Adhesive and Anticorrosive Properties of Poly(vinylidene fluoride) Powders Blended with Phosphonated Copolymers on Galvanized Steel Plates

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ABSTRACT: Fluoropolymers with adhesive and anticorrosive properties were investigated by blending statistical phosphonated copolymers with poly(vinylidene fluoride) (PVDF). In a first part, methacrylic monomers bearing dialkyl phosphonate and phosphonic acid groups were synthesized. Dimethyl(2-methacryloyloxyethyl)phosphonate was obtained by carrying out a one-step methacrylation of a commercial phosphonated alcohol. Then, a chemical conversion of the dimethyl phosphonate group to phosphonic acid groups was accomplished by two routes, including on the one hand a trimethyl-halosilane and on the other hand an inorganic halide as dealkylation reagents. The resulting monomers were analyzed by nuclear magnetic resonance (NMR) spectroscopy and results were discussed. In a second part, the phosphonated monomers were copolymerized with methyl methacrylate in the presence of 2,2'-azobis(isobutyronitrile) (AIBN) to give statistical copolymers in high yields. In a third and last part, copolymers were introduced into PVDF as adhesion promoters and anticorrosion inhibitors. Good dry and wet adhesion properties onto galvanized steel plates were obtained with blends containing mainly phosphonic acid groups. Results of corrosion tests show that the phosphonic acid groups maintain some level of adhesion, thereby preventing the spread of corrosion. However, the number of acid groups and their neighbors influence the adhesive and anticorrosive properties of the PVDF coatings. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2277–2287, 2002

Key words: phosphonic acid; steel substrates; poly(vinylidene fluoride); adhesion; corrosion resistance; fluoropolymers; coatings; adhesion; monomers; copolymerization

INTRODUCTION

Among the many ways to protect metals against corrosion, organic coatings are the most important one. The main property that characterizes a corrosion protective coating is its adhesion in presence of water or high humidity (wet adhesion).[1,2] Defects of organic coatings related to metal corrosion (e.g., blistering, delamination) are always preceded by a significant decrease of adhesion as a consequence of water diffusion to the coating–metal interface. To improve the wet adhesion, it is necessary to enhance the barrier properties and optimize the cooperative action of

adhesion bonds at the coating–metal interface. This improvement is generally accomplished with a multilayer system comprising a metallic coating, such as zinc coatings;[3] an inorganic and nonmetallic coating, for examples, phosphatizing and chromate conversion coatings;[4,5] and finally, organic layers containing barrier pigments, corrosion inhibitors,[6] and also reactive groups that induce polar forces and lead to the formation of firm bonds at the interface. In this article, we attempt to prepare a single-coat system with optimal barrier, wet adhesion, and passivation properties to protect galvanized steel plates against corrosion. Poly(vinylidene fluoride) (PVDF), characterized by a high thermal, chemical, and weather resistance, was used as a nonpolar polymer to obtain the required barrier properties. Organophosphorus copolymers synthesized by a radical way are introduced into PVDF to improve its well-known poor adhesiveness. Monomers bearing phosphonic acid groups are investigated in particular because of their wet adhesion resistance onto galvanized steel substrates[7] and their good anticorrosive surface passivation properties for steel and iron.[8,9] In this article, the synthesis of methacrylic monomers bearing phosphonated groups and their radical copolymerization with methyl methacrylate are described. The resulting organophosphorus copolymers blended with PVDF are applied onto galvanized steel plates and, finally, adhesive and anticorrosive properties of the polymer films are evaluated.

EXPERIMENTAL

Materials

Methyl methacrylate was purchased from Atochem (Serquigny, France) and required purification by distillation prior to use. All the syntheses were performed with commercial chemicals from Aldrich. Solvents like dichloromethane were purified by distillation. 2,2'-azobis(isobutyronitrile) (AIBN) was purchased from Merck and purified twice by recrystallization from methyl alcohol. Powdered PVDF Kynar 1000 LD was kindly supplied by Atochem. Galvanized steel plates (Zn 86 g/m^2, Cr <15 mg/m^2) supplied by Cockerill Sambre (Liege, Belgium) were washed with diethyl oxide in an ultrasonic sound tray to remove grease and oil traces.

Monomers and Copolymers Analyses

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC 250 spectrometer. CDCl$_3$ was used as internal lock. Tetramethylsilane (TMS) and orthophosphoric acid (H$_3$PO$_4$) were used as references for ^{1}H-NMR and ^{31}P-NMR, respectively. The letters s, d, t, q, and m designate singlet, doublet, triplet, quartet, and multiplet, respectively. Monomers and polymers were also analyzed by elemental analysis (Laboratory of Microanalysis of the National School of Chemistry, Montpellier, France). The given percentage values represent the amount of atom (g) per 100 g of pure product. Acid values were calculated from a conductimetric method using a Tacussel CD 6N conductimeter.

Synthesis of Dimethyl(2-methacryloyloxyethyl) phosphonate (I)

In a 2-L three-necked round-bottomed flask fitted with a magnetic stirrer, a condenser, a dropping funnel, and a nitrogen bubbler, 69.36 g (0.45 mol) of dimethyl(2-hydroxyethyl)phosphonate, 45.54 g (0.45 mol) of triethylamine, and 700 mL of dichloromethane CH$_2$Cl$_2$ were introduced. 2,6-Di-*tert*-butyl-4-methyl phenol (Ionol) was added as a polymerization inhibitor. The reaction mixture was cooled to 0 °C, and 56.93 g (0.54 mol) of methacryloyl chloride in 100 mL of CH$_2$Cl$_2$ were added in a dropwise manner for 30 min. Then, the mixture was stirred under nitrogen at room temperature for 16 h. A white precipitate of Et$_3$N·HCl was formed and filtered. The resulting solution was evaporated, and the compound **I** was distilled under a vacuum (85 °C, 2.10^{-3} mbar) to yield 60 g of a colorless liquid obtained (yield 60%).

Elemental analysis: C$_8$H$_{15}$PO$_5$ (FW = 222.18 g/mol); Calcd: C, 43.2%; H, 6.8%; O, 36.0%; P, 14.0%. Found: C, 42.88%; H, 6.85%; O, 36.4%; P, 13.9%. The structure of **I** was confirmed by ^{1}H-NMR (CDCl$_3$, δ ppm): 6.0–5.5 (d, 2H, **CH$_2$**=C(CH$_3$)—), 4.2 (t$_d$, $J^3_{\text{H-P}}$ = 13.2 Hz, 2H, —O—**CH$_2$**—), 3.7 (d, $J^3_{\text{H-P}}$ = 11.2 Hz, 6H, —P(O)(O**CH$_3$**)$_2$), 2.0 (t$_d$, $J^2_{\text{H-P}}$ = 16.0 Hz, 2H, —**CH$_2$**—P—), 1.7 (s, 3H, CH$_2$=C(**CH$_3$**)—). The subscript letter "d" means a dedoubled signal due to the phosphorus atom. The ^{31}P-NMR (dimethylsufoxide-d_6) spectrum exhibits one peak at 30 ppm, which is assigned to the dimethyl phosphonate function —P(O)(OCH$_3$)$_2$ of **I**.

Synthesis of (2-methacryloyloxyethyl)phosphonic Diacid (II)

In a 100-mL three-necked flask equipped with a magnetic stirrer, a condenser, and a dropping

funnel, and under nitrogen flow, 17.17 g (0.077 mol) of **I** and 40 mL of CH_2Cl_2 were introduced. Then, 25.94 g (0.169 mol) of bromotrimethylsilane $BrSi(CH_3)_3$ were added in a dropwise manner and the mixture was stirred at room temperature for 2 h. Then, solvent and volatile residues were evaporated (40°C, 26 mbar). The alcoholysis of the silylated intermediate was realized by adding an excess of methyl alcohol (20 mL). The mixture was stirred at 25°C for 2 h, and the solvent was evaporated. A colorless liquid (**II**) was quantitatively obtained (yield, 100%).

Elemental analysis: $C_6H_{11}PO_5$ (FW = 194.15 g/mol); Calcd: C, 37.08%; H, 5.67%; O, 41.20%; P, 16.0%. Found: C, 37.40%; H, 5.70%; O, 40.70%; P, 16.20%. ^{1}H-NMR (DMSO-d_6, δ ppm): 10.0 (s, 2H, —P(O)(**OH**)$_2$), 6.0–5.7 (d, 2H, **CH$_2$**=C(CH$_3$)—), 4.25 (t$_d$, J^3_{H-P} = 13.2 Hz, 2H, —O—**CH$_2$**—), 2.1 (t$_d$, J^2_{H-P} = 16.0 Hz, 2H, —**CH$_2$**—P—), 1.8 (s, 3H, CH$_2$=C(**CH$_3$**) —). The ^{31}P-NMR (DMSO-d_6) spectrum shows one single peak at 21 ppm corresponding to the phosphonic diacid function —P(O)(OH)$_2$ of **II**.

Synthesis of Methyl(2-methacryloyloxyethyl) phosphonic hemiacid (III)

Three reactions have been carried out according to the reagent used.

From Bromotrimethylsilane (III-a)

In the same manner as previously, 15.99 g (0.072 mol) of **I**, 40 mL of CH_2Cl_2, and 11.46 g (0.0746 mol) of $BrSi(CH_3)_3$ were used. Methanolysis was performed at 25 °C for 2 h. After evaporation of methyl alcohol, 14.8 g of a colorless liquid were obtained.

^{1}H-NMR (Acetone-d_6, δ ppm): 10.0 (s, 2H, —P(O)(**OH**)$_2$), 6.1–5.6 (d, 2H, **CH$_2$**=C(CH$_3$)—), 4.25 (t$_d$, J^3_{H-P} = 13.2 Hz, 2H, —O—**CH$_2$**—), 3.7 (two doublets juxtaposed, 9H, —P(O)(O**CH$_3$**)(OH) and —P(O)(O**CH$_3$**)$_2$, J^3_{H-P} = 11.2 Hz), 2.1 (t$_d$, J^2_{H-P} = 16.0 Hz, 2H, —**CH$_2$**—P—), 1.9 (s, 3H, CH$_2$=C(**CH$_3$**)—). The ^{31}P-NMR (acetone-d_6) spectrum exhibits three peaks at 30, 21, and 25 ppm corresponding to the —P(O)(OCH$_3$)$_2$ (24.8%), —P(O)(OH)$_2$ (23.8%), and —P(O)(OCH$_3$)(OH) (51.4%) functions, respectively.

From Chlorotrimethylsilane (III-b)

In a 100-mL three-necked flask equipped with a magnetic stirrer, a condenser, and a dropping funnel, and under nitrogen flow, 10.0 g (0.045 mol) of **I**, 4.63 g (0.0045 mol) of sodium bromide (NaBr), and 56 mL of acetonitrile CH_3CN were introduced. The mixture was heated to 40 °C. Then, 4.89 g (0.045 mol) of $ClSi(CH_3)_3$ were added in a dropwise manner and the solution was stirred for 3 h. The solid phase was filtered off and the filtrate was evaporated (40°C, 26 mbar). Then, the alcoholysis of the silylated ester function was performed with 20 mL of methyl alcohol at 25 °C for 2 h. The chemical shifts obtained by ^{1}H-NMR and ^{31}P-NMR are similar to the previous reaction from bromotrimethylsilane. Both spectra reveal a mixture of three-phosphonated functions with the following molar ratios: 58.9% (—P(O)(OCH$_3$)$_2$), 4.4% (—P(O)(OH)$_2$), and 36.7% (—P(O)(OCH$_3$)(OH)).

From Sodium Iodide NaI in Acetone (III-c)

In a 500-mL flask equipped with a magnetic stirrer, a calcium chloride tube inserted at the end of a condenser, and a nitrogen flow, 10.69 g (0.048 mol) of **I**, 8.81 g (0.059 mol) of NaI, and 240 mL of anhydrous acetone were introduced. The reaction mixture was heated under reflux (60 °C) with stirring for 8 h and then cooled to 25°C for 12 h. Sodium salt of **I** was precipitated, filtered, and washed several times with acetone to eliminate residues of **I**. The white powder was dried at 60 °C for 2 h, and 7.66 g (0.033 mol) were obtained (69% yield). Both ^{1}H-NMR (D$_2$O) and ^{31}P-NMR (DMSO-d_6) confirmed the structure of the sodium salt of (**III-c**). After acidification of the monomer salt with concentrated hydrochloric acid (2 N), extraction with chloroform, and drying over magnesium sulfate, the solvent was removed in vacuum to give a colorless liquid (**III-c**; 6.12 g, 61% yield).

Elemental analysis: $C_7H_{13}PO_5$ (FW = 208.18 g/mol); Calcd: C, 40.35%; H, 6.24%; O, 38.43%; P, 14.89%. Found: C, 39.51%; H, 6.40%; O, 39.45%; P, 14.64%. ^{1}H-NMR (DMSO-d_6, δ ppm): 7.1 (s, 1H, —P(O)(**OH**)(OCH$_3$)), 6.0–5.6 (d, 2H, **CH$_2$**=C(CH$_3$)—), 4.25 (t$_d$, J^3_{H-P} = 13.2 Hz, 2H, —O—**CH$_2$**—), 3.6 (d, J^3_{H-P} = 11.2 Hz, 3H, —P(O)(O**CH$_3$**)(OH)), 2.1 (t$_d$, J^2_{H-P} = 16.0 Hz, 2H, —**CH$_2$**—P—), 1.9 (s, 3H, CH$_2$=C(**CH$_3$**)—). The ^{31}P-NMR (DMSO-d_6) spectrum exhibits one single peak at 25 ppm corresponding to the —P(O)(OCH$_3$)(OH) function.

Statistical Copolymerization of I, II, and III(a, c) with Methyl Methacrylate (MMA)

Copolymerization of I with MMA

In a 100-mL two-necked flask equipped with a magnetic stirrer and a condenser and under ni-

Table I   Experimental Conditions of the Radical Copolymerizations

Monomers	Initial Molar Ratio	AIBN (%)	Yield (%)
I–MMA	20/80	1	95.3
II–MMA	10/90	2	60.0
III-a–MMA	10/90	0.5	85.0
III-c–MMA	10/90	0.5	85.7
III-c–MMA	20/80	0.5	86.0

trogen flow, 3.581 g (1.61 10^{-2} mol) of **I** and 6.429 g (6.42 10^{-2} mol) of MMA were dissolved in 80 mL of tetrahydrofuran (THF). The mixture was degassed by three freeze–pump–thaw cycles under high vacuum, sealed off, and placed in a constant-temperature bath at 70 °C. Then, 0.1328 g (8.09 10^{-4} mol) of AIBN were added, and the mixture was stirred for 48 h. The copolymer was precipitated in 700 mL of heptane, filtered, and dried at 60 °C for 8 h. A white powder was obtained (9.53 g, 95.3% by weight).

Copolymerization of II and III(a, c) with MMA

Statistical copolymerizations were carried out in *N,N*-dimethylformamide (DMF), under nitrogen flow, at 70 °C for 48 h. Experimental conditions are summarized in Table I. The initial molar ratio of each monomer, the molar percentage of initiator introduced, and the copolymer yield (by weight) are also shown in Table I.

Determination of the Amount of Phosphonated Units in Copolymers

By ^{1}H-NMR

The amount of phosphonated and MMA units in copolymers was evaluated by the height of the integration curve of the following signals: at 4.2 ppm, assigned to the methylene group in α of the ester function of the phosphonated monomer; at 3.5 ppm, assigned to the methoxy group of MMA; and at 3.6 ppm, assigned to the methoxy group of the phosphonated monomers **I** and **III** (**a** and **c**).

By Elemental Analysis

The amount of phosphonated units in copolymers could have been deduced from the phosphorus atom percentage as follows:

$$\%P = \frac{x \times M_p}{[(y \times M_{MMA}) + (x \times M_{\text{phosphonated monomer}})]} \quad (1)$$

where x, y, M_P, M_{MMA}, and $M_{\text{phosphonated monomer}}$ represent the molar ratio of phosphonated and methyl methacrylate units in copolymers, the P atomic weight (31 g/mol), and the molecular weight of MMA (100.12 g/mol) and of the phosphonated monomer, respectively.

By Conductimetric Titration

This method was performed with copolymers bearing phosphonic acid groups. The copolymers (0.625 g) were dissolved in 25 mL of DMF at room temperature, and 10 mL were titrated with a KOH/ethyl alcohol solution (N/10). The conductance noted G (in ms) was recorded for each volume of base added. By plotting G as a function of the volume of base added, two straight lines were obtained and the cross-point gave the volume at equilibrium.[10] To compare the adhesive and anticorrosive properties of the phosphonic acid functions, an acid value (I_a) was defined as the amount of potassium hydroxide (in mg) necessary to neutralize one gram of copolymers. I_a was evaluated as follows:

$$I_a = \frac{M_{KOH} \text{ (g/mol)} \times C_{KOH} \text{ (mol/L)} \times V_{KOH} \text{ (L)}}{m_{\text{copolymer}} \text{ (g)}} \times 10^3 \quad (2)$$

where M_{KOH}, C_{KOH}, V_{KOH}, and $m_{\text{copolymer}}$ represent the molecular weight of KOH (56 g/mol), the KOH/EtOH solution concentration, the volume at equilibrium, and the weight of the copolymer titrated, respectively.

Blends of Copolymers and PVDF

The blends were performed in a *N,N*-dimethylformamide/*N*-methylpyrrolidone (70/30 by weight) solution at 50 °C under vigorous stirring. The copolymers were added to PVDF in various percentages (5, 10, and 30%). Solutions with 20% by weight of solid were applied onto the galvanized steel plates using a Barcoater (120 μm, Braive Instruments), and solvents were evaporated in an aerated oven at 280 °C. A time of 31 s was required for the plates to reach 190 °C. This optimal temperature was related to the color appearance of the polymer films. The thickness of the films obtained was ~20–25 μm. Coated steel plates

were left at room temperature for 24 h, and the adhesion and corrosion resistance properties of the films were investigated.

Adhesive and Anticorrosive Properties

The adhesive properties were assessed by the Cross-cut Testing, the Conical Mandrel Bend Testing, the Water Immersion Testing, and the Boiling Water Testing, as in a previous study.[7] The anticorrosive behavior was evaluated in accordance with the Salt Spray Test (DIN 50021) on $100 \times 150 \times 1$-mm galvanized steel plates coated with a $20–25$-μm film and exhibiting a bare edge.

RESULTS AND DISCUSSION

Characterization of Monomers

Dimethyl(2-methacryloyloxyethyl)phosphonate **I** was obtained by a simple synthetic method starting from commercial products.[7,11] The structure was checked by ^{1}H-NMR and ^{31}P-NMR spectroscopy. The ^{31}P-NMR spectrum shows one single peak at 30 ppm corresponding to the dimethyl phosphonate function. The next step was the conversion of the dialkyl phosphonate **I** to the corresponding phosphonic acids **II** and **III**. The chemical change was generally accomplished by heating **I** in concentrated acidic solution (HCl or HBr)[12,13] or in alkaline solution[14–17] by using silylating reagents[18–23] or inorganic halides.[24–27] Because of the presence of other ester group in **I**, dealkylation was carried out under mild conditions. The conversion of the dimethyl phosphonate function $—P(O)(OCH_3)_2$ of **I** to the phosphonic diacid function $—P(O)(OH)_2$ was performed by using bromotrimethylsilane as a
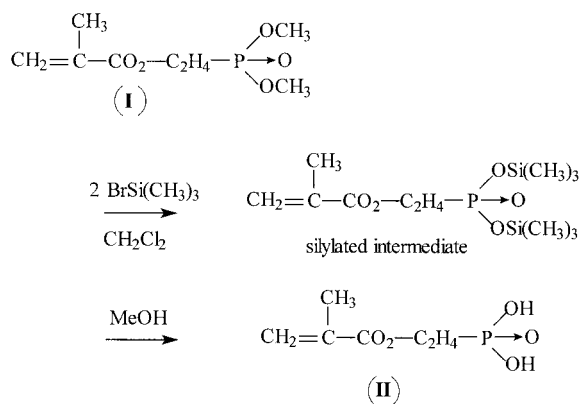
Scheme 1
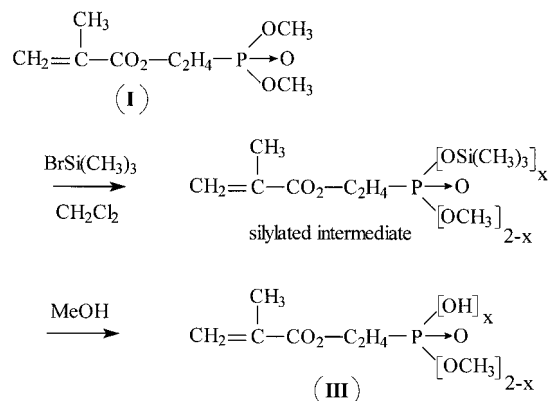
silylating reagent. With a dropwise addition of $BrSi(CH_3)_3$ to **I** (molar ratio of 2.1 to 1) in dichloromethane and under nitrogen flow, a complete reaction was observed by ^{1}H-NMR, leading to a silylated ester intermediate as shown in Scheme 1.

At this stage, the ^{1}H-NMR spectrum exhibits the absence of the doublet about 3.7 ppm corresponding to the ester group $—P(O)(OCH_3)_2$, whereas a singlet is observed at 0.3 ppm corresponding to the $—Si(CH_3)_3$ groups. A small singlet at 0.05 ppm is also observed, indicating the formation of the compound $(CH_3)_3Si—O—Si(CH_3)_3$ due to a partial hydrolysis by moisture. Then, the hydrolysis of the silylated intermediate by an excess of methyl alcohol leads to **II** in quantitative yield. The ^{1}H-NMR spectrum of **II** shows both the absence of the signal of $—Si(CH_3)$ and the presence of a signal at 10.8 ppm, corresponding to the phosphonic diacid function. The ^{31}P-NMR spectrum exhibits an upfield shift from 30 to 21 ppm.

By using an equivalent amount of bromated silane and **I**, **III** would be formed according to the reaction shown in Scheme 2.

The ^{1}H-NMR spectrum (Fig. 1) of (**III-a**) shows the appearance of the hydroxyl group of the phosphonic acid function at 9.5–10.0 ppm and a reduction by half of the doublet intensity assigned to the phosphonic ester at 3.7 ppm ($J^3_{H\text{-}P} = 11.2$ Hz). Place side by side, a second doublet appears at 3.6 ppm with an identical value of the coupling constant $J^3_{H\text{-}P}$. These observations reveal the presence of both **I** and the expected compound (**III**) in the crude product. Consequently, the half-reduced intensity of the signal at 3.7 ppm comes from the formation of **II** in an equivalent amount of **I**. The three products are clearly detected and quantified by ^{31}P-NMR spectroscopy, which was revealed as
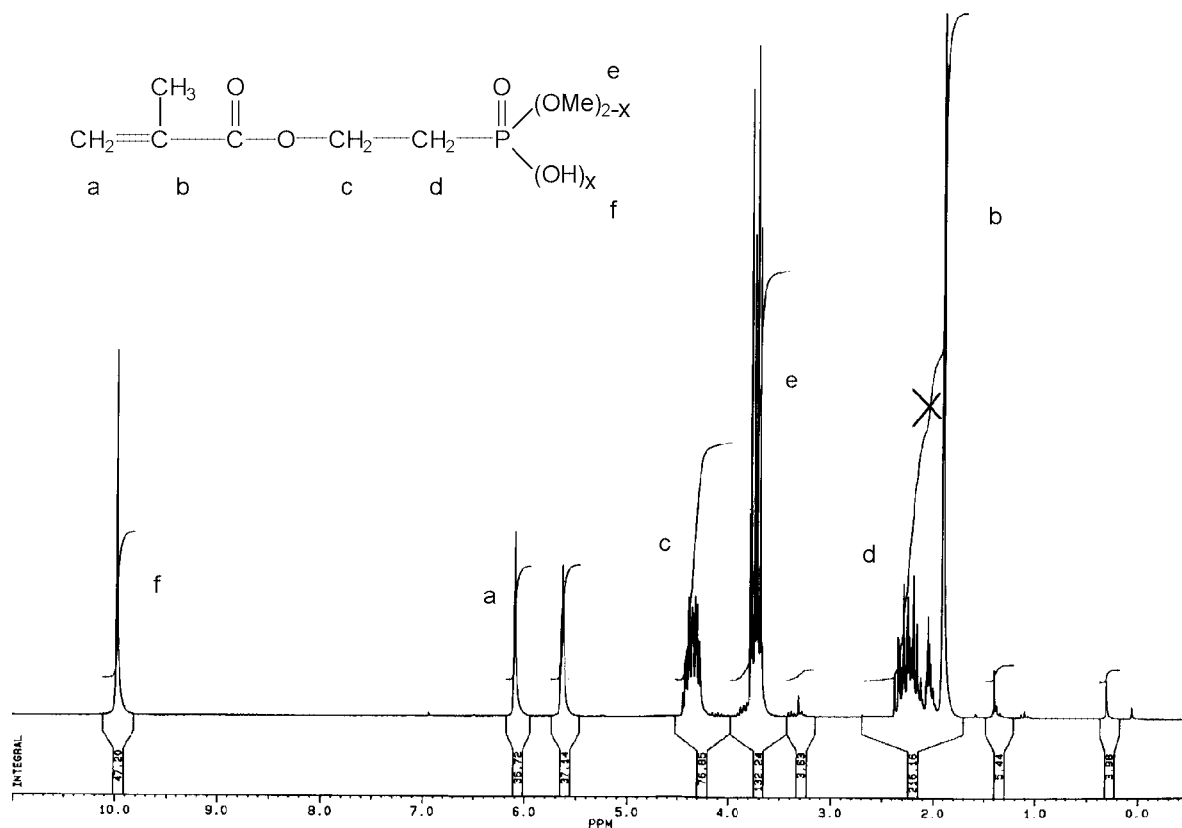
Scheme 2

Figure 1   ¹H-NMR spectrum of compound (**III-a**).

the most efficient method. Indeed, the ³¹P-NMR spectrum (Fig. 2) exhibits three peaks at 30, 21, and 25 ppm. By deduction, using the previous NMR results, the peaks are assigned to —P(O)(OCH₃)₂, —P(O)(OH)₂, and —P(O)(OCH₃)(OH) functions, respectively. The integration of these peaks gives the following molar ratio: (**I**), 24.8%; (**II**), 23.8%; (**III**), 51.4%. Based on these results, it can be noted that bromotrimethylsilane is too reactive to give **III** quantitatively. Another process using chlorotrimethylsilane in the presence of sodium bromide was investigated.²² Whatever the molar ratio of the silylating reagent to the dialkyl phosphonated monomer, a mixture of three-phosphonated functions was always obtained (**III-b**). This observation can be explained by the nucleophilic character of the sodium bromide leading to a further dealkylation of the two-phosphonic ester functions. Nevertheless, NaBr is not a high enough nucleophile to give a complete dealkylation of the dimethyl phosphonate groups leading to the corresponding phosphonic diacid groups. A third method noted (III-c) using sodium iodide as a dealkylation reagent gives the expected compound **III** by a two-step reaction (yield 61%), as shown in Scheme 3.

The ¹H-NMR spectrum of (**III-c**) shows the complete disappearance of the doublet assigned to the phosphonic ester functions and the presence of the signal at 3.6 ppm corresponding to the —P(O)(OCH₃)(OH) function. The ³¹P-NMR spectrum exhibits one single peak at 25 ppm, confirming the dealkylation of one ester group only. Among the many ways investigated to synthesize the **III**, the process using sodium iodide appears to be the most efficient one.

Statistical Copolymerizations

The radical and statistical copolymerizations were carried out using the previously synthesized monomers to introduce phosphonated functions in PVDF by a way other than by graft polymerization.⁷ Because of the well-known compatibility of poly(methyl methacrylate) and PVDF, MMA was used as a co-monomer.²⁸ Phosphonated methacrylates are used for their higher reactivity in copolymerization with MMA than their corresponding phosphonated acrylates.²⁹⁻³¹ As described in literature, the yield and the molecular weight of the copolymers in most case decreases
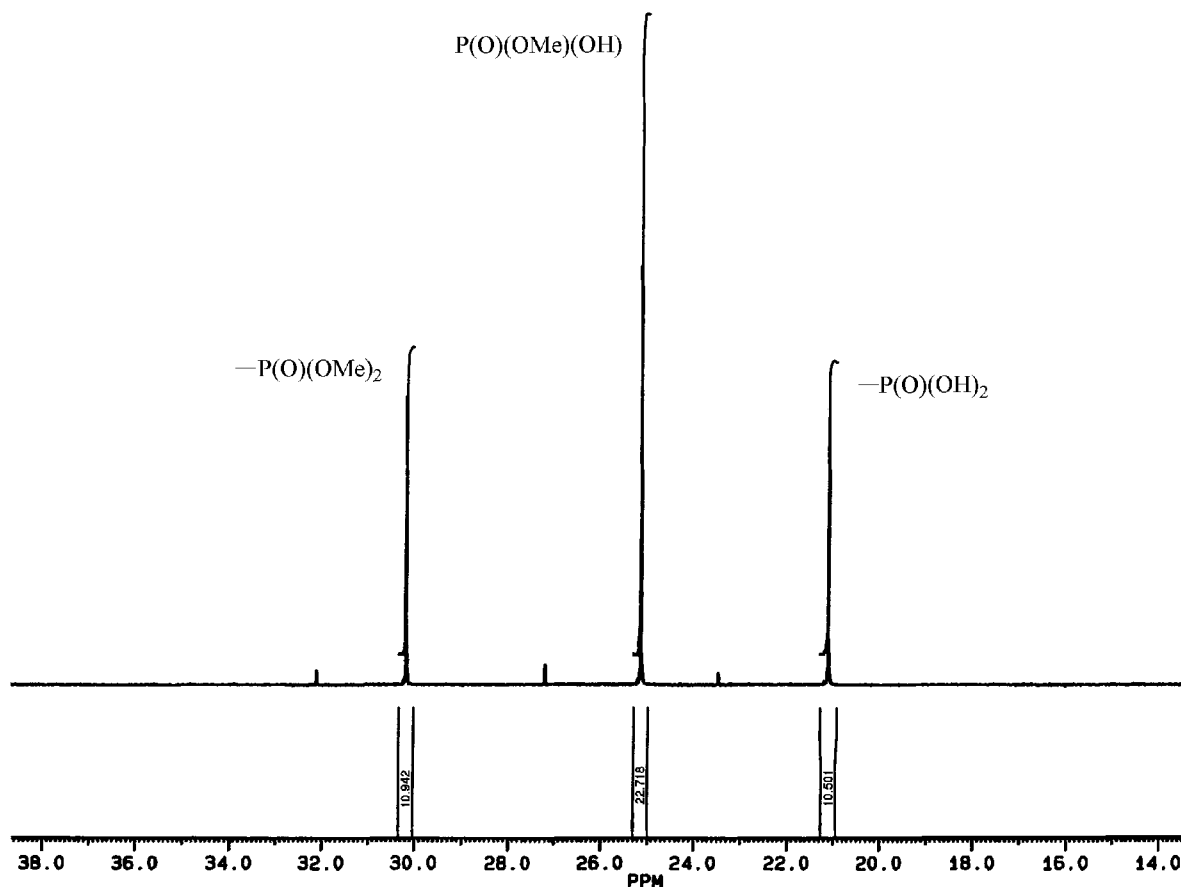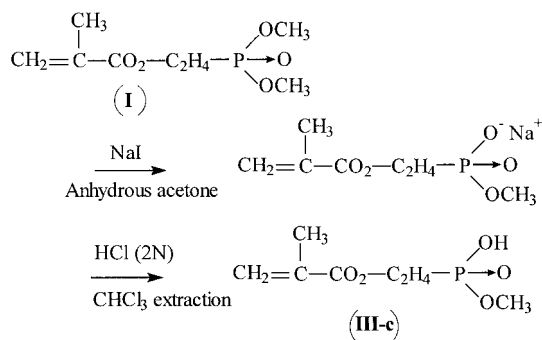
Figure 2 ^{31}P-NMR spectrum of compound (**III-a**).

with increasing content of phosphonated units in the macrochain.[32] So, small amounts of phosphonated monomers are employed to achieve high yields of copolymers. The final composition of the synthesized copolymers evaluated by ^{1}H-NMR, elemental analysis, and conductimetric titration is shown in Table II. In most case, the x and y values are close to the initial monomer mixture composition, and high copolymerization yields are obtained. The monomer (**II**) exhibits some difficulty in being copolymerized because of a decrease in solubility that is mainly induced by a polycondensation of the phosphonic diacid groups. Furthermore, x and y values are nearly identical whatever the technique employed. Based on these experiments, titration by conductimetry seems to be an accurate analytical technique to determine the molar ratio of phosphonic acid units in copolymers. The acid values (I_a) obtained by this method will be considered afterwards to estimate the adhesion and anticorrosion efficiency of the coatings resulting from the PVDF–copolymers blends (Table III).

Adhesive and Anticorrosive Properties

All the blends described in Table III were coated onto steel plates and their adhesive properties were evaluated. A commercially available PVDF paint system, coated onto anticorrosion-treated substrate with or without any adhesion primer,

Scheme 3

Table II   Final Composition of the Synthesized Copolymers

| No. | Monomers (Initial Molar Ratio) | Final Molar Composition of Phosphonated and Non-Phosphonated Units in Copolymers (x/y) | | | I_a (mg KOH/g) |
		^{1}H-NMR	Elemental Analysis ($\%P_{found}$)	Titration by Conductimetry	
1	**I**–MMA (20/80)	24/76	17/83 (4.3)	nd^a	nd
2	**II**–MMA (10/90)	5/95	8/92 (2.4)	9/91	92
3	**III-a**–MMA (10/90)	11/89	nd	nd	56
4	**III-c**–MMA (10/90)	pr^b	8/92 (2.2)	9/91	46
5	**III-c**–MMA (20/80)	24/76	17/83 (4.4)	17/83	80

^{a} nd, not determined.
^{b} pr, poor resolution NMR peaks.

was the reference. For each blend, the adhesive results are represented by one mean value (Table IV).

The cross-cut testing results clearly show an improvement in the adhesive properties of the blends containing phosphonated groups comparatively with the virgin PVDF, the PVDF paint coated without any adhesion primer, and the PVDF–PMMA blends (column 2). This improvement can be explained mainly by the polarity and the hydrophilicity of the phosphonated functional groups and to a lesser degree by the good properties of the coating under mechanical strain. Indeed, the T values resulting from the conical mandrel bend test (column 3) reveal the good film properties of the PVDF–organophosphorus copol-

ymer coatings. As a general rule, the phosphonic acid functions give better adhesive properties than the dialkyl phosphonate ones.[21] For example, the blends PVDF–no.2, 3, 4, and 5 act as more efficient adhesive coating than the PVDF–no.1 one, especially for an additive content <10%. For a copolymer addition of 30%, the difference of behavior between acid and ester groups is more pronounced in wet state than in dry state (columns 4 and 5). The blends containing 5% of additives bearing phosphonic acid functions exhibit poor adhesive properties. This amount of polar groups, which promotes good adhesion in dry conditions, is not sufficient to involve firm bonding at the coating–metal interface in the wet state. Therefore, the resulting molecular interactions at

Table III   PVDF–PMMA and PVDF–Organophosphorus Copolymer Blends

Blend	Percentage of Additives Blended (% by weight)	Percentage of Phosphorus (% by weight)	I_a of Blends (mg KOH/g)
PVDF + 5% PMMA	5	0	0
PVDF + 10% PMMA	10	0	0
PVDF + 30% PMMA	30	0	0
PVDF + 5% No. 1	5	0.22	0
PVDF + 10% No. 1	10	0.43	0
PVDF + 30% No. 1	30	1.29	0
PVDF + 10% No. 2	10	0.24	9.2
PVDF + 5% No. 3	5	0.13	2.8
PVDF + 10% No. 3	10	0.25	5.6
PVDF + 30% No. 3	30	0.75	16.8
PVDF + 5% No. 4	5	0.11	2.3
PVDF + 10% No. 4	10	0.22	4.6
PVDF + 30% No. 4	30	0.66	13.8
PVDF + 5% No. 5	5	0.22	4.1
PVDF + 10% No. 5	10	0.44	8.2
PVDF + 30% No. 5	30	1.32	24.6

Table IV   Adhesion Tests on PVDF Blend Coatings Compared with a PVDF Paint Reference Coated With or Without Adhesion Primer[a]

Sample	Cross-cut Testing (Quotation/5)	Conical Mandrel Bend Testing T Value	Water Immersion Testing (Quotation/5)	Boiling Water Testing (Quotation/5)
Virgin PVDF	5	> 3	5	5
PVDF paint without any primer	5	> 3	5	5
PVDF paint + primer	0	0	0	0
PVDF + 5% PMMA	5[b]			
PVDF + 10% PMMA	5[b]			
PVDF + 30% PMMA	5[b]			
PVDF + 5% No. 1	5[b]			
PVDF + 10% No. 1	5[b]			
PVDF + 30% No. 1	0–1	0.8	0	0
PVDF + 10% No. 2	0	1.1	0	0
PVDF + 5% No. 3	0	0	nd[c]	1
PVDF + 10% No. 3	0	0	0	0
PVDF + 30% No. 3	0	0.4	0	0
PVDF + 5% No. 4	0	0	nd	3
PVDF + 10% No. 4	0	1.0	nd	0
PVDF + 30% No. 4	0	2.8	nd	1
PVDF + 5% No. 5	1	0.4	nd	5
PVDF + 10% No. 5	0	2.8	nd	1
PVDF + 30% No. 5	0	1.8	nd	4

[a] Notation: 0, best adhesive properties; 5, worst adhesive properties.
[b] Further tests not performed.
[c] nd, Not determined.

metal surfaces are quite sensitive and also attract water molecules. For a value of 10% of additives, the interactions between phosphonic acid functions and the metal surface seem to exhibit higher resistance to water disbondment (column 5). Above this value of 10%, the wet adhesion decreases when the amount of phosphonic acid groups increases or, in other words, when the acid value increases. In this case, the neighborhood acid groups can gather and, therefore, further the diffusion of water at the interface. So, a limit acid value is required to obtain good adhesion properties in dry and wet states. The coatings with an I_a value ranged between 5.0 and 6.0 mg KOH/g give satisfactory adhesion results.

The blends with the higher adhesion properties underwent salt spray test to evaluate their anticorrosive properties. The results, listed in Table V, show that the percentage of corroded surfaces, in other words the spread of corrosion, increases when the acid value and the percentage of phosphorus in blends increase. Nevertheless, the sample PVDF + 10% no.3, with high wet adhesion properties, is also the coating with the better corrosion protection properties. The punctual corro-

sion attack observed on each salt-spray-treated coating probably stems from a semipermeable membrane behavior of the polymer film (Fig.3). However, in the neighborhood of the locations where blisters are formed, the adhesion is still sufficiently high to keep the coating to the substrate. The films are always bright, transparent, and without porosity. So, the phosphonic acid groups introduced in PVDF by statistical copolymers maintain some level of adhesion, resulting in preventing the spread of corrosion. These

Table V   Salt Spray Test on PVDF Blend Coatings

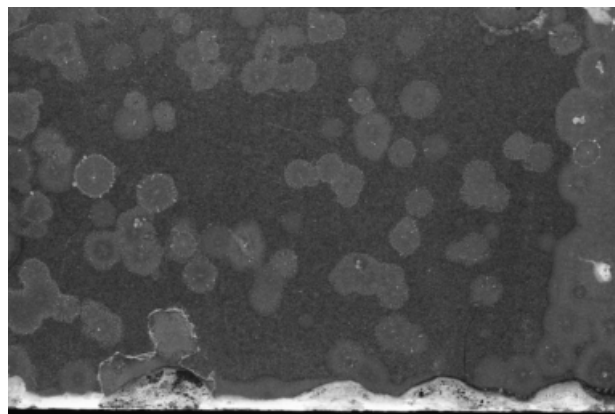| Sample	Salt Spray Test Percentage of Corroded Surface (%)
PVDF paint + primer	Delamination
PVDF + 10% No. 2	99
PVDF + 5% No. 3	84
PVDF + 10% No. 3	31
PVDF + 10% No. 4	96
PVDF + 10% No. 5	99

Figure 3 Results of salt spray test performed on PVDF + 10% no.3 coating.

groups may diffuse to and react with the metal surface, providing a corrosion protective layer. But, their random distribution into PVDF enhances the hydrophilicity of the polymer bulk. This fact probably leads to the formation of preferential ways for water diffusion through the coating. However, these results are interesting because no corrosion inhibitors were introduced into the blends and the galvanized steel plates did not proceeded to phosphatizing or chromating processes.

CONCLUSIONS

The blends of organophosphorus copolymers with PVDF powders were investigated to enhance adhesive and anticorrosive properties of fluoropolymer coatings. Based on the experiments described, it can be concluded that methacrylic monomers bearing phosphonic diacid and hemiacid groups can be synthesized from the corresponding dimethyl phosphonate monomer by two routes. The first one consists of using an excess of bromotrimethylsilane followed by a methyl alcohol hydrolysis, and the second one uses an equivalent amount of sodium iodide followed by an acidification step. The monomers are quite easily copolymerized with MMA to give statistical copolymers in high yields. This study clearly shows that dialkyl phosphonate and phosphonic acid groups introduced as additives into PVDF promote dry and wet adhesion of PVDF applied on galvanized steel plates. In the wet state, the adhesive bonds formed by the phosphonic acid groups at the coating–metal interface are stronger and more resistant to water disbondment than those of dialkyl phosphonate groups. Moreover, the salt spray exposure results show that the phosphonic acid groups maintain some level of adhesion and prevents the spread of corrosion at the PVDF coating–galvanized steel interface. Consequently, phosphonic acid groups are good adhesion promoters for fluoropolymers in dry and wet states, and their anticorrosive action onto galvanized steel substrates would be of great interest in the automotive paint domain.

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