visible light-curing characteristics to the BisGMA control, along with having better compressive strength, lower polymerization shrinkage and lower uptake of water and other liquids. This new type of multi-functional methacrylate oligomers has potential application in formulating dental composites with improved properties, as well as composites for a variety of industrial applications. However, until now, only the properties of unfilled EEBPA multi-methacrylate oligomer/TEGDMA blends have been evaluated. Further work is needed to mix these oligomer blends with appropriate inorganic fillers to formulate dental composites and compare their properties with commercial dental restoratives.

## ACKNOWLEDGEMENT

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