

# Synthesis and Polymerizations of Monomers Bearing Phosphonated Groups. I. Applications on Acrylates and Methacrylates

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## SYNOPSIS

The synthesis of (meth)acrylic monomer bearing phosphonic esters, phosphonic acids, and semisalts is presented. This synthesis was performed in four steps. The first concerns the phosphorylation of allyl bromide by Arbuzov reaction. Second is the monoaddition of 2-mercapto ethanol onto the allyl double bond, whereas the third consists of the acrylation of the previous phosphonated alcohol. The fourth step involves the dealkylation of the phosphonated ester by the mean of trimethyl halosilane and then the hydrolysis of the obtained silyl ester. Finally, the salification of the diacid is performed in order to stabilize the diacid. In the last part of this work two applications of these monomers in the field of additives for adhesives cured by UV or EB were studied. The results clearly show the superiority of phosphonic acid about the homologous esters. Moreover, the number of acid group and the neighbouring of this acid play an important part in adhesion phenomenon.

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## INTRODUCTION

It is well known that in coatings technology certain additives are used to improve adhesion on substrates. These compounds contain amine, silane, titanate, and phosphoric or carboxylic groups.<sup>1,2</sup> Actually, metal surfaces treated with poly(vinylphosphonic acid) exhibit a better corrosion resistance and an improved adhesion to coatings.<sup>3,4</sup> Presently 2-methacryloyloxy ethyl phosphoric acid (Ebecryl 169, Radcure) is commercially available and widely used. Such a product is often added in formulations cured by UV<sup>5</sup> or EB.<sup>6</sup> If acid chloride (P-Cl) is the starting material, hydrolysis by water in the presence of tertiary amine<sup>7</sup> or by caustic soda in methanol<sup>8</sup> easily leads to the corresponding acid. On the contrary, from esters a drastic acid or basic hydrolysis are necessary<sup>9,10</sup> that would modify other weak groups of the molecules.<sup>11</sup> In order to avoid these side-re-

actions, Rabinowitz<sup>12</sup> discovered a process in two steps: silylation by chloro or bromotrimethyl silane<sup>13,14</sup> followed by a water or an alcohol hydrolysis. This article deals with the synthesis and polymerization of new (meth)acrylic products that contain phosphonic acid linked by carbon—phosphorus bond. On the other hand some properties are given and compared to commercially available products.

## EXPERIMENTAL

Most starting materials were purchased from Aldrich and did not require any purification prior to use. AIBN was supplied by Merck.

Gel permeation chromatography (GPC) analyses were conducted with thermostated (25°C) columns, the diameters of the pores of which were 10,000, 1,000, 500, 100, and 50 Å. Tetrahydrofuran (THF) was used as the eluent (flow 1.5 mL min<sup>-1</sup>) at 25°C. The detection was performed by a differential refractometer type SP 8430.

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The different pure products were characterized by  $^1\text{H-NMR}$  spectroscopy at room temperature.  $^1\text{H-NMR}$  spectra were recorded on a Bruker CW 60 apparatus or for a higher resolution on a Bruker WM 360 or a Bruker AC 250, by using deuterated chloroform as the solvent and tetramethyl silane as the internal reference. The letters s, d, t, q, and m designate singlet, doublet, triplet, quartet, and multiplet, respectively.

Differential scanning calorimetry (DSC) measurements were conducted with a Perkin-Elmer DSC-4 apparatus equipped with a TADS micro-computer. The apparatus was calibrated with indium and with *n*-decane. After its insertion into the DSC apparatus, the sample was first cooled to  $-50^\circ\text{C}$  for 15 min. A first scan was made at a heating rate of  $40^\circ\text{C min}^{-1}$ , up to  $200^\circ\text{C}$ , where it stayed for 2 min. Then it was quenched to  $-50^\circ\text{C}$  at a cooling rate of  $320^\circ\text{C min}^{-1}$ . It was again left for 10 min at that temperature before a second scan at a heating-rate of  $20^\circ\text{C min}^{-1}$  gave the values of glass-transition temperature ( $T_g$ ) reported here, taken at the half-height of the heat capacity jump of the  $T_g$ .

The different homopolymers and copolymers were analyzed by elemental analysis at the Laboratory of Microanalysis (CNRS) of the Chemistry School (ENSCM). The indicated values for the elemental analyses designate the content of carbon, hydrogen in grams for 100 g of pure product.

#### Synthesis of Diethyl Allyl Phosphonate (I)

In a two-necked round-bottom flask, equipped with a dropping funnel and a distillation device, 182.6 g (1.1 *M*) of triethylphosphite was introduced. At  $80^\circ\text{C}$ , 121 g (1 *M*) of allyl bromide, which contain  $1.21 \cdot 10^{-2}$  g of hydroquinone, were added dropwise for about 30 min.

Then the temperature was progressively raised to  $100\text{--}110^\circ\text{C}$  in order to distilled the produced ethyl bromide. The reaction then last about 4 h. Diethyl allyl phosphonate, 160 g, was obtained by distillation. bp =  $45^\circ\text{C}/20$  mmHg. The yield was 90%.

ANAL:  $\text{C}_7\text{H}_{15}\text{PO}_3$ : Calcd: C, 47.19%; H, 8.43%; O, 26.97%; P, 17.42%; (FW = 178 g mol $^{-1}$ ). Found: C, 46.18%; H, 8.41%; O, 26.26%; P, 16.67%.

The structure of (I) was characterized by  $^1\text{H NMR}$  (solvent  $\text{CDCl}_3$ ). The signal of the vinyl protons appear in the  $5.0\text{--}6.0 \cdot 10^{-6}$  range whereas a doublet dedoubled by the P atom at  $2.46 \cdot 10^{-6}$  is assigned to the methylene group adjacent to the phosphonyl. The triplet at  $1.27 \cdot 10^{-6}$  and the multiplier at the 4.08 correspond to the ethyl group of the phosphonic ester.

#### Synthesis of Diethyl Hydroxy-6-thia-4-Hexyl Phosphonate (II)

In a 2-L 3-necked round-bottom flask (equipped with a condenser, a nitrogen flow, and a dropping funnel) 85.7 g (1.1 *M*) of 2-mercapto ethanol and 1 L of THF was introduced. The solution was heated to  $80^\circ\text{C}$ . Then, 178 g (1 *M*) of diethyl allyl phosphonate (I), which contained 1.64 g (0.01 *M*) of AIBN were added dropwise. The reaction was stirred for about 5 h. After evaporation of THF and volatile reactants, the solution was heated at  $35\text{--}40^\circ\text{C}$  under  $10^{-2}$  mmHg for 30 min. The 236 g of residue represent compound (II) (yield 92%).

ANAL:  $\text{C}_9\text{H}_{21}\text{O}_4\text{SP}$ : Calcd: C, 42.19%; H, 8.20%; O, 25.00%; S, 12.50%; P, 12.11%; (FW = 256 g mol $^{-1}$ ). Found: C, 41.86%; H, 8.34%; O, 24.65%; S, 11.50%; P, 12.30.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $10^{-6}$ ): 1.3 (t, 6H); 1.9 (m, 4H); 2.62 (t, 2H); 2.68 (t, 2H); 3.7 (t, 2H); 4.06 (dq, 4H).

#### Synthesis of Diethyl 6-(methacryloyloxy)-4-thia-hexyl Phosphonate (III, a)

In a 500-mL two-necked round-bottom flask containing 250 mL of freshly distilled toluene 64 g (0.25 *M*) of phosphonated alcohol (II), 25.25 g (0.25 *M*) of triethylamine, and 100 ppm of hydroquinone were stirred at room temperature for 5 min. Then the mixture was cooled in an ice bath. Methacryloyl chloride, 26 g (0.25 *M*), was added dropwise for 30 min, and then the reaction was maintained at room temperature for 16 h. The gross was filtered off and then diluted in 50 mL of toluene, washed four times with 30 mL of water to get rid of the ammonium salt. The organic layer was dried over sodium sulfate, the solvent and volatile products evaporated. Two hundred seventy-four grams were obtained as (III-a) (yield 85%).

ANAL:  $\text{C}_{13}\text{H}_{25}\text{SPO}_5$ : Calcd: C, 48.15%; H, 7.72%; S, 9.88%; P, 9.57%; (FW = 324 g mol $^{-1}$ ). Found: C, 48.44%; H, 7.73%; S, 9.07%; P, 8.85.

The  $^1\text{H NMR}$  spectrum exhibits the characteristic ethylenic protons in the  $5.45\text{--}6.10 \cdot 10^{-6}$  range and the triplet at  $4.1 \cdot 10^{-6}$  assigned to the  $\text{CH}_2$  in  $\alpha$  position to ester group.

#### Synthesis of Diethyl 6-(acryloyloxy)-4-thia-hexyl Phosphonate (III, b)

The synthesis was carried out in the same manner as for (III, a), using acryloyl chloride instead of methacryloyl chloride; 257 g (yield 83%) of product (III-b) was obtained.

ANAL:  $C_{12}H_{23}SPO_5$ : Calcd: C, 46.45%; H, 7.42%; S, 10.32%; P, 10%; (FW = 310 g mol<sup>-1</sup>). Found: C, 45.18%; H, 7.54%; S, 9.63%; P, 11.23%.

The <sup>1</sup>H NMR spectrum exhibits the three ethylenic protons in the 5.65–6.10<sup>-6</sup> range.

### Synthesis of Bis(trimethyl silyl)-6-(acryloyloxy)-4-thia-hexyl Phosphonate (IV)

#### From Chlorotrimethylsilane

Chlorotrimethyl silane (12 g, 0.11 M) was added to a stirred mixture of (III, b) (15.5 g, 0.05 M) and sodium iodide (16.2 g, 0.11 M) in 50 mL of acetonitrile under nitrogen at room temperature. The mixture was heated to 40°C for 15 min. The solid was filtered off and the filtrate was evaporated (17.9 g, 90% yield).

#### From Bromotrimethylsilane

In the same manner, 31 g of (III, b), 50 mL of CH<sub>2</sub>Cl<sub>2</sub>, and an excess of BrSi(Me)<sub>3</sub> (0.22 M) were used. Obtained were 39.8 g (92% yield) of product (IV).

ANAL:  $C_{14}H_{31}SSi_2PO_5$ : Calcd: C, 42.21%; H, 7.79%; P, 7.79%; Si, 14.07%; (FW = 398 g mol<sup>-1</sup>). Found: C, 41.78%; H, 7.71%; P, 8.04%; Si, 13.36. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 10<sup>-6</sup>): 0.3 (s, 18H); 1.8 (m, 4H); 2.62 (t, 2H); 2.78 (t, 2H); 4.28 (t, 2H) and 5.8–6.5 (ABX system, 3H).

### Synthesis of 6-(acryloyloxy)-4-thia-hexyl Phosphonic Acid (V)

#### Hydrolysis of Compound (IV) by Water

In an 100-mL Erlenmeyer, 7.96 g (0.02 M) of (IV) were introduced and 10 mL of water was added for 16 h at 25°C. The product was obtained after extraction of organic products by CHCl<sub>3</sub> and evaporation of water.

#### Hydrolysis by Methanol of Compound (IV)

In 19.9 g (0.05 M) of (IV), 20 mL of methanol was added and stirred for 10 min. After evaporation of excess of methanol, 12.7 g of (V) were obtained (100% yield).

ANAL:  $C_8H_{15}SPO_5$ : Calcd: C, 37.80%; H, 5.91%; S, 12.60%; P, 12.20%; (FW = 254 g mol<sup>-1</sup>). Found: C, 37.31%; H, 6.08%; S, 11.89%; P, 11.98%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 10<sup>-6</sup>): 1.95 (m, 4H); 2.7 (t, 2H); 2.8 (t, 2H); 4.32 (t, 2H) and 5.8–6.5 (ABX system, 3H).

### Synthesis of Dicyclohexyl Ammonium Salt of Acid (V)

A mixture of 12.7 g (0.05 M) of (V), 18 mL of dioxane, and 0.495 g (0.0275 M) of water were introduced in an Erlenmeyer. Then 4.98 g (0.0275 M) of dicyclohexylamine were added dropwise. The precipitate was filtered off and washed four times with diethylether and then dried in vacuum at 40°C for 10 h. Product (VI), 18.5 g, was obtained (85% yield).

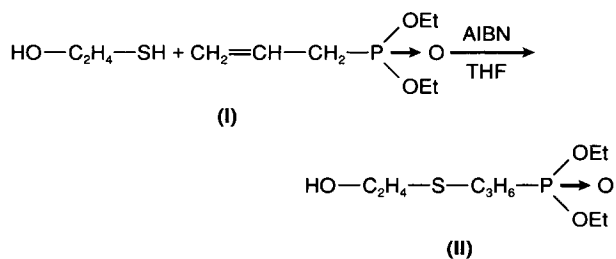
ANAL:  $C_{20}H_{38}NSPO_4$ : Calcd: C, 55.17%; H, 8.74%; S, 7.36%; N, 3.22%; (FW = 435 g mol<sup>-1</sup>). Found: C, 54.89%; H, 8.79%; S, 7.18%; N, 3.18%. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 10<sup>-6</sup>): 1.1–2.15 (m, 24H); 2.6 (t, 2H); 2.75 (t, 2H); 2.9 (t, 2H); 4.28 (t, 2H) and 5.8–6.5 (ABX system, 3H).

### Homopolymerization of Salt (VI)

In a 50-mL flask equipped with a condenser and under nitrogen flow, 4.35 g (0.01 M) of salt (VI) were introduced with 20 mL of CHCl<sub>3</sub> and the mixture was heated at 60°C. Then 10<sup>-4</sup> M of AIBN were added and the mixture was stirred for 10 h. We noticed the formation of a precipitate located in the bottom of the flask. The precipitate was dissolved in methanol and then precipitated from CHCl<sub>3</sub>. The obtained yellow powder was dried for 10 h at 50°C under vacuum with 85% yield.

## RESULTS AND DISCUSSION

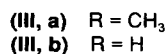
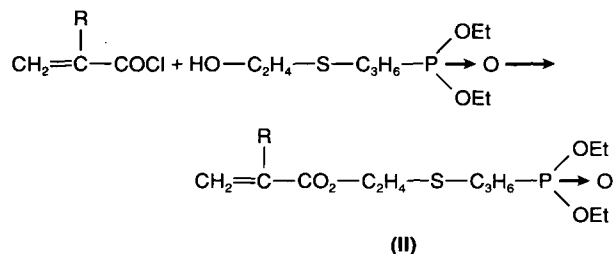
The diethyl allyl phosphonate (I) was obtained by the Arbuzov reaction<sup>15</sup> at about 100°C from diethyl phosphite and allyl bromide or chloride for 4 h.<sup>16,17</sup> Ethyl bromide was distilled in order to avoid the synthesis of diethyl ethyl phosphonate.<sup>18</sup> The structure, described previously, was checked by <sup>1</sup>H NMR spectroscopy. The second step of the synthesis was the addition of 2-hydroxy ethyl mercaptan onto the allyl compound (I) as follows:



Due to the allylic structure, only monoaddition product was obtained in a very good yield with a molar excess of 10% of thiol about the monomer.

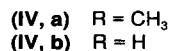
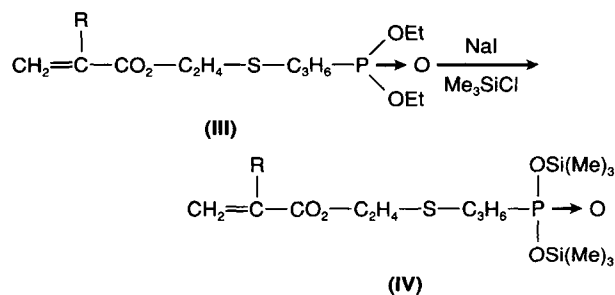
The  $^1\text{H}$  NMR spectrum clearly shows the selectivity of the addition. Both close triplets at 2.68 and  $2.62 \cdot 10^{-6}$  of the methylene groups adjacent to the thioether bridge were noted. The first one, with more low fields shifted, corresponds to the methylene group in the  $\beta$  position about the hydroxyl one.

The third step was performed by a dropwise addition, onto the mixture composed of alcohol (II),  $\text{N}(\text{C}_2\text{H}_5)_3$ , and hydroquinone, of (meth)acryloyl chloride at room temperature.<sup>19</sup>



The  $^1\text{H}$  NMR spectrum of (III, a) (Fig. 1) exhibits the chemical shift of the methylene group in  $\alpha$  of the ester at  $4.2 \cdot 10^{-6}$  low fields shifted of  $0.5 \cdot 10^{-6}$  by comparison with the corresponding methylene in the alcohol.

Finally, the last step of the synthesis consists of the chemical change of ester groups into the corresponding acids. Because such acrylic derivatives contain two kinds of esters, our choice of hydrolysis is very sharp, and the silylation was used. With a dropwise addition of chlorotrimethylsilane onto sodium iodide in acetonitrile at room temperature under nitrogen and heating at  $40^\circ\text{C}$  for 15 min, a complete reaction was observed by GPC leading to the silylated ester as follows:



with bromotrimethylsilane the reaction was less exothermic and lasted about 90 min.

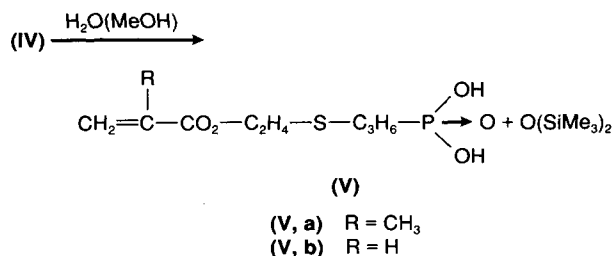
The  $^1\text{H}$  NMR spectrum shows the absence of the signal of the phosphonated ethyl ester whereas a

singlet is observed at  $0.3 \cdot 10^{-6}$  close to the peak of methyl groups of  $\text{Si}(\text{CH}_3)_4$ .

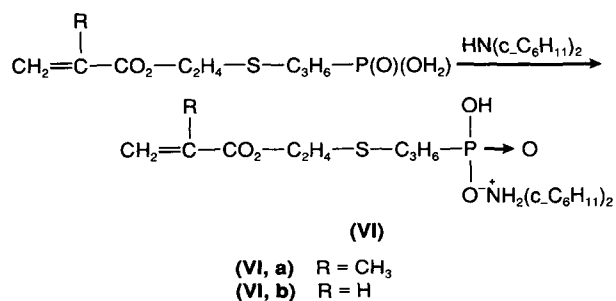
This spectrum also shows a small singlet ( $\delta = 0.08 \cdot 10^{-6}$ ) indicating the formation of  $(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3$  due to a partial hydrolysis by air moisture.

The hydrolysis can be carried out by water or methanol in excess. In the first case, the reaction was performed at room temperature for 16 h whereas in the second one the reaction at the same temperature lasted only 15 min. After distillation of the solvent and the formed silane, a viscous product was obtained. Its solubility in THF was decreasing with time. The  $^1\text{H}$  NMR spectrum of the soluble part shows the absence of the  $\text{SiCH}_3$ . On the contrary, the hydroxyl group of phosphonic acid appears at  $10.45 \cdot 10^{-6}$ . The insoluble part, like a gel, can easily be solubilized into water by adding amine.

Moreover, the acid titration of these two parts gives almost the same results corresponding to the diacid. Therefore all these data are consistent with the formation of the anhydride:



In order to stabilize the diacid (V), the salification was performed in dioxane at room temperature by an equivalent quantity of dicyclohexylamine<sup>20</sup> as follows:



Such a reaction was exothermic and the salt precipitated in the medium. Then it was washed, dried, and exhibited a good solubility into  $\text{CH}_3\text{OH}$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$ . The yield of this reaction was about 85%.

The  $^1\text{H}$  NMR characteristics are in particular the peaks of cyclohexyl at high field ( $1-2 \cdot 10^{-6}$ ) but

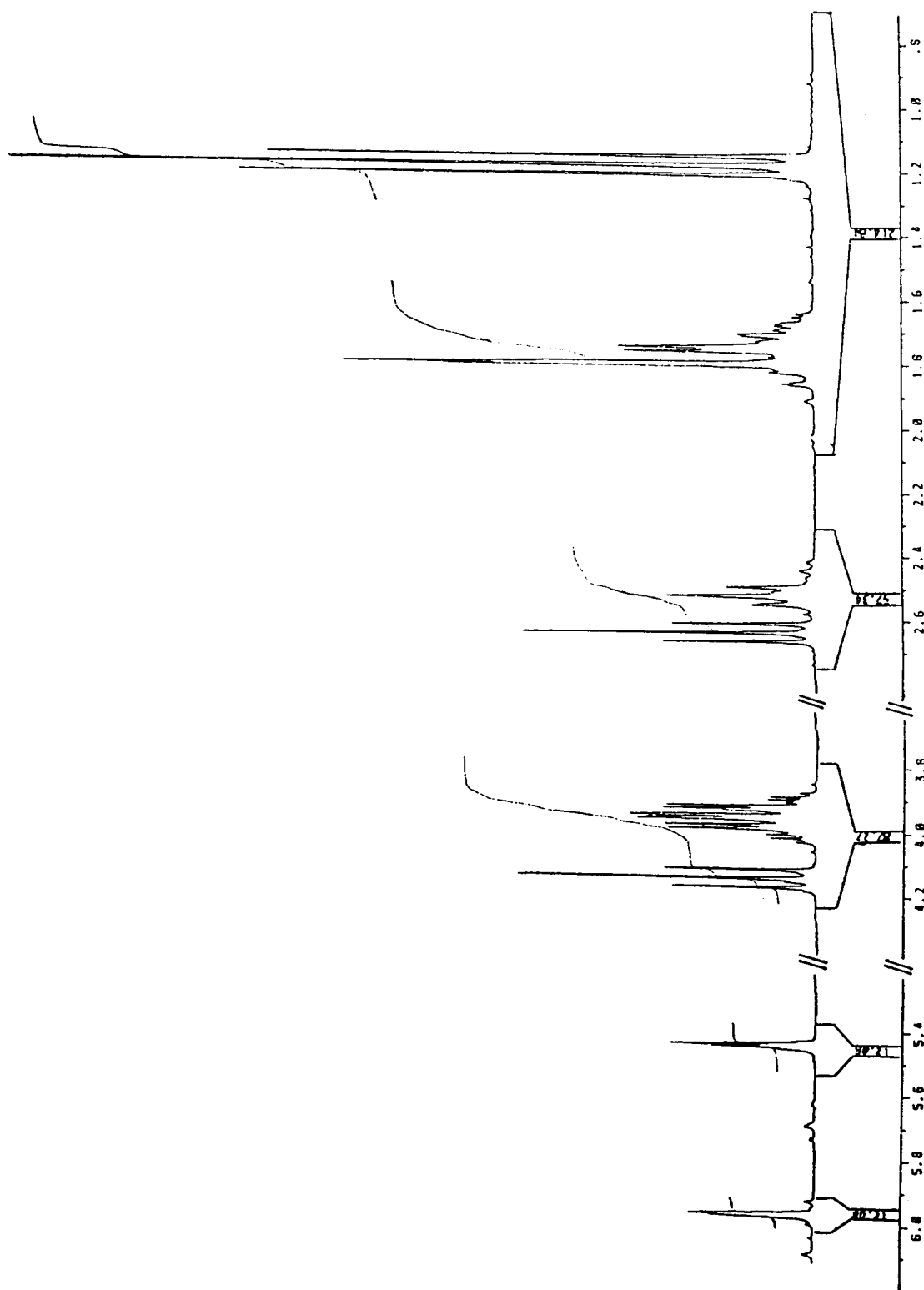


Figure 1  $^1\text{H}$  NMR spectrum of phosphonated methacrylate (III, a).

**Table I Comparative Results of Adhesion of Phosphonated Additives**

Phosphonated Additive	Wt %	Quality of Adhesion of Cross Cut
Without	—	Bad
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2 = \text{C} - \text{C} - \text{CO}_2 - \text{C}_2\text{H}_4 - \text{S} - \text{C}_3\text{H}_6 - \text{P}(\text{O})(\text{OEt})_2 \end{array}$	5	Bad
$\text{CH}_2 = \text{CH} - \text{CO}_2 - \text{C}_2\text{H}_4 - \text{S} - \text{C}_3\text{H}_6 - \text{P}(\text{O})(\text{OEt})_2$	5	Bad
Transol Chemical	5	Good
Ebecryl 169	5	Good
$\text{CH}_2 = \text{CH} - \text{CO}_2 - \text{C}_2\text{H}_4 - \text{S} - \text{C}_3\text{H}_6\text{P}(\text{O})(\text{OH})_2$	5	Good
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2 = \text{C} - \text{C} - \text{CO}_2 - \text{C}_2\text{H}_4 - \text{S} - \text{C}_3\text{H}_6 - \text{P}(\text{O})(\text{OH})_2 \end{array}$	5	Good

mainly both the protons adjacent to the nitrogen atom at  $2.9 \cdot 10^{-6}$ .

The homopolymerization of the salt (VI, b) was performed at  $60^\circ\text{C}$  in  $\text{CHCl}_3$  for 16 h. This led to a gel that precipitated. It was then dissolved in methanol followed by another precipitation into  $\text{CHCl}_3$ . A yellow powder was obtained in 82% yield. The nitrogen analysis gave 3.17% with 3.22 calculated. The  $T_g$  was  $82.5^\circ\text{C}$ .  $^1\text{H}$  NMR confirms the expected structure, mainly with the absence of the protons of the double bond.

## APPLICATIONS

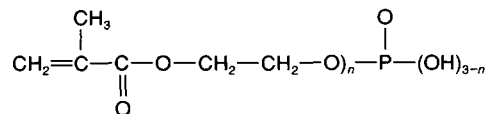
After these syntheses and the checking of the good stability of the salt, two applications of the above monomers were investigated: additive for improving

adhesion properties of coatings and additive for structural adhesives.

## Coatings

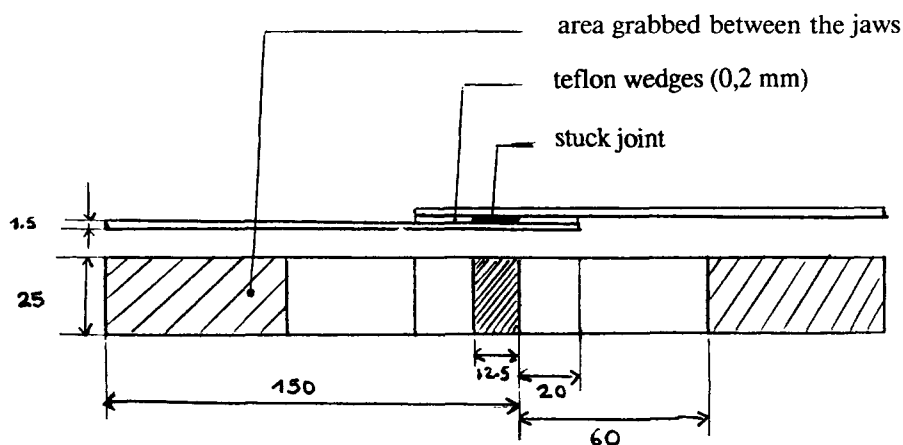
For the use of adhesion promoters, phosphonated additives are well known. Two main companies sell this kind of product: UCB and Transol Chemical.

The chemical formula is:



with  $n = 1$  or  $2$ .

It is very important to note that the product is a mix of mono- and difunctional acrylate but our acrylated phosphonated compound is strictly monofunctional.



**Figure 2** Strain-stress sample (thickness in millimeters).

Tests were performed on phosphated steel sheets using the following formulation:

halogenated unsaturated polyester (Ebecryl 524) 50 parts  
 acrylated urethane (Ebecryl 210) 30 parts  
 hexane diol diacrylated (HDDA) 15 parts  
 irgacure 500 4 parts

The formulations were layered down on the sheets with a threaded metal rod, to give a 20- $\mu$ m thick

layer. After UV hardening with a 80 W/cm lamp, the adhesion was evaluated by the cross cut test and the results are given in Table I.

At first, it is very interesting to note that phosphonated acrylic or methacrylic esters do not give better adhesion than the basic formulation without additive. On the other hand these results clearly show a better adhesive behavior of the diacid monofunctional acrylates to their homologue esters, and we note that our products give results similar to commercial compounds.

**Table II Adhesion Values for Tensile Tests for Different Phosphonated Products**

Product	$\tau$ (N/mm <sup>2</sup> )	$\tau_r$	Error
Standard resin	8.95 9.26 7.20 8.87 8.00 10.61	8.8	0.1
Standard resin with 5% Ebecryl 169	11.83 11.80 12.12 10.92 13.41 12.21	12.0	0.7
Standard resin with 5% compound (III, b)	9.90 8.83 11.07 8.90	9.5	0.9
$\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2)_2-\text{S}-(\text{CH}_2)_3-\overset{\text{O}}{\parallel}{\text{P}}(\text{OEt})_2$			
Standard resin with 5% product (VI, b)	10.75 10.56 9.59 9.15	10.0	0.7
$\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2)_2-\text{S}-(\text{CH}_2)_3-\overset{\text{O}}{\parallel}{\text{P}}(\text{OH})(\text{OH}_2^+\text{N}^{\oplus}(\text{c}\text{-C}_6\text{H}_{11})_2)$			
Standard resin with 5% derivative (V, b)	13.45 11.77 14.40 11.60	12.8	1.2
$\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2)-\text{S}-(\text{CH}_2)_3-\overset{\text{O}}{\parallel}{\text{P}}(\text{OH})_2$			
Standard resin with 5% compound (V, a)	11.28 11.97 14.00 12.57	12.5	1.0
$\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2)_2-\text{S}-(\text{CH}_2)_3-\overset{\text{O}}{\parallel}{\text{P}}(\text{OH})_2$			

### Additives for Structural Adhesives

The second application concerns the stuck joint test, that is, to stick two sheets of metal together by an adhesive curable by electron beam. Actually the resin is a urethane acrylic that contains 5% of additive to promote the adhesion. If the joint is made without any preparation of the surface metal, the adhesion is very low ( $\tau_r \approx 4 \text{ N/mm}^2$ ), but for industrial applications, a sandblasting is preferentially used. The tests are made with stainless steel sanded in an area  $2.5 \times 1.5 \text{ cm}$  by a corundum powder of 500- $\mu\text{m}$  granulation.

Before the application of the adhesive, the metal specimen was washed in a methylethyl ketone bath, dried in an oven, and the adhesive coated on the sanded surface. The thickness was obtained with Teflon wedges (0.2 mm). The assembly diagram of the sample is shown in the Figure 2.

Curing was done by a linear accelerator under nitrogen (50 kGy), and the adhesion was tested by the strain-stress method with an Instron apparatus (speed = 0.5 mm/min). The results are presented in Table II.

As in the previous case, phosphonated esters (III, b) do not improve the adhesive properties, and the hemi-salt (VI, b) exhibits the same behaviour. The commercial product (Ebercyl 169) increases the value of adhesion compared with the standard resin (30%), but better results has been obtained with (V, a) and (V, b) compounds.

As for the coatings, these results were obtained with the presence of a most important quantity of phosphonic acid groups in our products, where the acrylic or methacrylic functionality is strictly 1, so phosphonic acid functionality is strictly 2 (1, 2, or 3 acrylic functions so 2, 1, or 0 phosphonic acid functions).

### CONCLUSION

It can be concluded that our products do not give a very important improvement of properties in applications by comparison with those obtained from pluriacrylic commercially available products. However such products raise interest because of their

well-defined functionality that permits homopolymerization without curing and a high stability due to the C—P link.

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