

# Synthesis and characterization of a new dimethacrylate monomer based on 5,5'-bis(4-hydroxyphenyl)-hexahydro-4,7-methanoindan for root canal sealer application

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**Abstract** In this study, a new dimethacrylate monomer 5,5'-bis[4-(2'-hydroxy-3'-methacryloyloxy-propoxy)-phenyl]-hexahydro-4,7-methanoindan (5,5'-BHMPHM) with molecular weight of 640 and large molecular volume was designed and synthesized. The structure of monomer 5,5'-BHMPHM was confirmed by FT-IR, <sup>1</sup>H-NMR and elemental analysis. Degree of double bond conversion, volume shrinkage, contact angle, water sorption and solubility, diffusion coefficient value, flexure strength and modulus of 5,5'-BHMPHM/tri(ethylene glycol) dimethacrylate (TEGDMA) based resin were measured. 2,2-bis[4-(2'-hydroxy-3'-methacryloyloxy-propoxy)-phenyl]-propane (Bis-GMA)/TEGDMA based resin was used as reference. The result illustrated that the double bond conversion, polymerization shrinkage, and diffusion coefficient value of 5,5'-BHMPHM/TEGDMA based resin were significantly lower than that of Bis-GMA/TEGDMA based resin ( $P < 0.05$ ). Water sorption, solubility, flexure strength and modulus of 5,5'-BHMPHM/TEGDMA based resin were higher than that of Bis-GMA/TEGDMA based resin ( $P < 0.05$ ). There was no statistical difference between 5,5'-BHMPHM/TEGDMA based resin and Bis-GMA/TEGDMA based resin in contact angle ( $P > 0.05$ ).

## 1 Introduction

Root canal treatment is the most effective way of endodontic therapy [1], and root canal filling is the key step

for it. The core material and root canal sealer are the main root canal filling materials. They are used together to seal the root canal system tightly, so the ingrowth of bacteria from the oral cavity can be forbidden. Compared with the core material, root canal sealer is more important in filling irregularities that exist in the walls of the prepared canal system and entombing the remaining bacteria [2]. There are many kinds of root canal sealers used clinically, such as zinc oxide-eugenol, calcium hydroxide, glass ionomer, and resin-based root canal sealers [3]. Various characteristics of resin-based sealers, such as easy handling, superior aesthetic qualities, good mechanical properties and excellent adhesive ability with dentin, have attracted wide attention. Recently, epoxy resin-based sealers (e.g., AH26 and AHplus) and methacrylate resin-based sealers (e.g., Endoresin and Epiphany) are two main kinds of resin-based sealers. Although the epoxy resin-based sealers can filter into dentin tubules and enhance seal efficiency through adjusting epoxy value and molecular weight, there are two drawbacks that limit its application: one is the marginal gaps caused by polymerization shrinkage between sealer and root canal wall, which can influence the effectiveness of endodontic treatment [4, 5]; the other is hexamethylenetetramine used as a curing agent of epoxy, which can cause cytotoxicity [6–8]. Therefore, methacrylate resin-based sealers cured by light irradiation have become a focus of attention in recent investigations because of its excellent cohesiveness and biocompatibility. In general, methacrylate resin-based sealer consists of three parts: matrix resin, diluter, and filler, in which both matrix resin and diluter are methacrylate monomers. There are many methacrylate monomers used in commercial root canal sealers, such as 2,2-bis[4-(2'-hydroxy-3'-methacryloyloxy-propoxy)phenyl]-propane (Bis-GMA), urethane dimethacrylate (UDMA),

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and triethylene glycol dimethacrylate (TEGDMA) [9]. However, the main drawback of the methacrylate resin-based sealers is still volumetric shrinkage during their polymerization, which also forms marginal gaps between tooth and sealer, leading to microleakage and clinical failure.

Polymerization shrinkage is caused mainly by the change in distance from that between the free monomer molecules loosely bonded by weak van der Waals force to the distance between the monomers tightly linked by a covalent bond in a polymer [10]. To reduce the polymerization shrinkage of composite, the synthesis of novel monomers has been researched [11–13].

In this research work, a new monomer was synthesized and characterized with the aim of reducing polymerization shrinkage. It was mixed with TEGDMA to form the resin part of root canal sealer, and the properties of the resin system were studied. Bis-GMA/TEGDMA system was used as reference.

## 2 Materials and method

### 2.1 Materials and instrument

5,5'-bis(4-hydroxyphenyl)-hexahydro-4,7-methanoindan (5,5'-BPHM), Bis-GMA and TEGDMA were purchased from Aldrich Chemical Co., 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. Camphoroquinone (CQ) was purchased from Alfa Aesar Co., USA. 2-(*N,N*-dimethylamino)ethyl-methacrylate (DMAEMA) was purchased from Acros Organic Co., USA.

FT-IR spectra were measured on a Vector33 Model Fourier Transform Infrared Instrument (Bruker Co. Germany). The samples, in the form of KBr pellets, were scanned from 4000 to 400  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  spectra were recorded on an Avance AV 400 MHz 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 on a Vario EL CHNS Elemental Analyzer (Element AR Co. Germany). Exposure of samples was made on a Curing Light 2500 ( $\lambda = 400\text{--}520$  nm,  $I \approx 550$   $\text{mW cm}^{-2}$ , 3 M Co., USA).

### 2.2 Preparation of 5,5'-bis[4-(oxiranymethoxy)-phenyl]-hexahydro-4,7-methanoindan (5,5'-BOMPHM)

A mixture of 5,5'-BPHM (12.80 g, 0.04 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 further stirred for 4 h at  $110 \pm 2^\circ\text{C}$ . To hydrolyze residual epichlorohydrin, an additional aqueous NaOH solution (40 wt%, 16.00 g) was added and the mixture was stirred at  $90^\circ\text{C}$  for 4 h. Dichloromethane was added to the reaction mixture, and the resultant solution was washed with brine and dried over anhydrous sodium sulfate. After filtration to remove the drying agent, the solvent was stripped off and 5,5'-BOMPHM was obtained as a yellow viscose liquid (12.24 g, 70.82%). The results of spectroscopic studies for 5,5'-BOMPHM are as follows: IR (neat):  $\nu(\text{cm}^{-1})$  3054, 2943, 2860, 1607, 1508, 1453, 1246, 914.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  0.97–1.12, 1.41–1.43, 1.49–1.52, 1.61–1.65, 1.79, 2.07–2.11, 2.21–2.28, 2.86[14H, H in Aliphatic Ring], 2.70–2.71, 2.85–2.88[m, 4H, 2Ar–O–CH<sub>2</sub>CHCH<sub>2</sub>], 3.28–3.32[m, 2H, 2Ar–O–CH<sub>2</sub>CHCH<sub>2</sub>], 3.88–3.97, 4.11–4.13[m, 4H, 2Ar–O–CH<sub>2</sub>CHCH<sub>2</sub>], 6.75–6.78, 7.14–7.22[8H, 2Ar–O–CH<sub>2</sub>CHCH<sub>2</sub>]. Elemental analysis: calculated for  $\text{C}_{28}\text{H}_{32}\text{O}_4$ , C 79.43%, H 7.41%, O 13.16%; found, C 75.72%, H 7.32%, O 16.96%.

### 2.3 Preparation of 5,5'-bis[4-(2'-hydroxy-3'-methacryloyloxy-propoxy)-phenyl]-hexahydro-4,7-methanoindan (5,5'-BHMPHM)

A mixture of 5,5'-BOMPHM (8.64 g, 0.02 mol), methacrylic acid (6.88 g, 0.08 mol), *N,N*-dimethylbenzylamine (0.16 g) and hydroquinone (0.10 g) was stirred at  $90^\circ\text{C}$  for 9 h. Dichloromethane (50 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 5,5'-BHMPHM was obtained as a white crystalline (7.79 g, 65.29%). The results of spectroscopic studies for 5,5'-BHMPHM are as follows: IR (neat):  $\nu(\text{cm}^{-1})$  3418, 3035, 2946, 2861, 1716, 1635, 1608, 1509, 1454.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  0.97–1.09, 1.41–1.43, 1.50–1.53, 1.62–1.65, 1.81, 2.11, 2.16–2.29, 2.87[14H, H in Aliphatic Ring], 1.95[s, 6H, 2C=C–CH<sub>3</sub>], 3.78–4.35[m, 12, 2Ar–O–CH<sub>2</sub>CHOHCH<sub>2</sub>–COO], 5.60[s, 2H, 2H–C=C–COO (*trans*)], 6.14[s, 2H, 2H–C=C–COO (*cis*)], 6.75–6.78, 7.16–7.23[8H, 2Ar–O–CH<sub>2</sub>CHCH<sub>2</sub>]. Elemental analysis: calculated for  $\text{C}_{36}\text{H}_{44}\text{O}_8$ ,

C 71.52%, H 7.28%, O 21.20%; found, C 71.70%, H 7.46%, O 20.84%.

### 2.4 Preparation of resin formulations

Photo-cured resin formulations was a mixture of 5,5'-BHMPHM (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 5,5'-BHMPHM (or Bis-GMA)/TEGDMA/CQ/DMAEMA. All of resin formulations were stored in the dark before used.

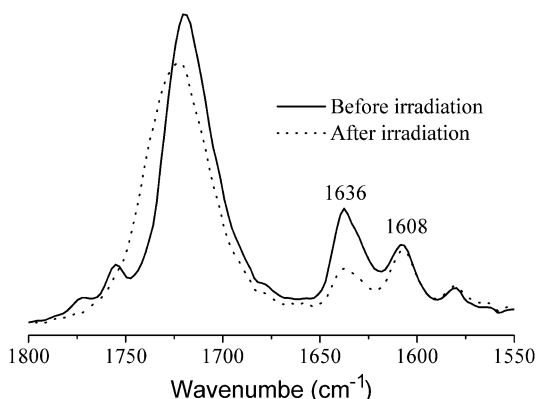
### 2.5 Measurement of double bond conversion

Conversion of double bond was measured by using FT-IR spectrometer. The basic principle is the Lambert–Beer law:

$$A = \varepsilon \times c \times l \tag{1}$$

where  $A$ ,  $\varepsilon$ ,  $c$  and  $l$  are the absorption area of peaks, the molar extinction coefficient, the concentration of sample and the thickness of sample, respectively.

The FT-IR spectra were recorded with 32 scans at a resolution of  $4\text{ cm}^{-1}$ . The sample was coated on KBr Pellets to form a very thin film and the absorbance peaks of uncured sample were obtained. Then photopolymerization of the sample was carried out by irradiation of a dental light source at room temperature and about 5 mm of distance between the light tip and the radiometer face. The FT-IR spectrum of sample at irradiation times of 300 s was collected. In order to quantify the concentration of double bond, the absorption peak at  $1636\text{ cm}^{-1}$  (methacrylate C=C: Bis-GMA or 5,5'-BHMPHM, TEGDMA and DMAEMA) was chosen, and its peak area decreased after being irradiated (as shown in Fig. 1). The absorption peak at  $1608\text{ cm}^{-1}$  (phenyl ring: Bis-GMA or 5,5'-BHMPHM) was



**Fig. 1** The absorption peaks at  $1636\text{ cm}^{-1}$  and  $1608\text{ cm}^{-1}$  varied as radiation time

chosen as an internal reference because its absorption peak area did not change during the polymerization. Thus, the conversion of double bond was then calculated as follows:

$$C(t) = \frac{(A_{C=C}/A_{Ph})_0 - (A_{C=C}/A_{Ph})_t}{(A_{C=C}/A_{Ph})_0} \tag{2}$$

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.

### 2.6 Measurement of polymerization shrinkage

Polymerization shrinkage was determined by density change of resin before and after curing [14, 15]. 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 5 times. The density of resin before curing ( $D_r$ ) was then calculated as:

$$D_r = (M_r/M_w) \times D(T) \tag{3}$$

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 300 s 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:

$$D_s = \frac{M_s \times D(T)}{M_w + M_s - M_{sw}} \tag{4}$$

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

$$S = \frac{D_s - D_r}{D_s} \times 100\%. \tag{5}$$

### 2.7 Measurement of contact angle

The 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.

## 2.8 Measurement of water sorption, solubility and diffusion coefficient

Resins were added into a cylindrical Teflon mold with an internal diameter of  $15 \pm 0.1$  mm and a height of  $1.0 \pm 0.1$  mm, then light-cured for 300 s using a dental light source at each side. Five 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. The time intervals were more during the first day (1 h, 3 h, 6 h, 12 h), preceding daily as the mass variation slowed at more extended intervals. 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.

$$WS = \frac{M_2 - M_3}{M_3} \times 100\% \quad (6)$$

$$SL = \frac{M_1 - M_3}{M_1} \times 100\% \quad (7)$$

The diffusion coefficient of water into cured resins was determined by plotting the  $\Delta M_t/\Delta M_\infty$  ratios as a function of the square root of time (where  $\Delta M_t$  was the mass gained after time  $t$  and  $\Delta M_\infty$  was the final mass gained). Since all

plotted curves were linear when  $\Delta M_t/\Delta M_\infty \leq 0.5$ , the diffusion coefficients of water ( $D$ ) in the resins could be calculated using the Stefan's approximation [15–17]:

$$\frac{\Delta M_t}{\Delta M_\infty} = \frac{4}{L} \left( \frac{D \cdot t}{\pi} \right)^{\frac{1}{2}} \quad (8)$$

where  $L$  is the thickness of the specimen

## 2.9 Measurement of flexural strength and modulus

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 mm  $\times$  4 mm  $\times$  2 mm, and five specimens were prepared for each formulation. A three-point bending test was carried out to evaluate the flexural strength and modulus 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.

## 2.10 Statistical analysis

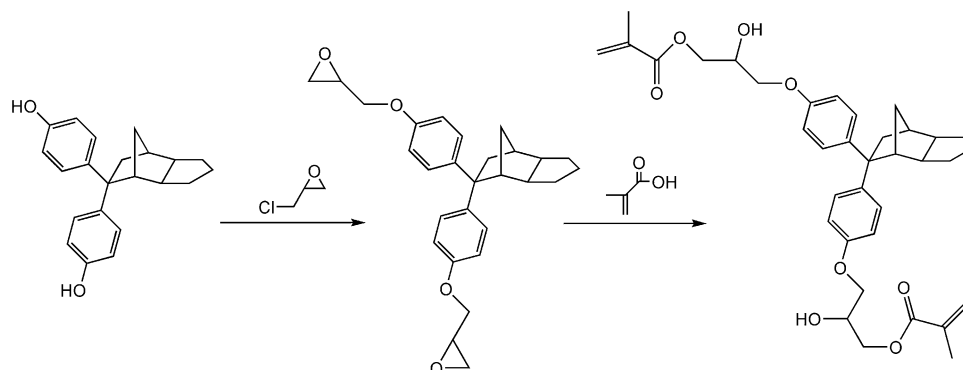
The results were analyzed and compared using one-way ANOVA and the Tukey test at the significance level of 0.05.

## 3 Results and discussion

### 3.1 Synthesis of 5,5'-BHMPHM

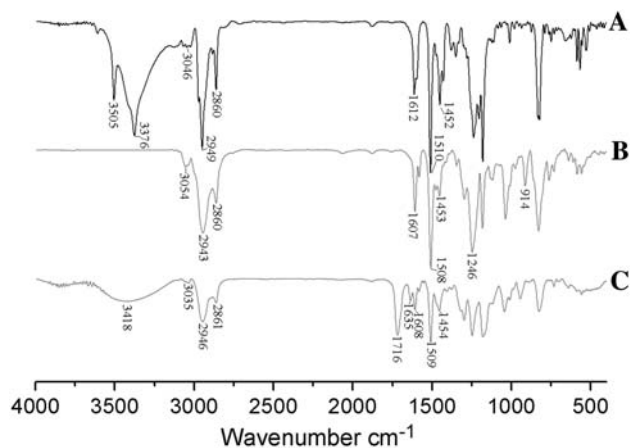
5,5'-BHMPHM was synthesized via a two steps reaction (Fig. 2). 5,5'-BPHM reacted with epichlorohydrin to afford 5,5'-BOPHM, and then 5,5'-BOPHM was converted to 5,5'-BHMPHM by the reaction with methacrylic acid. In the FT-IR spectrum of 5,5'-BOPHM (Fig. 3b), two typical absorption peaks were observed at  $914\text{ cm}^{-1}$  (epoxy group) and  $1246\text{ cm}^{-1}$  (C–O–C), while the absorption peak at  $3376\text{ cm}^{-1}$  (–OH) of 5,5'-BPHM (Fig. 3a) disappeared. This indicated that the hydroxyl group in 5,5'-BPHM had

**Fig. 2** Synthesis of 5,5'-BHMPHM



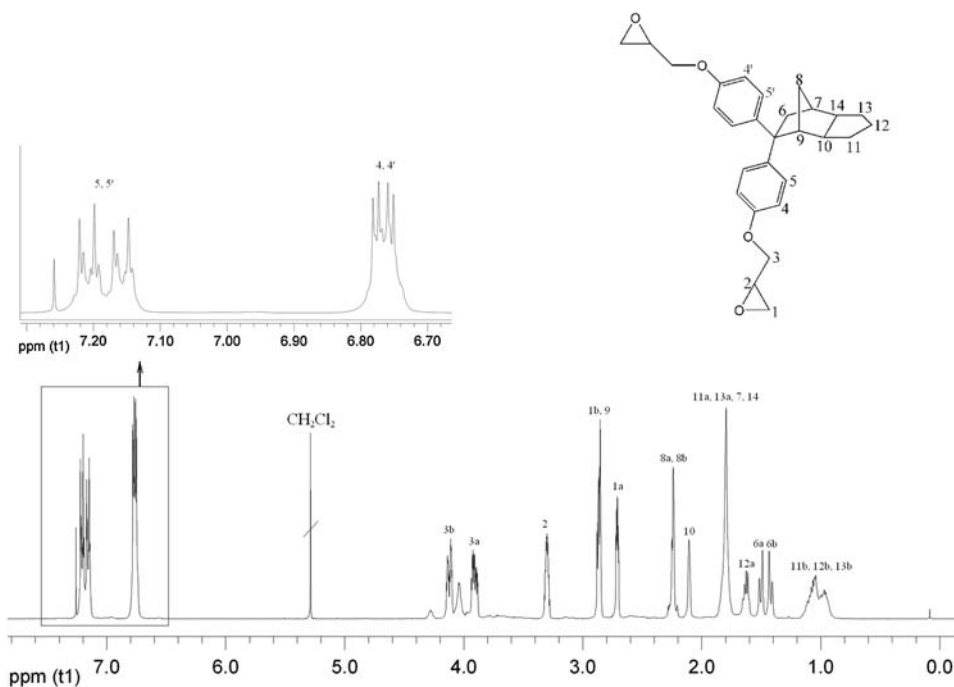
reacted with epichlorohydrin completely. The  $^1\text{H-NMR}$  spectrum (Fig. 4) and elemental analysis of 5,5'-BOMPHM could confirm the structure of 5,5'-BOMPHM.

The target monomer 5,5'-BHMPHM was synthesized via the ring-opening addition reaction between 5,5'-BOMPHM and methacrylic acid. Compared with the FT-IR spectrum of 5,5'-BOMPHM (Fig. 3b) mentioned above, the absorption peak at  $914\text{ cm}^{-1}$  disappeared and three new absorption peaks at  $3418\text{ cm}^{-1}$  ( $-\text{OH}$ ),  $1716\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ), and  $1635\text{ cm}^{-1}$  ( $\text{C}=\text{C}$ ) appeared in the FT-IR spectrum of



**Fig. 3** FTIR spectra of 5,5'-BPHM, 5,5'-BOMPHM and 5,5'-BHMPHM

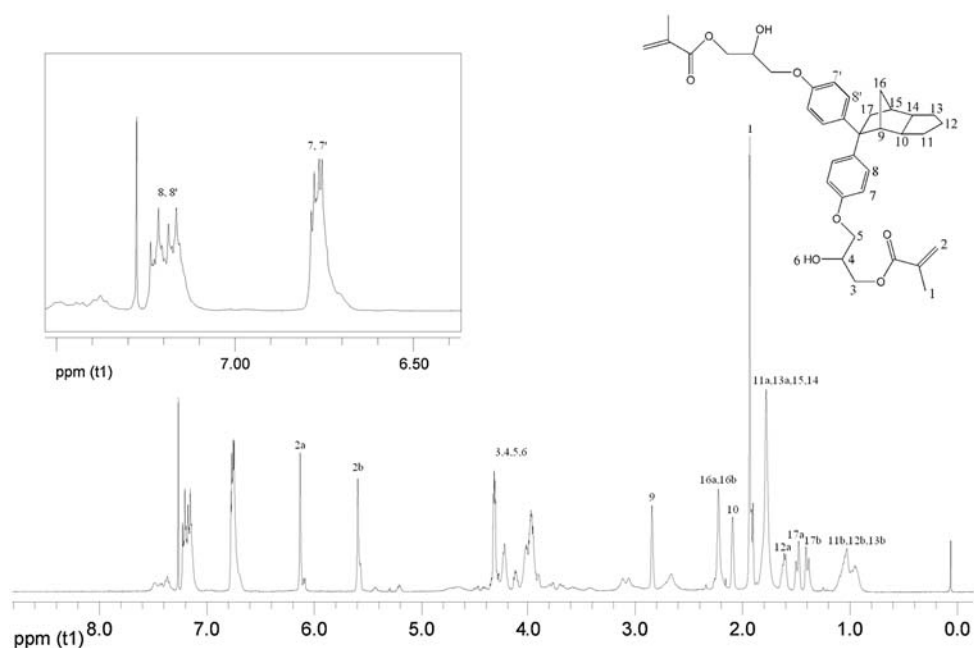
**Fig. 4**  $^1\text{H NMR}$  spectra of 5,5'-BOMPHM



5,5'-BHMPHM (Fig. 3c). Meanwhile, in  $^1\text{H-NMR}$  spectrum of 5,5'-BHMPHM (Fig. 5), distinctive signals assigned to  $\text{C}=\text{C}-\text{CH}_3$  (1.95 ppm),  $\text{Ar}-\text{O}-\text{CH}_2\text{CHOHCH}_2-\text{COO}$  (3.78–4.35 ppm),  $\text{H}-\text{C}=\text{C}-\text{COO}$  (5.60 ppm *trans*),  $\text{H}-\text{C}=\text{C}-\text{COO}$  (6.14 ppm *cis*) were observed, and the signals between 2.70 and 4.13 ppm corresponding to the epoxide CH and  $\text{CH}_2$  groups of 5,5'-BOMPHM disappeared. This suggests that the epoxy groups in 5,5'-BOMPHM reacted completely with methacrylic acid and methacrylate groups were introduced successfully.

### 3.2 Double bond conversion

The double bond conversion of 5,5'-BHMPHM/TEGDMA formulation and Bis-GMA/TEGDMA formulation are summarized in Table 1. As shown in Table 1, double bond conversion of Bis-GMA/TEGDMA formulation ( $83.3 \pm 3.8\%$ ) is higher than that of 5,5'-BHMPHM/TEGDMA formulation ( $77.5 \pm 2.2\%$ ) ( $P < 0.05$ ). The lower double bond conversion of 5,5'-BHMPHM based resin may be attributed to the large pendent aliphatic ring in the structure of the monomer. The bulkiness of 5,5'-BHMPHM may induce an earlier time to vitrification, so more unreacted monomers and macroradicals are trapped in the network early in the process [18], and reduce the double-bond conversion of 5,5'-BHMPHM based resin.

**Fig. 5**  $^1\text{H}$  NMR spectra of 5,5'-BHMPHM**Table 1** Double bond conversion of different systems

Formulation	Double bond conversion (%)
Bis-GMA/TEGDMA	83.1 ± 3.8
New monomer/TEGDMA	77.5 ± 2.2

### 3.3 Polymerization shrinkage

The variation of density and the polymerization shrinkage of each formulation are shown in Table 2. The shrinkage of 5,5'-BHMPHM based resin (4.56%) was significantly lower than that of Bis-GMA based resin (8.73%). It was reported that the extent of polymerization shrinkage depended on the relative mobility, the molecular weight, and functionality of the monomers. Comparing monomers of the same functionality, polymerization shrinkage increases when initial molecular weight decreases [19]. In

**Table 2** Polymerization shrinkage of different systems

Formulation	Density before cured (g/cm <sup>3</sup> )	Density after cured (g/cm <sup>3</sup> )	Shrinkage (%)
Bis-GMA/TEGDMA	1.108 ± 0.008	1.214 ± 0.004	8.73
New monomer/TEGDMA	1.152 ± 0.006	1.207 ± 0.001	4.56

**Table 3** Properties of the studied dental copolymers

Formulation	Contact angle (°)	Water sorption (%)	Water solubility (%)	Diffusion coefficient $D \times 10^8$ (cm <sup>2</sup> s <sup>-1</sup> )	Flexure strength (MPa)	Flexure modulus (GPa)
Bis-GMA/TEGDMA	83.4 ± 4.0	4.80 ± 0.42	1.51 ± 0.05	0.63 ± 0.07	66.88 ± 2.22	0.99 ± 0.13
New monomer/TEGDMA	84.1 ± 4.5	5.19 ± 0.18	1.81 ± 0.10	0.50 ± 0.06	81.40 ± 7.60	1.91 ± 0.12

this research, the higher molecular weight of 5,5'-BHMPHM might be the reason for its lower polymerization shrinkage. As a result, the lower polymerization shrinkage of 5,5'-BHMPHM make it suitable to replace Bis-GMA as base resin in root canal filling materials, because the probability of microleakage and treatment failure occurring in clinic might decrease with decreasing of polymerization shrinkage.

### 3.4 Properties of copolymer

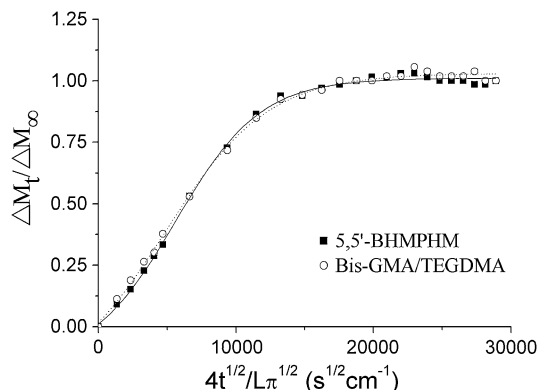
The properties of studied dental copolymers are listed in Table 3. As shown in Table 3, there is no statistical difference in contact angle ( $P > 0.05$ ) between Bis-GMA based copolymer and 5,5'-BHMPHM based copolymer. The water sorption and solubility, flexure strength and modulus of 5,5'-BHMPHM based copolymer are higher than that of

Bis-GMA based copolymer ( $P < 0.05$ ). The diffusion coefficient value of 5,5'-BHMPHM based copolymer is lower than that of Bis-GMA based copolymer ( $P < 0.05$ ).

It was reported that the water sorption of the copolymer was influenced by the hydrophilicity [20] and crosslinking density of copolymer [21]. 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 [22–24]. The same contact angle of these two copolymers implies that they have the same hydrophilicity. However, the crosslinking density of 5,5'-BHMPHM based copolymer is lower than that of Bis-GMA based copolymer because of its lower double bond conversion. So the higher water sorption of 5,5'-BHMPHM based copolymer might be attributed to its lower crosslinking density.

Water solubility of copolymers is concerned with the amount of unreacted monomers in it. The residual monomer molecules that remain unbound in a cured resin would be eluted into aqueous media [25], so the water solubility of a copolymer is higher if there is more unreacted monomers in it. In this research, the double bond conversion of 5,5'-BHMPHM based copolymer is lower than that of Bis-GMA based copolymer, so there might be more unreacted monomers in it. Therefore, 5,5'-BHMPHM based copolymer has higher water solubility than Bis-GMA based copolymer. The higher water solubility of 5,5'-BHMPHM based copolymer might be a disadvantage when comparing it with Bis-GMA based copolymer, because the release of unreacted monomers from resin composite may stimulate the growth of bacteria [26] and promote allergic reactions [27].

Plots of  $\Delta M_t/\Delta M_\infty$  against  $4t^{1/2}/L\pi^{1/2}$  of 5,5'-BHMPHM based copolymer and Bis-GMA based copolymer are shown in Fig. 6. From an observation of Fig. 6, it can be noticed that for all cured resins studied, the initial part of



**Fig. 6** Water sorption behavior of 5,5'-BHMPHM based copolymer and Bis-GMA based copolymer

the curves (i.e., until  $\Delta M_t/\Delta M_\infty \leq 0.5$ ) is always linear. Thus, from the slope of these lines and applying Eq. 8, the diffusion coefficient can be calculated. The value of diffusion coefficient was influenced by the crosslinking density of the polymer and the motion of polymer chain [26]. The diffusion coefficient value decreased with increasing crosslinking density and decreasing motion of polymer chain. In this work, the crosslinking density of 5,5'-BHMPHM based copolymer is lower than that of Bis-GMA based copolymer because of its lower double bond conversion. However, the diffusion coefficient value of it is still higher than that of Bis-GMA based copolymer. This might be attributed to the less motion ability of 5,5'-BHMPHM based copolymer network, for the ring structure of 5,5'-BHMPHM in the polymer network act as a barrier to rotation about carbon bonds [22]. The higher flexure strength and modulus are also attributed to this reason.

#### 4 Conclusions

In this study, a new dimethacrylate monomer based on 5,5'-bis(4-hydroxyphenyl)-hexahydro-4,7-methanoindan was synthesized in two steps successfully. The structures of the intermediate 5,5'-BOMPHM and target monomer 5,5'-BHMPHM were fully characterized by FT-IR,  $^1\text{H}$  NMR and elemental analysis. This study showed that the 5,5'-BHMPHM based resin had lower polymerization shrinkage, higher flexural strength and modulus than Bis-GMA based resin. These properties render 5,5'-BHMPHM with the potential to be used as a component of root canal sealer material. However, the higher water solubility of 5,5'-BHMPHM based resin, which is causing by its lower double conversion, might be a disadvantage of it. So further study to increase the double bond conversion of 5,5'-BHMPHM based resin is necessary.

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#### References

1. Ni XL, Wang SC. Modern endodontic therapy: root canal filling. J Pract Stomatol. 2005;21:712–4.
2. Lin ZM, Ling JQ. Development in root canal filling materials. Int J Stomatol. 2006;33:204–7.
3. Hauman CHJ, Love RM. Biocompatibility of dental materials used in contemporary endodontic therapy: a review. Part 2. Root-canal-filling materials. Int Endod J. 2003;36:147–60.
4. Shipper G, Orstavik D, Teixeira FB, Trope M. An evaluation of microbial leakage in roots filled with a thermoplastic synthetic polymer-based root canal filling material (Resilon). J Endod. 2004;30:342–7.

5. De Moor RJ, Hommez GM. The long-term sealing ability of an epoxy resin root canal sealer used with five gutta percha obturation techniques. *Int Endod J*. 2002;35:275–82.
6. Spangberg L, Barbosa SV, Lavigne GD. AH-26 releases formaldehyde. *J Endod*. 1993;19:596–8.
7. Willershausen B, Marroquín BB, Schäfer D, Schulze R. Cytotoxicity of root canal filling materials to three different human cell lines. *J Endod*. 2000;26:703–7.
8. Gerosa R, Menegazzi G, Borin M, Cavalleri G. Cytotoxicity evaluation of six root canal sealers. *J Endod*. 1995;21:446–8.
9. Moszner N, Salz U. New developments of polymeric dental composites. *Prog Polym Sci*. 2001;26:535–76.
10. Ellakwa A, Cho N, Lee IB. The effect of resin matrix composition on the polymerization shrinkage and rheological properties of experimental dental composites. *Dent Mater*. 2007;23:1229–35.
11. Khatri CA, Stansbury JW, Schultheisz CR, Antonucci JM. Synthesis, characterization and evaluation of urethane derivatives of Bis-GMA. *Dent Mater*. 2003;19:584–8.
12. Ge J, Trujillo M, Stansbury J. Synthesis and photopolymerization of low shrinkage methacrylate monomers containing bulky substituent groups. *Dent Mater*. 2005;21:1163–9.
13. Atai M, Ahmadi M, Babanzadeh S, Watts DC. Synthesis, characterization, shrinkage and curing kinetics of a new low-shrinkage urethane dimethacrylate monomer for dental applications. *Dent Mater*. 2007;23:1030–41.
14. Chung C-M, Kim M-S, Kim J-G, Jang D-O. Synthesis and photopolymerization of trifunctional methacrylates and their application as dental monomers. *J Biomed Mater Res*. 2002;62:622–7.
15. Labella R, Davy KWM, Lambrechts P, Meerbeek BV, Vanherle G. Monomethacrylate co-monomer for dental resin. *Eur J Oral Sci*. 1998;106:816–24.
16. Chung C-M, Kim J-G, Kim M-S, Kim K-M, Kim K-N. Development of a new photocurable composite resin with reduced curing shrinkage. *Dent Mater*. 2002;18:174–8.
17. Matsukawa S, Hayakawa T, Nemoto K. Development of high-toughness resin for dental applications. *Dent Mater*. 1994;10:343–6.
18. He JW, Luo YF, Liu F, Lin ZM, Ling JQ, Jia DM. Photopolymerization and properties of fluorene-based dimethacrylate monomer used as a root canal sealer. *Adv Polym Technol*. 2008;27:108–16.
19. Magali D, Delphine TB, Jacques D, Gaëtane L. Volume contraction in photocured dental resins: the shrinkage-conversion relationship revisited. *Dent Mater*. 2006;22:359–65.
20. Imazato S, Tarumi H, Kato S, Ebi N, Ehara A, Ebisu S. Water sorption, degree of conversion, and hydrophobicity of resins containing Bis-GMA and TEGDMA. *Dent Mater*. 1999;18:124–32.
21. Arima T, Hamada T, McCabe JF. The effects of cross-linking agents on some properties of HEMA-based resins. *J Dent Res*. 1995;74:1597–601.
22. Ronald EK, Lisa AK, Scott S, Benjamin G. Synthesis and evaluation of modified urethane dimethacrylate resins with reduced water sorption and solubility. *Dent Mater*. 2009;25:302–13.
23. Stansbury JW, Antonucci JM. Dimethacrylate monomers with varied fluorine contents and distributions. *Dent Mater*. 1999;15:166–73.
24. Wang G, Culbertson BM, Xie D, Seghi RR. Effect of fluorinated triethylene glycol dimethacrylate on the properties of unfilled, light cured dental resins. *J Macromol Sci Pure Appl Chem*. 1999;36:237–52.
25. Ferracane JL. Elution of leachable components from composites. *J Oral Rehabil*. 1994;21:453–62.
26. Hansel C, Leyhausen G, Mai UEH, Geurtsen W. Effects of various resin composite (co)monomers and extracts on two caries associated micro-organisms in vitro. *Dent Mater*. 1998;77:60–7.
27. Spahl W, Budzikiewicz H, Geursten W. Extractable residual monomers from various resin materials—a qualitative study. *J Dent Res*. 1994;73:295.