

Synthesis and characterization of two novel antibacterial dendritic methacrylate-based dental monomers

Mojtaba Abbasian¹, Mehdi Jaymand^{*,2,3}, Mehrdad Lotfi^{*,2,4} & Soodabeh Kimyai⁵

¹Department of Chemistry, Payame Noor University, P.O. BOX: 19395-3697, Tehran, Iran.

²Research Center for Pharmaceutical Nanotechnology, Tabriz University of Medical Sciences, P.O. BOX: 51656-65811, Tabriz, Iran.

³Immunology Research Center, Tabriz University of Medical Sciences, Tabriz, Iran.

⁴Department of Endodontics, Dental Faculty, Tabriz University of Medical Sciences, P.O. Box: 51666-14711, Tabriz, Iran.

⁵Department of Operative Dentistry, Dental Faculty, Tabriz University of Medical Sciences, P.O. Box: 51666-14711, Tabriz, Iran.

E-mail: m_jaymand@yahoo.com

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This study explores the synthesis and characterization of two novel antibacterial dendritic methacrylate-based dental monomers. For this purpose, two dendritic esters have been synthesized *via* condensation reaction and then reacted with methacryloyl chloride to afford methacrylate-end capped dendritic esters. These compounds are subsequently converted to quaternary ammonium fluoride monomers (QAFMs) with decyl substituted side chain to produce two novel antibacterial dendritic dental monomers. The chemical structures of synthesized samples have been characterized using Fourier transform infrared (FTIR) and proton nuclear magnetic resonance (¹H NMR) spectroscopies. The obtained monomers can be used to replace 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropyl)-phenyl]propane (Bis-GMA) as the base monomer of universal resin-based dental composites in the presence of a diluting monomer (*e.g.*, triethyleneglycoldimethacrylate; TEGDMA), mainly due to their superior characteristics such as multifunctionalities as well as antibacterial activities.

Keywords: Dendritic, Methacrylate, Quaternary ammonium fluoride, Antibacterial activity, Dental monomers

At current time, dental caries and dentin hypersensitivity are known as the main diseases regarding oral health. These diseases generally is caused by special types of microorganisms such as *Streptococcus sobrinus*, *Streptococcus mutans*, and *Lactobacilli* which live in the mouth and produce acid by the fermentation of residual food bits^{1,2}. In early stages, dental caries can be prevented through fluoride varnish or *in situ* remineralization approaches^{3,4}. In contrast, if caries break more than one-half of the depth of enamel, dentists have been removing the decayed area of tooth and fill the cavity with proper materials. Up to date, various types of materials including gold, glass ionomer, dental ceramic, amalgam, and resin-based composites (RBCs) have been used as restorative dental materials^{5,6}. Among these, RBCs have been attracted more attention for restore carious teeth mainly due to their excellent esthetic quality, maximum amount of tooth preserved, and good ability to bond to enamel surface. These type of dental materials generally composed from synthetic photopolymerizable monomer(s) (*e.g.*,

dimethacrylate), high percentage (up to 60 vol%) of inorganic filler(s) (*e.g.*, silica micro or nanoparticles), and a photoinitiator system⁷⁻¹⁰.

Polymerization shrinkage and low degree of conversion (DC) are the most important drawbacks of RBCs. Polymerization shrinkage may bring on marginal gaps between the tooth and the material that resulted to secondary caries^{3,11}. Low DC in these systems may be lead to undesirable side effects including allergic reactions and sensitization in patients due to *in vivo* leaching of residue monomers from the dental composites¹². Other disadvantages of RBCs can be listed as high cost and low mechanical properties in comparison with dental amalgam, water sorption, and oxygen inhibition^{3,13,14}. Given these thematic issues, the design and development of more efficient RBCs is necessary. Some of the mentioned issues can be circumvented through the use of multifunctional or dendritic monomers. In these compounds, high cross-link density, due to large number of polymerizable end groups would offer some advantages, including a three dimensional network,

decreases solubility and water sorption, improve the thermal and mechanical characteristics of the resin, and reduce shrinkage or shrinkage stress in comparison with other molecules that have similar weight^{3,15,16}.

On the other hand, these dental restorative materials have limited service life in part due to accumulation of bacterial (*e.g.*, *Streptococcus mutans*) or plaque, which lead to bonding failure of RBCs and finally secondary caries. Some researchers attempted to develop antibacterial RBCs through the incorporation of radiopacifying fillers (*e.g.*, BaSO₄, TiO₂, and ZrO₂)^{17,18} or antibacterial agents (*e.g.*, chlorhexidine)¹⁹. Unfortunately, these approaches bring some unwanted issues on the physicochemical and mechanical characteristics of the final composite materials. These problems can be solved through the using of fluoride-releasing dental materials, because fluoride has anticariogenic character due to its ability to enhance remineralization and the formation of acid-resistant fluorapatite^{20,21}. In this context, quaternary ammonium fluoride compounds are more attractive in part due to their low toxicity and broad spectrum antibacterial activity. In addition, the effect of fluoride does not depend on patient compliance^{22, 23}.

In this investigation, synthesis and characterization of two novel antibacterial dendritic methacrylate-based dental monomers is demonstrated. For this purpose, two dendritic esters were synthesized *via* condensation reaction and then reacted with methacryloyl chloride to afford methacrylate-ended dendritic esters. These compounds were subsequently converted to quaternary ammonium fluoride monomers with decyl substituted side chains to produce two novel antibacterial dental monomers. The resultant monomers can be used to replace Bis-GMA as the base monomer of universal resin-based dental composites in the presence of TEGDMA as diluting monomer.

Experimental Section

Materials

Triethanolamine (TEA), 1,2,3-benzenetricarboxylic acid anhydrate (BTCA), 2,2-bis(methylol)propionic acid (bis-MPA), methacryloyl chloride, silver(I) fluoride (AgF), *p*-toluenesulfonic acid (*p*-TSA), triethylamine (NEt₃), anhydrous stannous chloride (SnCl₂), *N,N*-dicyclohexylcarbodiimide (DCC), *N,N*-dimethylaminopyridine (DMAP), and 1-bromodecane were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received. Tetrahydrofuran (THF;

Merck, Darmstadt, Germany) was dried by refluxing over sodium, and distilled under argon protection before use. All other chemicals and solvents were of analytical grade (Sigma-Aldrich or Merck) and purified according to standard methods.

Synthesis of Compound 1

A 100 mL three-neck round-bottom reactor equipped with a stirrer, condenser, and a thermometer, was charged with a mixture of TEA (5 mL, 38 mmol), bis-MPA (19.4 g, 113 mmol), and a catalytic amount of *p*-TSA (0.05 g, 0.28 mmol). The content of the reactor was heated for 3 h at 140°C under argon protection, and the water formed during the reaction was removed. The product obtained was dissolved in *N,N*-dimethylformamide (DMF) and then precipitated in ethanol in order to remove unreacted reagents.

Synthesis of Compound 2

A 100 mL three-necked round-bottom reactor equipped with condenser, gas inlet/outlet, dropping funnel, and a magnetic stirrer, was charged with Compound 1 (10.0 g, 20 mmol), triethylamine (9.8 mL, 70 mmol), and 50 mL dried THF. The content of reactor was cooled to 4°C using an ice/water bath and then de-aerated by bubbling highly pure argon for some minutes. In a separate container, methacryloyl chloride (6.83 mL, 70 mmol) was dissolved in 10 mL of dried THF, and added to the reaction mixture dropwise using dropping funnel under argon protection. Thereafter, the temperature was allowed to increase to room temperature, and the reaction mixture was stirred under argon protection for about 24 h. At the end of this time, the solvent (THF) was removed using a rotary evaporator, added saturated sodium bicarbonate (50 mL), and the crude product was extracted with chloroform (3×70 mL). The organic phases were combined, dried using anhydrous Na₂SO₄, and the solvent removed using a rotary evaporator. The crude product was further purified using a short silica-gel column chromatography by ethyl acetate/*n*-hexane (60/40 v/v) as the eluent.

Synthesis of Monomer 1

The synthesized Compound 2 in previous section was converted to a quaternary ammonium salt in order to produce an antibacterial dental monomer. For this purpose, a 100 mL round-bottom flask was charged with Compound 2 (10 g, 10.1 mmol) and 1-bromodecane (3 mL, 14.5 mmol) and dried

acetonitrile (50 mL). The content of the flask was stirred at 60°C for about 24 h. At the end of this time, the solvent was removed under vacuum, the crude product was filtered, and washed with diethyl ether for several times in order to remove unreacted alkyl bromide. Afterward, the product was dissolved in ethyl acetate (100 mL), and then a AgF aqueous solution (0.80 g, in 5 mL distilled water) was added dropwise to the mixture under dimmed light. The reaction mixture was stirred for about 12 h, then centrifuged to remove the AgBr precipitate. The supernatant solution was then concentrated by rotary evaporation and purified through a short silica-gel column using ethyl acetate/*n*-hexane (50/50 v/v) as the eluent (Scheme 1).

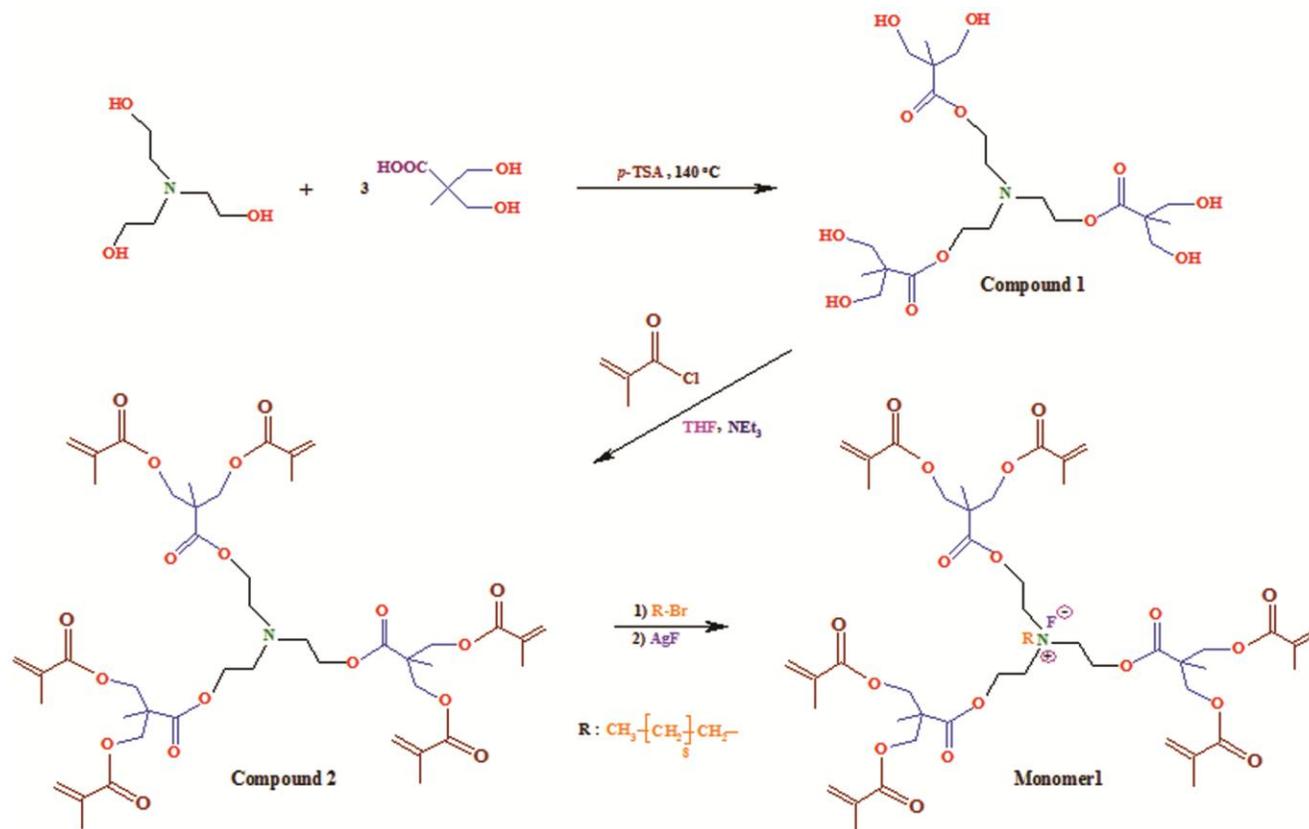
Synthesis of Compound 3

A 250 mL three-necked round-bottom flask equipped with condenser, gas inlet/outlet, and a magnetic stirrer, was charged with triethanolamine (10 mL, 75 mmol), 1,2,3-benzenetricarboxylic acid anhydride (58.0 g, 230 mmol), a catalytic amount of anhydrous SnCl₂ (0.20 g, 1 mmol), and dried DMF (100 mL). The reaction mixture was de-aerated by

bubbling highly pure argon for some minutes at room temperature, and then the flask was placed in an oil bath at 100°C. The content of the flask was stirred at this temperature for about 20 h under argon protection. At the end of this time, the most of DMF was distilled off in vacuum, and the residue mixture was precipitated in cold propanol, in order to remove unreacted reagents. The product (as a white powder) was dried in reduced pressure at room temperature.

Synthesis of Compound 4

A 250 mL three-necked round-bottom flask equipped with condenser, gas inlet/outlet, and a magnetic stirrer, was charged with Compound 3 (20.0 g, 27.5 mmol), DCC (37.2 g, 180 mmol), DMAP (5.625 g, 45 mmol), and dried DMF (120 mL). The reaction mixture was deaerated by purging argon for 15 min, and stirred magnetically at room temperature for about 5 h under an argon protection. After this time, the reaction mixture was filtered using filter paper (Whatman) in order to remove dicyclohexyl urea salts as the by-product. The solution was transferred in a new dried 250 mL flask, and then TEA (22.7 mL, 170 mmol) was



Scheme 1 — The overall strategy for synthesis of Monomer 1.

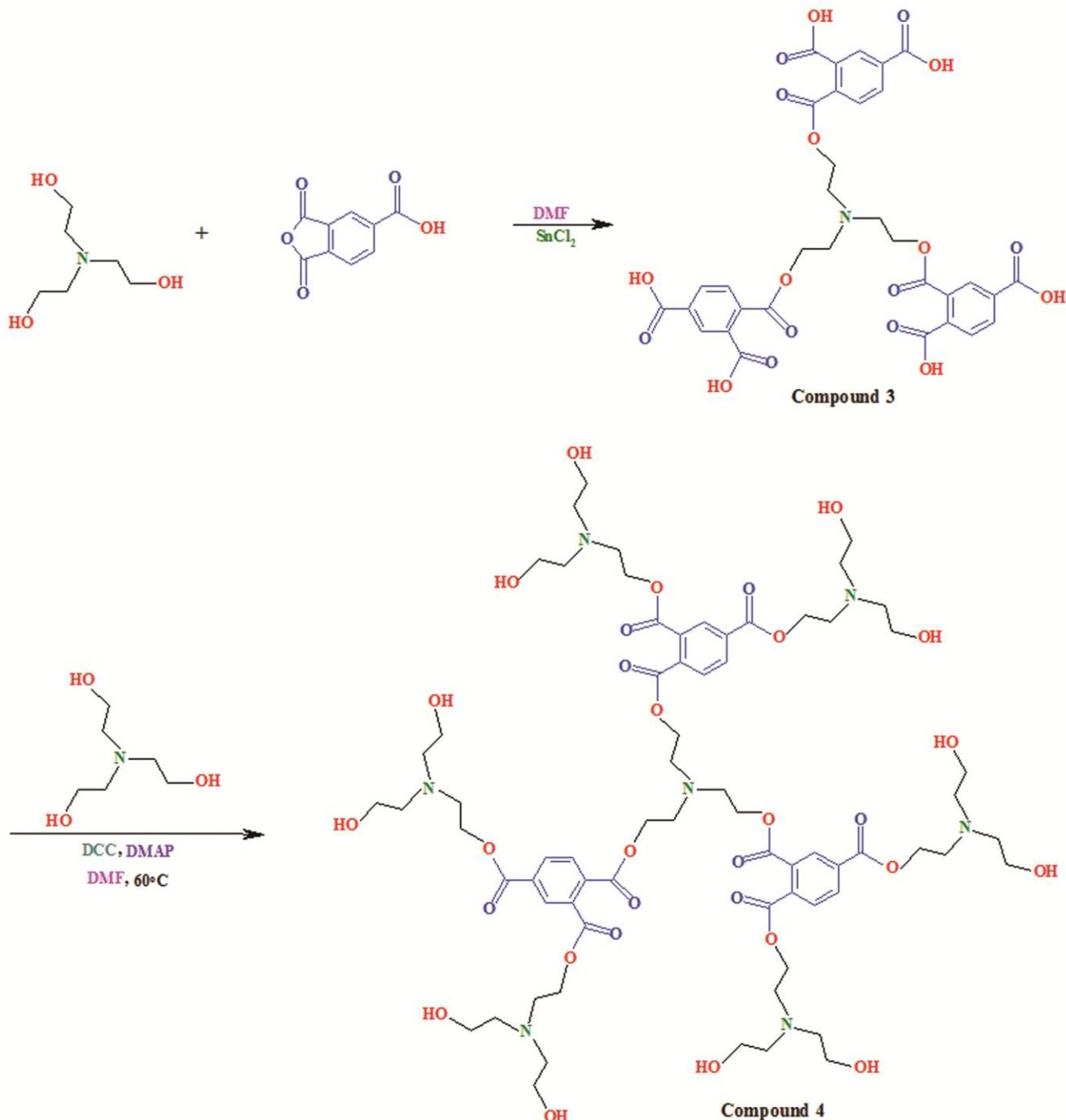
added. The reaction mixture was stirred for another 24 h at 40°C under an argon atmosphere. At the end of this time, the most of DMF was distilled off in vacuum, and the residue mixture was precipitated in cold propanol, in order to remove unreacted reagents. The product (as a white powder) was dried in reduced pressure at room temperature (Scheme 2).

Synthesis of Compound 5

The Compound 5 was synthesized through the esterification of hydroxyl end groups of Compound 4 with methacryloyl chloride using procedure that described in 2.3. section.

Synthesis of Monomer 2

Monomers 2 was synthesized through the conversion of Compound 5 to quaternary ammonium



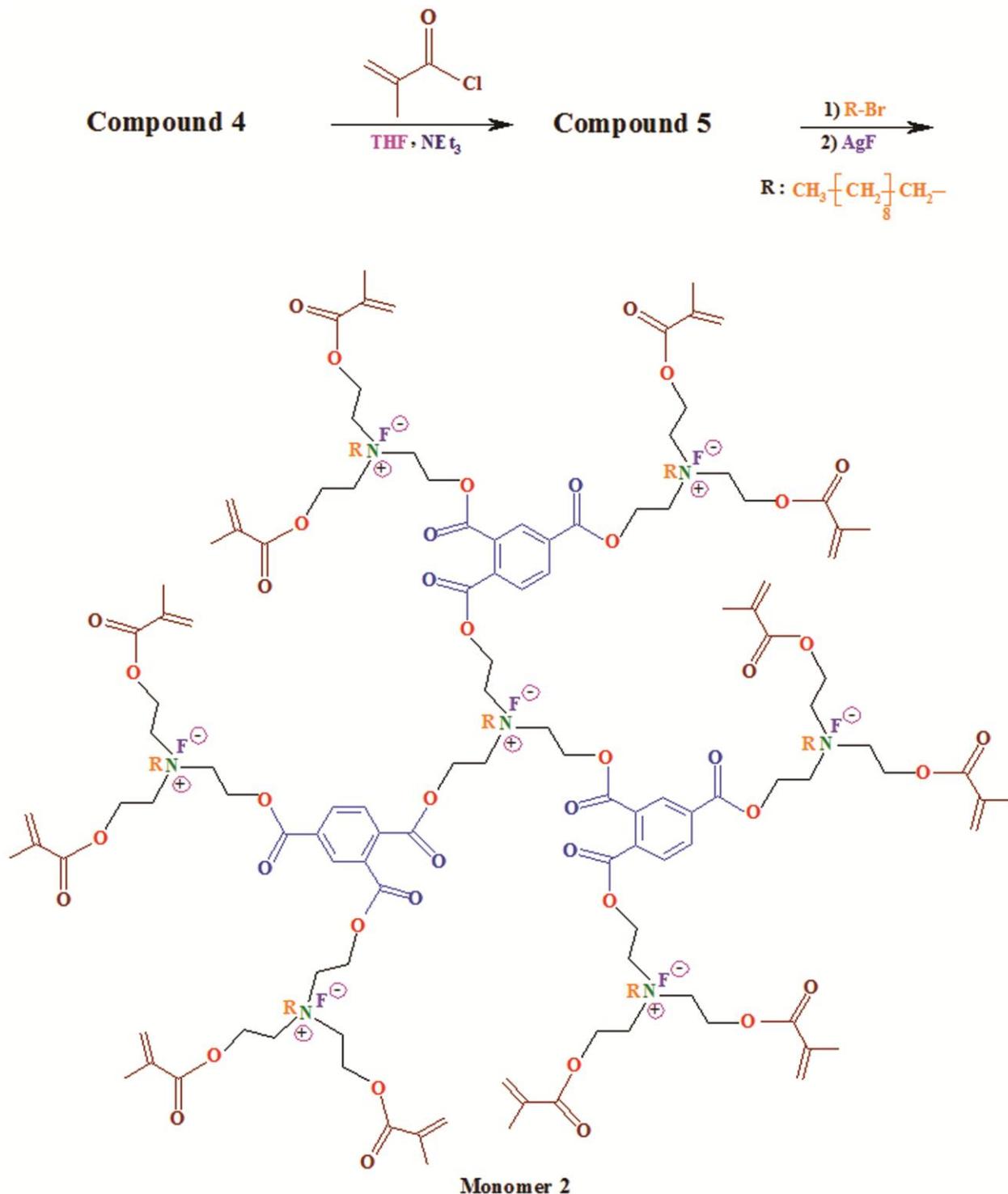
Scheme 2 — The overall strategy for synthesis of Compounds 3 and 4.

salts using the similar procedure that described in 2.4. section (see Scheme 3).

Characterization

Fourier transform infrared (FTIR) spectra of the samples were recorded using a Shimadzu 8101M

FTIR (Kyoto, Japan) in the wavenumber range of 4000 to 400 cm^{-1} at a wavenumber resolution of 4 cm^{-1} . The samples were prepared in the pellet form with spectroscopic-grade of potassium bromide (KBr) powder. Proton nuclear magnetic resonance (^1H NMR)



Scheme 3 — The overall strategy for the synthesis of Compound 5 and Monomer 2.

spectra were recorded at 25 °C on an FT-NMR (400 MHz) Bruker spectrometer (Ettlingen, Germany). The sample for NMR spectroscopy was prepared by dissolving about 10 mg of sample in 1 mL of deuterated dimethyl sulfoxide (DMSO-*d*₆) or chloroform (CDCl₃), and chemical shifts were reported in ppm units with tetramethylsilane (TMS) as an internal standard.

Results and Discussion

The need for enhanced RBCs as restorative materials in dentistry is rapidly increased during past few years. In this context, multifunctional dendrimers and dendritic compounds are particular of interest, mainly due to reduce polymerization shrinkage and enhance degree of monomer conversion as the most important drawbacks of RBCs materials. Furthermore, it is well established that RBCs tend to accumulate more biofilm and plaque *in vivo* than other restorative materials. This problem can be solved through the conversion of dental monomers into quaternary ammonium salts (more especially ammonium fluorides) in part due to excellent antibacterial activities of these compounds. Considering above mentioned facts, we try to design and develop two dendritic QAFMs as dental restorative materials.

Characterization of Monomer 1

The FTIR spectra of the TEA, bis-MPA, and Compound 1 are shown in Fig. 1. The FTIR spectrum of the TEA shows the characteristic absorption bands corresponding to the stretching vibration of C–O at 1062 cm⁻¹, the stretching vibration of C–N at 1153 cm⁻¹, the stretching vibrations of aliphatic C–H at 3050–2850 cm⁻¹ region, and the bending vibration of –CH₂ groups at 1461 cm⁻¹. The strong and broad band centered at 3410 cm⁻¹ is related to the hydroxyl groups. The FTIR spectrum of the bis-MPA exhibited the stretching vibration of C–O related to alcoholic and carboxylic acid groups at 1310–1020 cm⁻¹ region, the stretching vibrations of aliphatic C–H at 2950–2800 cm⁻¹ region, the bending vibrations of –CH₂ and –CH₃ groups at 1466 and 1399 cm⁻¹, respectively, the stretching vibration of carbonyl group at 1693 cm⁻¹, and the stretching vibrations of hydroxyl groups related to both carboxylic acid and alcohol are appeared at 3251 and 3376 cm⁻¹, respectively.

The FTIR spectrum of the Compound 1 revealed the successful synthesis of this compound. The most important bands in this spectrum can be listed as the

stretching vibration of C–O at 1043 cm⁻¹, the stretching vibrations of aliphatic C–H at 2950–2800 cm⁻¹ region, and the bending vibrations of –CH₂ and –CH₃ groups at 1466 and 1399 cm⁻¹, respectively. In addition, the stretching vibration of carbonyl group is shifted to higher wavenumber (1726 cm⁻¹), and the FTIR spectrum shows only one type of hydroxyl stretching vibration (alcohol) as a broad and strong band centered at 3308 cm⁻¹.

The FTIR spectrum of the Compound 2 and Monomer 2 are shown in Fig. 2. The most important change in the FTIR spectrum after incorporation of acrylate groups into Compound 1 are the appearance

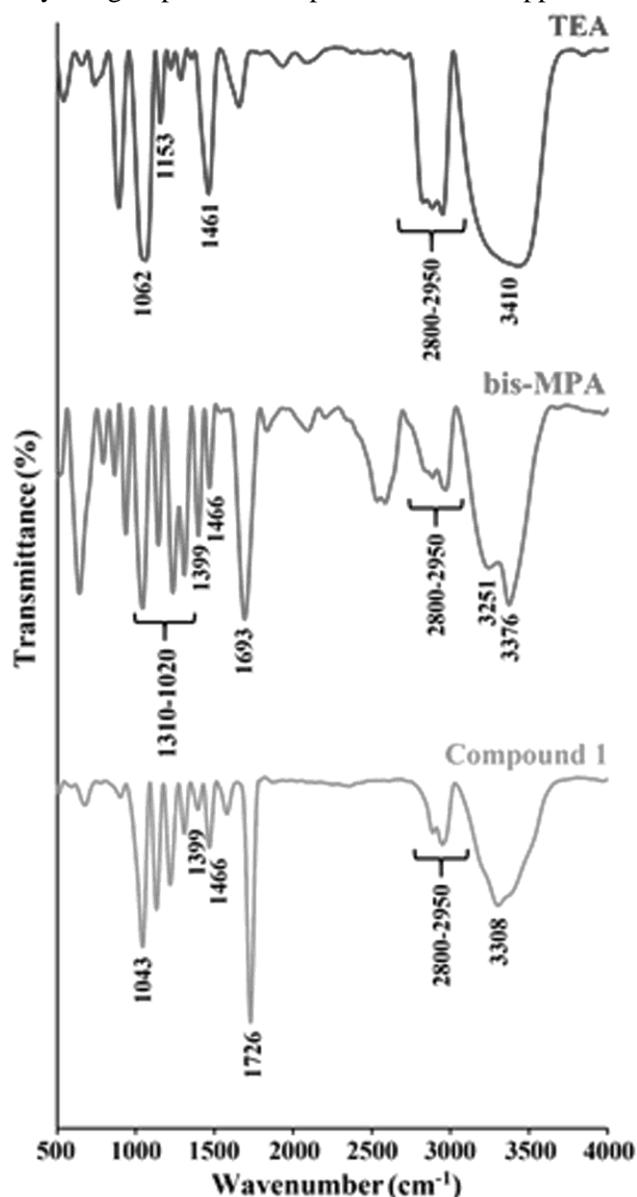


Fig. 1 — FTIR spectra of the TEA, bis-MPA, and Compound 1.

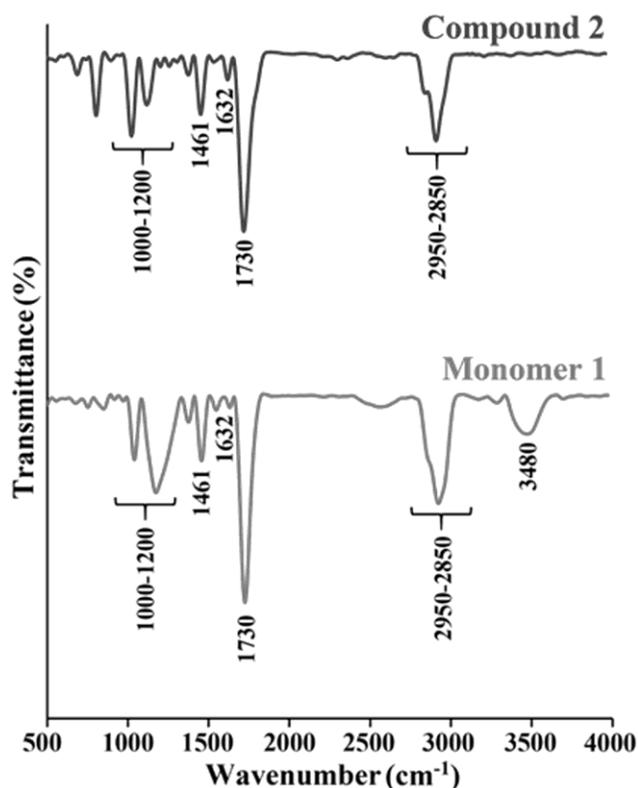


Fig. 2 — FTIR spectra of the Compound 2 and Monomer 1.

of new band at 1632 cm^{-1} related to the stretching vibration of C=C groups and disappearance of band at 3308 cm^{-1} corresponding to the stretching vibration of terminal hydroxyl groups due to their esterification with methacryloyl chloride as described in Experimental section. It should be pointed out that the bands at 1461 and $1200\text{--}1000\text{ cm}^{-1}$ in this spectrum are related to the bending and stretching vibrations of the --CH_2 and C–O groups, respectively. The FTIR spectrum of the Monomer 1 showed similar bands with minor differences. The most important change in this spectrum is the appearance of new broad band centered at 3480 cm^{-1} related to the ammonium fluoride.

Additional evidence regarding the successful synthesis of Compounds 1 and 2, and Monomer 1 were also obtained using ^1H NMR spectroscopy as shown in Fig. 3. In ^1H NMR spectrum of the Compound 1, the chemical shifts at 0.90 to 1.30 ppm correspond to the methyl groups (a), and the peak at $2.70\text{--}2.90$ ppm is related to the N– CH_2 groups (b). The chemical shifts of O– CH_2 (c), and $\text{CH}_2\text{--OH}$ (d) are appeared at $3.40\text{--}4.20$ ppm as labeled in the ^1H NMR spectrum. Finally, the chemical resonance at 4.9 ppm is corresponded to the terminal hydroxyl groups (e).

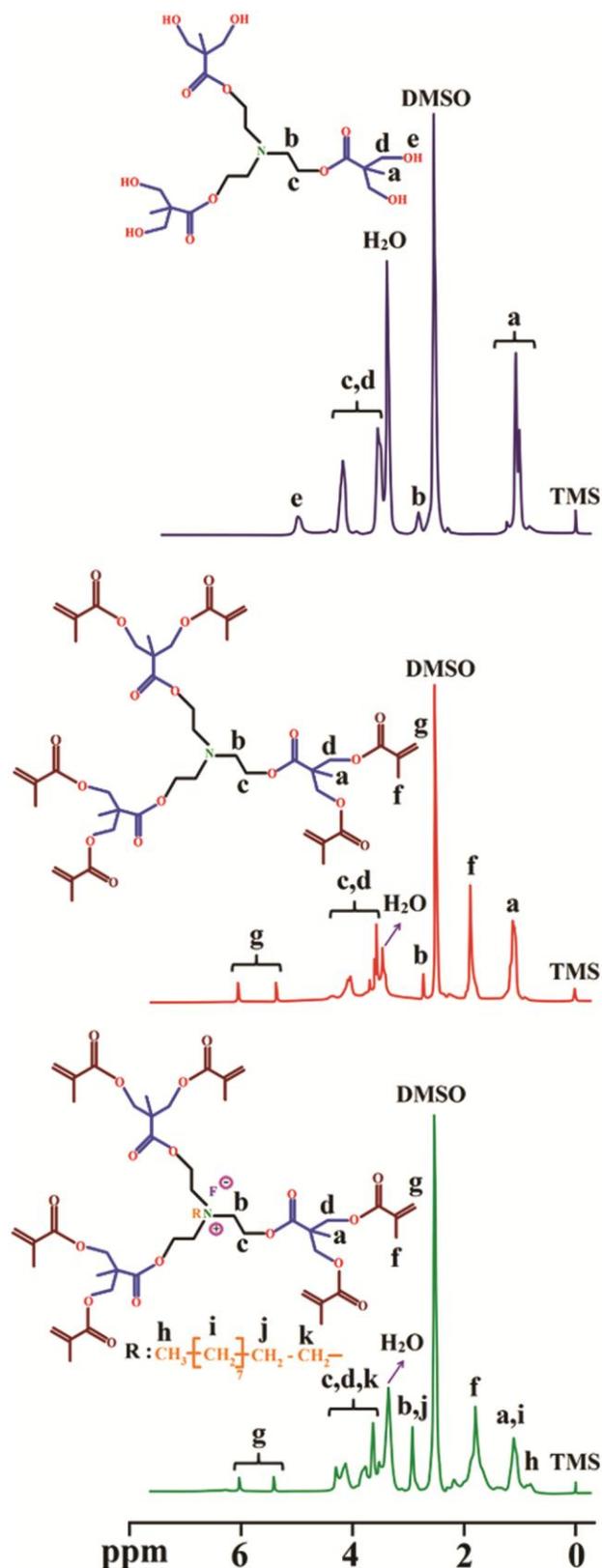


Fig. 3 — ^1H NMR spectra of the Compounds 1 and 2, and Monomer 1 (in $\text{DMSO-}d_6$).

The successful incorporation of methacrylate groups into the Compound 1 was confirmed by the appearance of characteristic chemical shifts at 1.80-2.10, and 5.40 and 6.10 ppm which related to the methyl(f) and vinyl protons(g) of methacrylate groups, respectively. The successful synthesis of Monomer 1 (conversion of Compound 2 into quaternary ammonium fluoride) was verified by the appearance of new chemical shifts related to the decyl moiety as labeled in the ^1H NMR spectrum.

Characterization of Monomer 2

The FTIR spectra of the BTCA, and Compounds 3 and 4 are shown in Fig. 4. The FTIR spectrum of the

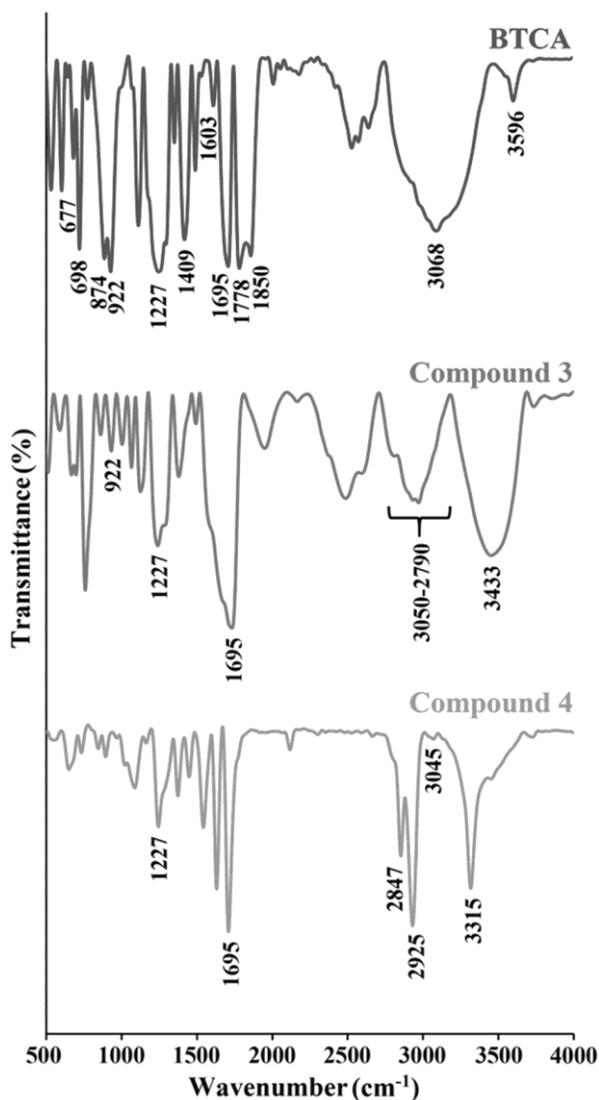


Fig. 4 — FTIR spectra of the BTCA, and Compounds 3 and 4.

BTCA reagent shows the absorption bands related to the aromatic C–H stretching vibrations at 3150–3000 cm^{-1} region, the stretching vibration of C–O at 1277 cm^{-1} , the symmetric stretching vibration of C–O–C at 922 cm^{-1} , hydroxyl stretching vibration at 3596 cm^{-1} , the stretching vibrations of the carbonyl groups related to anhydride group at 1778 and 1850 cm^{-1} , the carbonyl group of the carboxylic acid at 1695 cm^{-1} , aromatic C=C stretching vibration at 1603 cm^{-1} , and $\gamma(\text{C-H})$ in the aromatic ring at 874 cm^{-1} . In addition, the band at 1409 is related to the in-plane bending vibration of hydroxyl group²⁴.

The most important absorption bands in the FTIR spectrum of the Compound 3 can be listed as the symmetric stretching vibration of C–O–C at 922 cm^{-1} , the C–O stretching vibration at 1277 cm^{-1} , carbonyl stretching vibration at 1695 cm^{-1} , the stretching vibrations of aromatic and aliphatic C–H at 3050-2790 cm^{-1} region, and the stretching vibration of hydroxyl groups as a broad and strong band at 3433 cm^{-1} . Furthermore, as seen in this spectrum the stretching vibrations of the anhydride group at 1778 and 1850 cm^{-1} disappeared completely. This verifies the successful synthesis of the Compound 3 and remove the unreacted BTCA moiety as described in Experimental section.

The FTIR spectrum of Compound 4 shows an increase in the intensity of the stretching vibrations of aliphatic C–H as two sharp band at 2847 and 2925 cm^{-1} , in part due to esterification of carboxylic groups in the Compound 3 with TEA moiety through the Steglich approach²⁵.

The successful synthesis of Compound 3 and 4 was confirmed using ^1H NMR spectroscopy as seen in Fig. 5. The ^1H NMR spectrum of the Compound 3 shows the chemical shifts at 2.70-3.30 and 4.10-4.35 ppm correspond to the N–CH₂ (a) and O–CH₂ (b) groups, respectively. In addition, the chemical shifts at 7.40-8.30 ppm are related to the aromatic protons (c, d, and e) of the BTCA moiety. The successful synthesis of Compound 4 was verified through the change in the solubility after incorporation of TEA moiety into Compound 3 as well as the appearance of new chemical shift at 4.40 ppm (k) related to the terminal alcoholic hydroxyl groups.

The FTIR spectra of the Compound 5 and Monomer 2 are shown in Fig. 6. In comparison with FTIR spectrum of the Compound 4 (Fig. 4) the most

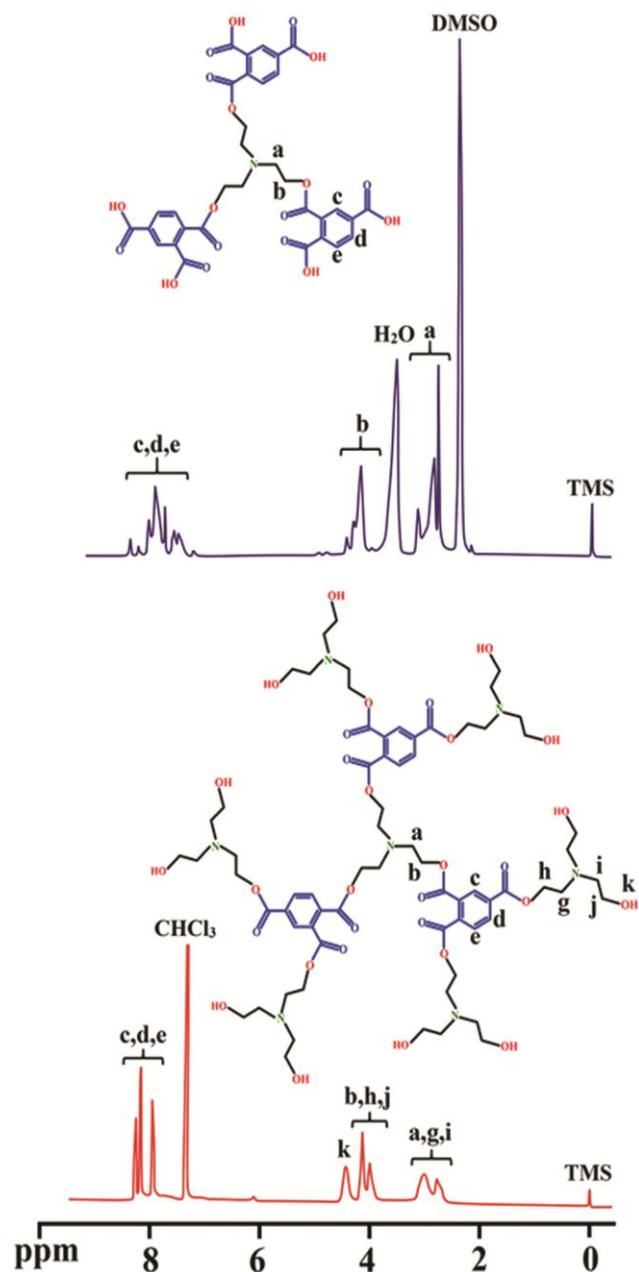


Fig. 5 — ^1H NMR spectra of the Compounds 3 (in $\text{DMSO-}d_6$) and 4 (in CDCl_3).

important changes in the FTIR spectrum of the Compound 5 are the appearance of new band at 1631 cm^{-1} related to the stretching vibration of the $\text{C}=\text{C}$ groups, disappearance of strong band related to the alcoholic hydroxyl groups at 3315 cm^{-1} due to their esterification, and shifts of stretching vibration of carbonyl group from 1695 to 1721 cm^{-1} . In addition, the bands at 1454 and 1378 cm^{-1} are related

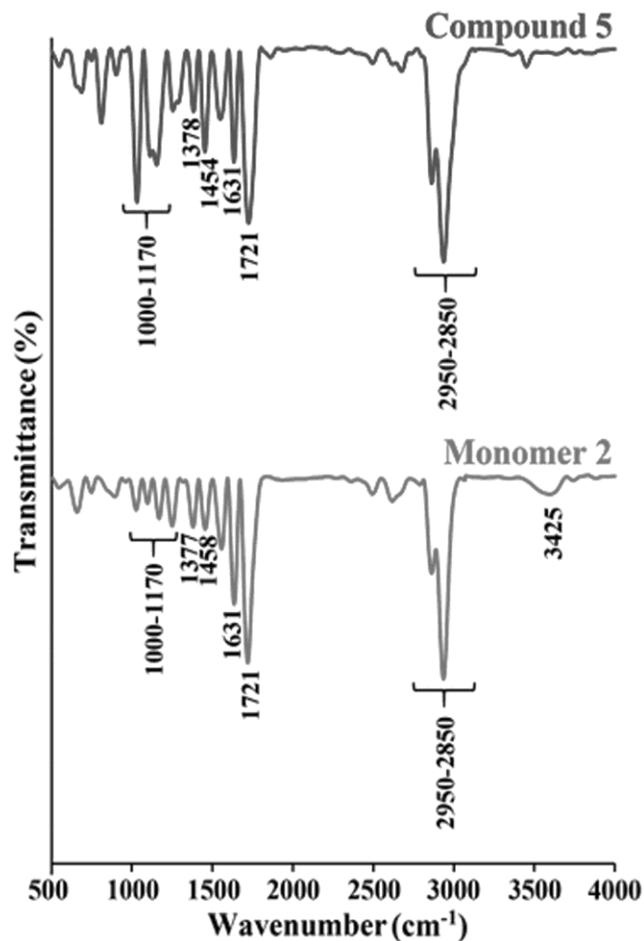


Fig. 6 — FTIR spectra of the Compound 5, and Monomer 2.

to the bending vibrations of $-\text{CH}_2$ and $-\text{CH}_3$ groups, respectively. As seen in Fig. 6, the FTIR spectrum of the Monomer 2 shows similar bands with minor differences. The most important change in this spectrum is the appearance of new band at 3425 cm^{-1} related to the ammonium fluoride groups.

The synthesized Compound 5 and Monomer 2 were further characterized using ^1H NMR spectroscopy as shown in Fig. 7. The successful synthesis of Compound 5 is verified by the appearance of new chemical shifts at 1.80 - 2.00 , and 5.40 and 6.10 ppm that corresponded to the methyl and vinyl protons of the methacrylate groups, respectively. As seen in Fig. 7, the successful synthesis of Monomer 2 was confirmed through the appearance of new characteristics peaks related to the decyl side chain as labeled in the ^1H NMR spectrum of this monomer.

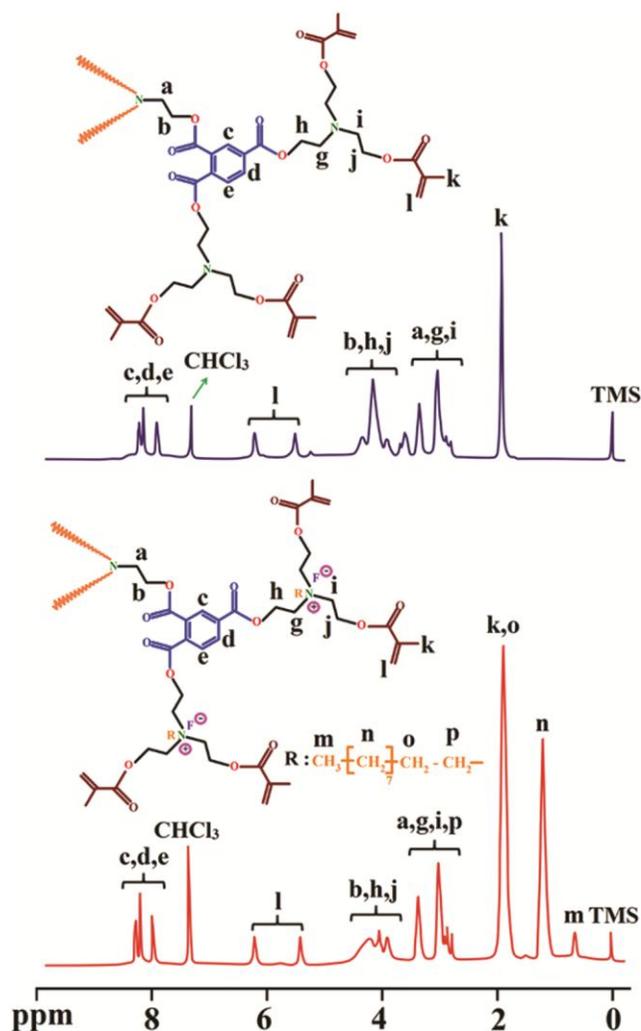


Fig. 7 — ^1H NMR spectra of the Compound 5, and Monomer 2 (in CDCl_3).

Conclusions

The synthesis and characterization of two novel antibacterial dendritic methacrylate-based dental monomers is demonstrated successfully. For this, two dendritic esters were synthesized through condensation reaction, and then reacted with methacryloyl chloride to produce two methacrylate-end capped dendritic esters. These compounds were subsequently converted to quaternary ammonium fluoride monomers with decyl substituted side chains to obtain two novel antibacterial dental monomers. The successful syntheses of all samples were demonstrated using FTIR and ^1H NMR spectroscopies. It is expected that the synthesized monomers used to replace Bis-GMA as the base monomer of universal resin-based dental composites in the presence of TEGDMA as diluting monomer,

due to their superior properties such as multi-functionality as well as antibacterial activities.

In conclusion, the formulation of resin-based dental composites using the synthesized monomers and investigation of their physicochemical properties including mechanical characteristics, water sorption and sol fraction, double bond conversion (DC), as well as some biological properties such as biocompatibility and antibacterial activity of the resultant (nano-)composites are under progress in our laboratory.

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