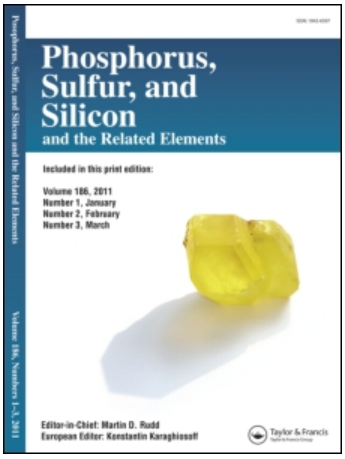

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Synthesis of a New Phosphonate Methacrylate Monomer

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In this work, a new methacrylate phosphonate monomer synthesis was described according to a two-step reaction. First the monoaddition of thioglycolic acid onto dimethylvinyl phosphonate monomer led to dimethyl–5-carboxymethyl-2-thiaethylphosphonate, a new phosphonate acid compound. This reaction also led to the thioester homologue of dimethyl–5-carboxymethyl-2-thiaethylphosphonate with a 15% yield by reaction of a thioglycolic acid thioester with dimethylvinyl phosphonate. Second, dimethyl carboxy-4-thia-butyl phosphonate reacted with glycidyl methacrylate. This epoxy-acid addition reaction was catalyzed by chromium salt at 70°C and led to the new methacrylate phosphonate monomer. We showed that only the secondary alcohol was obtained via a β addition. The two-step reaction final yield was calculated to be about 85%.

Keywords Methacrylate; phosphonate; thiol; transfer reaction

INTRODUCTION

Due to their specific properties, organophosphorus monomers are widely studied. These compounds are commonly used for flame-resistance improvement.[1–4] Among their flame-retardant properties, organophosphorus compounds find their application as adhesion promoters for paints and adhesives.[5] Recently, phosphonated monomers were used in emulsion polymerization,[6–8] conferring a very good stability to the corresponding lattices.

Many papers deal with the synthesis of phosphonated monomers.[9,10] Methacrylics one are of particular interest for their use in paints for metals.[11] Their salt forms can be used in detergent formulations.[12,13]

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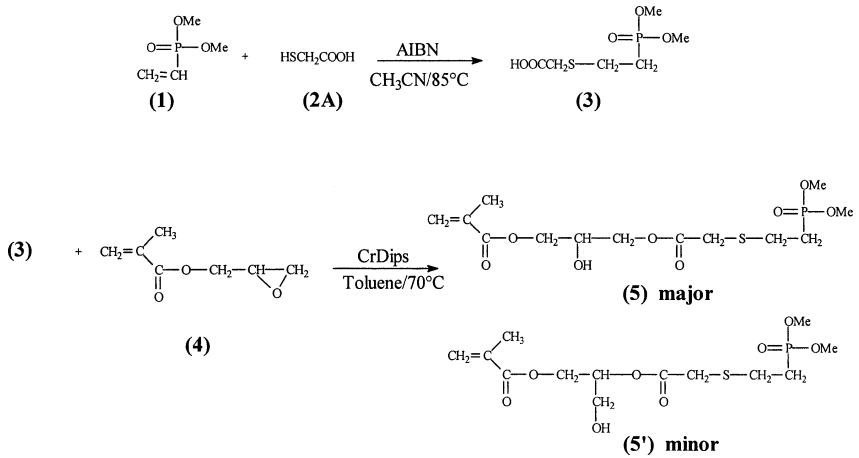
Methacrylic phosphonated monomers were mainly synthesized via the Arbusov reaction between a halogenated methacrylate and a trialkyl phosphite.[14] The radical pathway, using transfer agents, was extensively used. Misato and colleagues[15] described the radical addition of dialkylhydrogenophosphonate on a vinyl methacrylate. In our laboratory, Boutevin and colleagues[16] elaborated the synthesis in two steps of phosphonate methacrylate presenting a sulfur bridge. The first step is the addition of 2-hydroxy ethyl mercaptan onto allyldiethyl phosphonate. This new alcohol is slowly added to methacryloyl chloride in a second step leading to the phosphonate methacrylate. Recently, Jeanmaire and colleagues[11,17] synthesized a range of phosphonated alcohols followed by their methacrylation to give the corresponding phosphonate methacrylate monomers. Youssef and colleagues[18] also suggested an easier way to obtain phosphonate methacrylate monomers. They realized the reaction between diethyl(epoxy-2,3-propyl)phosphonate with methacrylic acid at 80°C, using tetraethylammoniumbromide (TEAB) as catalyst. However, they obtained only a 45% yield. They also developed a direct esterification reaction between a phosphonate alcohol, i.e., diethyl dihydroxy-1,2-propyl phosphonate and methacryloyl chloride. This reaction, carried out at room temperature, was more successful with a 64% yield.

Finally, in our laboratory[19] we synthesized a new phosphonate methacrylate from an isocyanate bearing a methacrylate function, i.e., isocyanatoethyl methacrylate. This methacrylate reacted with a phosphonate alcohol at C1 or C2, which was previously synthesized, to give the corresponding phosphonate methacrylate.

DISCUSSION

The synthesis of the new phosphonate methacrylate monomer (**5**) was performed in two steps and is represented in Scheme 1.

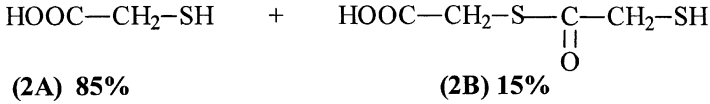
The first step consists of a monoaddition between a thioglycolic acid (**2A**) transfer agent and a dimethylvinyl phosphonate (**1**) monomer. The monoadduct product is targeted to lead to a new phosphonate acid compound, dimethyl carboxy-4-thia-butyl phosphonate (**3**). In the second step, this new acid compound (**3**) is engaged in an epoxy-acid catalyzed addition reaction with the glycidyl methacrylate monomer (**4**) to get the desired phosphonate methacrylate monomer (**5**). The two-step reaction is discussed below and the different reaction products are characterized by means of FTIR and NMR.



SCHEME 1 Reaction scheme for the synthetic route to the new methacrylate phophonate monomer (**5**).

Synthesis of Dimethyl-5-carboxymethyl-2- thiethyl-phosphonate (3)

This new acid phosphonate compound can be obtained easily by using a radical process based on a transfer reaction of a thiol compound to dimethyl vinylphosphonate (**1**). The transfer agent used is thioglycolic acid (**2A**). Thioglycolic acid always contains an impurity, i.e., the thioester of thioglycolic acid (**2B**) (Scheme 2).



SCHEME 2 Thioglycolic acid (**2A**) and its thioester homologue (**2B**) used in the synthesis of dimethyl–5-carboxymethyl-2-thiaethylphosphonate (**3**).

This compound (**2B**) is obtained by intrinsic thioesterification of thioglycolic acid (**2A**) at room temperature with a 15% yield. This compound may also react with dimethyl vinylphosphonate monomer. Dimethyl–5-carboxymethyl-2-thiaethylphosphonate (**3**) targeted product can be obtained only by the monoaddition of thioglycolic acid with dimethyl vinylphosphonate. This monoaddition is possible by using a R_0 ratio ([transfer agent]/[monomer]) equal to 1. This reaction is carried out at 85°C in acetonitrile. Azobisisobutyronitrile (AIBN) is used to initiate the radical process.

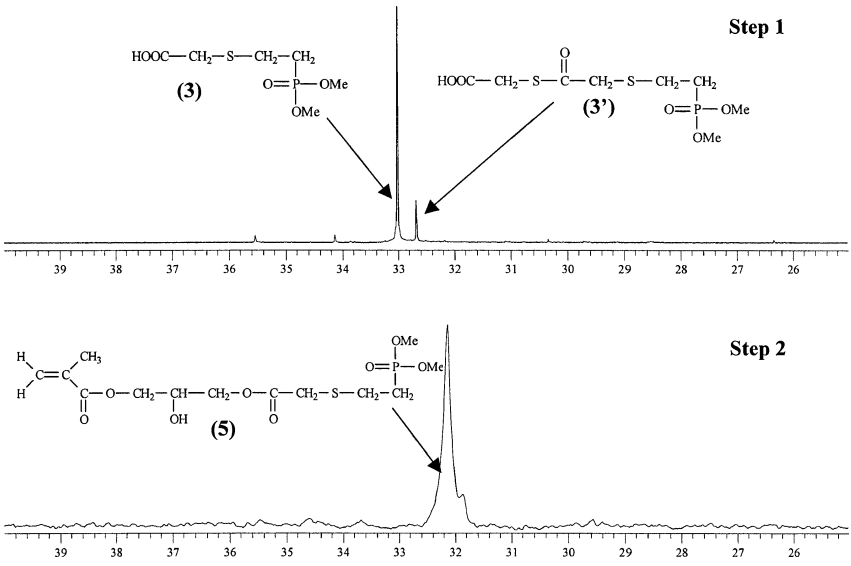


FIGURE 1 ^{31}P NMR (DMSO) spectra of dimethyl–5-carboxymethyl-2-thiaethylphosphonate (**3**) and (**3′**) in step 1 and of the methacrylate phosphonate monomer (**5**) in step 2.

First, we characterized this monoaddition by ^{31}P NMR (Figure 1, step 1).

^{31}P NMR clearly shows 2 peaks. The main sharp peak is observed at 33 ppm and is attributed to dimethyl–5-carboxymethyl-2-thiaethylphosphonate. The last peak observed at 32.5 ppm is probably the reaction product of thioester of glycolic acid with dimethyl vinylphosphonate.

We tried to confirm and quantify this monoaddition by ^{1}H NMR (Figure 2).

^{1}H NMR spectrum shows the disappearance of the triplet for SH from both thioglycolic acid and its thioester homologue, proving the complete reaction of the thiol. At 2.7 and 2 ppm we observe two multiplets for CH_2, respectively, in α and β positions of the phosphonate group. The doublet for the methyl of the phosphonate group remains at 3.5 ppm. Finally, 1H NMR confirms the structure of both monoadduct compounds. The CH_2 in α position of the carboxy group for dimethyl–5-carboxymethyl-2-thiaethylphosphonate is observed at 3.1 ppm. Hence, the same CH_2 is observed at 3.6 ppm for the monoadduct of its thioester homologue. The ratio of both monoadducts is calculated to be 85% for dimethyl–5-carboxymethyl-2-thiaethylphosphonate (**3**) and 15% for the

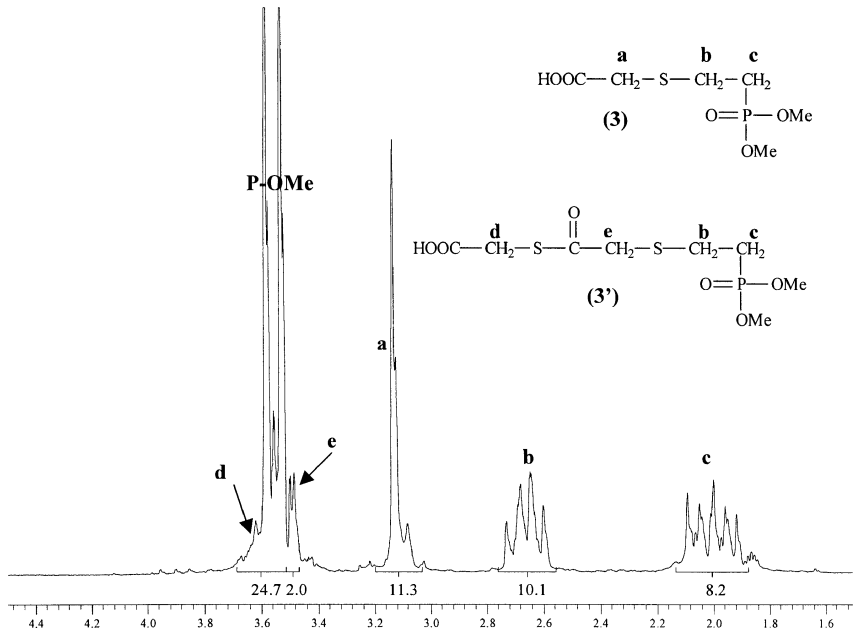


FIGURE 2 ^{1}H NMR (DMSO) spectra of dimethyl carboxy-methyl-2-thia-ethyl-phosphonate (**3**).

thioester homologue monoadduct (**3′**). This ratio is identical to the thiol ratio (Scheme 2).

Synthesis of the Methacrylate Phosphonate Monomer (5)

This methacrylate phosphonate monomer (**5**) is obtained by the addition of an epoxide (**4**) to (**3**). The epoxy-acid reaction can be an α and a β addition. It was already demonstrated[20] that the β addition, leading to a secondary alcohol, is the major reaction. This reaction is usually catalyzed by tertiary amine at 100°C. To avoid any reaction of the methacrylate double bond, we performed this reaction at a lower temperature (70°C) and catalyzed it with chromium salt, as previously done by Loubat and colleagues.[21] The product resulting from this reaction is analyzed by FTIR, ^{31}PNMR and ^{1}H NMR.

From the FTIR spectrum (Figure 3), one can observe:

– the presence of an alcoholic OH bond at 3351 cm^{-1}, characterizing the reaction between the acid and epoxide groups;
– the peak of the acid group at 1700 cm^{-1} is shifted to 1720 cm^{-1} for the ester function;

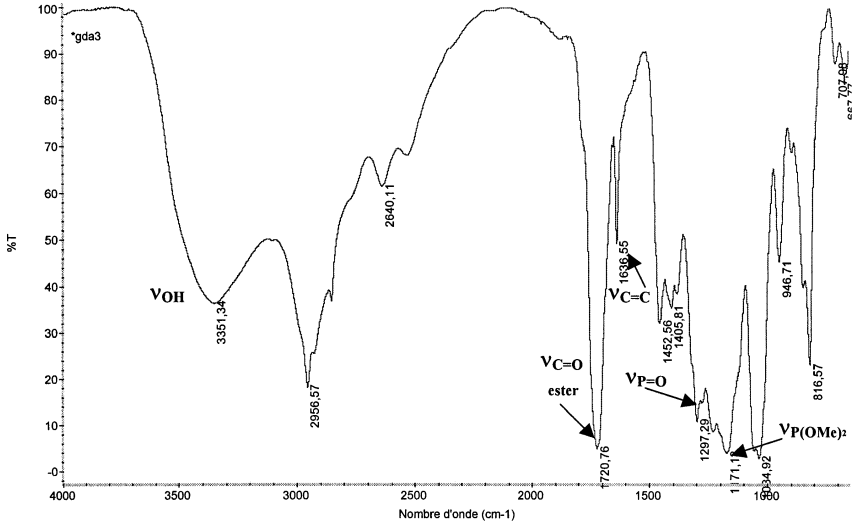


FIGURE 3 FTIR spectra of the methacrylate phosphonate monomer (**5**).

– the peak of the ethylenic double bond at 1636 cm^{-1} is observed characterizing the methacrylate double bond; and
– finally, the peaks at 1300 and 1170 cm^{-1} are still observed due to the phosphonate function.

^{31}P NMR of the final product is showed in Figure 1 (step 2). The spectrum for step 2 clearly shows that the sharp peaks from both monoadducts, previously observed in step 1, totally disappeared. Only one peak centred at 32 ppm is observed and is attributed to the phosphonate group from the methacrylate phosphonate monomer (**5**). ^{31}P NMR and FTIR prove that the reaction between dimethyl carboxy-4-thia-butyl phosphonate (**3**) and glycidyl methacrylate **(4**) is effective and quantitative.

But it is only the ^{1}H NMR (Figure 4) that confirms unambiguously the structure of the methacrylate phosphonate monomer (**5**).

In Figure 4, the assignments corresponding to the monomer (**5**) are reported. First, we can observe the total disappearance of the epoxide protons between 2.5 and 3.2 ppm. The signal for the CH_2 of the glycidyl group, previously at 3.2 ppm, is shifted to 4 ppm. We also remark that the signal for CH_2 in α position of the carboxy group for dimethyl carboxy-4-thia-butyl phosphonate (**3**), previously observed at 3.1 ppm, totally disappeared. The characteristic protons of the methacrylate group at 5.7 and 6.1 ppm are still observed. In Scheme 1, we also

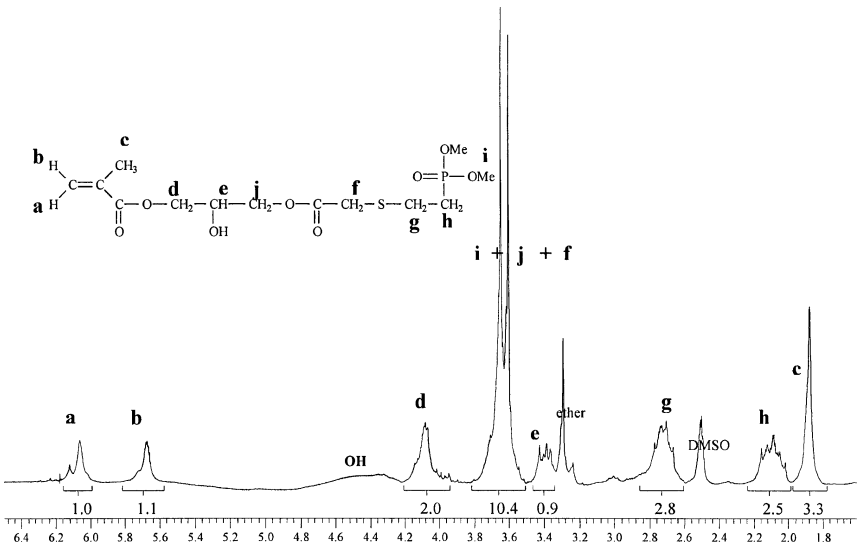


FIGURE 4 ^{1}H NMR (DMSO) spectra of the methacrylate phosphonate monomer (**5**).

annotated the structure (**5′**). This phosphonate methacrylate (**5′**) exhibits a primary alcohol that was obtained via an α addition. If this structure was obtained, we should see a signal in the ^{1}H NMR at 5ppm characterizing the CH in the β position of the OH function. As this is no signal around 5 ppm, we concluded that only the structure (**5**) is obtained. Finally, ^{1}H NMR confirms that the acid-epoxy reaction at 70°C is quantitative.

Thus, this two-step reaction leads to a new methacrylate phosphonate monomer (**5**) with an 85% yield.

EXPERIMENTAL PART

Thioglycolic acid, glycidyl methacrylate, chromium triacetate, diisopropylsalicylic acid, acetonitrile, and toluene were supplied by Aldrich and used without further purification. AIBN, supplied by Aldrich, was purified in methanol. Dimethylvinylphosphonate monomer, supplied by Aldrich, was distilled (b.p. = 195°C at 160 mmHg) and stored under an inert atmosphere at 5°C.

Synthesis of Dimethyl Carboxy-4-thia-butyl Phosphonate (3)

6.75 g (0.05 mol) of dimethyl vinylphosphonate (**1**), 4.6g (0.05 mol) of thioglycolic acid (**2A**), 0.08 g (0.5 mmol) of AIBN and 50 mL of

acetonitrile were introduced in a 100 mL round bottom flask fitted with a nitrogen flow. Nitrogen was bubbled into the solution at room temperature during 15 min. The mixture was then stirred under inert atmosphere at 85°C and maintained during 10 h. After cooling, acetonitrile was removed under vacuum. The residual dimethyl vinylphosphonate (5% by ^{1}H NMR) is removed by distillation. Finally, the product (**3**) was obtained with an 85% yield.

Synthesis of Diisopropylsalicylate Chromium (CrDips)

Cr Dips are obtained from the reaction of 3 g (0.013 mol) of chromic triacetate with 5.82 g (0.026 mol) of diisopropyl salicylic acid in refluxing methanol during 3 h and subsequent removal of acetic acid formed under vacuum at 85°C.

Synthesis of Methacrylate Phosphonate Monomer (5)

1 g (4.4 mmol) of dimethyl carboxy-4-thia-butyl phosphonate (**3**) and 50 mL of anhydrous toluene were introduced in a two-necked round bottom flask, which was fitted with a condenser, a dropping funnel, and a nitrogen flow. The solution was stirred under inert atmosphere at 70°C. To this solution, 0.62 g (4.4 mmol) of glycidyl methacrylate (**4**), 0.02 g (1% by weight of the mixture) of Cr dips, and 10 mL of anhydrous toluene were added dropwise through the dropping funnel. The mixture was maintained under magnetic stirring for 15 h. After cooling the solution, toluene was removed under vacuum. The methacrylate phosphonate monomer (**5**) was obtained with a quantitative yield.

Characterization

The chemical structure of the products was determined by ^{1}H and ^{31}P NMR (Bruker AC 200 MHz) at room temperature in DMSO solutions. The INVGATE procedure with delay D1 of 10s to get the quantified final yield. Infrared (FTIR) spectra are recorded on a Nicolet 510P FTIR spectrometer with a band accuracy of ± 2 cm^{-1}.

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