Synthesis and Photopolymerization of Phosphonic Acid Monomers for Applications in Compomer Materials

Yohann Catel, Loïc Le Pluart, Pierre-Jean Madec, Thi-Nhàn Pham

Laboratoire de Chimie Moléculaire et Thio-organique, ENSICAEN, Université de Caen Basse-Normandie, CNRS; 6 boulevard du Maréchal Juin, 14050 Caen, France

Received 17 March 2009; accepted 9 June 2009
DOI 10.1002/app.30952
Published online 27 April 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Novel methacrylate monomers bearing phosphonic acid groups **1** and **2** as well as new sulfur methacrylates **9** and **10** have been prepared in good yields from thiophenol. They have been fully characterized by ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR, and HRMS. Their copolymerization with a bis-GMA : TEGDMA (1 : 1) blend has been investigated with photodifferential scanning calorimetry at 50°C with camphorquinone as a photoinitiator and ethyl 4-(dimethylamino)benzoate (EDAB) as a coinitiator. The higher the content of acidic monomer **1** or **2** incorporated in the bis-GMA : TEGDMA (1 : 1) blend, the lower the mixtures reactivity. The phosphonic acid group has been proved to be responsible for this drop of reactivity. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2676–2687, 2010

Key words: dental polymers; monomers; phosphonic acid; photopolymerization; synthesis

INTRODUCTION

Compomers were introduced in the early 1990s to combine the advantageous properties of both dental composites (aesthetics, mechanical properties) and glass-ionomer cements (fluorine release).[1–4] The compomers composition is very close to that of composites. Indeed, compomers contain bulky monomers (e.g., bis-GMA, UDMA), viscosity-reducing diluents (e.g., TEGDMA) as well as nonreactive inorganic powders (quartz or other silicates).[1–4] Their polymerization is generally light-induced. Camphorquinone (CQ) combined with an aromatic tertiary amine is the most widely used initiating system.[5] Although compomers are very close to dental composites, they also contain specific components: an acidic monomer as well as an acid leachable fluoroaluminosilicate glass are added.[1–4] After polymerization, the material progressively absorbs small amounts of water. This absorption triggers a moderate acid–base reaction between the acidic monomer and the fluoroaluminosilicate glass resulting in a fluoride release.[6]

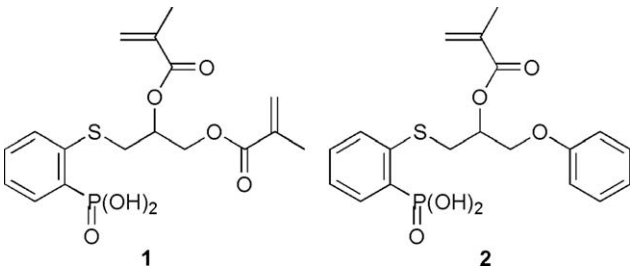
Despite this advantage, some concerns have been raised concerning the use of compomers. Indeed, it has been demonstrated that compomers generally exhibit lower mechanical properties (resistance to wear,[7] compressive strength,[4,8] flexural strength,[4,7] fracture toughness,[9] etc.) than the corresponding composite materials. According to Mou et al.,[10] this drop of mechanical properties could be partly attributed to the structure of the incorporated acidic monomers. Indeed, most of these monomers are aliphatic carboxylic acids and are not structurally analogous with the aromatic methacrylates commonly added in dental composites.[11] To address this problem, Mou et al.[10] suggested that the use of aromatic acidic monomers, structurally similar to the methacrylates incorporated in dental composites, should lead to materials exhibiting greater mechanical properties. Therefore, they prepared a new crosslinking methacrylate, similar to bis-GMA, bearing two phosphonic acid groups on the aromatic rings. Although the monomer preparation was reported, its polymerization behavior was barely described.[12] Moreover, this monomer exhibited a lower reactivity in free radical polymerization than bis-GMA.[12] This was attributed to a deactivation effect of the phosphonic acid groups. Outside this work, very few articles are dealing with the preparation of new aromatic acidic monomers for dental applications.[13–17] Therefore, there is a real need for the synthesis of such derivatives.

A few years ago, our group synthesized methacrylates bearing phosphonate groups for potential applications in dental materials.[18] These monomers were prepared according to a lithiation-rearrangement reaction previously developed in the laboratory.[19–20]

As an extension of this work, we would like to report in this article, the preparation and the photopolymerization of the new aromatic sulfur

Correspondence to: L. Le Pluart (loic.le-pluart@ensicaen.fr).

Contract grant sponsors: Ministère de la Recherche et des Nouvelles Technologies, Centre National de la Recherche Scientifique (CNRS), Région Basse-Normandie, European Union (FEDER Funding).



1 2

Figure 1 Structure of acidic monomers **1** and **2**.

phosphonic acids **1** and **2** for application in dental materials (Fig. 1). Phosphonic acid group being well known to favor adhesion of a restorative material to the dental tissues,[21] using of acidic monomers **1** and **2** in compomers formulation could improve both biocompatibility and adhesive properties of these materials.

EXPERIMENTAL

Materials

All reactions were carried out under a dry nitrogen atmosphere in oven-dried glassware. Triethylamine was distilled over calcium hydride before use. Unless stated otherwise, all reagents were purchased from Sigma-Aldrich and were used without further purification. Diisopropyl 2-sulfanylphenylphosphonate **4**[18] and 1-thiophenyl-3-phenoxypropan-2-ol[22] were prepared according to the literature. Dichloromethane was purified with a PURESOLVTM apparatus developed by Innovative Technology. Column chromatography was performed on Merck silica gel Si 60 (40–63 μm). Thin layer chromatography (TLC) was performed on silica gel 60 F-254 plates.

Measurements

^{1}H-NMR, ^{13}C-NMR, and ^{31}P-NMR spectra were recorded on Bruker DPX 250 (250 MHz) or AC 400 (400 MHz) spectrometers with TMS as internal reference for ^{1}H-NMR, ^{13}C-NMR chemical shifts and with H_3PO_4 (85%) as external reference for ^{31}P-NMR chemical shifts. Data are given in the following order: chemical shift in ppm, multiplicity (s, singlet; d doublet; t, triplet; and m, multiplet), coupling constant in Hertz, assignment broad band ^{1}H decoupling.

FTIR absorption spectra were recorded on a PerkinElmer Spectrum One FTIR Spectrometer with an ATR accessory. The mentioned IR absorptions are observed as strong bands in cm^{-1}.

High-resolution mass spectra (HRMS) were obtained with a Waters Q-TOF Micro instrument in electrospray ionization positive (ES+) or negative (ES−) mode and lockspray with orthophosphoric acid. These analyses have been performed with an infusion introduction of 10 μL min^{-1}, a source temperature of 80°C, a desolvation temperature of 120°C and an external calibration with NaI.

Syntheses

Diisopropyl 2-(2,3-dihydroxypropanylsulfanyl) phenylphosphonate (5)

Glycidol (1.9 mL, 28.6 mmol) was added to a solution of diisopropyl 2-sulfanylphenylphosphonate **4** (7.1 g, 25.8 mmol) and potassium carbonate (0.18 g, 1.3 mmol) in anhydrous dichloromethane (40 mL). The solution was refluxed for 3 h and the solvent was evaporated. Distilled water (10 mL) was added and the solution was extracted with ethyl acetate. The combined extracts were dried over anhydrous magnesium sulfate and the solvent was evaporated. The crude product was purified by flash column chromatography providing phosphonate **5** (293 mg, 0.61 mmol) as a yellow oil.

Yield: 79%. Column chromatography: Eluent = methanol/ethyl acetate: 3/97. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 1.37 (d, $^{3}J_{HH}$ = 6.2 Hz, 3H, POCHCH_3), 1.39 (d, $^{3}J_{HH}$ = 6.2 Hz, 3H, POCHCH_3), 1.42 (d, $^{3}J_{HH}$ = 6.2 Hz, 3H, POCHCH_3), 1.43 (d, $^{3}J_{HH}$ = 6.2 Hz, 3H, POCHCH_3), 2.25–2.40 (s, 1H, OH), 2.84 (dd, $^{2}J_{HH}$ = 13.7 Hz, $^{3}J_{HH}$ = 9.5 Hz, 1H, SCH_2), 3.16 (dd, $^{2}J_{HH}$ = 13.7 Hz, $^{3}J_{HH}$ = 2.4 Hz, 1H, SCH_2), 3.30–3.70 (m, 3H, CHOH and CH_2OH), 4.75–5.00 (m, 2H, PO$CH$$CH_3$), 5.75–5.90 (m, 1H, OH), 7.29–7.40 (m, 1H, CHarom), 7.43–7.54 (m, 1H, CHarom), 7.60–7.72 (m, 1H, CHarom), 7.82 (ddd, $^{3}J_{HP}$ = 13.7 Hz, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, CHarom). ^{13}C-NMR (101 MHz, $CDCl_3$, δ): 23.8 (d, $^{3}J_{CP}$ = 5.8 Hz, POCHCH_3), 23.9 (d, $^{3}J_{CP}$ = 5.0 Hz, POCHCH_3), 24.1 (d, $^{3}J_{CP}$ = 3.3 Hz, POCHCH_3), 24.2 (d, $^{3}J_{CP}$ = 3.8 Hz, POCHCH_3), 42.1 (s, SCH_2), 65.6 (s, CH_2OH), 68.8 (s, CHOH), 71.6 (d, $^{2}J_{CP}$ = 6.5 Hz, PO$CH$$CH_3$), 71.8 (d, $^{2}J_{CP}$ = 6.5 Hz, PO$CH$$CH_3$), 127.6 (d, $^{3}J_{CP}$ = 14.0 Hz, CHarom), 133.1 (d, $^{4}J_{CP}$ = 2.6 Hz, CHarom), 133.7 (d, $^{2}J_{CP}$ = 8.5 Hz, CHarom), 134.2 (d, $^{1}J_{CP}$ = 196.2 Hz, Carom), 135.7 (d, $^{3}J_{CP}$ = 13.2 Hz, CHarom), 138.2 (d, $^{2}J_{CP}$ = 9.0 Hz, Carom). ^{31}P-NMR (162 MHz, $CDCl_3$, δ): 14.5. FTIR (ATR, cm^{-1}): 3360 (O—H), 1580, 1560, 1451, 1426 (C=C arom), 1220 (P=O), 980 (P—O). HRMS (m/z): calcd for $C_{15}H_{25}O_5PS$, 349.1239; found, 349.1232 $[M + H]^+$.

Diisopropyl 2-(2,3-dimethacryloyloxypropylsulfanyl) phenylphosphonate (6)

Methacrylic anhydride (0.32 mL, 2.15 mmol) was added dropwise, under stirring, to a solution of phosphonate **5** (250 mg, 0.72 mmol), triethylamine (0.30 mL, 2.15 mmol), and 4-dimethylaminopyridine (DMAP, 7 mg, 0.06 mmol) in anhydrous dichloromethane (3 mL). After stirring for 6 h, the solution was

washed with distilled water (3 × 3 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated. The crude product was purified by flash column chromatography to give phosphonate **6** (293 mg, 0.61 mmol) as a yellow oil.

Yield: 84%. Column chromatography: Eluent = ethyl acetate/pentane: 1/1. ^{1}H-NMR (250 MHz, $CDCl_3$, δ): 1.19 (d, $^{3}J_{HH}$ = 6.2 Hz, 6H, POCHCH_3), 1.31 (d, $^{3}J_{HH}$ = 6.4 Hz, 6H, POCHCH_3), 1.83 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 3.19 (dd, $^{2}J_{HH}$ = 14.0 Hz, $^{3}J_{HH}$ = 7.4 Hz, 1H, SCH_2), 3.30 (dd, $^{2}J_{HH}$ = 14.0 Hz, $^{3}J_{HH}$ = 5.8 Hz, 1H, SCH_2), 4.34 (dd, $^{2}J_{HH}$ = 12.0 Hz, $^{3}J_{HH}$ = 5.5 Hz, 1H, CH_2O), 4.44 (dd, $^{2}J_{HH}$ = 12.0 Hz, $^{3}J_{HH}$ = 3.6 Hz, 1H, CH_2O), 4.57–4.78 (m, 2H, PO*C*HCH_3), 5.17–5.28 (m, 1H, *C*HOH), 5.46–5.51 (m, 2H, C=CH_2), 5.99 (s, 1H, C=CH_2), 6.05 (s, 1H, C=CH_2), 7.13–7.22 (m, 1H, CHarom), 7.35–7.43 (m, 1H, CHarom), 7.43–7.57 (m, 1H, CHarom), 7.89 (ddd, $^{3}J_{HP}$ = 13.7 Hz, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, CHarom). ^{13}C-NMR (63 MHz, $CDCl_3$, δ): 18.5 (s, CH_3), 18.6 (s, CH_3), 24.1 (d, $^{3}J_{CP}$ = 4.8 Hz, POCHCH_3), 24.2 (d, $^{3}J_{CP}$ = 4.9 Hz, POCHCH_3), 24.4 (d, $^{3}J_{CP}$ = 4.0 Hz, POCHCH_3), 24.5 (d, $^{3}J_{CP}$ = 4.0 Hz, POCHCH_3), 34.0 (s, SCH_2), 64.0 (s, CH_2O), 70.9 (s, *C*HOH), 71.5 (d, $^{2}J_{CP}$ = 5.7 Hz, POCHCH_3), 71.6 (d, $^{2}J_{CP}$ = 5.9 Hz, POCHCH_3), 125.9 (d, $^{3}J_{CP}$ = 14.5 Hz, *C*Harom), 126.4 (s, C=*C*H_2), 126.7 (s, C=*C*H_2), 129.6 (d, $^{3}J_{CP}$ = 12.6 Hz, *C*Harom), 130.3 (d, $^{1}J_{CP}$ = 190.0 Hz, *C*arom), 132.9 (d, $^{4}J_{CP}$ = 2.5 Hz, *C*Harom), 135.3 (d, $^{2}J_{CP}$ = 9.4 Hz, *C*Harom), 136.1 (s, *C*=CH_2), 136.2 (s, *C*=CH_2), 139.8 (d, $^{2}J_{CP}$ = 7.5 Hz, *C*arom), 166.8 (s, C=O), 167.0 (s, C=O). ^{31}P-NMR (101 MHz, $CDCl_3$, δ): 14.5. FTIR (ATR, cm^{-1}): 1718 (C=O), 1637 (C=C), 1579, 1560, 1452, 1427 (C=C arom), 1240 (P=O), 984 (P—O). HRMS (*m*/*z*): calcd for $C_{23}H_{33}O_7PS$, 485.1763; found, 485.1766 $[M + H]^+$.

2-(2,3-Dimethacryloyloxypropylsulfanyl) phenylphosphonic acid (1)

Trimethylsilyl bromide (TMSBr) (1.63 mL, 12.4 mmol) was added to a solution of dimethacrylate **6** (1.0 g, 2.1 mmol) in anhydrous dichloromethane (10 mL). After stirring for 24 h at room temperature, the mixture was concentrated under reduced pressure. Methanol (10 mL) was added and the mixture was stirred for 1 h at room temperature. The solvent was evaporated and the product was dried to a constant weight under vacuum.

Crude yield: 100%. Aspect: highly viscous yellow oil. ^{1}H-NMR (400 MHz, D_2O, δ): 1.68–1.69 (m, 3H, CH_3), 1.77–1.78 (m, 3H, CH_3), 3.34 (d, $^{3}J_{HH}$ = 6.4 Hz, SCH_2), 4.30 (dd, $^{2}J_{HH}$ = 12.1 Hz, $^{3}J_{HH}$ = 6.0 Hz, 1H, CH_2O), 4.55 (dd, $^{2}J_{HH}$ = 12.1 Hz, $^{3}J_{HH}$ = 3.6 Hz, 1H, CH_2O), 5.22–5.28 (m, 1H, *C*HOH), 5.51–5.53 (m, 1H, C=CH_2), 5.59–5.61 (m, 1H, C=CH_2), 5.83 (s, 1H, C=CH_2), 5.97 (s, 1H, C=CH_2), 7.21–7.27 (m, 1H, CHarom), 7.37–7.43 (m, 1H, CHarom), 7.52–7.58 (m, 1H, CHarom), 7.71 (ddd, $^{3}J_{HP}$ = 13.7 Hz, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, CHarom). ^{13}C-NMR (101 MHz, D_2O, δ): 17.3 (s, CH_3), 17.4 (s, CH_3), 34.6 (s, SCH_2), 64.0 (s, CH_2O), 71.3 (s, *C*HOH), 125.6 (s, C=*C*H_2), 125.8 (s, C=*C*H_2), 126.3 (d, $^{3}J_{CP}$ = 13.8 Hz, *C*Harom), 131.6 (d, $^{3}J_{CP}$ = 12.3 Hz, *C*Harom), 132.4 (d, $^{4}J_{CP}$ = 2.1 Hz, *C*Harom), 133.0 (d, $^{1}J_{CP}$ = 194.0 Hz, *C*arom), 133.6 (d, $^{2}J_{CP}$ = 9.2 Hz, *C*Harom), 136.3 (s, *C*=CH_2), 136.4 (s, *C*=CH_2), 139.3 (d, $^{2}J_{CP}$ = 8.2 Hz, *C*arom), 166.9 (s, C=O), 167.2 (s, C=O). ^{31}P-NMR (162 MHz, CD_3OD, δ): 13.9. HRMS (*m*/*z*): calcd for $C_{17}H_{21}O_7PS$, 399.0651; found, 399.0667 $[M - H]^-$.

Diisopropyl 2-(2-hydroxy-3-phenoxypropylsulfanyl) phenylphosphonate (7)

Phenyl glycidyl ether (2.2 mL, 16.4 mmol) was added to a solution of diisopropyl 2-sulfanylphenylphosphonate **4** (4.5 g, 16.4 mmol) and potassium carbonate (110 mg, 0.82 mmol). The solution was stirred for 15 h at 30°C. Ethyl acetate (25 mL) was added and the solution was washed with distilled water (10 mL). The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated. The crude product was purified by flash column chromatography providing phosphonate **7** (5.9 g, 13.9 mmol) as a yellow oil.

Yield: 85%. Column chromatography: Eluent = ethyl acetate/pentane: 3/7. ^{1}H-NMR (250 MHz, $CDCl_3$, δ): 1.26–1.37 (m, 12H, POCHCH_3), 2.95 (dd, $^{2}J_{HH}$ = 14.0 Hz, $^{3}J_{HH}$ = 8.3 Hz, 1H, SCH_2), 3.31 (dd, $^{2}J_{HH}$ = 14.0 Hz, $^{3}J_{HH}$ = 2.4 Hz, 1H, SCH_2), 3.77–4.05 (m, 3H, *C*HOH and CH_2O), 4.75–4.88 (m, 2H, PO*C*HCH_3), 5.53–5.60 (massif, 1H, OH), 6.78 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, CHarom), 6.83 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, CHarom), 7.10–7.28 (m, 3H, H_5, CHarom), 7.32–7.44 (m, 1H, CHarom), 7.55–7.63 (m, 1H, CHarom), 7.74 (ddd, $^{3}J_{HP}$ = 13.7 Hz, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, CHarom). ^{13}C-NMR (63 MHz, $CDCl_3$, δ): 24.2 (d, $^{3}J_{CP}$ = 5.2 Hz, POCHCH_3), 24.3 (d, $^{3}J_{CP}$ = 4.6 Hz, POCHCH_3), 24.5 (d, $^{3}J_{CP}$ = 3.5 Hz, POCHCH_3), 24.6 (d, $^{3}J_{CP}$ = 3.8 Hz, POCHCH_3), 43.0 (s, SCH_2), 67.8 (s, *C*HOH), 70.7 (s, CH_2O), 71.9 (d, $^{2}J_{CP}$ = 6.5 Hz, POCHCH_3), 71.8 (d, $^{2}J_{CP}$ = 6.6 Hz, POCHCH_3), 114.9 (s, *C*Harom), 121.2 (s, *C*Harom), 127.6 (d, $^{3}J_{CP}$ = 13.8 Hz, *C*Harom), 129.8 (s, *C*Harom), 133.1 (d, $^{4}J_{CP}$ = 3.1 Hz, *C*Harom), 133.7 (d, $^{2}J_{CP}$ = 8.8 Hz, *C*Harom), 134.1 (d, $^{1}J_{CP}$ = 195.6 Hz, *C*arom), 135.6 (d, $^{3}J_{CP}$ = 13.2 Hz, *C*Harom), 139.4 (d, $^{2}J_{CP}$ = 8.8 Hz, *C*arom), 159.0 (s, *C*Harom). ^{31}P-NMR (102 MHz, $CDCl_3$, δ): 14.7. FTIR (ATR, cm^{-1}): 3337 (O—H), 1599, 1587, 1560, 1496, 1452, 1427 (C=C arom), 1241 (P=O), 984 (P—O). HRMS (*m*/*z*): calcd for $C_{21}H_{29}O_5PS$, 425.1528; found, 425.1538 $[M + H]^+$.

Diisopropyl 2-(2-methacryloyloxy-3-phenoxypropylsulfanyl)phenylphosphonate (8)

Methacrylic anhydride (1.32 mL, 8.8 mmol) was added dropwise, under stirring, to a solution of hydroxyphosphonate **7** (2.5 g, 5.9 mmol), triethylamine (1.23 mL, 8.8 mmol) and DMAP (58 mg, 0.47 mmol) in anhydrous dichloromethane (15 mL). After stirring for 6 h, the solution was washed with distilled water (3 × 5 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated. The crude product was purified by flash column chromatography providing phosphonate **8** (2.5 g, 5.1 mmol) as a yellow oil.

Yield: 87%. Column chromatography: Eluent = ethyl acetate/pentane: 2/3. ^{1}H-NMR (250 MHz, $CDCl_3$, δ): 1.17 (d, $^{3}J_{HH}$ = 6.4 Hz, 6H, POCHC*H*$_3$), 1.29 (d, $^{3}J_{HH}$ = 6.2 Hz, 3H, POCHC*H*$_3$), 1.30 (d, $^{3}J_{HH}$ = 6.2 Hz, 3H, POCHC*H*$_3$), 1.85 (s, 3H, CH_3), 3.36 (d, $^{3}J_{HH}$ = 7.4 Hz, 2H, SCH_2), 4.17 (dd, $^{2}J_{HH}$ = 10.5 Hz, 1H, CH_2O), 4.25 (dd, $^{2}J_{HH}$ = 10.5 Hz, 1H, CH_2O), 4.62–4.80 (m, 2H, POC*H*CH$_3$), 5.25–5.35 (m, 1H, *CH*OH), 5.49 (sl, 1H, C=CH_2), 6.01 (s, 1H, C=CH_2), 6.79 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, CHarom), 6.88 (t, $^{3}J_{HH}$ = 6.9 Hz, 1H, CHarom), 7.11–7.23 (m, 3H, CHarom), 7.32–7.40 (m, 1H, CHarom), 7.47–7.53 (m, 1H, CHarom), 7.88 (ddd, $^{3}J_{HP}$ = 13.7 Hz, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, CHarom). ^{13}C-NMR (101 MHz, $CDCl_3$, δ): 18.6 (s, CH_3), 24.2 (d, $^{3}J_{CP}$ = 5.2 Hz, POCHCH$_3$), 24.3 (d, $^{3}J_{CP}$ = 5.0 Hz, POCHCH$_3$), 24.5 (d, $^{3}J_{CP}$ = 3.5 Hz, POCHCH$_3$), 24.6 (d, $^{3}J_{CP}$ = 3.8 Hz, POCHCH$_3$), 33.8 (s, SCH_2), 67.5 (s, *C*HOH), 71.5 (d, $^{2}J_{CP}$ = 6.5 Hz, POCHCH$_3$), 71.6 (d, $^{2}J_{CP}$ = 6.5 Hz, POCHCH$_3$), 71.8 (s, CH_2O), 115.1 (s, *C*Harom), 121.6 (s, *C*Harom), 125.6 (d, $^{3}J_{CP}$ = 14.1 Hz, *C*Harom), 126.9 (s, C=*C*H$_2$), 129.1 (d, $^{3}J_{CP}$ = 12.8 Hz, *C*Harom), 129.8 (d, $^{1}J_{CP}$ = 189.6 Hz, *C*arom), 129.9 (s, *C*Harom), 132.9 (d, $^{4}J_{CP}$ = 2.7 Hz, *C*Harom), 135.4 (d, $^{2}J_{CP}$ = 9.1 Hz, *C*Harom), 136.2 (s, *C*=CH_2), 140.4 (d, $^{2}J_{CP}$ = 7.8 Hz, *C*arom), 158.8 (s, *C*Harom), 167.1 (s, C=O). ^{31}P-NMR (101 MHz, $CDCl_3$, δ): 14.7. FTIR (ATR, cm^{-1}): 1716 (C=O), 1637 (C=C), 1599, 1588, 1560, 1496, 1452, 1426 (C=C arom), 1239 (P=O), 984 (P—O). HRMS (*m*/*z*): calcd for $C_{25}H_{33}O_6PS$, 493.1814; found, 493.1800 $[M + H]^+$.

2-(2-Methacryloyloxy-3-phenoxypropylsulfanyl) phenylphosphonic acid (2)

The preparation of **2** was carried out according to synthesis of **1**, from phosphonate **8** (2.49 g, 5.0 mmol) and TMSBr (4.0 mL, 30.0 mmol). Acidic monomer **2** (2.0 g, 4.9 mmol) was obtained as a light orange solid.

Yield: 97%. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 1.84–1.86 (m, 3H, CH_3), 3.33 (dd, $^{2}J_{HH}$ = 14.2 Hz, $^{3}J_{HH}$ = 6.2 Hz, 1H, SCH_2), 3.39 (dd, $^{2}J_{HH}$ = 14.2 Hz, $^{3}J_{HH}$ = 6.4 Hz, 1H, SCH_2), 4.16 (dd, $^{2}J_{HH}$ = 10.4 Hz, $^{3}J_{HH}$ = 4.0 Hz, 1H, CH_2O), 4.20 (dd, $^{2}J_{HH}$ = 10.4 Hz, $^{3}J_{HH}$ = 4.8 Hz, 1H, CH_2O), 5.28–5.37 (m, 1H, *CH*OH), 5.49–5.52 (m, 1H, C=CH_2), 6.00 (s, 1H, C=CH_2), 6.84 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, CHarom), 6.91 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, CHarom), 7.17–7.25 (m, 3H, CHarom), 7.39–7.46 (m, 1H, CHarom), 7.58–7.64 (m, 1H, CHarom), 7.93 (ddd, $^{3}J_{HP}$ = 13.7 Hz, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.2 Hz, 1H, CHarom), 9.62–9.75 (massif, 2H, POH). ^{13}C-NMR (101 MHz, $CDCl_3$, δ): 18.5 (s, CH_3), 35.7 (s, SCH_2), 67.6 (s, *C*HOH), 72.4 (s, CH_2O), 115.1 (s, *C*Harom), 121.5 (s, *C*Harom), 127.0 (d, $^{3}J_{CP}$ = 14.6 Hz, *C*Harom), 127.1 (s, C=*C*H$_2$), 129.8 (s, *C*Harom), 130.3 (d, $^{1}J_{CP}$ = 201.4 Hz, *C*arom), 132.6 (d, $^{3}J_{CP}$ = 13.1 Hz, *C*Harom), 133.4 (d, $^{4}J_{CP}$ = 2.5 Hz, *C*Harom), 134.4 (d, $^{2}J_{CP}$ = 9.3 Hz, *C*Harom), 136.0 (s, *C*=CH_2), 139.4 (d, $^{2}J_{CP}$ = 8.8 Hz, *C*arom), 158.7 (s, *C*Harom), 167.5 (s, C=O). ^{31}P-NMR (101 MHz, $CDCl_3$, δ): 20.0. HRMS (*m*/*z*): calcd for $C_{19}H_{21}O_6PS$, 409.0875; found, 409.0891 $[M + H]^+$.

3-Thiophenylpropane-1,2-diol (11)

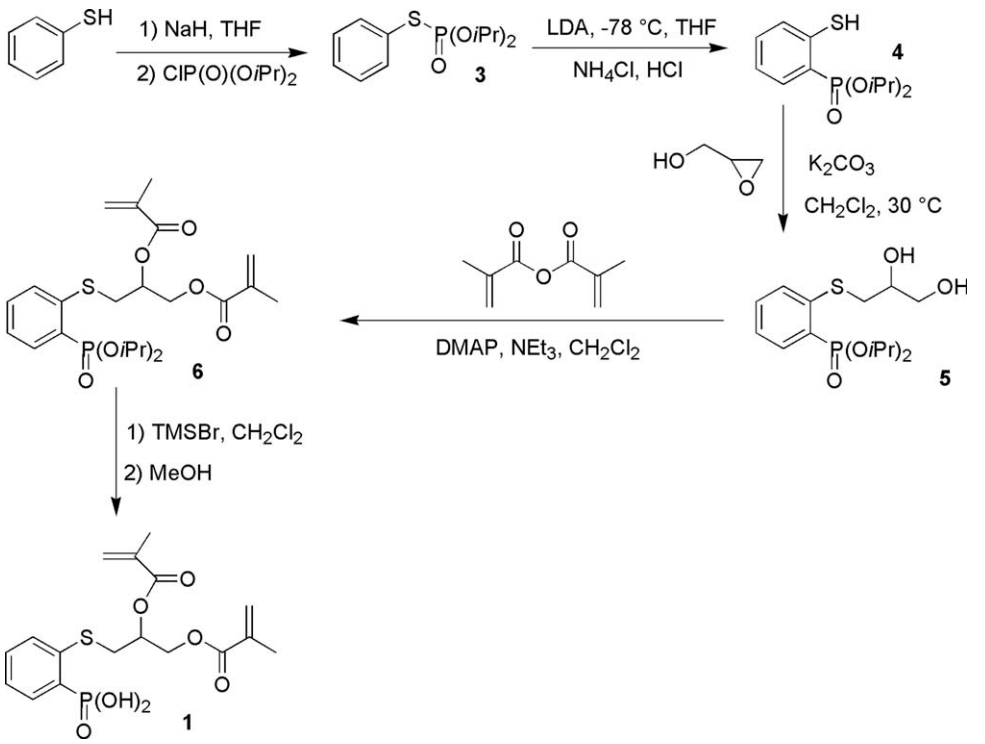
According to a different procedure,[23,24] glycidol (0.83 mL, 12.7 mmol) was added to a solution of thiophenol (1.39 g, 12.7 mmol) and potassium carbonate (84 mg, 0.61 mmol) in anhydrous dichloromethane (20 mL). The solution was stirred for 2 h and the solvent was evaporated. Distilled water (10 mL) was added and the solution was extracted with ethyl acetate. The combined extracts were dried over anhydrous magnesium sulfate and the solvent was evaporated. The crude product was purified by recrystallization in cyclohexane. Diol **11** (2.19 g, 11.9 mmol) was isolated as a white solid.

Yield: 94%. ^{1}H-NMR (250 MHz, $CDCl_3$, δ): 2.72–2.91 (m, 2H, OH), 2.97 (dd, $^{2}J_{HH}$ = 13.7 Hz, $^{3}J_{HH}$ = 7.8 Hz, 1H, SCH_2), 3.08 (dd, $^{2}J_{HH}$ = 13.7 Hz, $^{3}J_{HH}$ = 5.0 Hz, 1H, SCH_2), 3.56 (dd, $^{2}J_{HH}$ = 11.4 Hz, $^{3}J_{HH}$ = 5.8 Hz, 1H, *CH*$_2$OH), 3.73 (dd, $^{2}J_{HH}$ = 11.4 Hz, $^{3}J_{HH}$ = 3.2 Hz, 1H, *CH*$_2$OH), 3.73–3.83 (m, 1H, *CH*OH), 7.16–7.41 (m, 5H, CHarom). ^{13}C-NMR (63 MHz, $CDCl_3$, δ): 38.0 (SCH_2), 65.6 (CH_2OH), 70.4 (*C*HOH), 127.2 (*C*Harom), 129.6 (*C*Harom), 130.4 (*C*Harom), 135.4 (*C*arom).

2-Methacryloyloxy-3-thiophenylpropyl methacrylate (9)

The preparation of 9 was carried out according to synthesis of 6, from 3-thiophenylpropane-1,2-diol (660 mg, 3.58 mmol), methacrylic anhydride (1.6 mL, 10.7 mmol), triethylamine (1.50 mL, 10.7 mmol), and DMAP (45 mg, 0.29 mmol). Dimethacrylate 9 (810 mg, 2.53 mmol) was obtained as a colorless liquid.

Yield: 71%. Column chromatography: Eluent = ethyl acetate/pentane: 5/95. ^{1}H-NMR (250 MHz,



Scheme 1 Synthesis of acidic monomer **1**.

$CDCl_3$, δ): 1.81 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 3.09 (dd, $^2J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, SCH_2), 3.19 (dd, $^2J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, SCH_2), 4.29 (dd, $^2J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, CH_2O), 4.38 (dd, $^2J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 3.8 Hz, 1H, CH_2O), 5.14–5.24 (m, 1H, *CH*OH), 5.46–5.52 (m, 2H, C=CH_2), 5.97 (s, 1H, C=CH_2), 6.00 (s, 1H, C=CH_2), 7.09–7.37 (m, 5H, CHarom). ^{13}C-NMR (63 MHz, $CDCl_3$, δ): 18.6 (CH_3), 18.7 (s, CH_3), 34.7 (SCH_2), 64.1 (CH_2O), 71.1 (*C*HOH), 126.5 (C=*C*H_2), 126.7 (C=*C*H_2), 127.2 (*C*Harom), 129.5 (*C*Harom), 130.4 (*C*Harom), 135.4 (*C*arom), 136.1 (*C*=CH_2), 136.2 (*C*=CH_2), 166.8 (C=O), 167.1 (C=O). FTIR (ATR, cm^{-1}): 1716 (C=O), 1637 (C=C), 1583, 1481, 1450, 1440 (C=C arom). HRMS (*m*/*z*): calcd for $C_{17}H_{20}O_4S$, 343.0980; found, 343.0998 $[M + Na]^+$.

1-Phenoxymethyl-2-thiophenylethyl methacrylate (10)

The preparation of 10 was carried out according to synthesis of 8, from 1-thiophenyl-3-phenoxypropan-2-ol (1.0 g, 3.8 mmol), methacrylic anhydride (0.86 mL, 5.8 mmol), triethylamine (0.80 mL, 5.8 mmol), and DMAP (48 mg, 0.31 mmol). Methacrylate 10 (1.0 g, 3.0 mmol) was obtained as a colorless liquid.

Yield: 80%. Column chromatography: Eluent = ethyl acetate/pentane: 5/95. ^{1}H-NMR (250 MHz, $CDCl_3$, δ): 1.81 (s, 3H, CH_3), 3.27 (d, $^3J_{HH}$ = 6.4 Hz, 1H, SCH_2), 4.10 (dd, $^2J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 4.4 Hz, 1H, CH_2O), 4.16 (dd, $^2J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 4.7 Hz, 1H, CH_2O), 5.20–5.29 (m, 1H, *CH*OH), 5.45 (s, 1H, C=CH_2), 5.97 (s, 1H, C=CH_2), 6.76–6.91 (m, 3H, CHarom), 7.05–7.23 (m, 5H, CHarom), 7.29–7.37 (m, 2H, CHarom). ^{13}C-NMR (63 MHz, $CDCl_3$, δ): 18.6 (s, CH_3), 34.4 (SCH_2), 67.5 (CH_2O), 71.9 (CHOH), 115.1 (*C*Harom), 121.6 (*C*Harom), 126.8 (C=CH_2), 126.9 (*C*Harom), 129.5 (*C*Harom), 129.9 (*C*Harom), 130.0 (*C*Harom), 135.8 (*C*arom), 136.2 (*C*=CH_2), 158.8 (*C*Harom), 167.1 (C=O). FTIR (ATR, cm^{-1}): 1715 (C=O), 1637 (C=C), 1599, 1588, 1496, 1482, 1452, 1440 (C=C arom). HRMS (*m*/*z*): calcd for $C_{19}H_{20}O_3S$, 351.1031; found, 351.1032 $[M + H]^+$.

Photopolymerization procedure

Photopolymerizations were carried out on a Perkin-Elmer DSC 7 calorimeter. Resins were formulated and methylene chloride solutions of photoinitiator [CQ] and coinitiator [ethyl 4-(dimethylamino)benzoate (EDAB)] were added via a microsyringe to lead, after solvent evaporation, to the following final concentrations in the mixture : 1.0 mol % CQ, 1.0 mol % EDAB. The solvent was evaporated under reduced pressure for 2 h. Three to four milligrams of each mixture was placed in an uncovered aluminum DSC pan. The samples were irradiated for 60 s at 50°C with a LED light-curing unit (Radii Plus SDI, Australia), with an incident light intensity of

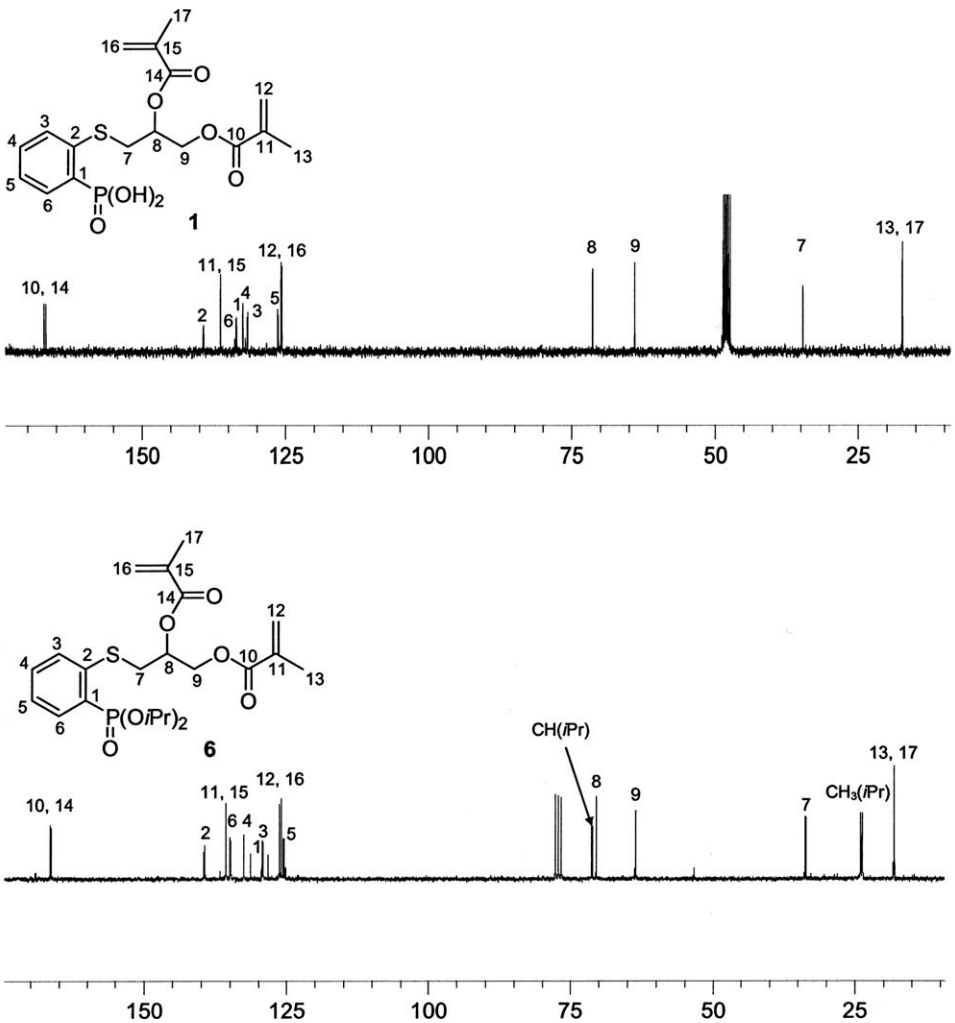
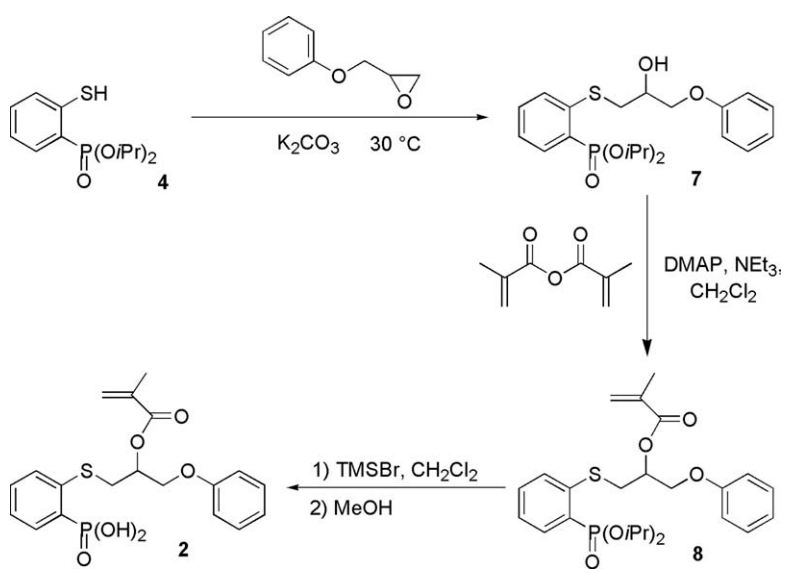


Figure 2 ^{13}C-NMR spectra of monomers **1** and **6**.



Scheme 2 Synthesis of acidic monomer **2**.

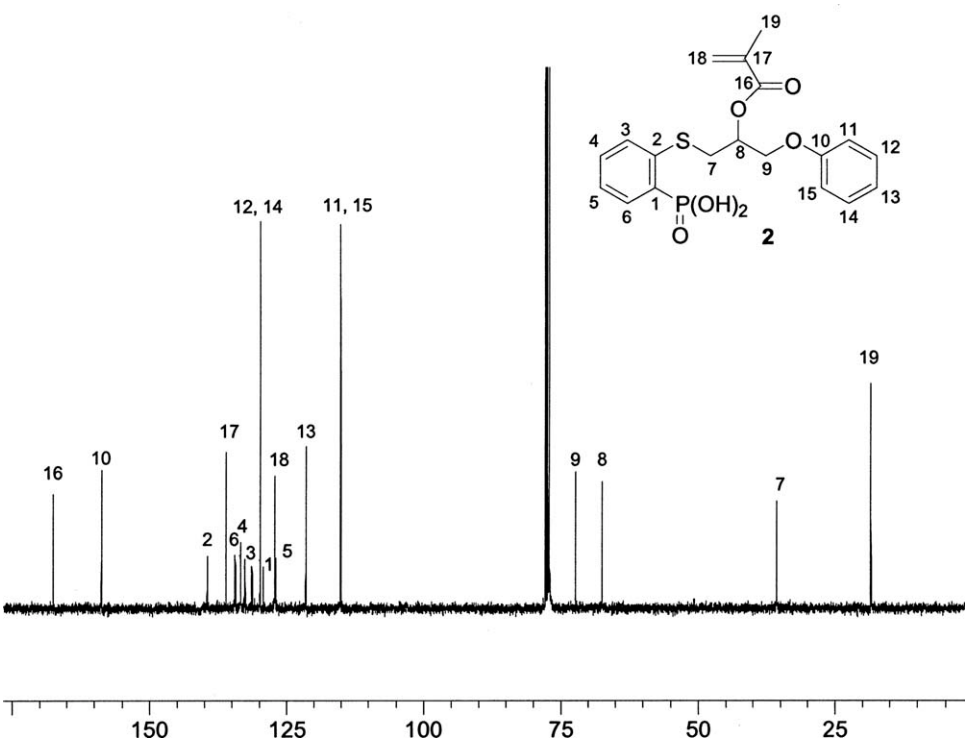


Figure 3 ^{13}C-NMR spectrum of monomer **2**.

40 mW cm^{-2}. Each experiment was repeated at least three times.

The heat flux as a function of time were monitored with DSC under isothermal conditions. Double-bond conversion (DBC) was calculated as the quotient of the overall enthalpy evolved [ΔH_p (J g^{-1})] and the theoretical enthalpy obtained for 100% conversion of the mixtures [ΔH_{0p} (J g^{-1})] [eq. (1)].

$$\mathrm{DBC} = \Delta H_p / \Delta H_{0p} \quad (1)$$

ΔH_{0p} was calculated according to the following formula [eq. (2)]:

$$\Delta H_{0p} = \sum \Delta H_{0i}{}^{*} P_i / M_i \quad (2)$$

where ΔH_{0i} is the theoretical enthalpy of monomer i (i = monomethacrylate, ΔH_{0i} = 54.8 kJ mol^{-1}, i = dimethacrylate, ΔH_{0i} = 109.7 kJ mol^{-1}),[25] M_i its molar mass and P_i the amount used in the formulation (% wt).

The rate of polymerization (R_p) was calculated according to the following formula [eq. (3)]:

$$R_p = Q / m^{*} \Delta H_{0p} \quad (3)$$

where Q is the heat flow and m the mass of the mixture in the sample.

RESULTS AND DISCUSSION

Synthesis of the acidic monomers 1 and 2

Monomer **1** has first been prepared in five steps, from thiophenol (Scheme 1). At first, treatment of thiophenol with sodium hydride, followed by addition of diethylchlorophosphate, has led to the

TABLE I
Composition of Resins 0–5

	Resin 0 (wt %)	Resin 1 (wt %)	Resin 2 (wt %)	Resin 3 (wt %)	Resin 4 (wt %)	Resin 5 (wt %)
Bis-GMA	50.0	47.6	40.0	33.3	47.6	40.0
TEGDMA	50.0	47.6	20.0	33.3	47.6	20.0
1	0	4.8 (4.4 mol %)	20.0 (18.6 mol %)	33.3 (31.4 mol %)	–	–
2	–	–	–	–	4.8 (4.3 mol %)	20.0 (18.4 mol %)

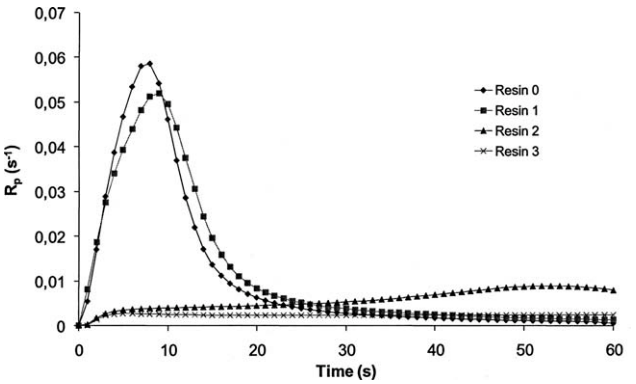


Figure 4 Rate of polymerization of resins 0–3 as a function of irradiation time.

thiophosphate **3** in a 90% yield. Based on an efficient method for the preparation of *ortho*-substituted thiophenols, the lithiation-rearrangement of thiophosphate **3** has provided the desired thiol **4** in a quantitative crude yield. Thiol **4** has then been reacted with glycidol, in the presence of a catalytic amount of potassium carbonate, to furnish the diol **5** in a 79% yield. Then, acylation of diol **5** by methacrylic anhydride, in the presence of triethylamine and of a catalytic amount of DMAP, has been carried out. After purification by flash column chromatography, dimethacrylate **6** has been isolated in 84% yield. Finally, dealkylation of the phosphonate group has been performed: reaction of phosphonate **6** with an excess of TMSBr, followed by subsequent methanolysis, has been provided the expected acidic monomer **1** in a quantitative crude yield.

The structures of monomers **6** and **1** have been confirmed by ^{1}H-NMR, ^{31}P-NMR, ^{13}C-NMR, and HRMS. The ^{13}C-NMR spectra of dimethacrylates **6** and **1** are reported in Figure 2. The disappearance of the characteristic signals of the diisopropyl groups of the phosphonate ester is observed on the acidic monomer **1** spectrum. Hence, dealkylation of the phosphonate group is complete.

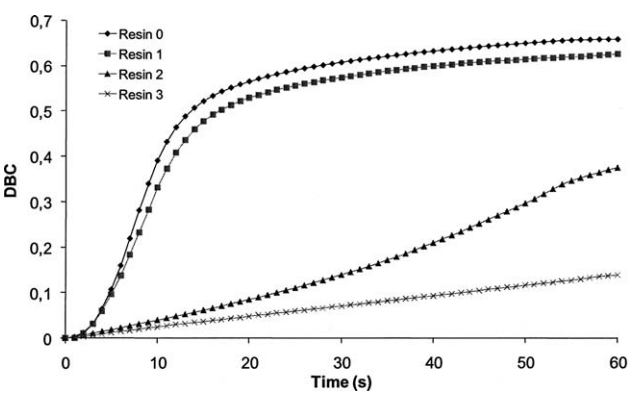


Figure 5 Double bond conversion of resins 0–3 as a function of irradiation time.

TABLE II
DBC of Resins 2 and 3 as a Function of the Irradiation Time

	Irradiation time = 60 s	Irradiation time = 120 s	Irradiation time = 180 s
DBC resin 2	37	52	54
DBC resin 3	13	29	41

Monomer **1** is identified by two methyl groups at 17.3 and 17.4 ppm and by three methylene groups at 34.6, 64.0, and 71.3 ppm. The $H_2C{=}C$ carbons of the methacrylate groups are identified by the presence of two singlets at 125.6 and 125.8 ppm (one for each methacrylate group) and by two other singlets at 136.3 and 136.4 ppm. Because of the coupling with the phosphorus atom, aromatic carbons are identified by doublets at 126.3, 136.1, 132.4, 133.0, 133.6, and 139.3 ppm.

Acidic monomer **2** has been prepared according to a similar synthetic pathway (Scheme 2). It has been synthesized in five steps, from thiophenol, in a 65% global yield. Thiol **4** has been obtained as previously described and has then been reacted with phenyl glycidyl ether, in the presence of a catalytic amount of potassium carbonate. This step has been carried out according to solvent-free conditions developed by Fringuelli et al.[22] After purification by flash chromatography, alcohol **7** has been isolated in 85% yield. Acylation and subsequent dealkylation of the phosphonate group have led to the desired acidic monomer **2**. The structure of this new aromatic phosphonic acid has been confirmed by ^{1}H-NMR, ^{31}P-NMR, ^{13}C-NMR, and HRMS. ^{13}C-NMR spectra of methacrylate **2** is reported in Figure 3.

The effect of acidic monomers 1 and 2 incorporation on the polymerization of bis-GMA : TEGDMA (1 : 1) blends

To check whether these new monomers could enter compomer formulations, we have then developed

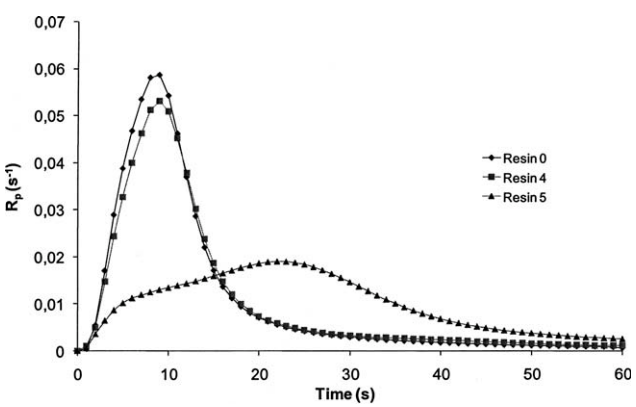


Figure 6 Rate of polymerization of resins 0, 4, and 5 as a function of irradiation time.

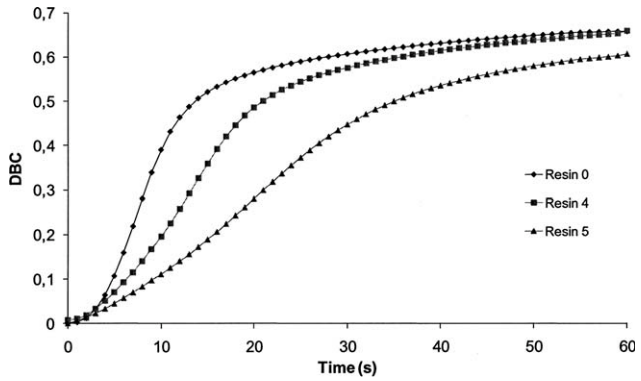


Figure 7 Double bond conversion of resins 0, 4, and 5 as a function of irradiation time.

new resins and we have studied their reactivities in free radical polymerization. Compomers are made up of three different kinds of monomers: a bulky macromonomer, a diluent, and an acidic monomer. The most commonly used bulky monomer and diluent in commercial formulations are respectively bis-GMA and TEGDMA. Therefore, we have taken an interest in the preparation of bis-GMA : TEGDMA mixtures in which acidic monomer **1** or **2** would be introduced in various ratios.

First, four different mixtures of bis-GMA, TEGDMA, and methacrylate **1** have been prepared which differed only in their acidic monomer content (i.e., bis-GMA : TEGDMA: **1** of 1 : 1 : 1, 1 : 1 : 0.5, 1 : 1 : 0.1, and 1 : 1 : 0 as described in Table I). The objective was to investigate the influence of the proportions of acidic monomer **1** incorporated on the mixture reactivity. 1 mol % CQ and 1 mol % EDAB have been added in each mixture and a photo-DSC study has been carried out. All copolymerizations have been performed under the same conditions of temperature (50°C), light intensity (40 mW cm^{-2}), and time of irradiation (60 s). The rate of polymerization (R_p) and the DBC are respectively plotted, as a function of irradiation time, in Figures 4 and 5. The results clearly demonstrate that addition of acidic monomer **1** in great proportions results in a strong inhibition of polymerization. Indeed, the greater the ratio of acidic monomer **1** incorporated, the lower the R_p and the final DBC. Although photopolymerization of resin 1 leads to similar final DBC than the resin 0 (final DBC resin 1 = 63%, final DBC resin 0 = 65%), resins 2 and 3 do not reach such a DBC (final DBC resin 2 = 37%, final DBC resin 3 = 14%). Longer irradiation time results in an increase of DBC (Table II). Indeed, after three successive irradiations of 60 s, the DBC of resins 2 and 3 are significantly higher (Table II). Anyway, such long irradiation times are inconsistent with a potential application in restorative dentistry. Hence, acidic monomer **1** can only be incorporated in bis-GMA : TEGDMA blends in small proportions.

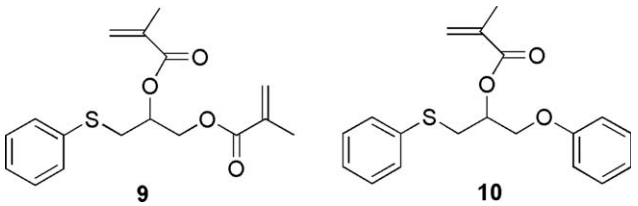
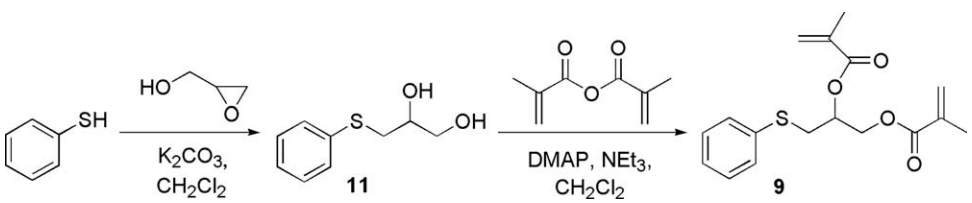
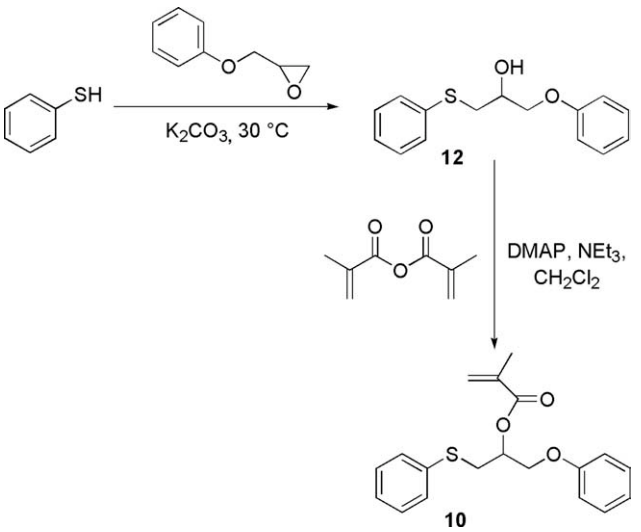


Figure 8 Structure of methacrylates **9** and **10**.

Two different mixtures of bis-GMA, TEGDMA, and methacrylate **2** have also been prepared (i.e., bis-GMA : TEGDMA: **2** of 1 : 1 : 0.5 and 1 : 1 : 0.1; Table I). Unfortunately, we have not been able to formulate the blend bis-GMA : TEGDMA: **2** (1 : 1 : 1) because monomer **2** is not soluble in such proportions. 1 mol % CQ and 1 mol % EDAB have been added in each mixture and a photo-DSC study has been performed. The R_p and the DBC are respectively plotted, as a function of irradiation time, in Figures 6 and 7. Similarly to the previous copolymerization study, results show that the higher the proportion in acidic monomer **2** incorporated, the lower the mixtures reactivity (lower R_p and final DBC). However, it should be noticed that, in the same proportions, incorporation of acidic monomer **2** to bis-GMA : TEGDMA (1 : 1) leads to a significantly lower polymerization inhibition than addition of dimethacrylate **1**. Indeed, the DBC obtained after 60 s of irradiation is higher with resin 5 (20 wt % of **2**, DBC = 61%) than with resin 2 (20 wt % of **1**, DBC = 37%). Thus, monomer **2** can be added in suitable quantities without compromising the final degree of cure of the material. As a consequence, it constitutes a great candidate to enter compomer formulations.



Scheme 3 Synthesis of dimethacrylate **9**.



Scheme 4 Synthesis of methacrylate **10**.

The inhibition effect observed when adding significant proportions of acidic monomers **1** or **2** to the bis-GMA : TEGDMA blend could be attributed to the presence of the phosphonic acid group. Indeed, it has been reported in the literature that the use of phosphonic acid monomers could lead to a strong inhibition of polymerization. Some authors stated that it could be due to a deactivation effect of the phosphonic group arising from its ability to withdraw electrons by both mesomeric and inductive effects.[12,26] However, the results we obtain cannot be explained by such an effect. Indeed, when looking at the structures of monomers **1** and **2**, it has to be noticed that the acidic group is too far from the polymerizable group to be able to stabilize the formed radical. One other hypothesis could arise from the protonation of the coinitiator (EDAB) by the acidic monomer.[27] In this case, higher proportions of acidic monomer would result in a higher amount of protonated coinitiator and thus in a lower amount of available radicals during initiation. Moreover, the pK_a of the acidic monomer must be a key parameter to quantify the importance of this protonation. Hence, the difference of behavior between acidic monomer **1** and **2** could partly be explained by their different pK_a.

TABLE III
Composition of Resins 6–8

	Resin 6 (wt %)	Resin 7 (wt %)	Resin 8 (wt %)
Bis-GMA	41.7	35.7	41.7
TEGDMA	41.7	35.7	41.7
9	16.6 (18.6 mol %)	28.6 (31.4 mol %)	–
10	–	–	16.6 (18.4 mol %)

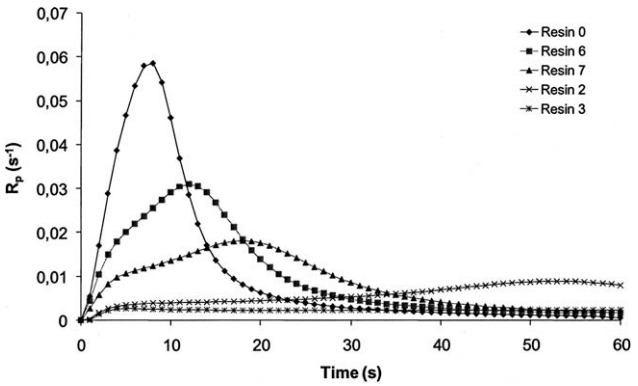


Figure 9 Rate of polymerization of resins 0, 2, 3, 6, and 7 as a function of irradiation time.

To quantify the role of the phosphonic group on the polymerization inhibition, we have then focused on the preparation and the reactivity in free radical polymerization of methacrylates **9** and **10**, which are structurally similar to acidic monomers **1** and **2**, except that the acidic group was replaced by a proton (Fig. 8).

Synthesis of the acidic methacrylates 9 and 10

Dimethacrylate **9** has been prepared in three steps from thiophenol (Scheme 3). Thiophenol has first been reacted with glycidol, in the presence of a catalytic amount of potassium carbonate, to provide diol **11** in 94% yield. Subsequent acylation led to the desired monomer **9** in 71% yield. According to a similar synthetic pathway, methacrylate **10** has been obtained, from thiophenol, in a 72% global yield (Scheme 4).

The structures of these monomers have been confirmed by ^{1}H-NMR, ^{31}P-NMR, ^{13}C-NMR, and HRMS. After isolating these new methacrylates, we have taken an interest in their copolymerization with a bis-GMA : TEGDMA (1 : 1) blend.

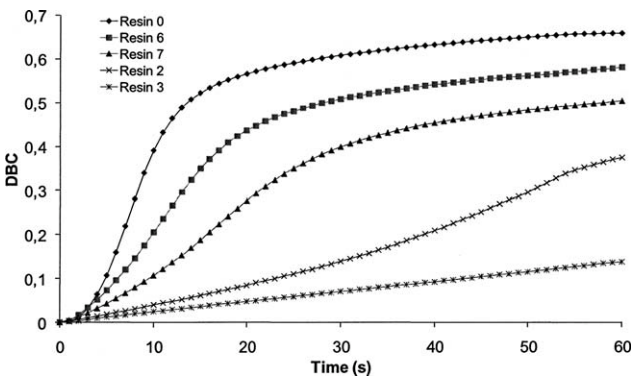


Figure 10 Double bond conversion of resins 0, 2, 3, 6, and 7 as a function of irradiation time.

The effect of monomers 9 and 10 incorporation on the polymerization of bis-GMA : TEGDMA blends

To compare the reactivities of acidic monomer **1** and methacrylate **9**, resins 6 and 7 have first been prepared similarly to resins 2 and 3: Acidic monomer **1** has been substituted by dimethacrylate **9**, in the same molar ratio (Table III). 1 mol % CQ and 1 mol % EDAB have been added and the mixtures have been irradiated for 60 s. The R_p and the DBC of resins 6 and 7 as well as of resins 0, 2, and 3 are respectively plotted, as a function of irradiation time, in Figures 9 and 10.

The results show that addition of dimethacrylate **9** to bis-GMA : TEGDMA (1 : 1) blends results in a decrease of both R_p and final DBC. First, the higher the monomer **9** content added, the lower the R_{pmax} and the higher the time to reach R_{pmax} are (Fig. 9). This could be attributed to the low viscosity of monomer **9**. Indeed, as TEGDMA, monomer **9** can be considered as a reactive diluent. When added to the bis-GMA : TEGDMA blend, monomer **9** lowers the mixture viscosity. It results in an increase of the gelation time due to a lower diffusion effect on the termination reaction during gelation and on propagation during vitrification.

Although addition of **9** to bis-GMA : TEGDMA (1 : 1) leads to a lower reactivity of the mixtures, the inhibition effect is much less pronounced than when phosphonic acid **1** is incorporated. Indeed, irradiation of resin 6 ($R_{pmax} = 0.031\ s^{-1}$; final DBC = 58%) leads to significantly higher R_p and final DBC than photopolymerization of resin 2 ($R_{pmax} = 0.009\ s^{-1}$; final DBC = 37%). The same observation is made when comparing resins 7 ($R_{pmax} = 0.018\ s^{-1}$; final DBC = 50%) and 3 ($R_{pmax} = 0.002\ s^{-1}$; final DBC = 14%). As a consequence, this photo-DSC study clearly demonstrates the significant role of the phosphonic group on the inhibition effects observed while polymerizing resins 2 and 3.

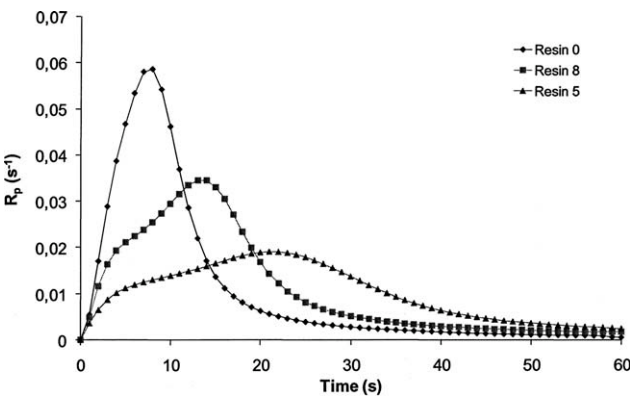


Figure 11 Rate of polymerization of resins 0, 5, and 8 as a function of irradiation time.

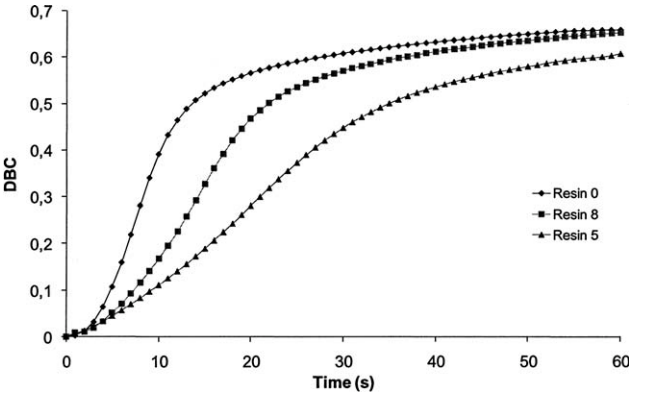


Figure 12 Double bond conversion of resins 0, 5, and 8 as a function of irradiation time.

To confirm this assessment, we have compared the reactivities of both acidic monomer **2** and methacrylate **10**. Thus, resin 8 has been formulated by incorporating **10** in the bis-GMA : TEGDMA blend, in the same molar ratio as monomer **2** in resin 5 (Table III). 1 mol % CQ and 1 mol % EDAB have been added and the resin has been irradiated for 60 s. The R_p and the DBC of resin 8 as well as of resins 0 and 5 are respectively plotted, as a function of irradiation time, in Figures 11 and 12. Once more, the lower reactivity of resin 8 compared to the resin 0 can be attributed to the diluent properties of the low-viscosity monomer **10**. Contrary to dimethacrylate **9**, monomer **10** is monofunctional. Therefore, its use should increase the final DBC of the mixtures because of a lower crosslink density of the network.

As for the comparison of reactivity between methacrylate **10** and acidic monomer **2**, it has been clearly evidenced that the presence of the acidic group leads to a decrease of the mixture reactivity. Indeed, irradiation of resin 8 leads to both higher R_p and final DBC than irradiation of resin 5 (Figs. 11 and 12).

CONCLUSIONS

New acidic methacrylates **1** and **2** as well as methacrylates **9** and **10** have been prepared. The proposed structures have been confirmed by HRMS and NMR spectra. Monomers **1**, **2**, **9**, and **10** have then been incorporated in different amounts to a bis-GMA : TEGDMA (1 : 1) blend. The reactivity of the mixtures was investigated by photo-DSC. Results show that the more monomers **1**, **2**, **9**, or **10** added, the lower the rate of polymerization and the final DBC. Moreover, we have demonstrated that the presence of the phosphonic acidic group leads to a strong inhibition of polymerization when the acidic monomer is incorporated in great quantities. However, results have shown that the mixtures containing acidic monomer **2** are more reactive than those containing dimethacrylate **1**. Thus, acidic methacrylate **2** is a

great candidate to enter compomer formulations and might be used to improve some properties of compomers. The investigation of mechanical properties of dental materials containing monomer **2** will soon be carried out.

This work has been performed within the "PUNCHOrga" interregional network (Pôle Universitaire de Chimie Organique) and the "RMPP" (Réseau Matériaux, Polymères, Plasturgie).

References

1. Nicholson, J. W. Dent Mater 2007, 23, 615.
2. Dorin Ruse, N. J Can Dent Assoc 1999, 65, 500.
3. Mc Cabe, J. F. Biomaterials 1998, 19, 521.
4. Meyer, J. M.; Cattani-Lorente, M. A.; Dupuis, V. Biomaterials 1998, 19, 529.
5. Jakubiak, J.; Allonas, X.; Fouassier, J. P.; Sionkowska, A.; Andrzejewska, E.; Linden, L. A.; Rabek, J. F. Polymer 2003, 44, 5219.
6. Forsten, L. Biomaterials 1998, 19, 503.
7. Peutzfeldt, A. Am J Dent 1996, 9, 259.
8. El-Kalla, I. H.; Garcia-Godoy, F. Oper Dent 1999, 24, 2.
9. Yap, A. U.; Chung, S. M.; Chow, W. S.; Tsai, K. T.; Lim, C. T. Oper Dent 2004, 29, 29.
10. Mou, L.; Singh, G.; Nicholson, J. W. Chem Commun 2000, 5, 345.
11. Nicholson, J. W. Int J Adhes 1998, 18, 229.
12. Adusei, G.; Deb, S.; Nicholson, J. W.; Mou, L.; Singh, G. J Appl Polym Sci 2003, 88, 565.
13. Sahin, G.; Albaynak, A. Z.; Sarayli, Z.; Avci, D. J Polym Sci Part A: Polym Chem 2006, 44, 6775.
14. Xu, X.; Ding, X.; Ling, L.; Burgess, J. O. J Polym Sci Part A: Polym Chem 2005, 43, 3153.
15. Xu, X.; Ling, L.; Ding, X.; Burgess, J. O. J Polym Sci Part A: Polym Chem 2004, 42, 985.
16. Atai, M.; Nekoomanesh, M.; Hashemi, S. A.; Yeganeh, H. J Appl Polym Sci 2002, 86, 3246.
17. Hammersfahr, P. D. Polym Prepr 1997, 38, 131.
18. Sibold, N.; Madec, P.-J.; Masson, S.; Pham, T.-N. Polymer 2002, 43, 7257.
19. Masson, S.; Saint-Clair, J.-F.; Saquet, M. Synthesis 1993, 5, 485.
20. Masson, S.; Saint-Clair J.-F.; Dore, A.; Saquet, M. Bull Soc Chim Fr 1996, 133, 951.
21. Anbar, M.; St John, G. A. J Dent Res 1971, 50, 778.
22. Fringuelli, F.; Pizzo, F.; Tortoioli, S.; Vaccaro, L. Tetrahedron Lett 2003, 44, 6785.
23. Movassagh, B.; Soleiman-Beigi, M. Synth Commun 2007, 37, 3239.
24. Amantini, D.; Fringuelli, F.; Pizzo, F.; Tortoioli, S.; Vaccaro, L. Synlett 2003, 15, 2292.
25. Anseth, K. S.; Wang, C. M.; Bowman, C. N. Macromolecules 1994, 27, 650.
26. Adusei, G. O.; Deb, S.; Nicholson, J. W. Dent Mater 2005, 21, 491.
27. Moszner, N.; Salz, U.; Zimmermannn, J. Dent Mater 2005, 21, 895.