

Communication

Synthesis and Characterization of Dimethacrylate Monomer with High Molecular Weight for Root Canal Filling Materials

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Abstract: A new dimethacrylate monomer 9,9'-bis[4-(2'-hydroxy-3'-methacryloyloxypropoxy)phenyl] fluorene (**3**) with a molecular weight of 634 was synthesized in 51.4% yield by addition of a glycidyl ether group to 9,9'-bis(4-hydroxyphenyl) fluorene (**1**) by the reaction of compound **1** with epichlorohydrin, and then introducing the methacrylate moiety by the reaction of the epoxy group with methacrylic acid. The structure of monomer **3** was confirmed by FT-IR, ¹H-NMR, mass spectra and elemental analysis.

Keywords: Dimethacrylates, high molecular weight, synthesis, characterization.

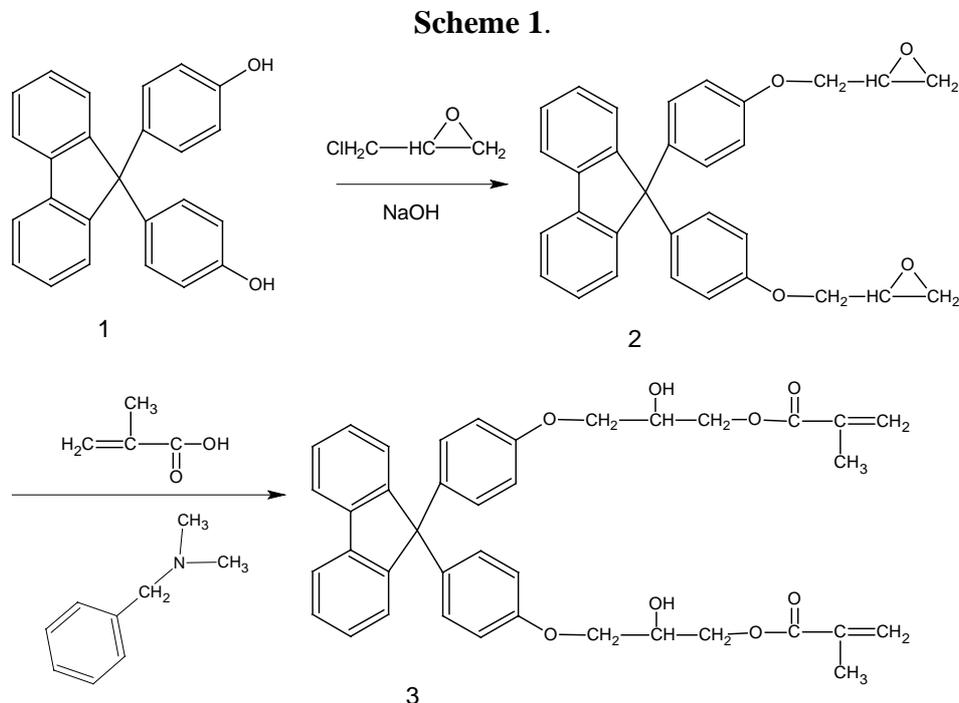
Introduction

Polymethyl methacrylate was firstly used in tooth restoration by German scientists in 1937. After that polymethacrylates were used extensively as dental materials, e.g. as dental restorative materials and primary resins of root canal sealers in root canal treatment, due to their good biocompatibility and adhesive properties [1]. The main drawback of methacrylate monomers is volumetric shrinkage during their polymerization, so marginal gaps between tooth and sealer, lead microleakage and clinical failure when these monomers were applied in root canal sealers are unavoidable. In order to decrease the polymerization shrinkage of methacrylate monomers, Bowen [2] had synthesized Bis-GMA with a

molecular weight of 512 using bisphenol A and glycidyl methacrylate (GMA) as raw materials. This new high molecular volume dimethacrylate monomer is the main organic component of the Epiphany™ root canal sealant, which has recently been applied in the clinic. Unfortunately, microleakage due to polymerization shrinkage of Epiphany™ still happens [3-6]. Based on their investigations of the relationship between polymerization shrinkage and the conversion of double bonds during polymerization of Bis-GMA, Venhoven *et al.* [7] revealed that polymerization shrinkage of monomers is directly influenced by the concentration and conversion of the double bonds. In order to solve this high polymerization shrinkage problem, urethane derivatives of Bis-GMA [8], dimethacrylate monomers having bulky substituent groups [9] and multifunctional methacrylate monomers [10-13] have been developed. These monomers are designed to decrease polymerization shrinkage by increasing the molecular weight and molecular volume. In this paper, the authors wish to report the synthesis and characterization of a dimethacrylate monomer with a high molecular weight (634) and a large molecular volume.

Results and Discussion

Monomer **3** had been previously reported as a component of photocurable resins with good light resistance [14] or protective coatings for optical materials and optical disks [15]. We synthesized this material in two steps by the reactions between 9,9'-bis(4-hydroxyphenyl) fluorene (**1**) and epichlorohydrin and then methacrylic acid. Scheme 1 illustrates this approach.



9,9'-Bis(4-oxiranylmethoxyphenyl) fluorene (**2**) was prepared in 83.0 % yield by the reaction of compound **1** and epichlorohydrin. The structure of this intermediate was fully characterized by spectral and elemental analysis data. In its FT-IR spectrum three typical glycidyl ether group absorption peaks were observed at 910 cm^{-1} ($\begin{matrix} \text{O} \\ | \\ \text{HC}-\text{CH}_2 \end{matrix}$), 2924 cm^{-1} (O-CH₂) and 3002 cm^{-1} (epoxide CH and CH₂) while the absorption peak at 3480 cm^{-1} (-OH) of starting compound **1** disappeared. This indicated that the

hydroxyl groups in compound **1** had reacted completely with epichlorohydrin and glycidyl ether groups had been introduced into compound **1**. The $^1\text{H-NMR}$ spectrum of compound **2** could be unambiguously assigned considering the features of $^1\text{H-NMR}$ spectra and the signal intensities. In the mass spectrum of compound **2**, a peak with $m/z = 462$ also supported the proposed structure.

The target monomer **3** was synthesized in 62.0% yield by the ring-opening addition reaction of methacrylic acid with compound **2**. This reaction was performed using a large excess of methacrylic acid so the excess methacrylic acid may further react with the $-\text{OH}$ group in monomer **3** to form the esterification product. Esterification reactions are usually catalyzed by acids such as H_2SO_4 , HCl , and HCOOH , and this reaction goes on very slowly in the absence of catalysts [16]. We chose to use a base, N,N -dimethylbenzylamine, as catalyst. Monomer **3** was the main product in our reaction and its structure was well characterized.

Compared with FT-IR spectrum of compound **2**, mentioned above, the absorption peak at 910 cm^{-1} disappeared and a new absorption peak at 3413 cm^{-1} ($-\text{OH}$) appeared in the FT-IR spectrum of compound **3**. In $^1\text{H-NMR}$ spectrum of monomer **3**, distinctive signals assigned to $-\text{C}=\text{C}-\underline{\text{H}}$ (6.112 ppm), $-\text{C}=\text{C}-\underline{\text{H}}'$ ($5.556\text{--}5.578\text{ ppm}$), $-\text{O}-\underline{\text{CH}}_2-\underline{\text{CHOH}}-\underline{\text{CH}}_2$ ($3.925\text{--}4.324\text{ ppm}$) and $-\text{C}-\underline{\text{CH}}_3$ ($1.905\text{--}1.928\text{ ppm}$) were observed, while two signals between $3.301\text{--}3.338\text{ ppm}$ and $2.728\text{--}2.895\text{ ppm}$ corresponding to the epoxide CH and CH_2 groups of the starting material **2** disappeared. This suggests that the epoxy groups in compound **2** reacted completely with methacrylic acid and methacrylate groups were this introduced successfully. In mass spectra of monomer **3**, we could observe the $m/z = 634$ peak corresponding to the M^+ ion.

Conclusions

A dimethacrylate monomer 9,9'-bis[4-(2'-hydroxy-3'-methacryloyloxypropoxy)phenyl] fluorene (**3**) with a molecular weight of 634 and a large molecular volume was synthesized in 51.4% total yield in two steps utilizing 9,9'-bis(4-hydroxyphenyl) fluorene (**1**), epichlorohydrin and methacrylic acid as raw materials. The structures of the intermediate 9,9'-bis(4-oxiranylmethoxyphenyl)fluorene (**2**) and target monomer **3** were fully characterized by FT-IR, $^1\text{H-NMR}$, mass spectra and elemental analysis.

Experimental

General

Chemicals (analytical reagent, unless otherwise stated) were used without further purification. 9,9'-Bis(4-hydroxyphenyl) fluorene (**1**, 97%), was purchased from Aldrich Chemical Co. (China); epichlorohydrin and anhydrous magnesium sulfate were obtained from Shanghai No. 1 Chemical Reagent Co. Ltd. (China); methacrylic acid (chemical reagent) was purchased from Guangzhou Chemical Reagent Co. Ltd. (China); N,N -dimethylbenzylamine (chemical reagent) was purchased from Shanghai No. 3 Chemical Reagent Co. Ltd. (China); sodium hydroxide, dichloromethane and anhydrous ethanol were purchased from Tianjin Chemical Reagent Co. Ltd. (China); hydrochloric acid was purchased from Guangzhou Donghong Chemical Co. Ltd. (China). 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 cm^{-1} . $^1\text{H-NMR}$ spectra were recorded on an Avance AV 400MHz Instrument (Bruker Co., Switzerland); chemical shifts are reported in ppm on the δ scale with tetramethylsilane as the internal reference and CDCl_3 as the solvent. Mass spectra were taken on DSQ Low Resolution Mass Spectrometer (Thermo Co. USA). Elemental analysis was done on a Vario EL CHNS Elemental Analyzer (Element AR Co. Germany). Spectral and elemental analysis data are given in Table 1.

Table 1. Spectral and elemental analysis data for **1-3**.

Compound	$^1\text{H-NMR}$ δ ppm	FT-IR (KBr) cm^{-1}	MS m/z (%)	Elemental analysis Formula Calculated % Found %
1	–	3480 (OH)	350 (100), 333 (9.43), 257 (39.17)	–
2	6.775-7.776 (16H, <u>Ar-O</u>) 4.134-4.170 (dd, J = 11 Hz, 3.3 Hz, 2H, $\text{O}-\text{CH}_2-\text{HC}-\text{CH}_2$) 3.897-3.939 (dd, J = 11 Hz, 5.5 Hz, 2H, $\text{O}-\text{CH}_2-\text{HC}-\text{CH}_2$) 3.301-3.338 (m, 2H, $\text{O}-\text{CH}_2-\text{HC}-\text{CH}_2$) 2.728-2.734 (dd, J = 4.8 Hz, 2.5 Hz, 2H, 4H, $\text{O}-\text{CH}_2-\text{HC}-\text{CH}_2$) 2.873-2.895 (t, J = 4.5 Hz, 2H, $\text{O}-\text{CH}_2-\text{HC}-\text{CH}_2$)	3002 ($\text{HC}-\text{CH}_2$ and $\text{HC}-\text{CH}_2$) 2924 (O-CH ₂) 910 ($\text{HC}-\text{CH}_2$)	462 (100), 405 (17.82), 348 (3.59), 257 (16.73)	$\text{C}_{31}\text{H}_{26}\text{O}_4$ C: 80.52 H: 5.63 C: 79.99 H: 5.66
3	6.708-7.744 (16H, <u>Ar-O</u>) 6.112 (2H, -C=C- <u>H</u>) 5.556-5.578 (2H, -C=C- <u>H</u>) 3.925-4.324 (12H, -O-CH ₂ - <u>CHOH-CH₂</u>) 1.905-1.928 (6H, -C- <u>CH₃</u>)	3413 (OH) 2952 (CH ₃) 1717 (C=O) 1635 (C=C)	634 (7.81), 566 (2.76), 548 (14.18), 492 (5.13), 423 (4.08), 349 (8.25), 257 (31.73), 143 (100), 69 (31.84)	$\text{C}_{39}\text{H}_{38}\text{O}_8$ C: 73.82 H: 5.99 C: 74.04 H: 6.01

Preparation of 9,9'-bis(4-oxiranylmethoxyphenyl)fluorene (**2**)

A mixture of compound **1** (8.00 g, 0.023 mol) and epichlorohydrin (20.80 g, 0.223 mol) was stirred until a clear solution was obtained. Aqueous NaOH solution (40 wt %, 5.50 g) was added and the mixture was further stirred for 7h at 110 ± 2 °C. The reaction mixture was filtered, and the filtrate was

dried under vacuum to remove excess epichlorohydrin, affording a viscous product which was dissolved in small amount of dichloromethane and the resulting solution was added to a mixture of ethyl alcohol/water (3:1, v/v), giving a white precipitate. The precipitate was dissolved in dichloromethane, reprecipitated twice from mixture of ethyl alcohol/water (3:1, v/v) and dried to a constant weight under vacuum at 40 °C to give 8.50 g (83.0% yield) of compound **2**.

Preparation of 9,9'-bis[4-(2'-hydroxy-3'-methacryloyloxypropoxy)phenyl] fluorene (3)

A mixture of methacrylic acid (11.50 g, 0.134 mol), N,N-dimethylbenzylamine (0.1035 g, 7.667×10^{-4} mol) and compound **2** (7.00 g, 0.020 mol) was stirred at 90 ± 2 °C for 10 h. Dichloromethane (50 mL) was then added to the reaction mixture. The resulting solution was washed successively with 0.5 M 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. The product was dried under vacuum at 50 °C to a constant weight to give 5.59 g (62.0 % yield) of monomer **3** as a white powder.

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Sample Availability: Available from the authors.

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