Synthesis and Polymerization Kinetics of Acrylamide Phosphonic Acids and Esters as New Dentine Adhesives

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Received 15 June 2012; accepted 9 August 2012; published online
DOI: 10.1002/pola.26339

ABSTRACT: In restorative dentistry, acrylamide monomers bearing phosphonic acid moieties have proved to be useful species for the formulation of dental self-etch adhesives since they provide enhanced adhesion to hydroxyapatite and are not subject to hydrolysis, thus potentially improving their adhesive durability. Previous studies have demonstrated that phosphonic acid acrylamides increase the rate of photopolymerization of diacrylamide monomers. To understand whether this rate acceleration is specific to the acrylamide function of the monomer, or due to the phosphonic acid group *per se*, or is applicable only with a crosslinking reaction, we have synthesized several acrylamide and methacrylate monomers bearing phosphonic acid or phosphonate moieties and studied their photopolymerization kinetics. The acrylamide phosphonic acid was found to accelerate the polymerization rate but similar monomers bearing a phosphonate ester group had a much smaller effect. A similar accelerating effect was observed when the phosphonic acid-based monomers were copolymerized with a monofunctional acrylamide monomer, excluding the possibility that the rate acceleration might be related to the crosslinking process. This rate effect is also observed when a nonpolymerizable organic phosphonic acid is present in the polymerizing medium. We suggest that the increase of the medium polarity is responsible for this rate enhancement effect. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: acrylamide phosphonic acids; adhesives; dental materials; DSC; photopolymerization kinetics; polarity

INTRODUCTION Because of their simplicity of use, dental self-etch adhesives (SEAs) are widely employed to adhere restorative materials to dentine and enamel.[1–3] SEAs are aqueous acidic solutions containing various monomers (acidic, hydrophilic, and hydrophobic monomers) which are able to simultaneously etch and infiltrate dental tissues mediating the formation of a bond to the restorative material.[4–7] Various monomers have been described in the literature[5,8–10] for dental SEAs and typically they contain phosphate esters, carboxylic acids, and phosphonic acids. In our previous studies,[2,3] we have focused on the synthesis of novel phosphonic acid derivatives since it was demonstrated that phosphonic acids were able to chemically adhere to hydroxyapatite (HAp), and that they were not subject to potential hydrolysis in acidic aqueous solutions contrary to their phosphate equivalents, and this feature could help improve the SEAs durability.[2,3,11–15] Using the camphorquinone (CQ)/amine photo redox initiator system which is commonly used for photoinitiation of dental restoratives,[16,17] we have also demonstrated that the adhesive properties of dental adhesives containing phosphonic acid monomers were competitive with commercial formulations and that these novel monomers had a significant effect on the photopolymerization kinetics.

In radical polymerization, when radical transfer reactions can be neglected, the overall polymerization rate is proportional to the concentration of the vinyl monomer units and the radical concentration. In many situations, the steady state hypothesis for the radical concentration can be used, which states that the rate of change in the radical concentration is negligible compared with the rate of radical formation (given by the initiation rate) and the rate of radical loss (usually by bimolecular termination or radical disproportionation).[18,19] As a result, in the classic theory of free radical polymerization, the rate of monomer consumption is given by[18]:

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_\mathrm{p}[\mathrm{M_n}\cdot][\mathrm{M}] = \left(\frac{\mathrm{R}_i k_\mathrm{p}^2}{k_\mathrm{t}}\right)^{0.5}[\mathrm{M}] \qquad (1)$$

where [M] and [M·] are the concentrations of vinyl groups and radicals, R_i is the rate of initiation of propagating chains and k_p and k_t are the rate constants for propagation and termination. However, radical polymerization generally shows

an important autoacceleration step in the early stages of the reaction, called the Trommsdorff or gel effect.[20–22] This observed acceleration is due to the diffusion-controlled character of the recombination or disproportionation termination reactions. The magnitude of the Trommsdorff effect depends on the mobility of the radicals. As the reaction proceeds, chains grow and consequently macroradical mobility and radical termination rates decrease, leading to a strong increase in the overall rate of polymerization, since the propagation rate of the reaction remains unchanged.[23,24] Indeed the addition of monomer molecules to the growing chain is not significantly affected by the mobility of the macromolecules unless the matrix vitrifies.[25]

The reaction is even more complex when the free radical polymerization of monomers leads to the formation of a polymer network. During the crosslinking process, the termination rate decreases dramatically when gelation occurs,[18,23,26] which makes the Trommsdorff effect even more important and produces a significant increase in rate. As the reaction proceeds, the radical translational and segmental diffusion mechanisms are so retarded that a third diffusion mechanism, termed reaction diffusion, dominates. Reaction diffusion is the movement of radicals by successive propagating steps which eventually leads to their mutual termination. Since this process is proportional to the rate of propagation, eq 1 shows that the overall rate constant for polymerization will be approximately proportional to $[M]^{0.5}$, and so the reaction rate decreases as the monomer is consumed. In some cases, the increase in the glass transition temperature (T_g) due to crosslinking process reduces the molecular mobility to such an extent that the material vitrifies and this process leads to cessation of the propagation and termination reactions.[26,27] In other cases where the T_g is still below the curing temperature, the polymerization may cease prior to full reaction because the radicals and/or the reactive vinyl groups are buried in the surrounding polymerized matrix and are not able to reach fresh monomer.[28–30]

In previous studies of the copolymerization of *N*,*N*′-diethyl-1,3-bis(acrylamido)propane (DEBAAP, a hydrophobic crosslinking monomer commonly used in hydrolytically stable dental adhesives formulations[31]) with acrylamide phosphonic acid monomers, we observed that these acidic monomers accelerated the DEBAAP photopolymerization kinetics but we were not able to fully explain the cause.[3] Ullrich et al.[32] also found that when DEBAAP was copolymerized with the phosphonic acid monomer, ethyl-4-(dihydroxyphosphoryl)-2-oxa-butylacrylate, the rate of polymerization and final double bond conversion (DBC) were raised compared with DEBAAP alone. These authors suggested that this increase in DBC was caused by the lower crosslink density in the copolymerizing system which allowed greater access of radicals to the double bonds. However, the increase in polymerization rate is inconsistent with the Trommsdorff effect[16,20–22] because the greater mobility of the radicals should increase the termination rate and thus reduce the polymerization rate. This prediction is contrary to that found by Ullrich et al.[32] and our previous study.[3]

Another possible mechanism for the enhanced polymerization rate that we considered[3] is the potential for the phosphonic acid to act as a reducer for the photoactivated CQ. However, we have reported[3] that the CQ-induced photopolymerization of the mixture of DEBAAP with acrylamide phosphonic acid monomers without any tertiary amine co-initiator (normally considered to be the most effective reducer for CQ) proceeded at a much lower rate than DEBAAP homopolymerization with CQ and amine co-initiator, proving that the observed behavior is not due to a co-initiating activity of bisphosphonic acids.

Several groups of researchers[33–37] have proposed that monomers capable of hydrogen bond formation have raised reaction rates caused by lower termination rates due to enhanced medium viscosity, or higher propagation rates due to their role in pre-organizing the monomer units. However such effects would not be expected to be very important for monomers that develop a three-dimensional network because the developing gel has a massive impact on molecular mobility and has a strong influence on the arrangement of the monomers and their reactive groups.

In addition to the effect of H-bonding, several alternative ideas have been considered by Jansen et al.[33,34,37] to explain the anomalously high photopolymerization rate of some monomers. These authors found that the maximum rate of polymerization is highly and positively correlated with the dipole moment of their monomers. Four potential explanations relating to medium polarity were given for this correlation.[33,34,37] The photoinitiator effectiveness may be increased by a solvent effect on primary radical recombination which leads to more propagating radicals.[38] The propagation rate may be raised by the solvent polarity, leading to a faster polymerization.[39] In a more polar medium, the propagating radical is charged to a greater extent, resulting in less bimolecular termination.[33,34] Finally, because the solvent cage around the radical has stronger secondary bonding in a more polar medium, this could reduce the termination reaction rate and lower the polymerization rate.[33,34,37] In addition, Jansen et al.[33,34,37] noted that the polymerization rate was higher for monomers that are capable of H-bonding—by comparison of a series of H-bonding and non-H-bonding, Jansen et al. concluded that a higher dipole moment of the polymerizing medium reduced k_t but H-bonding raised k_p. In contradiction, Kilambi et al.[40] found no correlation between the maximum polymerization rate and the monomer or solvent polarity.

In the present work, we further investigate the role played by the phosphonic acid moiety on the photopolymerization rate of dental monomers in an effort to understand the rate enhancing mechanism. We have synthesized several species bearing phosphonic acid or phosphonate moieties to help answer four questions that emerged from our previous studies[3]: is the observed rate enhancement due to the phosphonic acid group *per se*; is it specific to the acrylamide function in the phosphonic monomer; is the effect associated with the changes in polymerization rates inherent to a crosslinking reaction. We have therefore focused this study

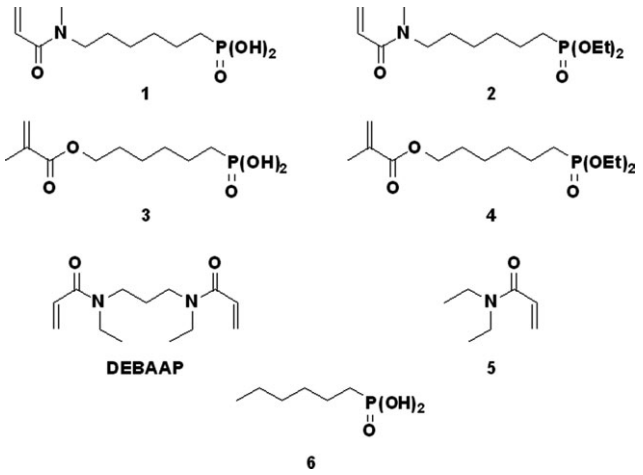

FIGURE 1 Structures of DEBAAP and species **1–6**.

around the behavior of Monomer **1** (see Fig. 1), which is an acrylamide phosphonic acid monomer with six methylene units as a spacer between the amide and the phosphonic acid moiety. Monomer **2** was synthesized to determine if the activity of Monomer **1** was due to its acidic nature. Methacrylate Monomers **3** and **4** (see Fig. 1) were synthesized to establish whether the nature of the polymerizable group on the phosphonic acid/phosphonate was involved in the observed rate enhancement effect. In addition, hydroxyhexylphosphonic acid **6** (see Fig. 1), a nonpolymerizable species analogous to the polymerizable monomers, was synthesized to be able to isolate the effect on the polymerization rate due to the phosphonic acid moieties. Finally, to test whether the rate acceleration effect was associated with network formation, Monomer **5** (see Fig. 1) was prepared because it is the monofunctional equivalent of the diacrylamide DEBAAP crosslinking monomer that we have used in our previous studies.

EXPERIMENTAL

Material

The synthesis reactions were carried out under a dry nitrogen atmosphere in oven-dried glassware. Triethylamine was distilled over calcium hydride prior to use. Unless stated otherwise, all reagents were purchased from Sigma-Aldrich and were used without further purification. Dichloromethane was purified with a PURESOLV^{TM} apparatus developed by Innovative Technology Inc. Column chromatography was performed with Merck silica gel Si 60 (40–63 μm). Thin layer chromatography was performed on silica gel 60 F-254 plates.

Nuclear Magnetic Resonance (NMR)

^{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 and ^{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; q, quadruplet; sx, sextuplet; m, multiplet), coupling constant in Hertz, assignment broad band ^{1}H decoupling.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR absorption spectra were recorded on a Perkin Elmer Spectrum One FTIR Spectrometer with an ATR accessory. The characteristic IR absorptions mentioned in the text were strong bands and are reported in cm^{-1}.

High-Resolution Mass Spectroscopy (HRMS)

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 were 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.

Photodifferential Scanning Calorimetry

The photoinitiator CQ (0.54 mol %, Aldrich) and co-initiator ethyl-4-(dimethylamino)benzoate (0.54 mol % EDAB, Aldrich) respectively, were added to each mixture for photopolymerization studies. It is important to note that the same initiating system was used for the whole study since interactions between this initiating system and the synthesized monomers may also be invoked to try to explain the observed behaviors.

Photopolymerization kinetics were monitored using a Perkin Elmer differential scanning calorimetry (DSC) 7 differential scanning calorimeter calibrated with indium and zinc standards, was modified to allow for irradiation of the sample and reference pans by use of a bifurcated fiber optic lead, thus minimizing the thermal heating effect of the photocuring source.[41] Approximately 3 mg of material was spread as a thin layer over the base of the 4.5-mm diameter, aluminum DSC pan. Since the maximum decadic molar absorption coefficient of CQ is $\sim 3.8 \times 10^4$ cm^2 mol^{-1} at 470 nm, films of this thickness with the standard concentration of CQ resulted in <8% variation in radiation intensity through the film.[16] Previous studies[42] have shown that for the present photoinitiation conditions, the influence of CQ depletion on the polymerization kinetics can be neglected. To minimize the effect of dissolved oxygen on the polymerization kinetics, all samples were equilibrated in the apparatus for at least 5 min under a 20 mL min^{-1} flow of N_2 at 50 °C before commencing the experiment. All photopolymerizations were performed at 50 °C, using a Rofin Polilight source with a light intensity of 40 mW cm^{-2} near 470 nm for an irradiation time of 600 s.

The heat flow was monitored as a function of time with the DSC under isothermal conditions. DBC was calculated as the quotient of the overall enthalpy evolved (ΔH_p in J g^{-1}) and the theoretical enthalpy obtained for 100% conversion of the mixtures (ΔH_{0P} in J g^{-1}) using eq 2:

$$\mathrm{DBC} = \frac{\Delta H_p}{\Delta H_{0p}} \tag{2}$$

ΔH_{0P} (in J/g) was calculated according to the following formula (eq 3):

$$\Delta H_{0p} = \frac{x_a \cdot \Delta H_{0a} + x_b \cdot \Delta H_{0b}}{x_a \cdot M_a + x_b \cdot M_b} \quad (3)$$

where x_a and x_b are the molar percentages of Monomers *a* and *b* in the mixture, respectively, while M_a and M_b are their molecular weights. ΔH_{0a} and ΔH_{0b} are their theoretical enthalpy of reaction which have been determined from the values of 120.6 kJ mol^{-1} for DEBAAP,[43] 60.3 kJ mol^{-1} for Monomers **1**, **2**, and **5**[40] and 54.8 kJ mol^{-1} for Monomers **3** and **4**.[44] The rate of polymerization (R_p in units of fractional conversion/s) was calculated according to the following formula:

$$R_p = Q/(m\Delta H_{0P}) \quad (4)$$

where Q is the heat flow per second during the reaction and m is the mass of the sample. The rate of polymerization (R_p) and the DBC were plotted as a function of irradiation time.

Syntheses

N,N′-Diethyl-1,3-bis-(acrylamido)-*propane (DEBAAP*)

In a 500-mL three-necked round-bottomed flask supplied with a dropping funnel under nitrogen atmosphere, *N,N′*-diethyl-propane-1,3-diamine (12.9 mL, 81.0 mmol), freshly distilled triethylamine (23.7 mL, 170 mmol, 2.1 eq.) and 100 mL of anhydrous dichloromethane are introduced. After cooling at 0 °C, a solution of acryloylchloride (13.2 mL, 160 mmol, 2.0 eq.) diluted in 100 mL of anhydrous dichloromethane is added dropwise. The reaction was kept under agitation for 15 min at 0 °C, then for 2 h at RT. The reaction was concentrated under reduced pressure and distilled water was added to the crude product. After three extractions with ethyl acetate, the organic layers were combined and dried on magnesium sulfate. The solution was concentrated on a rotary evaporator, and after column chromatography on silica gel with acetone, the purification provided 10.8 g (45 mmol) of a yellowish viscous product.

Yield: 56 %. ^{1}H NMR ($CDCl_3$, 250.1 MHz, δ): 0.98–1.15 (m, 6H, H_7), 1.75 (qt, $^3J_{HH}$ = 7.5 Hz, 2H, H_1), 3.21–3.41 (m, 8H, H_2, and H_6), 5.52–5.61 (m, 2H, H_{5a}), 6.15–6.29 (m, 2H, H_{5b}), 6.34–6.52 (m, 2H, H_4). ^{13}C NMR ($CDCl_3$, 62.9 MHz, δ): 13.3 and 15.0 (C_7), 26.5 and 28.6 (C_1), 41.5 (C_2 or C_6), 43.0 (C_2 or C_6), 43.1 (C_2 or C_6), 43.9 (C_2 or C_6), 44.2 (C_2 or C_6), 45.8 (C_2 or C_6), 127.7 (s, C_5), 128.0 (s, C_5), 128.5 (s, C_4), 166.0, 166.2, and 166.4 (C_3).

N-Diethyl-1-acrylamido-*propane (Monomer* 5)

In a 100-mL three-necked round-bottomed flask supplied with a dropping funnel under nitrogen atmosphere, diethylamine (3.6 mL, 34.0 mmol), fresh distilled triethylamine (2.8 mL, 38.0 mmol, 1.1 eq.) and 25 mL of anhydrous dichloromethane were introduced. After cooling at 0°°C, a solution of acryloylchloride (2.5 mL, 34.0 mmol, 1.0 eq.) diluted in 25 mL of anhydrous dichloromethane was added dropwise. The reaction was kept under agitation for 15 min at 0°°C, then 2 h at room temperature. The reaction was concentrated under reduced pressure and distilled water was added to the crude product. After three extractions with ethyl acetate, the organic layers were combined and dried on magnesium sulfate. The solution was concentrated on a rotary evaporator, and after column chromatography on silica gel with acetone, the purification provided 2.15 g (17.0 mmol) of a yellowish viscous product.

Yield: 50%. ^{1}H NMR ($CDCl_3$, 400.1 MHz, δ): 1.01–1.18 (m, 6H, H_1), 3.25–3.41 (m, 4H, H_2), 5.53–5.61 (m, 2H, H_{5a}), 6.22–6.29 (m, 2H, H_{5b}), 6.42–6.52 (m, 2H, H_4). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 13.3 and 14.7 (s, C_1), 40.8 and 42.2 (s, C_2), 127.5 (s, C_5), 127.8 (s, C_4), 165.6 (C_3).

Diethyl hexylphosphonate

A mixture of triethylphosphite (5.2 mL, 30.3 mmol, 2.5 eq.) and bromohexane (2.0 g, 12.0 mmol) was heated at 150°°C for 15 h. Excess of triethylphosphite and by-products were removed under reduced pressure (P = 0.1 mbar, T = 170°°C). The phosphonate (1.8 g, 8.2 mmol) was obtained as a colorless liquid.

Yield: 68%. ^{1}H NMR ($CDCl_3$, 400.1 MHz, δ): 0.78–0.83 (t, $^3J_{HH}$ = 6.2 Hz, 3H, H_6), 1.18–1.37 (m, 6H, H_3, H_4, and H_5), 1.24 [t, $^3J_{HH}$ = 7.2 Hz, C**H$_3$**(OEt)], 1.47–1.59 (m, 2H, H_2), 1.61–1.72 (m, 2H, H_1), 3.95–4.09 [m, 4H, C**H$_2$**(OEt)]. ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 13.8 (s, C_6), 16.6 [d, $^3J_{HH}$ = 6.0 Hz, **C**H_3(OEt)], 21.7 (s, C5), 22.1 (s, C4), 23.8 (d, $^3J_{CP}$ = 17.4 Hz, C_3), 24.7 (d, $^2J_{CP}$ = 5.2 Hz, C_2), 25.5 (d, $^1J_{CP}$ = 140.7 Hz, C_1), 61.5 [d, $^3J_{HH}$ = 6.4 Hz, **C**H_2(OEt)]. ^{31}P NMR ($CDCl_3$, 162.0 MHz, δ): 32.7 [s, **P**(OEt)].

Hexylphosphonic acid (6)

Under inert conditions, a solution of diethyl hexylphosphonate (1.8 g, 8.2 mmol) in anhydrous dichloromethane (15 mL) was introduced in a round-bottomed flask. Then trimethylsilyl bromide (TMsBr) (3.2 mL, 24.6 mmol, 3.0 eq.) was added dropwise. After stirring for 3 h at room temperature, the mixture was concentrated under reduced pressure and methanol (10 mL) was added. The mixture was stirred for 1 h and the solvent was evaporated. The product was dried to a constant weight under vacuum. Phosphonic acid **6** (1.36 g, 8.2 mmol) was isolated with a quantitative yield as a yellowish oil.

Yield: 100%. ^{1}H NMR ($CDCl_3$, 400.1 MHz, δ): 0.78–0.81 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H_6), 1.05–1.22 (m, 4H, H_4, and H_5), 1.25–1.33 (m, H_3), 1.46–1.58 (m, 2H, H_2), 1.59–1.72 (m, 2H, H_1). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 13.8 (s, C_6), 21.9 (s, C_5), 22.0 (s, C_4), 23.9 (d, $^3J_{CP}$ = 17.2 Hz, C_3), 24.8 (d, $^2J_{CP}$ = 5.1 Hz, C_2), 25.5 (d, $^1J_{CP}$ = 140.6 Hz, C_1) ^{31}P NMR ($CDCl_3$, 162.0 MHz, δ): 32.0 [s, **P**(OH)]. HRMS (m/z): calcd for $C_6H_{15}O_3P$, 165.0681; found, 165.0674 [M − H]$^-$.

Diethyl N-(methylacrylamido)hexylphosphonate (Monomer 2) and N-(Methylacrylamido)hexylphosphonic acid (Monomer 1)

Diethyl *N*-(methylacrylamido)hexylphosphonate **2** and *N*-(methylacrylamido)hexylphosphonic acid **1** were prepared following the same protocol as described in our previous publication.[2]

2-(6-Bromohexyloxy)tetrahydro-2H-pyran

6-Bromohexanol (5.0 g, 27.6 mmol) and pyridinium *p*-toluenesulfonate (70.0 mg, 0.3 mmol) diluted in anhydrous

dichloromethane (30 mL) were introduced in a round-bottomed flask. Then dihydropyrane (2.5 mL, 27.6 mmol, 1 eq.) was added and the mixture was stirred for 3 h at room temperature. The crude product was washed with distilled water (50 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure. A bulb to bulb distillation under reduced pressure (180°°C, 0.1 mbar) provided the pure product (6.5 g, 20.2 mmol) as a colorless oil.

Yield: 89%. ^{1}H NMR ($CDCl_3$, 400.1 MHz, δ): 1.33–1.91 (m, 14H, H_2–H_5, and H_8–H_{10}), 3.39–3.42 (t, $^3J_{HH}$ = 5.2 Hz, 2H, H_1), 3.36–3.53 (m, 2H, H_6), 3.70–3.89 (m, 2H, H_8), 4.57 (t, $^3J_{HH}$ = 3.6 Hz, 2H, H_7). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 19.9 (s, C_{10}), 25.6 (s, CH_2), 25.6 (s, CH_2), 28.2 (s, CH_2), 29.7 (s, CH_2), 30.9 (s, CH_2), 32.9 (s, CH_2), 34.0 (s, C_1), 62.6 (s, C_6), 67.6 (s, C_8), 99.1 (s, C_7). HRMS (m/z): calcd for $C_{11}H_{21}BrO_2$, 287.0623; found, 287.0623 $[M + Na]^+$.

Diethyl 6-(tetrahydropyran-2-yloxy)hexylphosphonate

A mixture of triethylphosphite (6.2 mL, 35.8 mmol, 2.5 eq.) and 2-(6-bromohexyloxy)tetrahydro-2H-pyran (3.8 g, 14.3 mmol) was heated at 150°°C for 15 h. Excess triethylphosphite and by-products were removed under reduced pressure (P = 0.1 mbar, T = 180°°C). The phosphonate (3.6 g, 11.2 mmol) was obtained as a colorless liquid.

Yield: 79%. ^{1}H NMR ($CDCl_3$, 400,1 MHz, δ): 1.26–1.29 [t, $^3J_{HH}$ = 6.8 Hz, 3H, C**H$_3$**(OEt)], 1.30–1.41 (m, 2H, CH_2), 1.41–1.72 (m, 6H, CH_2), 3.30–3.47 (m, 2H, H_1), 3.65–3.69 (m, 2H, H_6), 4.02–4.11 [m, 4H, C**H$_2$**(OEt)], 4.51–4.53 (t, $^3J_{HH}$ = 3.6 Hz, 1H, H_7). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 16.6 [d, $^3J_{CP}$ = 6.0 Hz, **C**H_3(OEt)], 19.8 (s, C_{10}), 22.5 (d, $^2J_{CP}$ = 5.2 Hz, C_2), 25.1 (s; C_4), 25.6 (s, C_9), 25.8 (d, $^1J_{CP}$ = 140.6 Hz, C_1), 29.6 (s, C_5), 30.6 (d, $^3J_{CP}$ = 17.0 Hz, C_3), 30.9 (s, C_{11}), 61.5 [d, $^2J_{CP}$ = 6.5 Hz, **C**H_2(OEt)], 62.5 (s, C_6), 67.6 (s, C_8), 99.0 (s, C_7). ^{31}P NMR ($CDCl_3$, 162.0 MHz, δ): 32.4. HRMS (m/z): calcd for $C_{15}H_{31}O_5P$, 323.1987; found, 323.1978 $[M + H]^+$.

Diethyl 6-hydroxyhexylphosphonate

Diethyl 6-(tetrahydropyran-2-yloxy)hexylphosphonate **2** (0.70 g, 2.3 mmol) and Amberlyst H15 (8 mg) were introduced in a round-bottomed flask with methanol (5 mL). The reaction was heated at 45°°C under reflux for 1 h. After filtration and concentration under reduced pressure, diethyl 6-hydroxydecylphosphonate was obtained (0.54 g, 2.3 mmol) with a quantitative yield as a colorless oil.

Yield: 100%. ^{1}H NMR ($CDCl_3$, 400.1 MHz, δ): 1.33–1.37 [t, $^3J_{HH}$ = 5.6 Hz, 3H, C**H$_3$** (OEt)], 1.31–1.41 (m, 2H, CH_2), 1.49–1.74 (m, 8H, CH_2), 3.14 (sl, 1H, OH), 3.58–3.61 (t, $^3J_{HH}$ = 6.4 Hz, H_6), 4.03–4.08 [m, 4H, C**H$_2$**(OEt)]. ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 16.7 [d, $^3J_{CP}$ = 6.0 Hz, **C**H_3(OEt)], 22.5 (d, $^2J_{CP}$ = 5.0 Hz, C_2), 25.3 (s, C_4), 25.0 (d, $^1J_{CP}$ = 141.0 Hz, C_1), 30.3 (d, $^3J_{CP}$ = 16.4 Hz, C_3), 32.6 (s, C_5), 61.6 [d, $^2J_{CP}$ = 6.5 Hz, **C**H_2(OEt)], 62.9 (s, C_6). ^{31}P NMR ($CDCl_3$, 162.0 MHz, δ): 32.5. HRMS (m/z): calcd for $C_{10}H_{23}O_4P$, 239.1412; found, 239.1419 $[M + H]^+$.

Diethyl 6-(methacryloyloxy)hexylphosphonate (Monomer 4)

A solution of diethyl 6-hydroxyhexylphosphonate (3.3 g, 14.0 mmol) in anhydrous dichloromethane (60 mL) was mixed together with 4-dimethylamino pyridine (80.0 mg, 0.7 mmol) and redistilled triethylamine (2.9 mL, 21.0 mmol, 1.1 eq.). Then methacrylic anhydride was introduced (2.3 mL, 15.4 mmol). After 6 h at room temperature, water was added and the product was extracted. The organic layer was dried over magnesium sulfate and the crude product was purified by flash chromatography (eluent: ethyl acetate) providing Monomer **4** (3.7 g, 11.4 mmol) as a colorless oil.

Yield: 81%. ^{1}H NMR($CDCl_3$, 400.1 MHz, δ): 1.29–1.33 [t, $^3J_{HH}$ = 7.2 Hz, 3H, C**H$_3$**(OEt)], 1.34–1.48 (m, 2H, CH_2), 1.50–1.78 (m, 8H, CH_2), 1.93 (m, 3H, H_9), 4.06–4.14 [m, 6H, H_6, and C**H$_2$**(OEt)], 5.54 (m, 1H, H_{8a}), 6.08 (m, 1H, H_{8b}). ^{13}C NMR (CDCl3, 100.6 MHz, δ): 16.4 [d, $^3J_{CP}$ = 5.9 Hz, **C**H_3(OEt)], 18.3 (s, C_{10}), 22.3 (d, $^2J_{CP}$ = 5.1 Hz, C_2), 25.5 (s, C_4), 25.6 (d, $^1J_{CP}$ = 140.7 Hz, C_1), 28.3 (s, C_5), 30.1 (d, $^3J_{CP}$ = 16.8 Hz, C_3), 61.4 [d, $^2J_{CP}$ = 6.5 Hz, **C**H_2(OEt)] ; 64.5 (s, C_6), 125.1 (s, C_9), 136.4 (s, C_8), 167.4 (s, C_7). ^{31}P NMR ($CDCl_3$, 162.0 MHz, δ): 32.3. HRMS (m/z): calcd for $C_{14}H_{27}O_5P$, 307.1670; found, 307.1674 $[M + H]^+$.

6-(Methacryloyloxy)hexylphosphonic acid (Monomer 3)

Under inert conditions, a solution of diethyl 6-(methacryloyloxy)hexylphosphonate **4** (1.9 g, 5.3 mmol) in anhydrous dichloromethane (15 mL) was introduced in a round-bottomed flask. Then TMsBr (2.1 mL, 15.9 mmol, 3.0 eq.) was added dropwise. After stirring for 3 h at room temperature, the mixture was concentrated under reduced pressure and methanol (10 mL) was added. The mixture was stirred for 1 h and the solvent was evaporated. The product was dried to a constant weight under vacuum. The phosphonic acid Monomer **3** (1.6 g, 5.3 mmol) was isolated with a quantitative yield as yellowish oil.

Yield: 100%. ^{1}H NMR (D_2O, 400.1 MHz, δ): 1.36–1.82 (m, 10H, H_1–H_5), 1.93 (s, 1H, H_{10}), 4.21 (t, $^3J_{HH}$ = 6.4 Hz, 2H, H_6), 5.70 (s, 1H, H_{9a}), 6.12 (s, 1H, H_{9b}), 8.30 (sl, 2H, OH). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 18.4 (s, C_{10}), 23.8 (d, $^2J_{CP}$ = 4.8 Hz, C_2), 25.1 (s, C_4), 25.2 (d, $^1J_{CP}$ = 147.7 Hz, C_1), 28.7 (d, $^3J_{CP}$ = 17.9 Hz, C_3), 29.6 (s, C_5), 65.8 (s, C_6), 125.9 (s, C_9), 137.9 (C_8), 168.9 (s, C_7). ^{31}P NMR (D_2O, 162.0 MHz, δ): 32.3. HRMS (m/z): calcd for $C_{10}H_{19}O_5P$, 249.0892; found, 249.0889 $[M - H]^-$.

RESULTS AND DISCUSSION

Copolymerization of Monomer 5 with Monomers 1–4

To understand the effect on the kinetics of the copolymerization of phosphonic acid based monomers with the acrylamide moiety without overlaying the effect of the formation of a crosslinked network, we first studied the copolymerization of monovinyl phosphonic acid monomers, Monomers **1–4** with the monoacrylamide Monomer **5**. Mixtures of Monomer **5** with Monomers **1–4** were prepared in a 0.95/0.05 (i.e., 1.8/0.1) molar ratio so as to be consistent with our previous study of the copolymerization of difunctional DEBAAP and monofuctional acrylamide phosphonic acids where we used a 0.9/0.1 monomer ratio and thus a 1.8/0.1 or 0.9/0.05 molar ratio of acrylamide units.

Figure 2 shows the copolymerization rate of monoacrylamide Monomer **5** with the acrylamide phosphonate ester

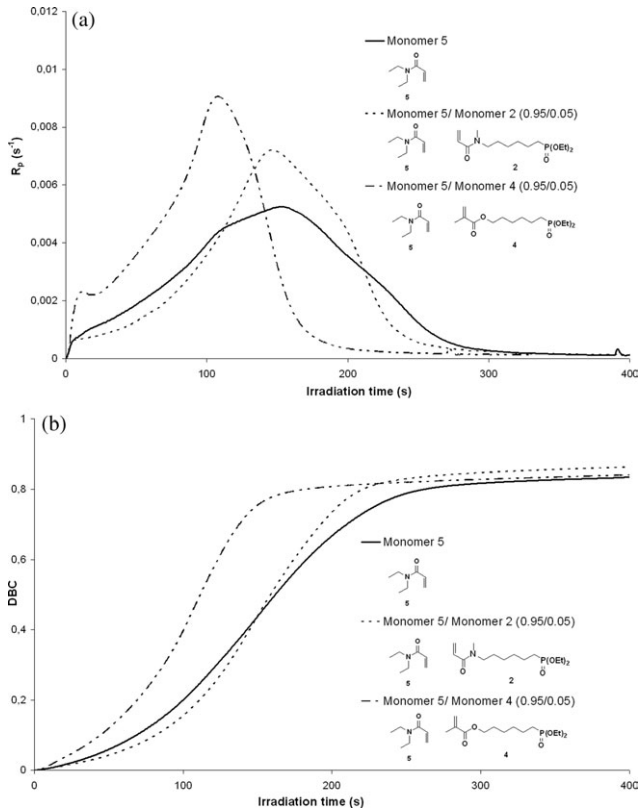

FIGURE 2 Fractional conversion rate (a) and fractional conversion (b) of double bonds versus irradiation time for the homopolymerization of Monomer 5 and its copolymerization with Monomers **2** or **4**.

Monomer **2** as a function of irradiation time in comparison with the homopolymerization of Monomer **5**. Although the maximum polymerization rate for the comonomer system is greater than that for the monoacrylamide, the introduction of Monomer **2** as a comonomer does not change the polymerization kinetics very much since the time at the peak rate, the overall shape of the rate curve and the final DBC are not greatly affected. This result does not necessarily disagree with a polarity effect because the phosphonate ester is expected to have a smaller effect than a phosphonic acid monomer.

In Figure 2, we also compare the kinetics of Monomer **5** homopolymerization with its copolymerization with Monomer **4** which is a methacrylate monomer bearing a phosphonate ester group. In this case, some significant differences can be noted. First, a shoulder is evident at the early times of the reaction which might be due to differences in reactivity ratios when a methacrylate monomer copolymerizes with an acrylamide monomer. The reactivity ratios for dimethylacrylamide (M1)/methylmethacrylate (MMA) (M2) copolymerization are typically close to $r_1 = 0.5$ and $r_2 = 2$ according to Brandrup et al.[45] Since $r_1 << r_2$, this means that an acrylamide radical will preferentially react with a MMA monomer and MMA radicals also prefer to react with MMA. Therefore, it is likely that the overall copolymerization reaction proceeds in two stages, the first being the preferential polymerization of all methacrylate monomers independently of the nature of the radicals formed during the initiation, followed by the polymerization of the acrylamide monomers. Since the methacrylate monomer are far less numerous than the former, only a small shoulder is observed at the start of the polymerization rate curve due to methacrylate consumption. Figure 2(b) reveals that despite the varying polymerization rates of these monomers, the final conversion is similar and about 85%. The glass transition temperature (T_g, determined by DSC) of the polymer from Monomers **5** is 69°C,[46] which is higher than the photocuring temperature (50°C). This suggests that the systems will vitrify before complete polymerization is achieved. The fact that the final conversions are virtually unaffected by the addition of the phosphonate ester monomers may be due to the relatively small amount added and the similarity of T_gs of the individual polymers.

Figure 3 compares the copolymerization kinetics of Monomer **5** with acrylamide Monomers **1** (a phosphonic acid) and **2** (a phosphonate ester) to determine the effect of the phosphonic acid function. In this case, the phosphonate ester increases the copolymerization rate slightly but a strong increase in the reaction rate is clearly evidenced with the acrylamide phosphonic acid since both the time of the maximum polymerization rate is strongly reduced and $R_{p(max)}$ is

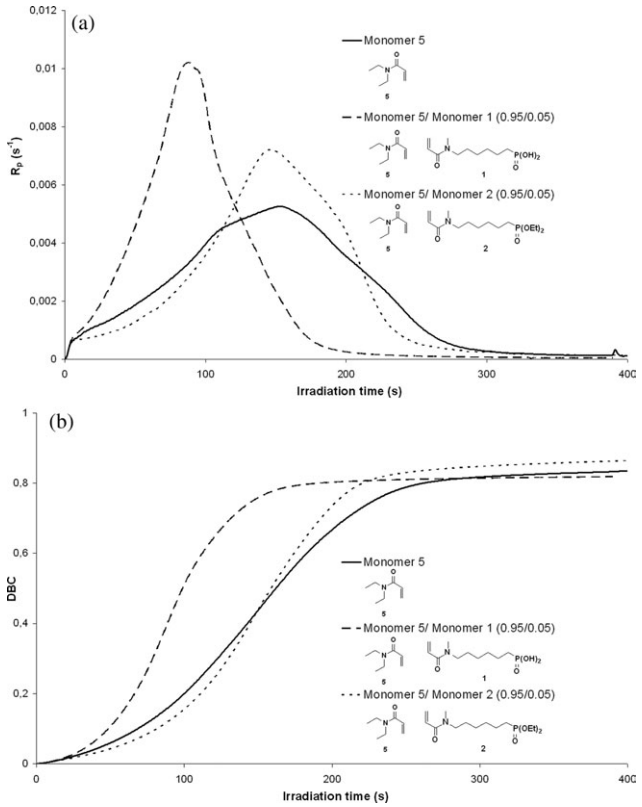

FIGURE 3 Fractional conversion rate (a) and fractional conversion (b) of double bonds versus irradiation time for the homopolymerization of Monomer **5** and its copolymerization with Monomers **1** and **2**.

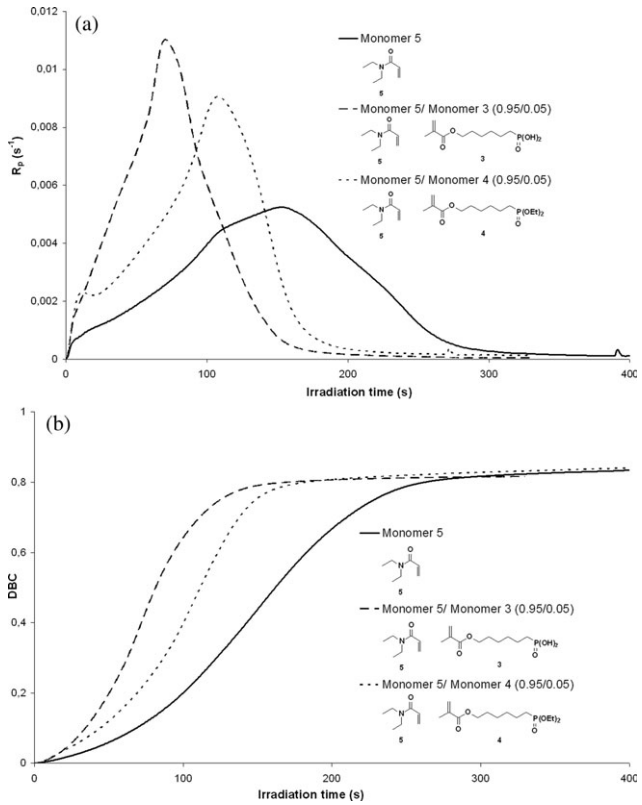

FIGURE 4 Fractional conversion rate (a) and fractional conversion (b) of double bonds versus irradiation time for the homopolymerization of Monomer **5** and its copolymerization with Monomers **3** and **4**.

increased. The final DBC is reached for a much shorter irradiation time but its value is unchanged at ~ 85%, presumably for the reasons discussed above. This result is consistent with the effect of polarity proposed by Jansen et al.,[33,34,37] because it is expected that the phosphonic acid would have a greater dipole moment compared with the phosphonate ester. In addition, since these systems do not contain crosslinking monomers, the effect of hydrogen bonding on the polymerization rate discussed above may also be responsible for the rate enhancement.

The data plotted in Figure 4 indicate that the rate enhancement by the phosphonic acid group is observed even when the phosphonic acid function is carried on a methacrylate monomer since the copolymerization of Monomer **5** with Monomer **3** is also much faster than it is with its phosphonate ester equivalent, Monomer **4.** These results are consistent with the effect of polarity as discussed above. Moreover, Figure 4 also shows that the phosphonate ester does accelerate the copolymerization with DEBAAP as suggested by the related data for the acrylamide phosphonate esters in Figures 2 and 3. As observed before, the final DBC remains unaffected by the nature of the monomers.

Copolymerization of DEBAAP with Monomers 1–4

It is well known that provided the double bonds are of equal reactivity, the homopolymerization of crosslinking monomers such as difunctional DEBAAP instead of the monofunctional Monomer **5** enhances the polymerization rate due to the effect of gelation on reducing the termination rate[18,23,26] and this is observed by a comparison of Figures 3 and 5—DEBAAP homopolymerizes much more quickly that does Monomer **5** even though the peak polymerization rate is similar. The analogy also continues for the copolymerization reactions—the copolymerization of DEBAAP with Monomers **1** and **2** (Fig. 5) are faster than the copolymerization of the monoacrylamide Monomer **5** with Monomers **1** and **2** (Fig. 3). However, the effect of the phosphonic acid–based monomers on the copolymerization kinetics is consistent with the effect of polarity proposed by Jansen et al.[33,34,37]

Figures 3 and 5 also show the final DBC obtained with DEBAAP and its copolymers with Monomers **1** and **2** are ~ 75% which is much lower than that found for Monomer **5** and its copolymers. This is expected because vitrification (which stops the polymerization reaction) would be expected to occur at a lower conversion for DEBAAP-based systems due to the formation of a crosslinked network which increases the T_g above that of the uncrosslinked analog. In addition, topological trapping of monomer in the network structure formed from DEBAAP which will lower conversion compared with the uncrosslinked polymer from Monomer **5**.

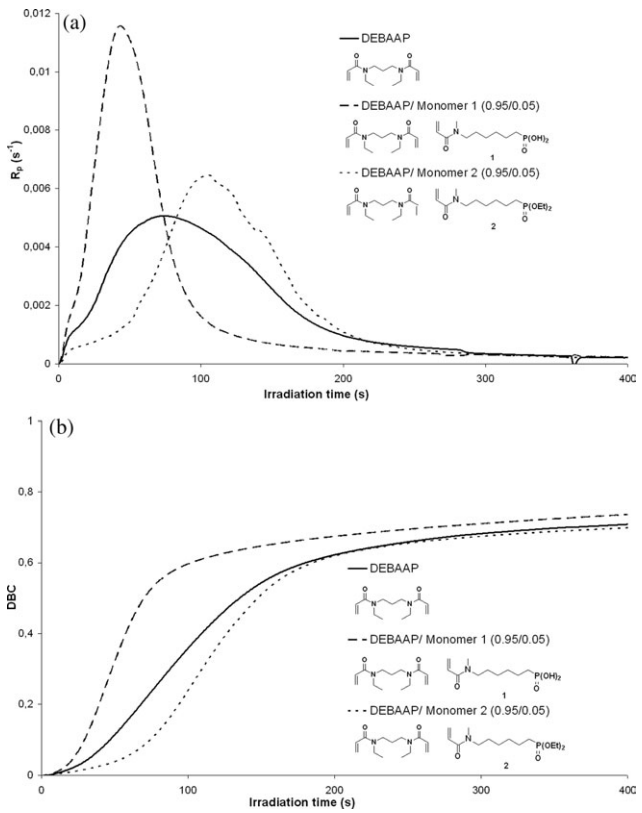

FIGURE 5 Fractional conversion rate (a) and fractional conversion (b) of double bonds versus irradiation time for the homopolymerization of DEBAAP and its copolymerization with Monomers **1** and **2**.

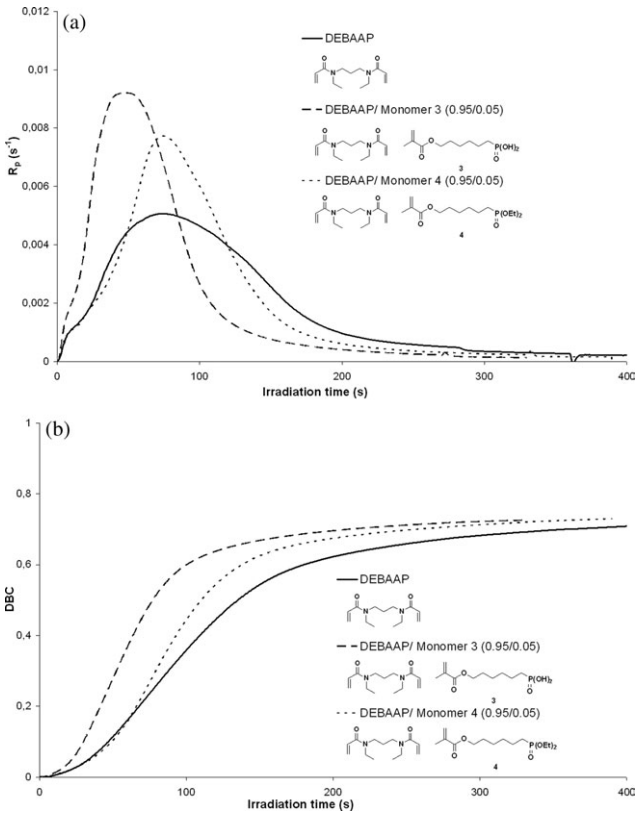

FIGURE 6 Fractional conversion rate (a) and fractional conversion (b) of double bonds versus irradiation time for the homopolymerization of DEBAAP and its copolymerization with Monomers **3** and **4**.

Figure 5 shows that addition of the monofunctional acrylamide phosphonate, Monomer **2**, with difunctional DEBAAP decreases the polymerization rate because it delays gelation and the Trommsdoff effect. However, copolymerization of DEBAAP with the phosphonic acid-based Monomer **1** proceeds much faster than with DEBAAP or with the DEBAAP/Monomer **2** (the phosphonate-based acrylamide) system, which is consistent with what we observed during our previous study[2] and that shown in Figure 3 for the diethyl acrylamide, Monomer **5**. This indicates that the phosphonic acid function increase the rate of photopolymerization of the acrylamide function when initiated by the CQ/EDAB system, possibly due to the effect of polarity proposed by Jansen et al.[33,34,37]

The rate enhancement effect of phosphonic acid groups shown in Figures 3–5 on the vinyl polymerization is not restricted to the polymerization of acrylamide units. Similar trends in the kinetics are observed in Figure 6 when the methacrylate phosphonic acid, Monomer **3**, was copolymerized with DEBAAP in agreement with that found for the acrylamide Monomers **1** and **2**. Again this is consistent with a polarity effect. Monomer **4**, also enhances the polymerization of DEBAAP as found for the monofunctional acrylamide shown in Figure 2.

To determine if the rate enhancement is due to the polymerizable phosphonic comonomer *per se*, the photopolymerization of DEBAAP was studied in the presence of hexylphosphonic acid (species **6**) which has no polymerizable vinyl group. Figure 7 shows that the polymerization of DEBAAP is markedly enhanced by hexylphosphonic acid and that this effect is not associated with the copolymerization process itself. This result is also consistent with the view that polarity enhances polymerization.

CONCLUSIONS

We have investigated the photocopolymerization of difunctional acrylamide monomers, used in dental adhesives, with monofunctional acrylamide comonomers bearing phosphonic acid groups, which we have used to promote adhesion and improve bond durability. It has been shown the acrylamide phosphonic acid accelerates that polymerization kinetics but similar monomers bearing a phosphonate ester group have a smaller effect. Similar behavior was observed when the difunctional acrylamide monomer was substituted by a monofunctional acrylamide monomer. This effect is also observed when a phosphonic acid methacrylate was used and also when a nonpolymerizable organic phosphonic acid was present in the polymerizing medium. Since hypotheses concerning potential interactions of the phosphonic acid moiety with the photoinitiating system, and the potential role of the acidic functions protonating the amide have been previously eliminated,[3] it is likely that, as proposed by Jansen

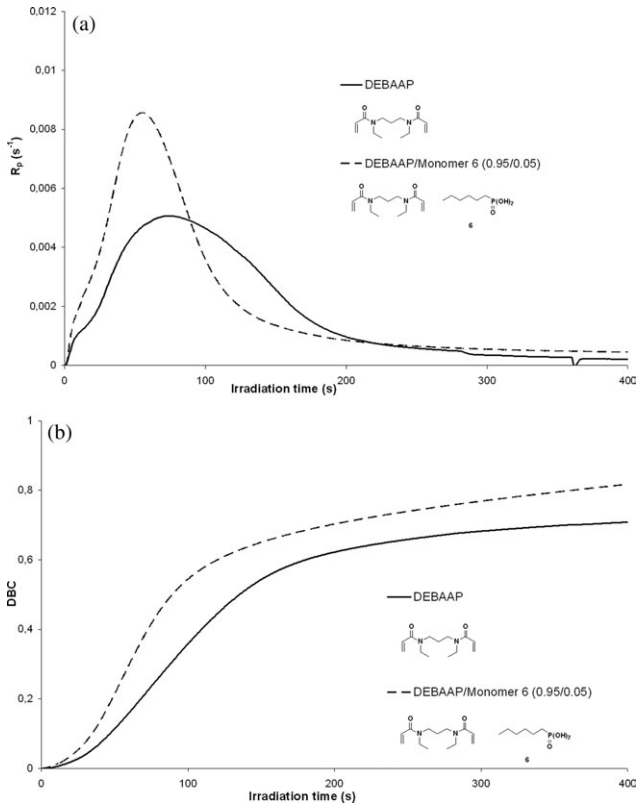

FIGURE 7 Fractional conversion rate (a) and fractional conversion (b) of double bonds versus irradiation time for the homopolymerization of DEBAAP and its copolymerization with species **6**.

et al. the increase of medium polarity brought by the presence of phosphonic acid groups is responsible for the increased polymerization rate of acrylamide monomers.

ACKNOWLEDGMENTS

This work was supported by EGIDE, Partenariat Hubert Curien French/Australian Science and Technology FAST2008 18603VH and FAST2010 23205WC grant and by the Australian Department of Innovation, Industry, Science and Research FR080034 and FR100037 grants, which provided funding for collaboration between the Laboratoire de Chimie Moléculaire et Thioorganique within the Institute of Chemistry INC3M FR 3038 and the "RMPP" (Réseau Matériaux, Polymères, Plasturgie) in France and the Department of Materials Engineering, Monash University in Australia. The authors also gratefully acknowledge the financial support from the "Ministère de la Recherche et des Nouvelles Technologies," CNRS (Centre National de la Recherche Scientifique), the "Région Basse-Normandie," and the European Union (FEDER funding).

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