

# An Efficient Process for Synthesizing and Hydrolyzing a Phosphonated Methacrylate: Investigation of the Adhesive and Anticorrosive Properties

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**ABSTRACT:** A new phosphonated methacrylate, namely dimethyl(methacryloyloxy)-methyl phosphonate (MAPC<sub>1</sub>), has been synthesized using paraformaldehyde and potassium carbonate according to the Pudovik reaction. The quantitative synthesis of MAPC<sub>1</sub> was followed by selective hydrolysis of the ester group with sodium bromide to replace NaI (imparting non-negligible ecological impact). Pure MAPC<sub>1</sub>(OH) was obtained in high yield and efficiently copolymerized with MMA. The  $r_1$  for MAPC<sub>1</sub>(OH) and  $r_2$  (for MMA) values are 0.99 and 1.02, respectively, which indicates that the monophosphonic groups are statistically linked to the methacrylate backbone. When blended with PVDF, MMA/MAPC<sub>1</sub>(OH) copolymers show very good adhesion promoters in both dry and wet conditions and subsequently provide good anticorrosive properties. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 4794–4803, 2008

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## INTRODUCTION

Phosphorus-containing polymers are very promising compounds as their field of applications are very large, that is, ion-exchange resins, dental adhesives, and adhesion promoters for paints.<sup>1–5</sup> Recently, some authors have demonstrated the potential use as agents for controlling drug release.<sup>6</sup> Among phosphorus compounds, phosphate- and phosphonate-containing polymers have elicited much interest over deca-

des,<sup>7–11</sup> for instance, polyphosphates and polyphosphonates are known as excellent fire retardant candidates.<sup>2,12–14</sup> This article focuses on phosphonate compounds as the phosphate derivatives are known to be much more sensitive towards hydrolysis.<sup>15</sup> There are several strategies to introduce the phosphonate functionality into the polymeric backbone, one of them consists of the radical (co)polymerization of a phosphonate-containing monomer. Four different types of phosphonate-containing monomers can be listed from the literature; the allylic, vinylic, styrenic, and (meth)acrylic. Both phosphonate-containing allylic and vinylic monomers do not show good reactivity in radical (co)polymerizations with low molecular weight oligomers

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usually obtained.<sup>16–20</sup> The radical (co)polymerization of phosphonate-containing styrenic monomers generally leads to high molecular weight polymers, but the synthesis of the monomers usually requires a chemical modification of halogenated precursors, for instance, Boutevin et al. performed the synthesis (via the Michaelis-Arbuzov reaction with chlorovinylbenzene) and the controlled radical polymerization of dimethyl vinylbenzylphosphonate.<sup>21,22</sup> Because of their high reactivity in radical (co)polymerization, the phosphonate methacrylic derivatives are probably the most extensively studied monomers. To our knowledge, the usual phosphonate containing methacrylate structure is as follows:  $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{P}(\text{O})(\text{OR}_1)(\text{OR}_2)$  and can be obtained using different organic pathways, recently reviewed by Senhaji et al.<sup>23</sup> These reaction may proceed as follows: Arbuzov reaction<sup>24,25</sup> using a trialkylphosphite, radical addition onto vinyl methacrylate,<sup>26</sup> Michael addition onto vinyl phosphonate,<sup>27</sup> and methacrylation using a hydroxyphosphonate precursor under the Schotten-Baumann conditions.<sup>28</sup> More recently, Jeanmaire et al. obtained dimethyl (2-methacryloyloxyethyl)phosphonate and dimethyl(2-methacryloyloxypropyl)phosphonate by a quantitative alcoholysis of MMA in the presence of  $\text{Zr}(\text{AcAc})_4$  Lewis acid catalyst.<sup>29</sup>

Phosphonate-containing methacrylates in their acidic form are required when the corresponding (co)polymers are used as adhesion promoters. Brondino et al.<sup>30</sup> observed that the monoacid group, that is,  $\text{PO}(\text{OR})(\text{OH})$  is sometimes preferred to the diacid one, that is,  $\text{PO}(\text{OH})_2$ ; this last may confer a too strong hydrophilic behavior to the (co)polymers. Condensable reactions may also occur for  $\text{PO}(\text{OH})_2$  groups between adjacent phosphonic groups, which therefore will increase the viscosity.<sup>31</sup> The most conventional route toward hydrolysis of the phosphonate ester groups into phosphonic acid is based on the use of bromosilane<sup>32</sup>; however, this hydrolysis is not selective and the bromosilane reagents are often very expensive. A selective way to efficiently obtain the monoacid form consists on a monodealkylation in the presence of NaI sodium iodide.<sup>33–36</sup> But it is necessary to replace NaI by other selective reagents due to its non-negligible ecological impact and also because of its high cost.

This article deals with the synthesis of a phosphonate containing methacrylate (dimethyl (methacryloyloxy)methyl phosphonate, MAPC<sub>1</sub>),

with only one  $\text{CH}_2$  spacer, by the use of paraformaldehyde and potassium carbonate, followed by the selective hydrolysis of the ester group with sodium bromide. Both the synthesis and hydrolysis will allow ecological and economical benefits as all the reagents are much less hazardous and expensive compared to other phosphonate methacrylate syntheses (described earlier). The reactivity in radical (co)polymerization of MAPC<sub>1</sub> with MMA is also investigated, and the anticorrosive properties of these newly formed copolymers will be evaluated.

## EXPERIMENTAL

### Reagents

Powdered PVDF SOLEF 1010/1001 was kindly supplied by Solvay (France). All chemicals were reagent grade (purity > 98%), purchased from Sigma-Aldrich, and used without further purification. Methyl methacrylate (MMA) was vacuum distilled, and 2,2'-azobisisobutyronitrile (AIBN, Fluka, 98%) was recrystallized in methanol before use. Potassium carbonate was reagent grade, anhydrous (purity p.a.  $\geq 99\%$ ), and purchased from Fluka.

### Measurements

The chemical structure of the products was determined by <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR (Bruker AC 400 MHz) at room temperature in  $\text{CDCl}_3$  solutions. s, d, t, q, and m abbreviations stand for singlet, doublet, triplet, quadruplet, and multiplet, respectively. The INVGATE procedure with delay  $D_1$  of 10 s was used to quantify the final yield. The elemental analysis was also performed by the Service Central d'Analyses (Verneuil, France). Infrared (FTIR) spectra are recorded on a Nicolet 510P FTIR spectrometer with a band accuracy of  $\pm 2 \text{ cm}^{-1}$ .

### Dimethyl- $\alpha$ -Hydroxymethylphosphonate Synthesis

Ten grams (0.09 mol) of dimethyl hydrogenophosphonate, 2.73 g (0.09 mol) of paraformaldehyde, 30 mL of methanol, and 0.62 g of anhydrous  $\text{K}_2\text{CO}_3$  were introduced in a two-necked flask equipped with a condenser. The solution was vigorously stirred under methanol refluxing for 2 h. Dimethyl- $\alpha$ -hydroxymethylphosphonate is obtained under high vacuum with 98% yield.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  ppm : 3.6 (d, 6H,  $\text{PO}(\text{OCH}_3)_2$ ,  $^3J_{\text{H-P}} = 10.5$ ); 3.9 (d, 2H,  $\text{CH}_2\text{P}$ ); 5.3 (sl, 1H, OH).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  ppm : 28.2 (s, 1P) ( $R-\text{P}(\text{O})(\text{OMe})_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  ppm : 56 (d,  $\text{C}^b$ ), 53 (d,  $\text{C}^c$ ). FTIR ( $\text{CCl}_4$ ):  $3600\text{ cm}^{-1}$  ( $\nu_{\text{O-H}}$ ),  $3300\text{ cm}^{-1}$  ( $\nu_{\text{Csp}^3\text{-H}}$ ),  $2910\text{ cm}^{-1}$  ( $\nu_{\text{Csp}^3\text{-H}}$ ),  $1480\text{ cm}^{-1}$  ( $\delta_{\text{Csp}^3\text{-H}}$ ),  $1225\text{ cm}^{-1}$  ( $\delta_{\text{P=O}}$ ),  $1137\text{ cm}^{-1}$  ( $\delta_{\text{C-O}}$ ),  $1022\text{ cm}^{-1}$  ( $\delta_{\text{P-O-CH}_3}$ ).

Elemental analyses : C (25.72%), H (6.48%), O (45.69%), P (22.11%).

### Dimethyl(methacryloxy)methyl Phosphonate (MAPC<sub>1</sub>) Synthesis

Ten grams (0.071 mol) of dimethyl- $\alpha$ -hydroxymethylphosphonate, 6.15g (0.071 mol) of methacrylic acid, and 30 mL of chloroform were introduced in a two-necked flask equipped with a condenser. Temperature was dropped until  $0\text{ }^\circ\text{C}$  and, after degassing, 14.73 g (0.0071 mol) of dicyclohexylcarbodiimide (DCCI), 0.872 g (0.0071 mol) of *N,N*-dimethyl-4-aminopyridine (DMAP) were added in a dropwise manner. The solution was vigorously stirred at room temperature for 2 h. After filtration, MAPC<sub>1</sub> is obtained by distillation under high vacuum ( $100\text{ }^\circ\text{C}$  with  $2 \times 10^{-2}$  mmHg) with 90% yield.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  ppm : 3.7 (d, 6H,  $\text{PO}(\text{OCH}_3)_2$ ,  $^3J_{\text{H-P}} = 10.5$ ); 1.8 (s, 3H,  $\text{C}(\text{CH}_3)-\text{C}(\text{O})$ ); 4.45 (d, 2H,  $\text{CH}_2\text{P}$ ,  $^2J_{\text{H-P}} = 13.2$ ); 5.5 (s, H,  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)$ ); 6.1 (s, H,  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  ppm : 22.5 (s, 1P) ( $R-\text{P}(\text{O})(\text{OMe})_2$ ). FTIR ( $\text{CCl}_4$ ):  $3311\text{ cm}^{-1}$  ( $\nu_{\text{Csp}^3\text{-H}}$ ),  $2923\text{ cm}^{-1}$  ( $\nu_{\text{Csp}^3\text{-H}}$ ),  $1740\text{ cm}^{-1}$  ( $\nu_{\text{C=O}}$ ),  $1620\text{ cm}^{-1}$  ( $\nu_{\text{C=C}}$ ),  $1499\text{ cm}^{-1}$  ( $\delta_{\text{Csp}^3\text{-H}}$ ),  $1239\text{ cm}^{-1}$  ( $\delta_{\text{P=O}}$ ),  $1147\text{ cm}^{-1}$  ( $\delta_{\text{C-O}}$ ),  $1022\text{ cm}^{-1}$  ( $\delta_{\text{P-O-CH}_3}$ ).

Elemental analyses : C (40.92%), H (6.27%), O (37.75%), P (13.97%).

### Methyl(methacryloxy)methyl Phosphonic Hemi-Acid MAPC<sub>1</sub>(OH) Synthesis

Four grams (0.019 mol) of MAPC<sub>1</sub>, 2 g (0.019 mol) of NaBr, and 20 mL of methylethylketone are introduced in a two-necked flask equipped with a condenser and with a magnetic stirrer. The reaction mixture was heated under reflux with stirring for 13 h and at room temperature for 4 h. The sodium salt was precipitated, filtered, and washed several times with acetone to remove residues. The white powder was dried under high vacuum for 2 h (88% yield). The salt was solubilized in methanol and passed through

a column filled with sulfonic acid resin (Amberlite IR 120). The column was washed with methanol until reaching neutral pH, and the final MAPC<sub>1</sub>(OH) was obtained with 97% yield.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  ppm : 3.6 (d, 3H,  $\text{PO}(\text{OCH}_3)$ ,  $^3J_{\text{H-P}} = 10.5$ ); 1.8 (s, 3H,  $\text{C}(\text{CH}_3)-\text{C}(\text{O})$ ); 4.3 (d, 2H,  $\text{CH}_2\text{P}$ ,  $^2J_{\text{H-P}} = 13.2$ ); 5.5 (s, 1H,  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)$ ); 6.1 (s, 1H,  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  ppm : 18.2 (s, 1P) ( $R-\text{P}(\text{O})(\text{OMe})(\text{OH})$ ).

Elemental analyses : C (37.32%), H (5.09%), O (41.11%), P (15.12%).

### Homo and Copolymerization of MAPC<sub>1</sub> and MAPC<sub>1</sub>(OH) with MMA

Kinetics were conducted in a three-necked flask equipped with a condenser, a septum cap (to be able to take aliquots), and a magnetic stirrer in acetonitrile refluxing and with AIBN as initiator. Monomer conversions were followed by means of  $^1\text{H}$  NMR. Two kinetic methods were used to determine the reactivity ratios:

#### Jaacks Method

If an excess of  $M_1$  compared to  $M_2$  is added into the mixture ( $f_1 > f_2$ ); one can write

$$\ln \frac{[M_1]}{[M_1]_0} = r_1 \ln \frac{[M_2]}{[M_2]_0} \quad (1)$$

From eq 1,  $r_1$  can be reached by plotting  $\ln([M_1]/[M_1]_0)$  versus  $\ln([M_2]/[M_2]_0)$ . Similarly, if an excess of  $M_2$  compared to  $M_1$  is added into the mixture ( $f_2 > f_1$ ),  $r_2$  will be reached by plotting  $\ln([M_2]/[M_2]_0)$  versus  $\ln([M_1]/[M_1]_0)$ .

As an example, kinetic of radical polymerization of MAPC<sub>1</sub> ( $M_1$ ) with MMA ( $M_2$ ) was conducted with  $f_1 = 0.20$  ( $f_1$  is the initial molar fraction of monomer  $M_1$ ):

#### Finemann-Ross Method

From  $f_1$ ,  $f_2$ ,  $F_1$  (molar fraction of monomer  $M_1$  after copolymerization), and  $F_2$ , Finemann and Ross developed the eq 2:

$$\frac{f_1(2F_1 - 1)}{F_1(1 - f_1)} = r_1 \frac{f_1^2(1 - F_1)}{F_1(1 - f_1)^2} + r_2 \quad (2)$$

By plotting  $\frac{f_1(2F_1 - 1)}{F_1(1 - f_1)}$  versus  $\frac{f_1^2(1 - F_1)}{F_1(1 - f_1)^2}$ , a straight line is obtained from which  $r_1$  and  $r_2$  represent the slope and the origin, respectively.

As an example, kinetic of MAPC<sub>1</sub> ( $M_1$ ) with MMA ( $M_2$ ) radical polymerizations was performed with different  $f_1$  fractions and  $F_1$  fractions into the copolymer were calculated at low monomer conversion (<20%):

### Adhesive and Anticorrosive Properties of PVDF and Copolymers Blends

#### Preparation of Blends

PVDF SOLEF 1010/1001 (9% w:w) was first solubilized in *N*-methyl pyrrolidone (90% w:w) at room temperature. To this solution, MAPC<sub>1</sub>(OH)/MMA (10/90%mol) copolymers (1% w:w) was added in a dropwise manner. The solution was deposited onto galvanized steel plates using a BarCoater (120  $\mu$ m Braive instruments). After the removal of solvents (heating to 190 °C), the thickness of the films measured with Byko-test 7500 apparatus was about 10  $\mu$ m. The same blend was realized by using MAA/MMA (10/90% mol) copolymer (1% w:w) instead.

#### Adhesive Tests

After 24 h of storage, graft copolymers adhesive properties were tested by two techniques: The crosscut testing (ISO 2409 or NFT 30-038), dry adhesion test, consisted of crosscutting the surface with a multiple knife and applying scotch tape and then peeling it. When bits of the coating were removed, the appraisalment of residual adhesive areas was quantified on a scale from zero (perfect adhesive coating) to five (all the coating was eliminated). The boiling water testing, wet adhesion test, consisted of putting the plates into boiling water (30 min) and after 1 h of drying, making a crosscut testing.

#### Anticorrosive Test

The salt spray test (DIN 50,021) was used to evaluate the anticorrosive properties. The samples were galvanized steels plates coating like the last technique.

#### Determination of Acid Value

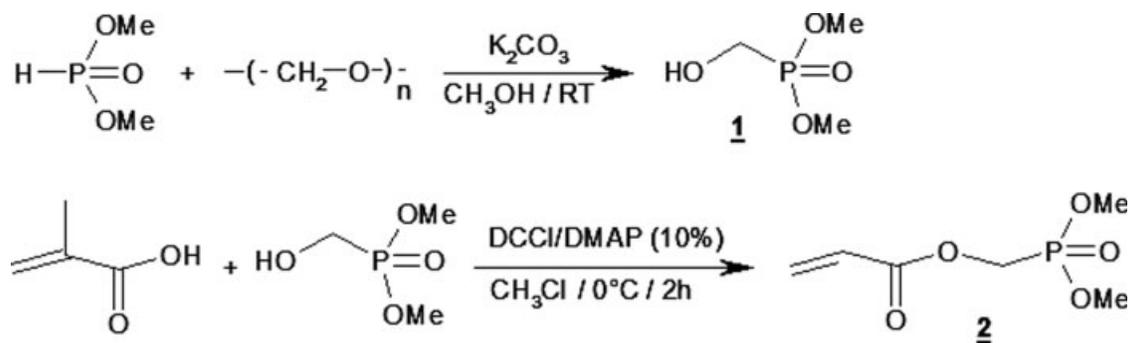
The phosphonic acid groups bring adhesive and anticorrosive properties, so that the titration of these functions was necessary. Acid value ( $I_a$ ) was defined as the amount of potassium hydroxide necessary to neutralize one gram of copolymers. The copolymer was dissolved into dimethylformamide, 10 mL of this solution was titrated with a KOH/EtOH solution (*N*/10). The values used to calculate  $I_a$  are the molecular weight of KOH (56 g/mol)  $M_{\text{KOH}}$ , the concentration of KOH  $C_{\text{KOH}}$ , the volume at equilibrium  $V_{\text{KOH}}$ , and the weight of copolymer titrated  $m_{\text{copo}}$ .

$$I_a = \frac{M_{\text{KOH}}(\text{g/mol}) \times C_{\text{KOH}}(\text{mol/L}) \times V_{\text{KOH}}(\text{L})}{m_{\text{copo}}(\text{g})} \times 10^3$$

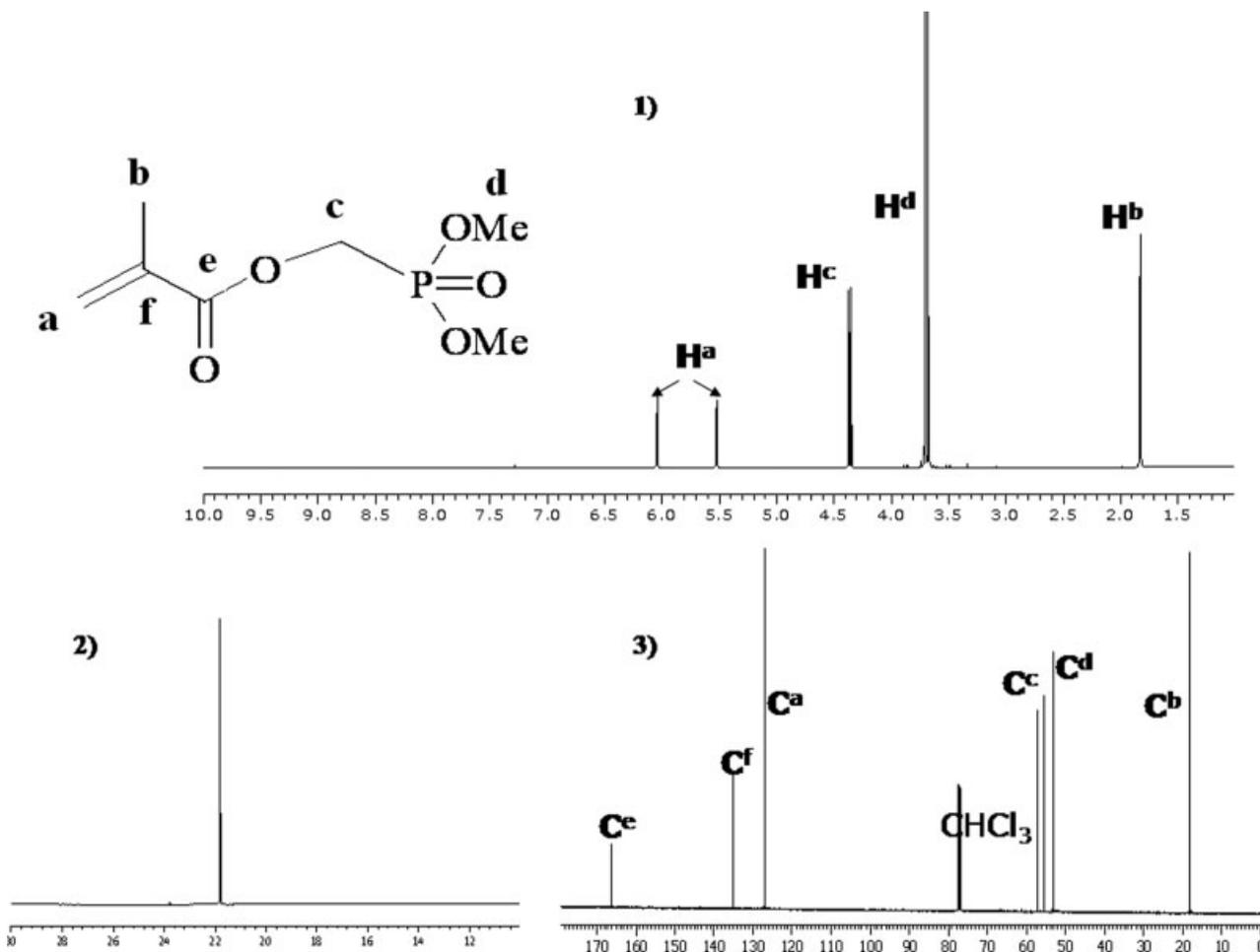
## RESULTS AND DISCUSSION

### Synthesis and Hydrolysis of MAPC<sub>1</sub>

As mentioned in the Introduction, the synthetic methods for phosphonated methacrylate are numerous, but none of them can be reproduced at an industrial scale. This work aims at producing a low cost monomer bearing a phosphonate group. The synthesis of dimethyl(methacryloyloxy)methyl phosphonate (MAPC<sub>1</sub>) via a two-steps reaction is suggested (Fig. 1) with consideration of using nonhazardous and low cost reagents at



**Figure 1.** Two-step synthesis of dimethyl(methacryloyloxy)methyl phosphonate (MAPC<sub>1</sub>) **2**.

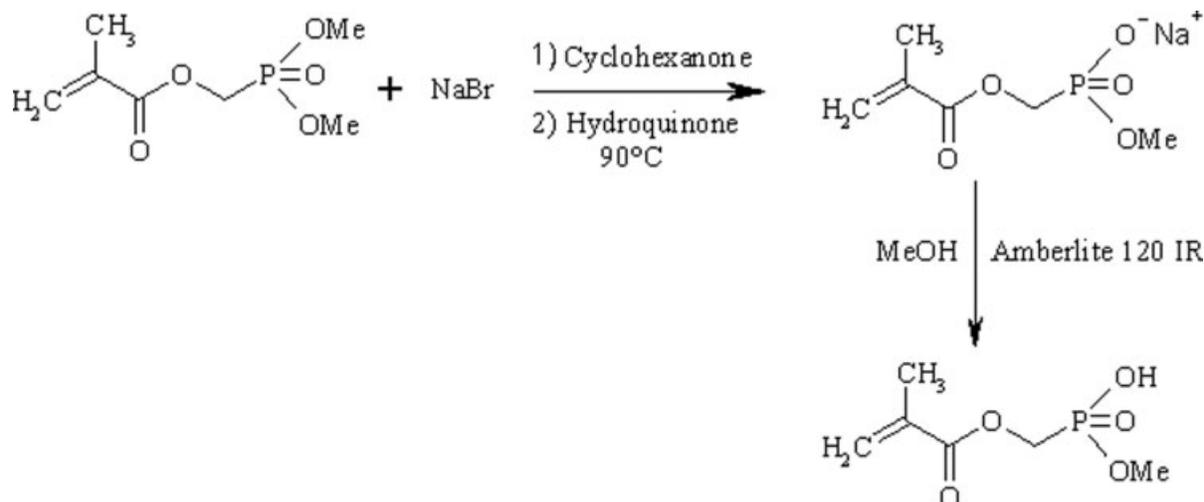


**Figure 2.** <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR analysis (CDCl<sub>3</sub>) of MAPC1.

low temperature. This concern led to the reaction being performed in heterogeneous medium at room temperature with commercially available products: dimethyl hydrogenophosphonate, paraformaldehyde, and anhydrous potassium carbonate. This last compound is usually used as non-nucleophilic base in heterogeneous medium and can be easily eliminated by filtration. According to the well-known Pudovik<sup>37,38</sup> reaction mechanism, anhydrous potassium carbonate will exchange the K<sup>+</sup> cation with dimethyl hydrogenophosphonate in the methanol phase. The resulting (OMe)<sub>2</sub>PO<sup>-</sup> anion will then be able to react with paraformaldehyde at room temperature to give dimethyl- $\alpha$ -hydroxymethylphosphonate (HOPC<sub>1</sub>) almost quantitatively.

The structure of HOPC<sub>1</sub> was definitively assessed by NMR spectroscopy, <sup>1</sup>H NMR spectrum shows the methylene in  $\alpha$  position of the

hydroxy group observed at 3.8 ppm as a doublet due to the coupling of the phosphorus, and <sup>31</sup>P NMR shows a single peak at 28.5 ppm, indicating a pure compound. The second step (Fig. 1) is the esterification reaction of dimethyl- $\alpha$ -hydroxymethylphosphonate (HOPC<sub>1</sub>) with methacrylic acid. Once again, the reaction is performed under mild conditions, that is, 0 °C in chloroform for 2 h, allowing a potential scale up for this reaction. This synthesis is allowed by using dicyclohexylcarbodiimide (DCCI) coupling agent in the presence of a small amount of DMAP (10 mol %/DCCI).<sup>39,40</sup> The coupling reaction between DCCI and methacrylic acid is thermodynamically favored as it leads to an urea compound, such as dicyclohexylurea (DCU). An azeotropic extraction of water is required to avoid any DCU formation by coupling of DCCI with water. The esterification of HOPC<sub>1</sub> was performed for



**Figure 3.** Synthesis of MAPC<sub>1</sub>(OH) by using NaBr.

2 h, DCU was filtered, and dimethyl(methacryloxy)methyl phosphonate (MAPC<sub>1</sub>) was obtained by solvent evaporation.

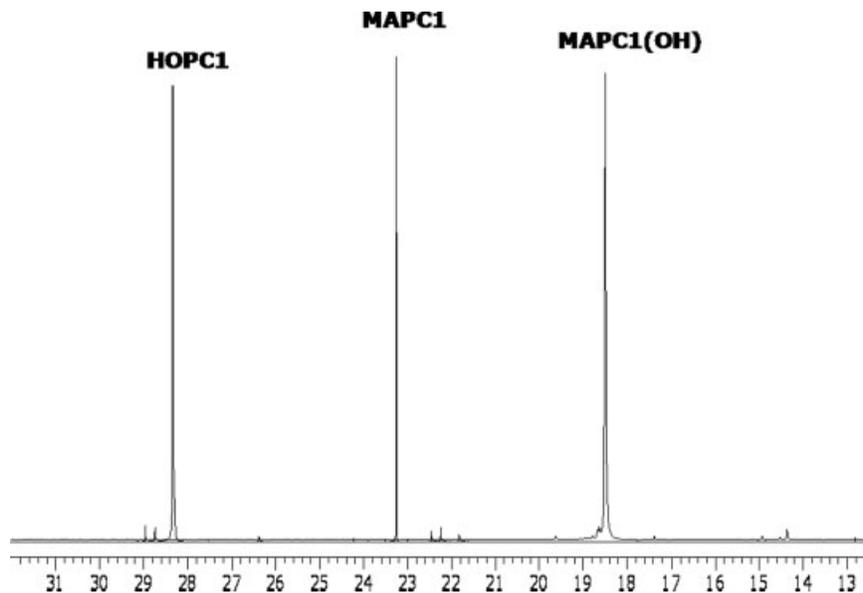
The monomer was characterized by means of NMR spectroscopy (Fig. 2), the <sup>31</sup>P spectrum shows a single peak at 22.5 ppm, indicating the quantitative esterification of HOPC<sub>1</sub>. The same observation can be done from the <sup>1</sup>H NMR spectrum where the methylene **H<sup>c</sup>** has high-field shifted at 4.3 ppm. The two methacrylic protons are observed at 5.5 and 6 ppm. The <sup>13</sup>C NMR spectrum definitively proves the MAPC<sub>1</sub> structure, from which the **C<sup>c</sup>** carbon signal (centered at 58 ppm) appears as a doublet due to the phosphorus coupling. The presence of the ester bond was determined both by the **C<sup>e</sup>** signal (centered at 170 ppm) and by the  $\nu_{C=O}$  vibration at 1640  $\text{cm}^{-1}$  from the IRTF.

The last step is the conversion of the dimethylphosphonate to the corresponding monophosphonic acid, that is, methyl(methacryloxy)methyl phosphonic hemi-acid MAPC<sub>1</sub>(OH). Brondino et al. showed that diacid groups are not specifically required and even sometimes avoided for anticorrosive applications. A too high concentration of acid groups may favor water diffusion at the interface and as a consequence will decrease the PVDF blend adhesion.<sup>30,41</sup> As mentioned in the Introduction, NaI sodium iodide allows the monodealkylation of alkyl phosphonate groups. However, NaI is a hazardous compound and should be replaced by another halogenated compound, such as NaCl or NaBr. A cleavage based on the use of NaCl would be of major interest, but this requires

high temperatures (>130 °C) to be performed, from which degradation of the methacrylic monomer starts to occur. Monodealkylation of MAPC<sub>1</sub> was performed at 80 °C in cyclohexanone in the presence of NaBr to give the corresponding monosalt (Fig. 3), and MAPC<sub>1</sub>(OH) is subsequently obtained by acidification of the monosalt passed through a column filled with sulfonic acid resin. The <sup>1</sup>H NMR spectral analysis does not give insight on the structure, apart from the signal intensity of **H<sup>d</sup>** (methyl ester), which decreased compared to that of MAPC<sub>1</sub>. <sup>31</sup>P NMR spectrum (Fig. 4) brings more evidence on the quantitative monodealkylation of MAPC<sub>1</sub> where the <sup>31</sup>P signal has high-field shifted to 18.5 ppm. In this part, MAPC<sub>1</sub> and MAPC<sub>1</sub>(OH) were obtained by the use of nonhazardous and low cost reagents at low temperature, thus the synthesis shows potential for scale up. The next part is the radical copolymerization of these two monomers with MMA.

#### Radical (co)polymerizations of MAPC<sub>1</sub> and MAPC<sub>1</sub>(OH) with MMA

Methacrylic monomers are known to be highly efficient in radical polymerization (i.e., high  $k_p$  propagation rate); initially, it is interesting to gain some insight on the behavior of dimethyl(methacryloxy)methyl phosphonate (MAPC<sub>1</sub>) radical homopolymerization and also to compare its reactivity with MMA and with other phosphonate methacrylic derivatives. Some insight to the value for  $k_p$  can be found by determining the square of the propagation rate over the ter-



**Figure 4.**  $^{31}\text{P}$  NMR analysis ( $\text{CDCl}_3$ ) of HOPC1, MAPC1, and MAPC1(OH).

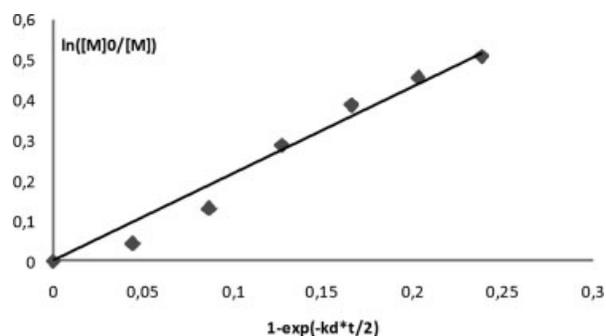
mination rate,  $k_p/kt$ , using the Tobolsky law (eq 3).<sup>42</sup>

$$\ln \frac{[M]_0}{[M]} = 2 \frac{k_p}{\sqrt{k_t}} \times \sqrt{\frac{f}{k_d}} \times \sqrt{[I_2]_0} \times \left(1 - \exp\left(-\frac{k_d t}{2}\right)\right) \quad (3)$$

Radical polymerization of MAPC<sub>1</sub> was performed at 80 °C in acetonitrile, initiated with AIBN (1 mol %) for 2 h, and the MAPC<sub>1</sub> conversion was followed over time. From eq 3, the plot of  $\ln([M]_0/[M])$  versus  $(1 - \exp(-k_d t/2))$  gives a slope of 2.17 at 80 °C (Fig. 5), enabling assessment of the  $k_p/kt$  ratio from knowledge of the values for  $k_d$  and  $f$  obtained from the literature ( $k_d$  and  $f$  being decomposition rate of initiator and initiator efficiency).<sup>43</sup> The resulting  $k_p/kt$  ratio is  $4.5 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ , this ratio is almost one order of magnitude lower than that of MMA ( $35 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$  at 80 °C)<sup>44</sup>; this preliminary result suggests that phosphonate methacrylate and MMA should have a similar reactivity in radical copolymerizations.

Radical copolymerizations of both MAPC<sub>1</sub> and MAPC<sub>1</sub>(OH) with MMA were then carried out in acetonitrile at 80 °C initiated by AIBN (1 mol %). The evolution of both MAPC<sub>1</sub> and MAPC<sub>1</sub>(OH) as well as MMA conversions over time were followed by  $^1\text{H}$  NMR spectroscopy to determine the  $r_1$  and  $r_2$  reactivity ratios. From monomer conversions, several methods can be used to reach  $r_1$  and  $r_2$  values.<sup>45–47</sup> In this study, the

methods of Jaacks<sup>45</sup> and of Finemann-Ross<sup>47</sup> have been applied, the first one simply requires to follow the concentrations of both monomers over time, whereas the second one implies the determination of  $f_1$  (initial molar fraction of monomer  $M_1$ ) and  $F_1$  (molar fraction of monomer  $M_1$  after copolymerization). The  $r_1$  [for MAPC<sub>1</sub> and MAPC<sub>1</sub>(OH)] and  $r_2$  (for MMA) values are gathered in Table 1; we can note a good correlation between the two methods with an error as low as 0.04. For MAPC<sub>1</sub>/MMA copolymerization, the average  $r_1$  and  $r_2$  ratios are 0.97 and 1.02, respectively, whereas for MAPC<sub>1</sub>(OH)/MMA copolymerization values of 0.99 and 1.02 are obtained, respectively. These two copolymerizations proceed as quasi-ideal copolymerizations, that is, statistical copolymers are obtained. In other words, neither block nor gradient copolymers have been synthesized and the



**Figure 5.** Radical polymerization of MAPC1 at 80 °C initiated with AIBN.

**Table 1.**  $r_1$  and  $r_2$  Reactivity Ratio Values for the Radical Copolymerizations of MAPC<sub>1</sub> and MAPC<sub>1</sub>(OH) (M<sub>1</sub>) with MMA (M<sub>2</sub>)

$M_1$	Jaacks		Finemann-Ross		Average $r_1$ and $r_2$ Ratios	
	$r_1$	$r_2$	$r_1$	$r_2$	$r_1$	$r_2$
MAPC <sub>1</sub>	0.95	1.04	0.99	1.08	0.97	1.02
MAPC <sub>1</sub> (OH)	0.98	1.03	1	1.09	0.99	1.02

phosphonate (or monophosphonic) group is statistically linked to the methacrylate backbone, this will increase the adhesive and anticorrosive properties for these copolymers (next part). It can be noted that both copolymerizations give similar  $r_1$  and  $r_2$  values, that is, the phosphonic group does not modify the polymerizability of the methacrylate monomer.

#### Adhesive and Anticorrosive Properties

Bressy-Brondino et al.<sup>41</sup> have prepared a single-coat system to protect galvanized steel plate against corrosion. This system consisted of a blend of PVDF, acting as gas barrier, with organophosphorus copolymers, promoting PVDF adhesion onto galvanized steel plate. This system showed great performance, at preventing the spread of corrosion. The aim was to reproduce the adhesion and anticorrosion tests to check the efficiency of the additives, that is, MAPC<sub>1</sub>/MMA and MAPC<sub>1</sub>(OH)/MMA copolymers blended with PVDF. The blends of PVDF (90% w:w) with phosphonated methacrylate additives (10% w:w) were coated onto steel plates, and both their adhesive and anticorrosive properties were evaluated (Table 2). Three different additives were prepared, one based on MAPC<sub>1</sub>/MMA co-

polymer (initial molar ratios of 10% for MAPC<sub>1</sub>) and two others based on MAPC<sub>1</sub>(OH)/MMA copolymers with initial molar ratios of 10 and 20% for MAPC<sub>1</sub>(OH). The adhesion test consists of immersing the plates in boiling water and applying the crosscut testing (see experimental part). As expected, the phosphonate groups promote good adhesion properties, especially for the phosphonic hemi-acid. These blends have been subjected to the salt spray test for 14 days to evaluate their anticorrosive properties. The spread of corrosion, represented by the percentage of corroded surface (Table 2), is in accordance with the adhesion results. Indeed, the MAPC<sub>1</sub>(OH)/MMA copolymer shows only 40% of corroded surface (after 14 days subjected to the salt spray test) due to the high level of adhesion maintained by the phosphonic hemi-acid group. It can be noted that the MAPC<sub>1</sub>(OH)/MMA copolymer is less efficient when the initial molar ratio of MAPC<sub>1</sub>(OH) is higher (20%), that is, an acid content of 8.2 mg KOH/g. Bressy-Brondino et al. have already attested that a maximum acid value ranging between 5.0 and 6.0 mg KOH/g was required to reach good adhesion properties.

The blend of PVDF with MAPC<sub>1</sub>(OH)/MMA (10% w:w of additive compared to PVDF) was

**Table 2.** Adhesion and Anticorrosive Properties of PVDF Blended with MMA/MAPC1 and MMA/MAPC<sub>1</sub>(OH) Additives (10% w:w Compared to PVDF)

Additive (Initial Molar Ratio)	$I_a$ of Blend (mg KOH/g) <sup>a</sup>	Adhesion Test (Cotation/5) <sup>b</sup>	% of Corroded Surface <sup>c</sup>
MMA/MAPC1 (90/10)	0	4	99
MMA/MAPC1(OH) (90/10)	4.6	0	40
MMA/MAPC1(OH) (80/20)	8.2	1	99

<sup>a</sup> Amount of KOH necessary to neutralize one gram of copolymer.

<sup>b</sup> Boiling water and crosscut testing. Zero cotation corresponds to a perfect adhesive coating.

<sup>c</sup> Salt spray test for 14 days.

then subjected to the crosscut test in dry adhesion and compared to PVDF without any additive and also to PVDF blended with MAA/MMA (10% w:w of additive compared to PVDF) (Table 3). As expected, MAPC<sub>1</sub>(OH)/MMA additive brings high improvement to PVDF adhesion into the steel plate. A better adhesion notation was obtained for the phosphonic group compared to the carboxylic group of MAA, used in the same molar concentrations than the phosphonic group. Figure 6 presents the adhesion properties (obtained by the crosscut testing) versus the boiling water immersion time for these additives. The PVDF alone is pulled out after 2 min, whereas MAA/MMA additive brings an improvement of the adhesion properties, slightly decreasing after 20 min. Finally, when PVDF is blended with MAPC<sub>1</sub>(OH)/MMA, the adhesion remained unchanged even after 2 h immersed in boiling water. This result confirms that the phosphonic groups of MAPC<sub>1</sub>(OH) are very good adhesion promoters for PVDF both in dry and wet state, and as a consequence will allow to reach good anticorrosive properties. In conclusion, MAPC<sub>1</sub>(OH) is a very attractive monomer that will allow, after radical copolymerization with MMA, high adhesion performance.

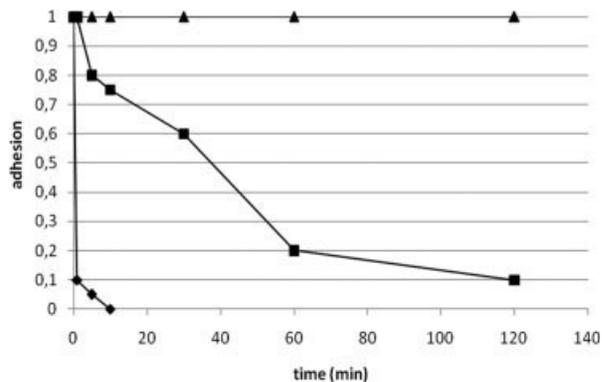
## CONCLUSIONS

Dimethyl(methacryloxy)methyl phosphonate (MAPC<sub>1</sub>) and methyl(methacryloxy)methyl phosphonic hemi-acid MAPC<sub>1</sub>(OH) synthesis have been performed using nonhazardous and low cost reagents at low temperature. The selective hydrolysis of the phosphonate group into phosphonic hemi-acid was for the first time quantitatively conducted in the presence of NaBr, replacing the usual NaI reagent, and showing promise

**Table 3.** Adhesion Properties of PVDF Solef and PVDF Solef Blended with MMA/MAA and MMA/MAPC<sub>1</sub>(OH) Additives (10% w:w Compared to PVDF)

	Cross-Cut Test <sup>a</sup>
PVDF Solef	5
PVDF Solef + MMA/MAA(90/10)	2
PVDF Solef + MMA/MAPC <sub>1</sub> (OH)(90/10)	0

<sup>a</sup> Crosscut testing (dry adhesion). Zero notation corresponds to a perfect adhesive coating.



**Figure 6.** Adhesion properties versus boiling water immersion time of PVDF Solef (♦) and PVDF Solef blended with MMA/MAA (■) and MMA/MAPC<sub>1</sub>(OH) (▲) additives (10% w:w compared to PVDF).

to be reproduced on an industrial scale. Both the methacrylic monomers were copolymerized with MMA leading to statistical copolymers where the phosphonate or the phosphonic hemi-acid groups were distributed along the polymethacrylate backbone. This statistical repartition afforded very good adhesive and anticorrosive properties for a blend of PVDF with copolymers, coated onto a galvanized steel plate. Only 40% of the surface was corroded after being subjected to the salt pray test for 14 days, which shows very high level of efficiency for these additives. These new monomers and corresponding copolymers show promise for industrial development in several domains, such as automotive paint.

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