Synthesis and Photopolymerizations of New Phosphonated Methacrylates from Alkyl α-Hydroxymethacrylates and Glycidyl Methacrylate

Gorkem Sahin,[1] Duygu Avci,[1] Ozlem Karahan,[1] Norbert Moszner[2]

[1]*Department of Chemistry, Bogazici University, Bebek 34342, Istanbul, Turkey*
[2]*Ivoclar Vivadent AG, Bendererstrasse 2, Schaan FL-9494, Liechtenstein*

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ABSTRACT: Novel aromatic mono- and di(phosphonate) or phosphonic acid monomers for use in dental composites were synthesized. Synthesis of monomer **1a** involved three steps: (i) reaction of *t*-butyl α-bromomethacrylate (*t*-BuBMA) and Bisphenol A, (ii) conversion to diacid chloride derivative using thionyl chloride, (iii) reaction of diacid chloride with diethyl (2-hydroxyphenyl) phosphonate. Monomer **2a** was synthesized from the reaction of 2-chloromethacryloyl chloride and diethyl (2-hydroxyphenyl) phosphonate. Synthesis of monomer **3a** involved reaction of glycidyl methacrylate (GMA) with diethyl (2-hydroxyphenyl) phosphonate. Hydrolysis of the phosphonate groups of monomers **1a** and **2a** with trimethylsilyl bromide (TMSBr) gave monomers **1b** and **2b** with phosphonic acid functionality, which is intended to improve binding ability of dental composites. The homopolymerization and copolymerization behaviors of the synthesized monomers with (Bis-GMA) were investigated using photo-differential scanning calorimetry at 40°C with 2,2′-dimethoxy-2-phenyl acetophenone as photoinitiator. The interaction of the monomer **1b** with hydroxyapatite (HAP) was investigated using Fourier transform infrared technique. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 97–106, 2009

Key words: *o*-hydroxyaryl phosphonates; crosslinking; dental polymers; α-hydroxymethyl acrylates; photopolymerization

INTRODUCTION

Commonly used dental composites are composed of dimethacrylate monomers such as 2,2-bis[4-(2-hydroxy-3-methacryloyloxy propyloxy)phenyl]propane (Bis-GMA) or 1,6-bis-(2-methacryloyloxyethoxycarbonylamino)-2,4,4-trimethylhexane (UDMA), an inorganic filler coated with methacrylate-functional silane coupling agents and a polymerization initiator system.[1,2] A comonomer such as triethylene glycol dimethacrylate (TEGDMA) is added to adjust the viscosity of the dental resin. One of the major problems encountered with the dental composites is the lack of bonding to the tooth material. To address that problem, novel monomers with binding ability have been designed.[3–15] In general, this binding ability is provided by acid functional groups such as carboxylic, phosphonic, and phosphoric acids, which form chelates with the calcium ions in the tooth surface.

Recently, we have reported synthesis and photopolymerization behavior of new mono- and di(phosphonate) containing monomers based on *t*-butyl α-hydroxymethacrylate (TBHMA) from *o*-hydroxyaryl phosphonates. Some of these monomers contain both phosphonic and carboxylic acid groups to improve adhesive properties.[16] The objective of this study is to develop new dental monomers based on alkyl α-hydroxymethyl acrylates and glycidyl methacrylate (GMA) with improved adhesion, volume shrinkage, solubility in common dental monomers and mechanical properties and investigate their photopolymerization behavior and interactions with HAP.

EXPERIMENTAL

Reagents

T-butyl α-hydroxymethacrylate (TBHMA), *t*-butyl α-bromomethacrylate (*t*-BuBMA), 2-chloromethacryloyl chloride (CMAC), diethyl (2-hydroxyphenyl) phosphonate and 2,2′-(4,4′-(propane-2,2-diyl)bis(4,1-phenylene)) bis(methylene) diacryloyl chloride (monomer B) were prepared according to literature procedures.[17–23] The photoinitiators, 2,2-dimethoxy-2-phenylacetophenone (DMPA) and bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (BAPO) were obtained from Aldrich. Tetrahydrofuran (THF) was

Correspondence to: D. Avci (avcid@boun.edu.tr).
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obtained from JT Baker and dried over Na and freshly distilled before use. TMSBr (Aldrich, Taufkirchen, Germany) was distilled before use. All other solvents and starting materials were reagent grade and used as received.

Characterization

The monomer characterization involved ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy (Varian Gemini 400 MHz) and Fourier transform infrared (FTIR) spectroscopy on thin films on NaCl plates (Mattson 5000). Photopolymerizations were carried out on a TA Instruments Q100 differential photocalorimeter. Thermogravimetric analysis (TGA) was carried out on a TA Instruments (Q50).

Synthesis of monomers

Monomer **1a**

To a mixture of diethyl (2-hydroxyphenyl) phosphonate (2.71 g, 11.8 mmol) and triethyl amine (TEA) (1.19 g, 11.8 mmol), 2,2′-(4,4′-(propane-2,2-diyl)-bis(4,1-phenylene)) bis(methylene) diacryloyl chloride (monomer B) (2.3 g, 5.4 mmol) in 15 mL THF was added dropwise in an ice bath under nitrogen purge. After 24 h of stirring at room temperature, THF was evaporated. The solution was diluted with 30 mL of CH_2Cl_2 and extracted with water (3 × 15 mL). The organic layer was dried with anhydrous Na_2SO_4. Removal of solvent left thick brown paste (97% yield) and it was washed with petroleum ether to remove excess diethyl (2-hydroxyphenyl) phosphonate. The pure product was obtained as a light yellow viscous liquid after column chromatography (silica gel 0.063–0.200 mm), starting EtAc : hexane (50 : 50) elutant and changing to EtAc : MeOH (99 : 1). Yield: 45%.

^{13}C-NMR ($CDCl_3$): δ = 15.2 (CH_3—CH_2), 30.0 [$(CH_3)_2$—C], 40.7 [C—$(CH_3)_2$], 61.2 (CH_3—CH_2), 64.8 (CH_2—O), 113.1 (Ar—CH), 119.4, 121.2 (d, C—P), 122.8, 125.0 (Ar—CH), 126.7 (Ar—CH), 127.6 (C=CH_2), 132.8, 133.9 (Ar—CH), 134.5 (Ar—C), 142.6 (C=CH_2), 151.0, 155.2 [C(Ar)—O], 162.6 ppm (C=O).

^{1}H-NMR ($CDCl_3$): δ = 1.18 (t, 12H, CH_2—CH_3), 1.56 (s, 6H, [$(CH_3)_2$—C]), 3.95 (m, 8H, CH_2—CH_3), 4.81 (s, 4H, CH_2—O), 6.15, 6.62 (s, 4H, CH_2=C), 6.81, 7.08 (d, 8H, Ar—CH), 7.16 (dd, 2H, Ar—CH), 7.27 (td, 2H, Ar—CH), 7.53 (t, 2H, Ar—CH), 7.90 ppm (qd, 2H, Ar—CH).

FTIR (NaCl): 2964 (C—H), 1745 (C=O), 1641 (C=C), 1599 (C=C, arom.), 1257 (P=O), 1087 (C—O), 1021, 972 cm^{-1} (P—O—Et).

^{31}P NMR ($CDCl_3$): δ = 16.1 ppm.

Monomer **1b**

TMSBr (0.79 g, 5.2 mmol) was added dropwise to a solution of monomer **1a** (0.97 g, 1.2 mmol) in 1 mL freshly dried CH_2Cl_2 in an ice bath under nitrogen, and then the solution was refluxed for 2 h. After the evaporation of the solvent, 2 mL of MeOH was added, and the mixture was stirred at room temperature overnight. Methanol was evaporated and the product was obtained in 62% yield after several washings with acetonitrile.

^{13}C-NMR ($CDCl_3$): δ = 30.4 [$(CH_3)_2$—C], 41.6 [C—$(CH_3)_2$], 66.1 (CH_2—O), 114.5, 117.2 (Ar—CH), 123.5, 125.4 (d, C—P), 123.8, 126.1 (Ar—CH), 127.6 (Ar—CH), 127.8 (C=CH_2), 133.9 (Ar—CH), 136.2 (Ar—C), 143.7 (C=CH_2), 152.2, 156.5 [C(Ar)—O], 164.1 ppm (C=O).

^{1}H-NMR ($CDCl_3$): δ = 1.52 (s, 6H, [$(CH_3)_2$—C]), 4.83 (s, 4H, CH_2—O), 6.04, 6.57 (s, 4H, CH_2=C), 6.82, 7.05 (d, 8H, Ar—CH), 7.16 (t, 2H, Ar—CH), 7.28 (t, 2H, Ar—CH), 7.53 (t, 2H, Ar—CH), 7.81 ppm (dd, 2H, Ar—CH).

FTIR (NaCl): 3500–2000 (OH), 2964 (C—H), 1715 (C=O), 1644 (C=C), 1602 (C=C, arom.), 1262 (P=O), 1009 and 929 cm^{-1} (C—O).

^{31}P-NMR ($CDCl_3$): δ = 12.3 ppm.

Monomer **2a**

To a stirring mixture of diethyl (2-hydroxyphenyl) phosphonate (0.90 g, 3.9 mmol) and TEA (0.51 g, 5.0 mmol) in 5 mL dry THF in an ice bath, CMAC (0.22 g, 1.9 mmol) was slowly added. After 24 h of refluxing at 55°C, THF was evaporated. The solution was diluted with 10 mL of CH_2Cl_2 and extracted with 3 × 5 mL water. The organic layer was dried with anhydrous Na_2SO_4. Removal of solvent left thick brown paste, and it was washed with petroleum ether to remove excess diethyl (2-hydroxyphenyl) phosphonate. The residue was purified by reversed-phase column chromatography (C-18 silica gel), starting H_2O : MeOH (70 : 30) elutant and changing to 100% MeOH gradually. The pure product was obtained as a yellow viscous liquid in 45% yield.

^{13}C-NMR ($CDCl_3$): δ = 14.1 (CH_3—CH_2), 59.7, 60.0 (CH_3—CH_2), 63.6 (CH_2—O), 109.8 (Ar—CH), 113.2, 115.0 (d, C—P), 117.9, 119.7 (d, C—P), 118.6, 121.3, 123.7 (Ar—CH), 126.7 (C=CH_2), 131.7, 132.1, 132.2, 132.7 (Ar—CH), 133.0 (C=CH_2), 149.5, 157.3 [C(Ar)—O], 161.1 ppm (C=O).

^{1}H-NMR ($CDCl_3$): δ = 1.29 (m, 12H, CH_2—CH_3), 4.12 (m, 8H, CH_2—CH_3), 5.01 (s, 2H, CH_2—O), 6.59, 6.76 (s, 2H, CH_2=C), 7.07 (m, 2H, Ar—CH), 7.27, 7.37 (m, 2H, Ar—CH), 7.51, 7.61 (t, 2H, Ar—CH), 7.88, 7.98 ppm (dd, 2H, Ar—CH).

FTIR (NaCl): 2983 (C—H), 1746 (C=O), 1643 (C=C), 1593 (C=C, arom.), 1250 (P=O), 1091 (C—O), 1023, 969 cm^{-1} (P—O—Et).

Monomer **2b**

TMSBr (0.49 g, 3.2 mmol) was added dropwise to a solution of monomer **2a** (0.39 g, 0.7 mmol) in 1 mL

freshly dried CH_2Cl_2 in an ice bath under nitrogen, and then the solution was refluxed for 2 h. After evaporation of the solvent, 2 mL of MeOH was added and the mixture was stirred at room temperature overnight. Then MeOH was evaporated and the product was obtained as a yellow viscous liquid in 60 per cent yield.

^{1}H-NMR ($CDCl_3$): δ = 5.08 (s, 2H, CH_2—O), 6.43, 6.66 (s, 2H, CH_2=C), 7.05, 7.17 (m, 2H, Ar—CH), 7.32, 7.38 (m, 2H, Ar—CH), 7.54, 7.63 (t, 2H, Ar—CH), 7.80, 7.90 ppm (dd, 2H, Ar—CH).

^{13}C-NMR ($CDCl_3$): δ = 66.3 (CH_2—O), 112.5 (Ar—CH), 115.9, 118.1 (d, C—P), 120.5, 122.4 (d, C—P), 121.0, 124.0, 126.3 (Ar—CH), 127.4 (C=CH_2), 129.4, 134.1, 134.6, 135.2 (Ar—CH), 135.5 (*C*=CH_2), 152.1, 160.1 [C(Ar)—O], 163.6 ppm (C=O).

FTIR (NaCl): 3500–2000 (OH), 2924 (C—H), 1725 (C=O), 1643 (C=C), 1594 (C=C, arom.), 1284 (P=O), 1090 (C—O), 1003, 928 cm^{-1} (P—O).

^{31}P-NMR ($CDCl_3$): δ = 12.4, 16.0 ppm.

Monomer **3a**

Diethyl (2-hydroxyphenyl) phosphonate (1.28 g, 5.6 mmol), GMA (0.72 g, 5.1 mmol) and TEA (0.031 g, 0.3 mmol) are mixed at 85°C under nitrogen for 1 day. The mixture was washed with cyclohexane to remove excess diethyl (2-hydroxyphenyl) phosphonate and TEA. The pure product was obtained as a yellow viscous liquid after column chromatography (silica gel 0.063–0.200 mm), with ethyl acetate as an elutant. Yield: 68%.

^{13}C-NMR ($CDCl_3$): δ = 16.4 (CH_3—CH_2), 18.7 [CH_3—C], 62.5, 72.8 (CH_2—O), 65.2 (CH_3—CH_2), 68.3 (CH—OH), 114.7 (Ar—CH), 117.0, 118.8 (d, C—P), 121.5 (Ar—CH), 126.0 (C=CH_2), 133.6, 134.8 (Ar—CH), 136.3 (*C*=CH_2), 161.2 [C(Ar)—O], 167.4 ppm (C=O).

^{1}H-NMR ($CDCl_3$): δ = 1.26 (td, 6H, CH_2—CH_3), 1.86 (s, 3H, [CH_3—C]), 3.95 (m, 4H, CH_2—CH_3), 4.19 (s, 4H, CH_2—O), 4.24 (m, 2H, CH—O), 5.16 (s, 1H, —OH), 5.49, 6.05 (s, 2H, CH_2=C), 6.90 (t, 1H, Ar—CH), 6.97 (td, 1H, Ar—CH), 7.42 (t, 1H, Ar—CH), 7.60 ppm (qd, 1H, Ar—CH).

FTIR (NaCl): 3349 (—OH), 2981 (C—H), 1715 (C=O), 1637 (C=C), 1593 (C=C, arom.), 1283 (P=O), 1093 (C—O), 1022, 969 cm^{-1} (P—O—Et).

^{31}P-NMR ($CDCl_3$): δ = 18.5 ppm.

Photopolymerization procedure

Approximately 3.0 mg of sample was placed in an aluminium DSC pan. A CH_2Cl_2 solution of the photoinitiator was added with a microsyringe to give a final concentration in the monomer of 2.0 mol % after evaporation of the solvent. Heats of photoreactions were measured using a DSC equipped with a mercury arc lamp (lamp intensity 20 mW/cm^2). The DSC chamber was purged with nitrogen to remove air and CH_2Cl_2 for 10 min before polymerization and purging was continued during polymerization. We start to take data 60 s before we turn the light on. The samples were irradiated for 10 min at 40°C. The heat flux as a function of reaction time was monitored using DSC under isothermal conditions, and both the rate of polymerization and conversion were calculated as a function of time. The theoretical value used for the heats of reaction (ΔH_p) was 13.1 kcal/mol for methacrylate double bonds.[24,25] Rates of polymerization were calculated according to the following formula.

$$\text{Rate} = \frac{(Q/s)M}{n\Delta H_p m}$$

where Q/s is heat flow per second; M, the molar mass of the monomer; n, the number of double bonds per monomer molecule; and m, the mass of monomer in the sample.

Polymerization

All polymerizations (bulk or solution) were carried out at 60°C with azobisisobutyronitrile (AIBN) and 2,2′-azobis(2-amidinopropane)dihydrochloride (V-50) in septum-sealed glass tubes using standard freeze-evacuate-thaw procedures. The crosslinked polymer solutions were washed with methylene chloride to remove residual monomer and dried.

Calculation of dipole moments

Spartan '04 software is used to calculate the Boltzmann-averaged dipole moments of the given monomers.[26] A set of starting geometries were generated using threefold rotation between two sp^3 hybridized atoms and twofold rotation between two sp^2 hybridized atoms. The resulting conformations were minimized at the PM3 level of theory. The convergence criterion for the maximum gradient was 0.0001 a.u. and the maximum number of geometry optimization cycles was taken to be 20 + the number of independent geometrical parameters. The unique structures were sorted in the order of increasing energy. The dipole moments of the first 100 conformers are Boltzmann averaged at 298.15 K according to the following formula.

$$\langle \mu_{calc} \rangle = \sum D_j \frac{e^{\Delta H_j/RT}}{\sum_i e^{\Delta H_i/RT}} = \sum_j D_j p_j$$

where D_j is the dipole moment of the conformation j, ΔH_j is the difference between the heat of formation

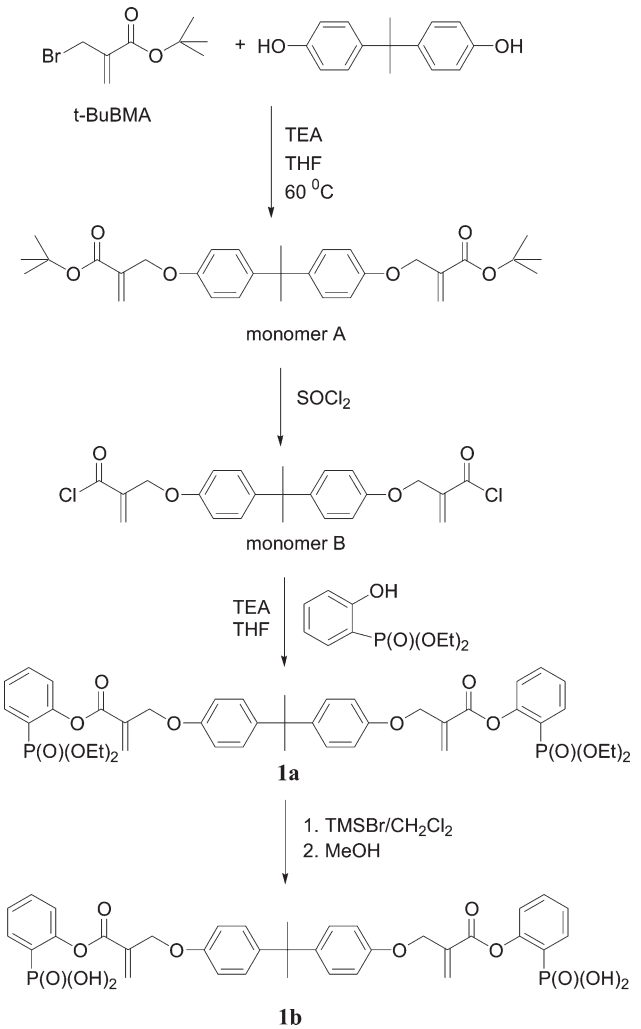

Figure 1 Synthesis of monomers **1a** and **1b**.

of conformation j and the heat of formation of the global minimum conformation, T is the absolute temperature, R is the Boltzmann constant, and p_j is the probability of finding the monomer in conformation j at the temperature T.[27]

RESULTS AND DISCUSSION

Synthesis of monomers

In the present work, we have designed new phosphonate and phosphonic acid monomers for use in dental composites. These monomers are expected to have the following properties: (a) rigid aromatic structures (either Bisphenol A or phenolic structure or both) which will result in materials with good mechanical properties and low volume shrinkage, (b) ability to form bonds with dental tissue due to incorporation of phosphonic acid function, (c) copolymerizability with common monomers used in dental composites such as Bis-GMA and TEGDMA.

Synthesis of the first pair of monomers (**1a** and **1b**), which contain both Bisphenol A and phenolic structures and phosphonate or phosphonic acid incorporated in the phenolic ring, is shown in Figure 1. They also have crosslinking ability which will further improve mechanical properties. Monomer **1a** was synthesized in three steps. The first step involved the reaction of Bisphenol A with t-BuBMA in the presence of TEA at 60°C to give an intermediate monomer (monomer A), which was a white solid after recrystallization from methanol. In the second step, this intermediate was converted to a diacid chloride (monomer B) by thionyl chloride reaction. The ^{1}H-NMR spectrum showed a complete disappearance of *t*-butyl ester groups. This intermediate was the precursor for the syntheses of other crosslinking monomers in our previous work.[23] In the third step, reaction of the diacid chloride with diethyl (2-hydroxyphenyl) phosphonate in TEA at room temperature gave diphosphonate containing monomer **1a**. The crude product yields were high (97%) but the pure product was obtained after column chromatography with 45% yield as a light yellow viscous liquid. This monomer was soluble in THF, diethyl ether, dichloromethane, and acetone, but insoluble in water (Table I). The ^{1}H-NMR spectrum of this monomer was characterized by ethyl protons of phosphonate ester at 1.18 and 3.95 ppm, methyl protons of Bisphenol A at 1.56 ppm, methylene protons at 4.81 ppm, double bond protons at 6.15 and 6.62 ppm, aromatic protons of Bisphenol A at 6.81 and 7.08 ppm, and aromatic protons of phenol phosphonate at 7.16, 7.27, 7.53, and 7.90 ppm (Fig. 2). The ^{31}P-NMR spectrum shows a singlet at 16.1 ppm.

The silylation of monomer **1a** with TMSBr, followed by methanolysis of the silyl derivative, gave a new phosphonic acid monomer **1b** as a very viscous

TABLE I
Solubilities of the Monozmers

	Solvent						
Monomer	H_2O	Methanol	Ethanol	THF	Acetone	Diethyl ether	CH_2Cl_2
1a	−	+	+	+	+	+	+
1b	+/−	+	+	−	−	−	−
2a	−	+	+	+	+	+	+
2b	+	+	+	+	−	−	−
3a	−	+	+	+	+	+	+

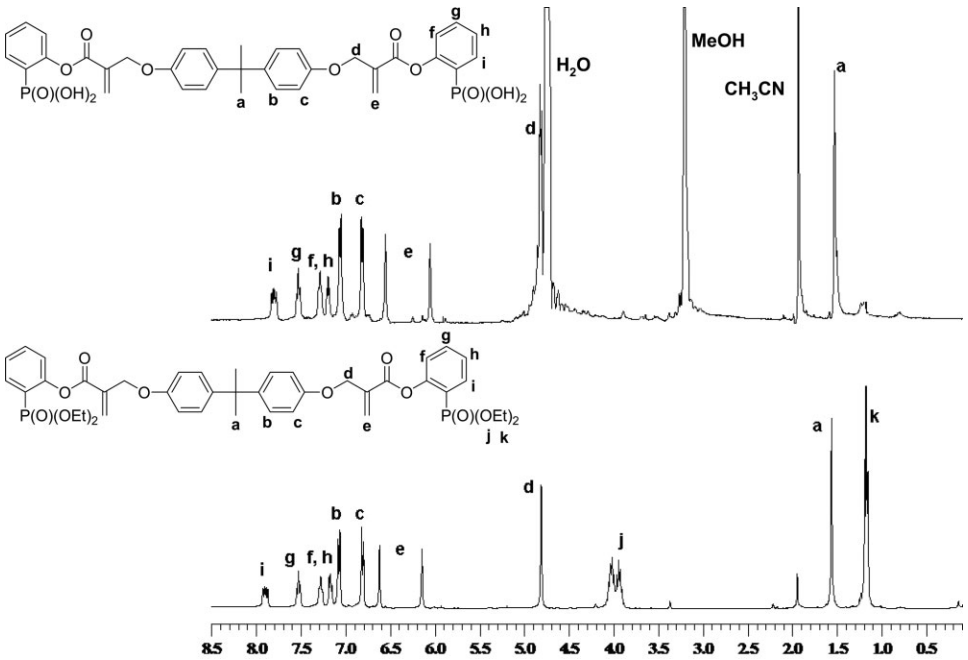

Figure 2 ^{1}H-NMR spectra of monomers **1a** and **1b**.

liquid. Monomer **1b** is soluble in EtOH, MeOH, insoluble in diethyl ether, THF, acetone, and CH_2Cl_2 and slightly soluble in water (Table I). Both ^{1}H-NMR (Fig. 2) and ^{13}C-NMR spectra show a complete disappearance of the ethyl groups of the phosphonate ester.

For the synthesis of the second pair of monomers, TBHMA was converted to CMAC in one-step reaction with thionyl chloride. CMAC was reacted with diethyl (2-hydroxyphenyl) phosphonate to obtain new pair of monomers (**2a** and **2b**) with identical ester and ether groups (Fig. 3). The pure product was obtained after reverse-phase column chromatography in 45% yield. The ^{1}H-NMR spectrum of this monomer was characterized by ethyl protons at 1.29 and 4.12 ppm, methylene protons at 5.01 ppm, double bond protons at 6.59, 6.76 ppm, and aromatic protons at 7.07, 7.27, 7.37, 7.51, 7.61, 7.88, and 7.98 ppm (Fig. 4).

The monomer **2a** was hydrolyzed after reaction with TMSBr under the same conditions as monomer **1a**. Monomer **2b** was obtained as a yellow viscous liquid, which was soluble in water, ethanol, methanol, THF, and insoluble in diethyl ether, acetone, and CH_2Cl_2. (Table I). Both ^{13}C-NMR and ^{1}H-NMR (Fig. 4) spectra show complete disappearance of the ethyl groups of the phosphonate ester. However, it was observed that this monomer was prone to cleavage at the methacrylate group to give carboxylic acid and 2-hydroxyphenyl phosphonic acid during

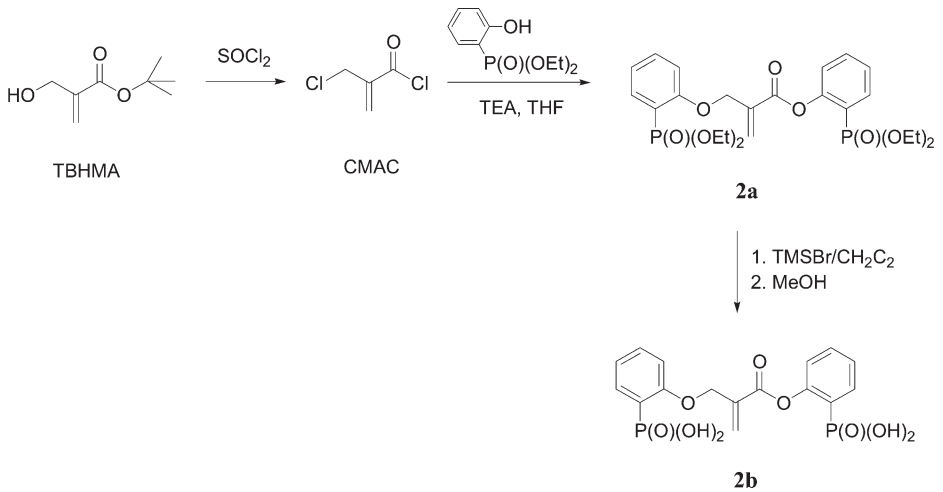

Figure 3 Synthesis of monomers **2a** and **2b**.

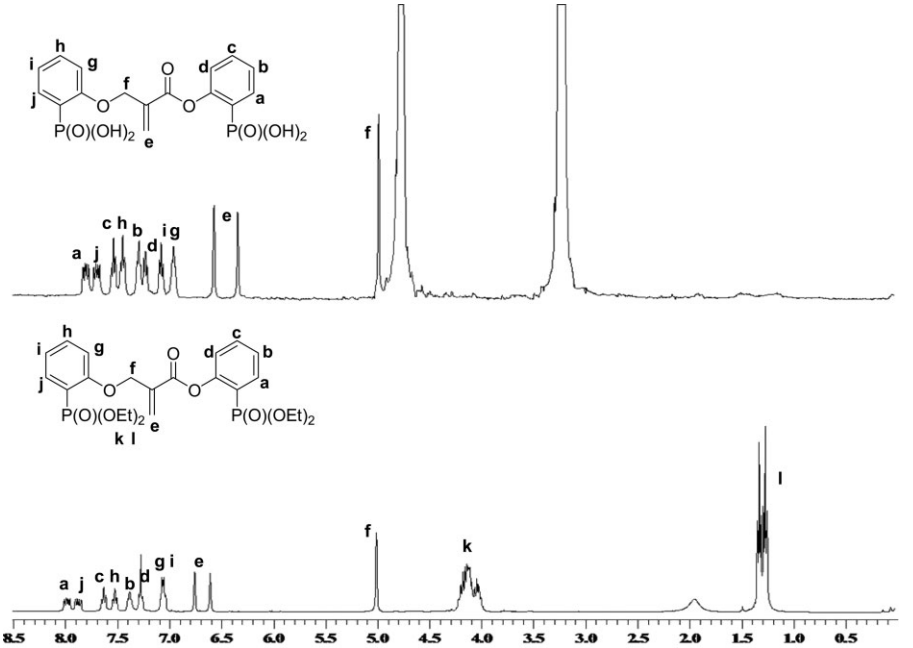

Figure 4 ^{1}H-NMR spectra of monomers **2a** and **2b**.

TMSBr hydrolysis. Purification of the product with several washings with acetonitrile in which the carboxylic acid and 2-hydroxyphenyl phosphonic acid are soluble was not always succesful.

The reason for the cleavage of this monomer may be due to the presence of phenyl phosphonate group in the ester part. Hydrolysis of a monomer containing phosphonate and phenyl ester groups was previously successfully done.[28] Apparently in our monomer, the presence of the phosphonate group on the ring increases the sensitivity to acid cleavage. Although monomer **1a** has also phenyl phosphonate group, it is not as sensitive to cleavage, probably due to its more hydrophobic structure.

The synthesis of monomer **3a** involved the reaction of (2-hydroxyphenyl) phosphonate with GMA in the presence of TEA at 85°C (Fig. 5). The ring opening reaction of the epoxides is not regiospecific. There are two possible sites for attack of alcohols, acids, and anhydrides.[29–31] If the attack occurs from the less hindered side the linear isomer is obtained otherwise the branched isomer or both isomers are produced. The crude product yield of our reaction was 87%, containing mostly the linear isomer with a very small amount of the branched isomer. When this mixture was subjected to a chromatographic separation on silica gel, fractions containing mixtures of isomers at different ratios were obtained. The ^{13}C-NMR spectrum of one of the fractions showed characteristic peaks for methyl carbons at 16.4 and 18.7 ppm, a tertiary carbon at 68.3 ppm, methylene carbons at 62.5, 72.8, and 65.2 ppm, aromatic carbons at 114.7, 117.0, 118.8, 121.5, 133.6, 134.8, 161.2 ppm, double bond carbons at 126.0 and 136.3 ppm, and a carbonyl carbon at 167.4 ppm (Fig. 6). The small peaks at 62.7 (CH_2), 66.3 (CH_2), and 70.2 (CH) ppm are due to the branched isomer. The FTIR spectrum of this fraction showed the presence of alcoholic OH bond at 3349 cm^{-1}, the characteristic ester C=O bond at 1715 cm^{-1}, the double bond at 1637 cm^{-1}, phosphonate group bonds at 1283, 1022, and 969 cm^{-1}. The ^{31}P-NMR spectrum showed a peak at 18.5 ppm. Monomer **3a** was soluble almost in all organic solvents such as ether, acetone, methanol, THF, and CH_2Cl_2 but it was insoluble in water (Table I).

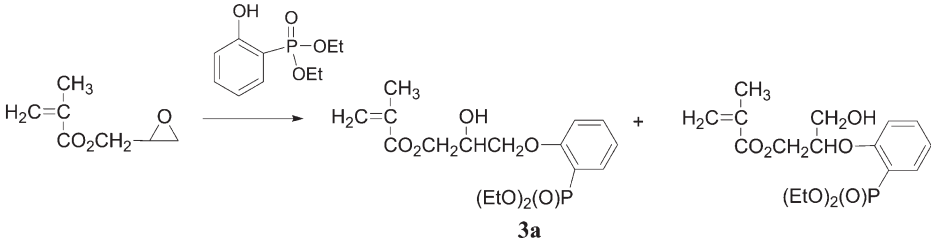

Figure 5 Synthesis of monomer **3a**.

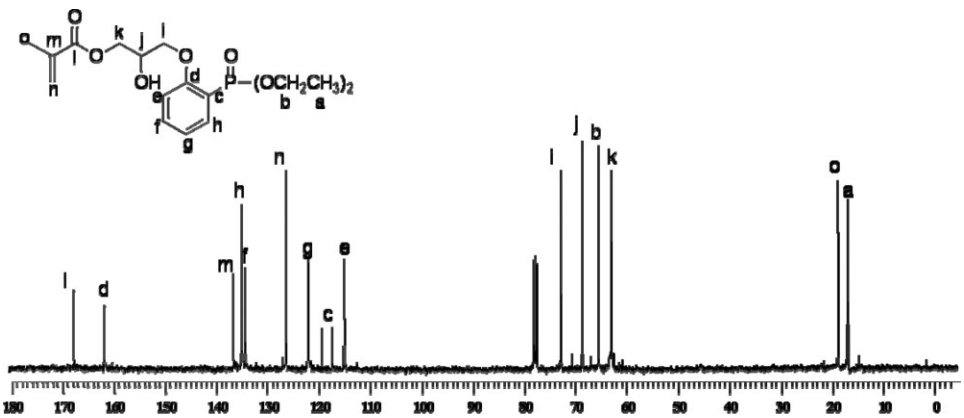

Figure 6 ^{13}C-NMR spectrum of monomer **3a**.

The attempted hydrolysis of monomer **3a** via TMSBr route under different conditions was unsuccessful. NMR spectrum of the product was too complicated to identify product(s) but did not show formation of the expected acid monomers. The ethyl peaks of the phosponate esters remained intact after the attempted reaction.

Photopolymerization

The polymerization behaviors of the monomers were investigated using photo-DSC. All the polymerizations were performed under identical conditions of initiator concentration (2.0 mol %), UV light intensity (20 mW/cm^2), and temperature (40°C).

First, the homopolymerization behavior of the synthesized monomers was investigated and compared with those of the commercial monomers such as Bis-GMA, 2-hydroxyethyl methacrylate (HEMA), and glycerol dimethacrylate (GDMA). The rate versus time and conversion versus time curves are shown in Figure 7 and polymerization results are also indicated at Table II.

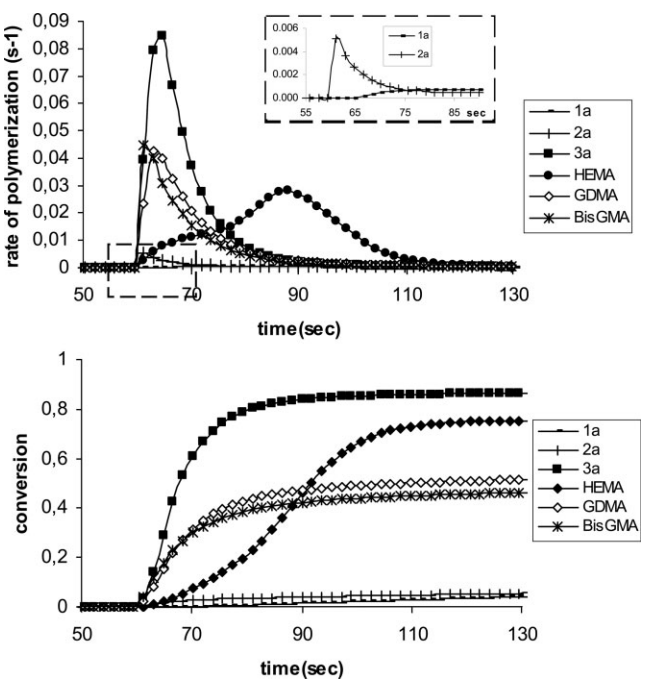

Figure 7 Rate of polymerizations and conversions of monomers **1a**, **2a**, **3a**, Bis-GMA, HEMA, and GDMA.

Monomer **1a** showed very low maximum rate of polymerization (0.00073 s^{-1}) and conversion (10.3%) (Figure 7, Table II). Monomer **2a** was more reactive than monomer **1a** with a maximum rate of polymerization of 0.0051 s^{-1} but it also gave very low conversion (11.8%). These monomers were less reactive than Bis-GMA, HEMA, and GDMA polymerized under the same conditions (Figure 7, Table II). We attributed this behavior to the presence of a bulky Bisphenol A and phenolic groups close to the double bond. Hydrolysis of the ethyl groups of these monomers (to produce monomers **1b** and **2b**) was expected to result in increased reactivity. However, monomer **1b** did not polymerize at all. This may be due to residual (2-hydroxyphenyl) phosphonic acid present due to ester cleavage reaction during TMSBr hydrolysis, which may act as a polymerization inhibitor. Photopolymerization of **2b** was not tried due to the same reason.

TABLE II
Photopolymerization Results

Monomer	R_p (s^{-1})	Conversion (%)
1a	0.00073	10.3
2a	0.0051	11.8
3a	0.084	87.2
HEMA	0.028	84.2
GDMA	0.043	57.2
Bis-GMA	0.044	51.6
Bis-GMA : **1a** (90 : 10)	0.035	69.2
Bis-GMA : **1b** (90 : 10)	0.010	44.1
Bis-GMA : **1b** (90 : 10)[a]	0.017	51.4
Bis-GMA : **2a** (90 : 10)	0.033	69.4
Bis-GMA : **3a** (90 : 10)	0.068	80.5

[a] Initiator: BAPO

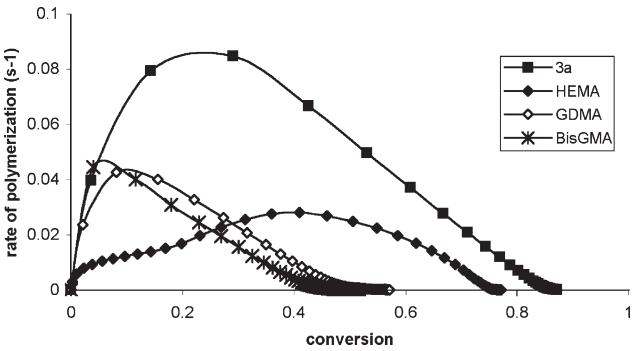

Figure 8 Rate of polymerization as a function of conversion for **3a**, Bis-GMA, HEMA, and GDMA.

Monomer **3a** showed much higher maximum rate of polymerization (0.084 s^{-1}) and conversion (87.2%) than monomers **1a** and **2a**. Unexpectedly, this monomer which is a monomethacrylate is more reactive than the dimethacrylate monomers, Bis-GMA, and GDMA. Figure 8 shows rate of polymerization as a function of conversion for Bis-GMA, HEMA, GDMA, and **3a**. During the polymerization of multifunctional monomers, such as Bis-GMA, the immediate autoacceleration caused by diffusion controlled termination in crosslinked systems is observed. After the polymerization reaches its maximum rate autodeceleration begins and then polymerization stops. It is known that as the flexibility of the monomer is increased, the maximum rate of polymerization decreases while the conversion at maximum rate of polymerization and total conversion increase. Figure 8 shows that autoacceleration for monomer **3a** begins at lower conversions similar to dimethacrylate systems but maximum rate of polymerization was observed at higher conversions unlike dimethacrylates but similar to monomethacrylates. The reason for this high rate of polymerization and conversion may be attributed to hydrogen bonding capability and flexibility of this monomer. Although this monomer has a rigid phenolic structure, this is far from the double bond. Our earlier studies on similar monomers indicated that hydrogen abstraction reaction from labile hydrogens lead to high rate of polymerization and crosslinked polymer formation (Fig. 9).[32] To see crosslinking tendency of monomer **3a,** we studied its bulk and solution polymerization (next section). Also, the photopolymerization reactivity of monomer **3a** was compared with the previously synthesized monomers with the maximum rate of polymerizations of 0.064 s^{-1} for monomer C and 0.025 s^{-1} for monomer D. The difference in polymerization rates of monomers shown in Figure 9 was attributed to the larger the dipole moment of the more reactive monomer. The dipole moment of monomer **3a** was found to have a higher value (4.69) than two of the monomers. Therefore, the reactivity of monomer **3a** was also expected to have higher than these monomers. Actually, monomer **3a** was found to be more reactive than either of the two. This suggests that the dipole moment may be one of the factors determining the reactivity of monomers.

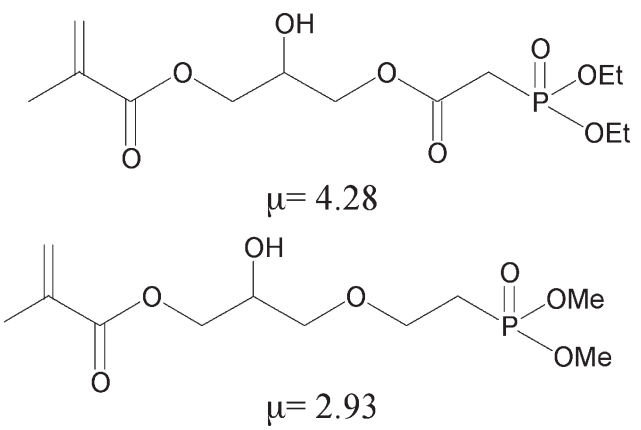

Figure 9 Structures and calculated dipole moments of the phosphonated monomers from the previous work.

We also investigated copolymerization behavior of our monomers with Bis-GMA (Fig. 10). Monomers **1a**, **1b**, **2a,** and **3a** (10 mol%) were added to Bis-

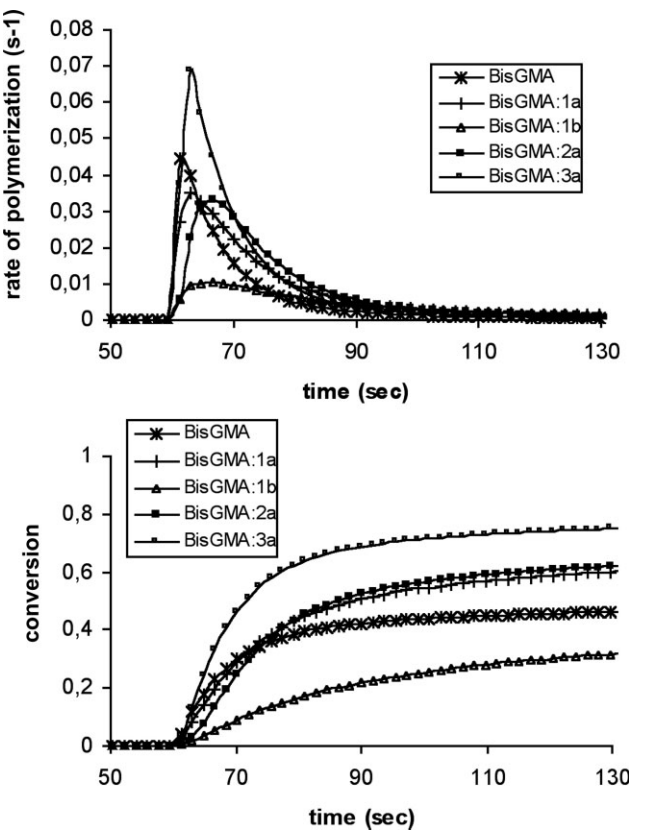

Figure 10 Rate of polymerization and conversions of Bis-GMA, Bis-GMA : **1a**, Bis-GMA : **1b**, Bis-GMA : **2a**, and Bis-GMA : **3a**.

TABLE III
Bulk and Solution Polymerization Results of Monomer 3a

[M]	[I] (10^{-2})	Solvent	Time (min)	Yield (%)
[a]	[b]	–	<25	Crosslinked
3.0	1.0[c]	Water	15	Crosslinked
1.0	1.0[c]	Water	40	Crosslinked

[a] Bulk polymerization.
[b] Amount of initiator (AIBN) was 3.0 wt % of the monomer.
[c] V-50.

GMA and clear solutions were obtained. It was observed that addition of monomers except monomer **3a** to Bis-GMA decreased rate of polymerization of Bis-GMA (Table II). However, conversions were improved by the addition of 10 mol % of monomers **1a**, **2a,** and **3a** to Bis-GMA. These higher conversions were probably due to a decrease in viscosity of Bis-GMA. Bis-GMA : monomer **1b** mixture gave the lowest rate of polymerization and conversion using DMPA (2 mol %), which were slightly improved by using a different initiator, BAPO (1 mol %).

Bulk and solution polymerization

Bulk and solution polymerizations of monomer **3a** were carried out with AIBN and V-50 at 60°C (Table III). This monomer polymerized very fast to give crosslinked polymers, as indicated by its swelling but not dissolving in various solvents.

Generally, polyphosphonates and polyphosphates are known as flame retardants.[33,34] During the combustion, poly(phosphoric acid) forms and catalyzes the formation of char to protect the surface from further burning.[35] The thermal stability of crosslinked poly-**3a** (residual monomer was removed by several washings with methylene chloride) was investigated by TGA under nitrogen (Fig. 11). The spectrum showed degradation starting around 275°C mainly due to ester thermolysis. The char residue of this polymer was 30% at 550°C and comparable with other phosphonate monomers synthesized by us with similar structures (32). The formation of char indicates a condensed phase mechanism for flame retardance.

Acidity and interactions with HAP of monomer 1b

The phosphonate monomers (**1a** and **2a**) do not dissolve in water, and monomer **2b** is unstable as discussed above. However, the aqueous solution of monomer **1b** (1 wt % in water) was acidic with pH value of 2.37. This value was higher than pH of 1 wt % aqueous phosphoric acid solution (pH = 1.17) but in the range of acidity expected from a mild self-etching dental adhesive monomer (pH around 2.0). The addition of 30-mg HAP, a model compound for dentin and enamel, to the solutions of monomer **1b** resulted in an increase in the pH value from 2.37 to 4.59.

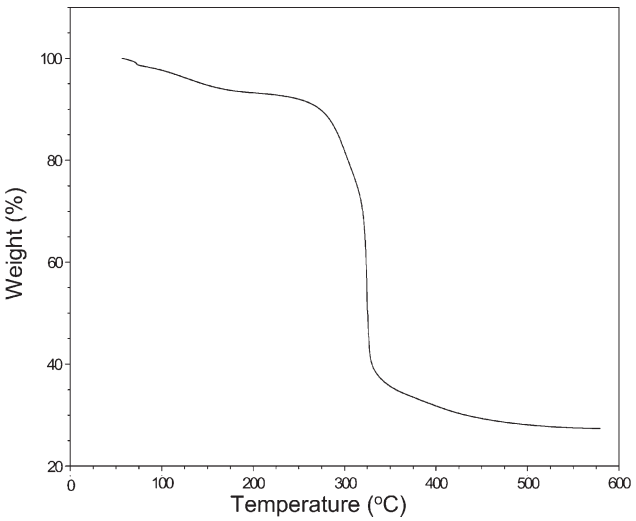

Figure 11 TGA thermogram of poly-**3a**.

The interaction of monomer **1b** with HAP was investigated using FTIR spectrometer (Fig. 12). The monomer **1b** showed OH peak of POOH at around 2500–2000 cm^{-1}, the C=O and P=O stretching vibrations are at ~ 1700 and ~ 1260 cm^{-1}. The C—O stretching bands are at ~ 1290 whereas P—O stretching bands are at ~ 1000 and ~ 925 cm^{-1}, respectively.

HAP spectrum showed surface PO—H groups at ~ 3690 cm^{-1}, sharp OH peak from lattice of HAP at 3570 cm^{-1}, symmetric and antisymmetric P—O stretching modes between 1200 and 900 cm^{-1}, and antisymmetric P—O bending modes in the 700–500 cm^{-1} region.[36]

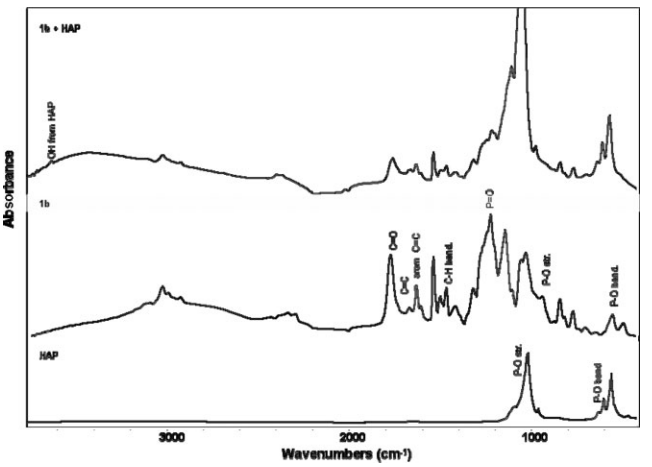

Figure 12 FTIR spectra of HAP, monomer **1b** without HAP and 30 mg HAP added.

After mixing with HAP, P=O ($\sim$ 1260 cm^{-1}) and P—O ($\sim$ 1000 and $\sim$ 925 cm^{-1}) stretching vibrations present in the pure monomer showed a sharp decrease in intensity, which is an indication of an interaction between the phosphonic acid functional groups in the monomer and the calcium ions of the HAP. Analysis of the P—O stretching region around 1000–1100 cm^{-1} is complicated due to strong absorbance of the HAP matrix.

D'Andrea and Fadeev proposed that the reduction in the sharp peak at 3570 cm^{-1} (OH from the lattice of HAP) was due to changes in the crystalline structure and bulk modification of the HAP matrix.[37] In the monomer **1b**–HAP mixture, this band remained unchanged at 3558 cm^{-1} (Fig. 12). This indicates that monomer **1b** was adsorbed on the HAP surface via probably formation of a surface complex or hydrogen bonding. In dentistry, although some acids are used to demineralize HAP, some other acids are used to adhere or bind to human calcified tissues.[38] We may say that monomer **1b** is of the second class.

CONCLUSIONS

New monomers containing phenyl phosphonate and phenyl phosphonic acid groups have been synthesized. During the hydrolysis of phosphonate groups via TMSBr route it was observed that phenyl ester linkages are also prone to hydrolysis. The interaction of one of the phosphonic acid monomer with HAP is observed with FTIR technique. The novel monofunctional (meth)acrylate synthesized from GMA homo and copolymerize rapidly to give crosslinked polymers. This monomer can be used as reactive diluents for Bis-GMA and improve the cure efficiency, material properties, and binding ability of dental composites.

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