Acrylate Based Anticorrosion Films Using Novel Bis-Phosphonic Methacrylates

KAMEL CHOUGRANI,[1] BERNARD BOUTEVIN,[1] GHISLAIN DAVID,[1] SHANE SEABROOK,[1] CÉDRIC LOUBAT[2]

[1]Institut Charles Gerhardt, UMR-CNRS 5253, Ingénierie et Architectures Macromoléculaires, ENSCM, 8 rue de l'école normale, 34296 Montpellier Cedex 5, France

[2]Spécific Polymers, Avenue de l'Europe, Cap Alpha 34830 Clapiers, France

ABSTRACT: Two novel phosphonated methacrylate monomers were successfully synthesized and subsequently incorporated into adhesion/anticorrosive coatings. Specifically, they were propyl N,N-tetramethyl-bis(phosphonate)-2-hydroxyl-bis(methylene) amine methylmethacrylate (MAC_3NP_2) and 2-[2,2-bis(diisopropoxyphosphoryl) ethoxy]-methylmethacrylate, (MAC_3P_2). The phosphonic forms of each monomer were blended with ∼85% w.w acrylates (tripropyleneglycol-diacrylate and hexanediol-diacrylate) and 6% w.w of the photo sensitive initiator Darocur®. Along with a monophosphonic monomer synthesized in a previous publication (MAC_3P), they were polymerized on Q-panels under ultraviolet light, and then subject to the salt spray test (ca. 0.5 mol/L NaCl at 35 °C) for a duration of up to 50 days. The results indicate that acrylate blends with low concentration of the bisphosphonic compound MAC_3P_2 have excellent resistance to corrosion, thus excellent adhesive properties. Importantly, these coatings were formed without the use of a hydrophobic polymer matrix or solvents. © 2008 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 46: 7972–7984, 2008

Keywords: adhesion; anticorrosion; phosphonated methacrylate

INTRODUCTION

The potential applications for polymer products containing phosphorus are numerous; dental adhesives, ion-exchange resins, and adhesion promotors are just three of the more common applications.[1–7] Compounds containing phosphorous are excellent promotors with respect to adhesion, and thus anticorrosion. Coatings with blends of fluoro-polymers and phosphorous compounds show high resilience to water due to the hydrophobic nature of the molecules. Commercial anticorrosion polymer compounds are generally formed from Sipomer® or Phosmer® monomers, which are phosphate-type (meth)acrylates, and can be readily polymerized via emulsion or solution.[8,9] Polymers with some phosphonate functionality have long been established as excellent adhesives and anticorrosion compounds,[10–17] however there has been very little investigation into the use of phosphonate-type methacrylates for the same purpose.[8,9]

The current study has two aims, the first involving the synthesis of a novel phosphonic methacrylate incorporating a bisphosphonic group and utilizing spacers between the ester bond and the phosphonate group (MAC_nP_2, where n refers to the number of methylene spacer groups),[17–20] as they have a wide range of

potential applications beyond adhesion promotors and anticorrosion; most recently, phosphonic compounds have been shown to be of high value in biomedical grafting applications,[21,22] and the monomers synthesized here could be used for a similar application. It has been established that spacer length does not influence the adhesive properties[23–25]; in this study the number of methylene spacers was fixed to 3 ($n = 3$). New N,N-amino-bisphosphonic-containing methacrylates (MAC$_n$NP$_2$) have also been synthesized,[26] as synthetic aminophosphonics have shown potential to mimic amino acids[27–29] and act as antihypercalcemics, i.e.; therapeutic agents for inhibiting bone deterioration and restoring normal calcium balance.[30,31] Outside the biomedical sphere, they are commonly used as antiscale agents to avoid the CaCO$_3$ precipitation into water.[32] Minimal investigation has been conducted on the use of aminophosphonic compounds, such as the monomer synthesized in this study, for use as adhesion or anticorrosion products.

The second aim is to test these bisphosphonic methacrylate monomers for use as metal adhesives and anticorrosive coatings. MAC$_2$P (the single P indicating a mono-phosphonic monomer) has been successfully copolymerized in its acidic form with MMA to be used as an additive with poly(vinylidenefluoride).[25,33] The incorporation of a phosphonic component results in a copolymer with highly enhanced adhesion onto the metallic surface, as alkanephosphonic acids are well known to form resonance stabilized phosphonate complexes with a wide range of metal alloys,[25] while remained soluble in the poly(VDF) matrix which inhibits water penetration and thus corrosion. The anticorrosive behavior was evaluated using the salt spray test, with only 30% of the metallic surface was corroded after 300 h. The salt spray test is well-established as the best standard by which to measure the adhesion/anticorrosive properties of a surface coating.[34] The same behavior was recently observed when MAC$_2$P was replaced by MAC$_1$P, the synthesis of this monomer being based on the use of paraformaldehyde and potassium carbonate.[24] However, to our knowledge, no study has been done to demonstrate the ability of bisphosphonic compounds to increase adhesion onto metal, when compared to mono-phosphonic based copolymers. In the current study, blends of acrylates with bisphosphonic methacrylates were polymerized via photo-polymerization to promote adhesion and inhibit corrosion. The primary difference, aside from the use

of bisphosphonics, is that the coatings are prepared without being blended into a hydrophobic polymer matrix, such as poly(VDF) or poly(VC). Photo-polymerization allows for a more efficient polymerization due to better activation of the radical species, especially with regard to the high surface to volume ratio as is the case for surface coatings. In addition, photopolymerization will proceed without any solvent, which is of increasing importance due to the environmental impact of industrial organic solvents.

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich and used without further purification. Fluoro-surfactant FC430 was purchased from 3 M.

Measurements

The chemical structure of the products were determined by ^{1}H, ^{31}P and ^{13}C NMR (Bruker AC 400 MHz) at room temperature in CDCl$_3$ solutions. S, d, t, q, m abreviations stand for singlet, doublet, triplet, quadruplet and multiplet, respectively. The INVGATE procedure with delay D1 of 10 s was used to quantify the final yield. Infrared (FTIR) spectra were recorded on a Nicolet 510P FTIR spectrometer with a band accuracy of $\pm$ 4 cm^{-1}. Scanning electronic microscopy, coupled with X-ray diffraction (SEM-EDX), was used to visualize the morphology of the coatings and define localized concentrations of phosphorus. Analyses were performed on cross-sections of the coating material. SEM-EDX analyses were performed on a FEI apparatus (resolution between 1.5 and 500 nm). X-ray spectrometry induced by the electron beam allowed for determination of all elements present, with the exception of hydrogen.

MAC$_3$P Synthesis

The MAC$_3$P synthesis was reproduced according to the procedure previously described in the literature.[18]

MAC$_3$P Dimethyl(2-methacryloyloxypropyl)phosphonate

85% yield. ^{1}H NMR (CDCl$_3$) δ: 1.7 (s, 3H, CH$_2$=C(*CH$_3$*)); 1.7 (m, 2H + 2H, *CH$_2$CH$_2$*—PO); 3.7 (d, 6H, PO*CH$_3$*); 4.1 (t, 2H, —O—*CH$_2$*); 5.4–6

(d, 2H, CH_2=C(CH_3)). ^{31}P NMR (CDCl$_3$) δ: 35.18 (s).

## MAC$_3$NP$_2$ Synthesis

The MAC$_3$NP$_2$ synthesis follows a two steps procedure which has been extensively described in a previous publication.[26]

HOC$_3$NP$_2$ N,N-Tetramethyl-bis(phosphonate)-3-hydroxylpropyl-bis(methylene) Amine
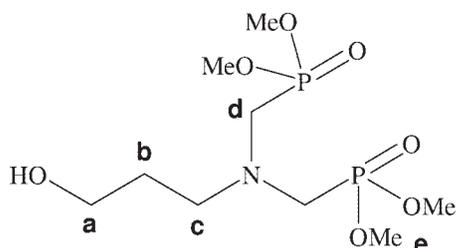
95% yield. ^{1}H NMR (CDCl$_3$, δ, ppm): 3.79 (sl, 1H, OH), 3.30 (d, 12H, H$_\mathbf{e}$, $^3J_{\mathbf{H\text{-}P}}$ = 10.5), 3.34 (t, 2H, H$_\mathbf{a}$, $^3J_{\mathbf{H-H}}$ = 5.7), 2.98 (d, 4H, H$_\mathbf{d}$, $^2J_{\mathbf{H-P}}$ = 8.0), 2.88 (tt, 2H, H$_\mathbf{c}$, $^3J_{\mathbf{H-H}}$ = 7.0 et $^4J_{\mathbf{H-H}}$ = 1.1), 2.01 (m, 2H, H$_\mathbf{b}$). ^{31}P NMR (CDCl$_3$, δ, ppm): 27.5. ^{13}C NMR (CDCl$_3$, δ, ppm): 60.6 (s, C$_\mathbf{a}$), 59.0 (t, C$_\mathbf{c}$, $^3J_{\mathbf{C-P}}$ = 6.7), 53.3 (m, C$_\mathbf{e}$), 49.6 (dd, C$_\mathbf{d}$, $^1J_{\mathbf{C-P}}$ = 157.3 et $^3J_{\mathbf{C-P}}$ = 5.9), 27.5 (s, C$_\mathbf{b}$). IRTF (CCl$_4$, cm^{-1}): 3615 F ($v_{\mathrm{O-H}}$), 2920 m ($v_{\mathrm{Csp3-H}}$), 1490 F ($\delta_{\mathrm{Csp3-H}}$), 1241 ($\delta_{\mathrm{P=O}}$), 1150 ($\delta_{\mathrm{C-O}}$), 1020 ($\delta_{\mathrm{P-O-CH3}}$). Mass spectrum (ESI$^+$: 20 V): [MH$^+$] = 320.35.

### MAC$_3$NP$_2$ Propyl N,N-Tetramethyl-bis(phosphonate)-bis(methylene)-amine Methylmethacrylate
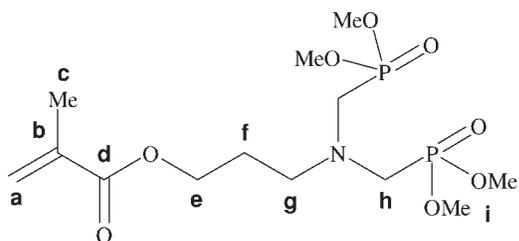
57% yield. ^{1}H NMR (CDCl$_3$, δ, ppm): 6.05–5.51 (2m, 2H, H$_\mathbf{a}$), 4.20 (t, 2H, H$_\mathbf{e}$, $^3J_{\mathbf{H-H}}$ = 5.4 Hz), 3.71 (d, 12H, H$_\mathbf{i}$, $^3J_{\mathbf{H-P}}$ = 10.6), 3.18 (d, 4H, H$_\mathbf{h}$, $^2J_{\mathbf{H-P}}$ = 10.5), 3.08 (tt, 2H, H$_\mathbf{g}$, $^3J_{\mathbf{H-P}}$ = 5.5 et $^4J_{\mathbf{H-P}}$ = 1.0), 2.12 (m, H$_\mathbf{f}$), 1.87 (m, 3H, H$_\mathbf{c}$). ^{31}P

NMR (CDCl$_3$, δ, ppm): 28.1. ^{13}C NMR (CDCl$_3$, δ, ppm): 166.7 (s, C$_\mathbf{d}$), 130.1 (s, C$_\mathbf{b}$), 127.7 (s, C$_\mathbf{a}$) 62.8 (s, C$_\mathbf{e}$), 55.0 (t, C$_\mathbf{g}$, $^3J_{\mathbf{C-P}}$ = 7.0), 52.7 (dd, C$_\mathbf{i}$, $^2J_{\mathbf{C-P}}$ = 8.2 et $^6J_{\mathbf{C-P}}$ < 1.0), 50.4 (dd, C$_\mathbf{h}$, $^1J_{\mathbf{C-P}}$ = 157.3 et $^3J_{\mathbf{C-P}}$ = 6.52), 23.2 (s, C$_\mathbf{f}$), 18.2 (s, C$_{\mathbf{C},}$). IRTF (CCl$_4$, cm^{-1}): 3070 m ($v_{\mathrm{Csp2-H}}$), 2905 m ($v_{\mathrm{Csp3-H}}$), 1730 f ($v_{\mathrm{C=O}}$), 1642 m ($v_{\mathrm{C=C}}$), 1499 F ($\delta_{\mathrm{Csp3-H}}$). 1230 ($\delta_{\mathrm{P=O}}$), 1145 ($\delta_{\mathrm{C-O}}$), 1011 ($\delta_{\mathrm{P-O-CH3}}$). Mass spectrum (ESI$^+$: 20 V): [MH$^+$] = 388.28.

MAC$_3$P$_2$ Synthesis

HOC$_3$P$_2$ Tetraisopropyl-bis(phosphonate)-[2-(2-hydroxyethoxy)ethane-1,1-diyl]
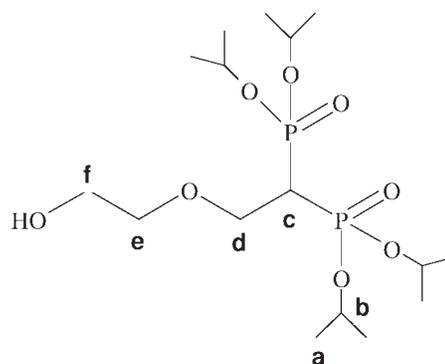
Two hundred and fifty milliliter of ethylene glycol was introduced, under argon, into a two-necked round bottom flask equipped with a condenser and a magnetic stirrer. Subsequently, five molar equivalents of paraformaldehyde and one molar equivalent of diethylamine (DEA) were added dropwise. Finally, one molar equivalent of bisphosphonate methylene was added and the reaction temperature increased to 55 °C for duration of 12 h, under agitation. The excess of ethylene glycol is removed under high vacuum and the crude product solubilized in chloroform and washed with a basic aqueous solution (NaOH 0.1 mol L^{-1}). The organic phase was dried and purified by running through a silica gel column.

70% yield. ^{1}H NMR (CDCl$_3$, δ, ppm): 4.79 (m, 4H, H$_\mathbf{b}$), 3.92 (dt, 2H, H$_\mathbf{d}$, $^3J_{\mathbf{H-P}}$ = 16.1 et $^3J_{\mathbf{H-H}}$ = 5.9), 3.60 (m, 4H, H$_e$ et H$_f$), 2.63 (tt, 1H, H$_\mathbf{c}$, $^2J_{\mathbf{H-P}}$ = 23.6 et $^3J_{\mathbf{H-H}}$ = 5.9), 1.30–1.48 (m, 24H, H$_\mathbf{a}$). ^{31}P NMR (CDCl$_3$, δ, ppm): 19.7. ^{13}C NMR (CDCl$_3$, δ, ppm): 72.2 (s, C$_\mathbf{f}$), 71.4 (m, C$_\mathbf{b}$), 65.9 (t, C$_\mathbf{d}$, $^3J_{\mathbf{C-P}}$ = 6), 60.7 (s, C$_\mathbf{e}$), 40.1 (t,C$_\mathbf{c}$, $^1J_{\mathbf{C-P}}$ = 135), 23.7–24.2 (m, C$_\mathbf{a}$). Mass spectrum (ESI$^+$: 20 V): [M+H$^+$] = 419.32.

MAC₃P₂ 2-[2,2-bis(diisopropoxyphosphoryl)-ethoxy]methylmethacrylate
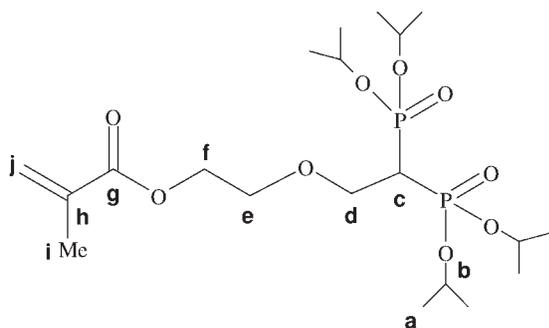
1 M equivalent of HOC_3P_2 and 1.5 M equivalent of triethylamine and anhydrous chloroform were introduced under argon into a two-necked round bottom flask equipped with a condenser. The reaction solution temperature was decreased to 0 °C, and then 1.5 M equivalents of methacryloyl chloride were added dropwise. The mixture was vigorously stirred, remaining at 0 °C, for 1 h and then at RT for an additional 12 h. Following this, the mixture was washed with an aqueous solution (three times excess) in an effort to extract any remaining methacryloyl chloride and triethylamine. The final product was dried over $MgSO_4$.

80% yield. ^{1}H NMR (CDCl$_3$, δ, ppm): 6.06–5.50 (2m, 2H, H$_\mathbf{j}$), 4.77 (m, 4H, H$_\mathbf{b}$), 4.20 (m, 2H, H$_\mathbf{f}$), 3.92 (dt, 2H, H$_\mathbf{d}$, $^3J_{\mathbf{H-P}}$ = 16.1 et $^3J_{\mathbf{H-H}}$ = 5.9), 3.66 (m, 2H, H$_\mathbf{e}$), 2.63 (tt, 1H, H$_\mathbf{c}$, $^2J_{\mathbf{H-P}}$ = 23.6 et $^3J_{\mathbf{H-H}}$ = 5.9), 1.87 (m, 3H, H$_\mathbf{i}$), 1.30–1.48 (m, 24H, H$_\mathbf{a}$). ^{31}P NMR (CDCl$_3$, δ, ppm): 19.2. ^{13}C NMR (CDCl$_3$, δ, ppm): 167.3 (s, C$_\mathbf{g}$), 136.0 (s, C$_\mathbf{h}$), 125.8 (s, C$_\mathbf{j}$), 72.2 (s, C$_\mathbf{f}$), 71.4 (m, C$_\mathbf{b}$), 65.9 (t, C$_\mathbf{d}$, $^3J_{\mathbf{C-P}}$ = 6), 60.7 (s, C$_\mathbf{e}$), 40.1 (t, C$_\mathbf{c}$, $^1J_{\mathbf{C-P}}$ = 135), 23.7–24.2 (m, C$_\mathbf{a}$), 18.2 (s, C$_\mathbf{i}$). Mass spectrum (ESI$^+$: 20 V): [M+H$^+$] = 487.2, [2M+H$^+$] = 973.3.

The phosphonate group was hydrolyzed to a phosphonic group using BrSi(Me)$_3$, a method which is reported elsewhere,[33] and applied to MAC₃NP₂, MAC₃P₂, and MAC₃P.

UV Photopolymerization of Methacrylate Monomers and Film Coating

The UV photopolymerization of mixtures of (meth)acrylates (composed of tripropyleneglycol diacrylate, hexanedioldiacrylate, and phosphonic methacrylate), pentaerythritoltetrakis (3%, w:w) as mercaptan allowing reticulation and Darocur 1173 (6%, w:w) as a photoinitiator was studied by real time FTIR spectroscopy with a Nicolet Nexus

apparatus with 2 cm^{-1} accuracy using OMNIC software. To this formulation, 3% (w:w) of the fluoro-surfactant FC430 (fluorinated aliphatic ether oligomer provided by 3 M) was added to reduce the surface tension and decrease surface defects. The UV intensity was measured using a Solatell UV spectroradiometer apparatus (4D Controls Limited, Cornwall, UK). The reagents were blended without solvent and different formulations were made by changing the (metha)acrylates w%, according to Table 2).

The samples were coated on a Q-panel plate with a SHEEN bar coater apparatus. Coated samples were then photopolymerized and the thickness was measured with a Bykotest 7500 apparatus (e = 20–22 μm). The UV source was placed perpendicular to the sample surface thus inducing the crosslinking reaction, and monitored in real-time via FTIR. Complete conversion of monomer to polymer was obtained after ca. 60 s, confirmed by following the intensity of the IR absorption at 812 cm^{-1} (characteristic of the C=C methacrylate monomer double bond).

Adhesive and Anticorrosive Properties of Films

The salt spray test (DIN 50,021) was used to evaluate the adhesive/anticorrosive properties. A series of 10 Q panels coated on each of the five acrylate/methacrylate coatings were subject to the salt spray test for 1200 h (50 days). A solution of 0.5 mol/L of NaCl in purified water was dispersed on the samples using a Ascott S120T salt spray machine, at a constant temperature of 35 °C. At regular intervals (ca. every 50 h) a plate for each of the five samples was removed from the machine and visually assessed for corrosion (Fig. 8). The assessment was achieved by dividing the plate into 10 × 10 squares and giving a value of one (for noncorroded segment) or a value of zero (for corroded segments), and finally reported as percentage of corrosion. The salt spray test is widely accepted as the most intense of the anticorrosive/adhesive test methods.

RESULTS AND DISCUSSION

Two different bisphosphonic methacrylate monomers have been synthesized: propyl *N,N*-tetramethyl-bis(phosphonate)-2-hydroxyl-bis(methylene) amine methylmethacrylate (MAC₃NP₂ – compound **2** in Fig. 1) and 2-[2,2-bis(diisopropoxyphosphoryl) ethoxy]-methylmethacrylate, (MAC₃P₂ – compound
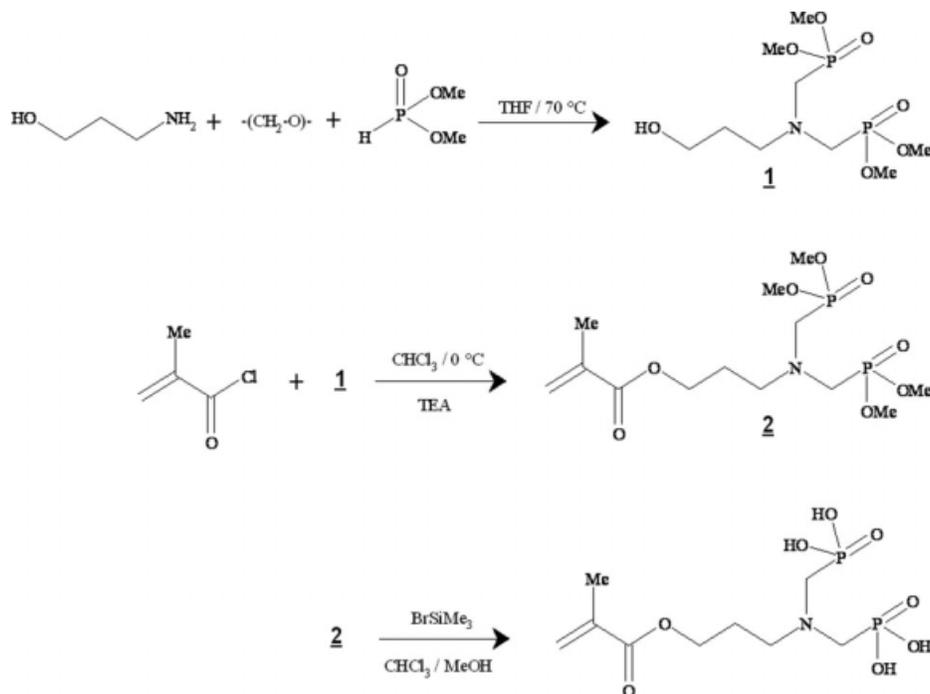
Figure 1. Synthesis of propyl N,N-tetramethyl-bis(phosphonate)-2-hydroxyl-bis (methylene) amine methylmethacrylate (MAC$_3$NP$_2$ – compound **2**) and conversion to the phosphonic acid form (MAC$_3$NP$_2$(OH)$_4$).

4 in Fig. 2). The primary difference between these two monomers is the amine functionality found in MAC$_3$NP$_2$.

Synthesis and Characterization of Propyl *N,N*-Tetramethyl-bis(phosphonate)-2-hydroxyl-bis(methylene) Amine Methylmethacrylate (MAC$_3$NP$_2$)

The amine containing bisphosphonic methacrylate (MAC$_3$NP$_2$) was synthesized via a three-step reaction, where the corresponding aminodiphosphonate hydroxy compound (*1* of Fig. 1) was synthesized by the Kabachnik-Field process.[35–37] It was subsequently esterified, and the obtained aminobisphosphonate methacrylate monomer was finally hydrolyzed resulting in the bisphosphonic methacrylate monomer at a 60% yield. The synthesis, as well as the characterization, of a series of aminobisphophonic methacrylate monomers was presented elsewhere.[26] The structures of the hydroxy precursor as well as the corresponding methacrylate were proved by means of both ^{1}H and ^{31}P NMR (Fig. 3). After hydrolysis with BrSi(Me)$_3$, the CH$_3$ protons of the aminobisphosphonate ester, which are centered at 3.8 ppm (as seen in Fig. 3) are no longer present, indicating successful hydrolysis. In support of this,

the peak corresponding to the P—O—CH$_3$ at 28 ppm shifted to 12.3 ppm for P—OH (Table 1).

Synthesis and Characterization of 2-[2,2-bis(diisopropoxyphosphoryl)ethoxy]-methylmethacrylate (MAC$_3$P$_2$)

The synthesis of 2-[2,2-bis(diisopropoxyphosphoryl)ethoxy]-methylmethacrylate (MAC$_3$P$_2$), is described in Figure 2. The synthetic strategy is similar to that of the MAC$_3$NP$_2$ monomer, where a bisphosphonate hydroxy compound is first synthesized and reacted with methacryloyl chloride. The main difficulty arises with the conversion to a bisphosphonate hydroxy compound. This reaction has been already performed by Degenhardt et al.[38] and involves reacting diisopropyl bisphosphonate methylene with methanol in the presence of paraformaldehyde, in basic medium, to introduce the methoxy function. To obtain the diisopropyl bisphosphonate hydroxy compound (*3* in Fig. 2), this reaction has been adapted by replacing methanol with ethylene glycol, for a duration of 24 h at 55 °C, thus obtaining compound *3* with a 70% yield. The [1]H-^{13}C HMQC spectrum (Fig. 4) proves the successful synthesis of compound *3*.

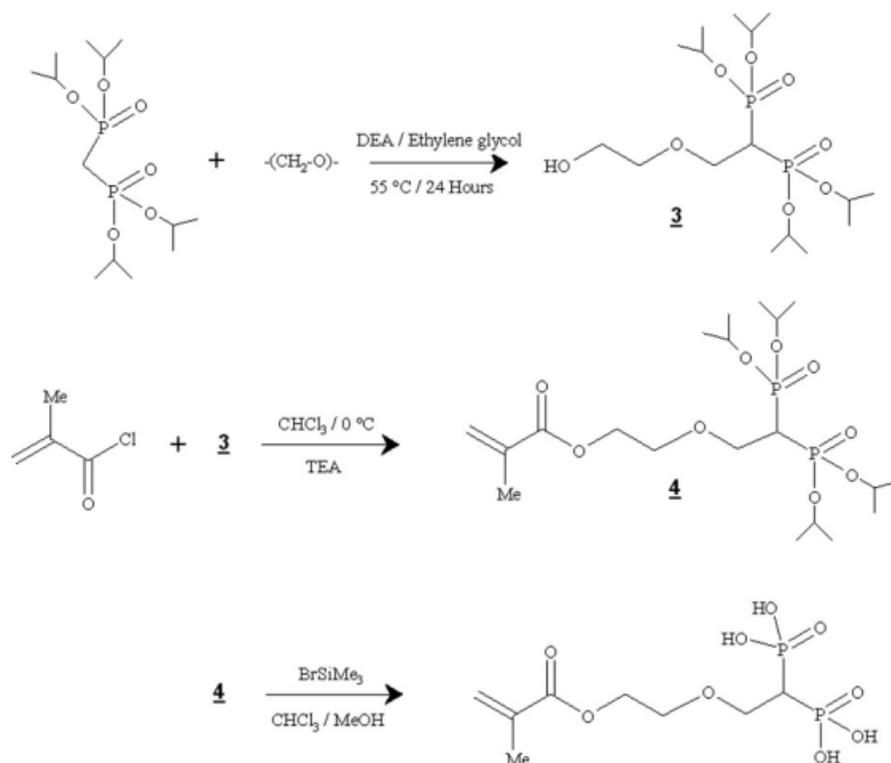Specifically, it is possible to distinguish in region **a** the presence of CH$_3$ from the isopropyl

Figure 2. The synthesis of 2-[2,2-bis(diisopropoxyphosphoryl)ethoxy]-methylmethacrylate (MAC$_3$P$_2$ – compound **4**) and conversion to the phosphonic acid form (MAC$_3$P$_2$(OH)$_4$).
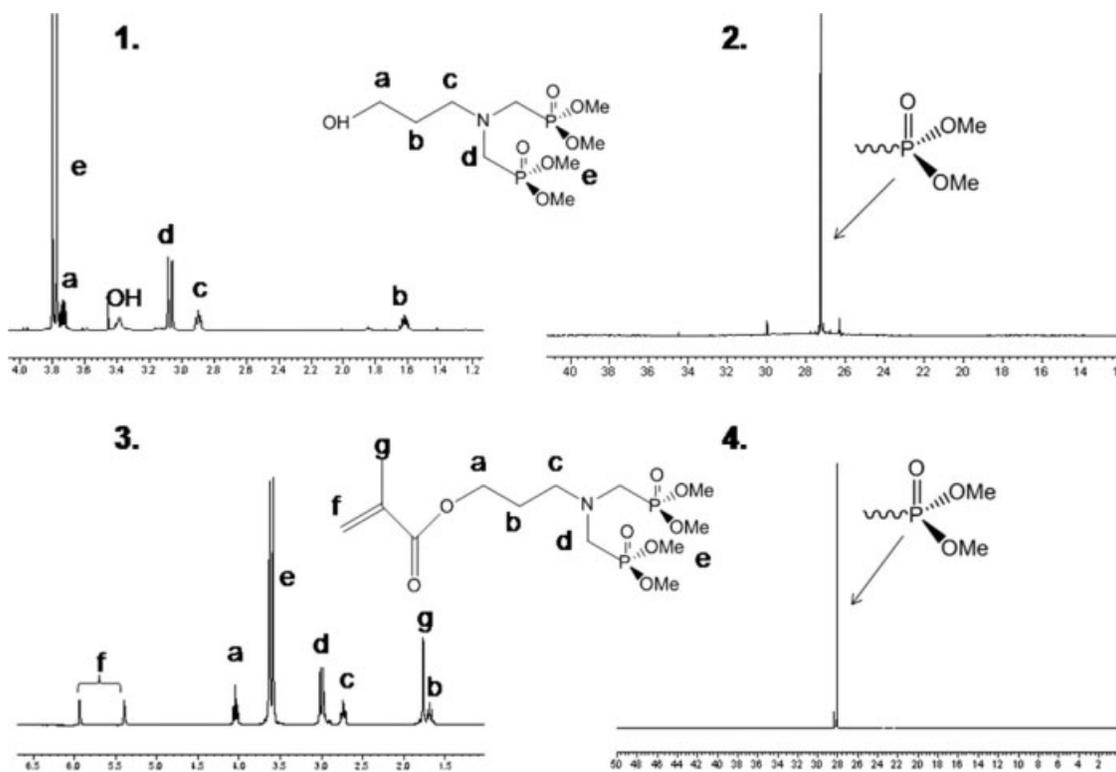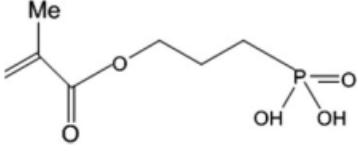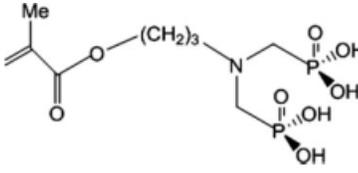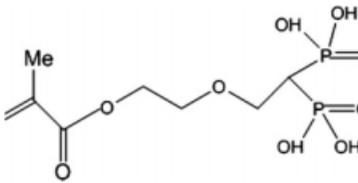

Figure 3. ^{31}P and ^{1}H NMR spectra of the precursor and final product for propyl *N,N*-tetramethyl-bis(phosphonate)-2-hydroxyl-bis(methylene) amine methylmethacrylate (MAC$_3$NP$_2$).

Table 1.   The Structure of Each Phosphonic Methylmethaacrylate Used in the Anticorrosion Formulas and their Corresponding ^{31}P NMR Chemical Shifts

Formula	Monomer	Yield (%)	^{31}P NMR Chemical Shift (ppm)
	MAC$_3$P	65	29.2
	MAC$_2$NP$_2$	57	12.3
	MAC$_3$P$_2$	80	16.2

The two bis-phosphonic monomers were synthesized specifically for this study, while the mono-phosphonic monomer was included for comparison, the synthesis of which is outlined in a previous paper.
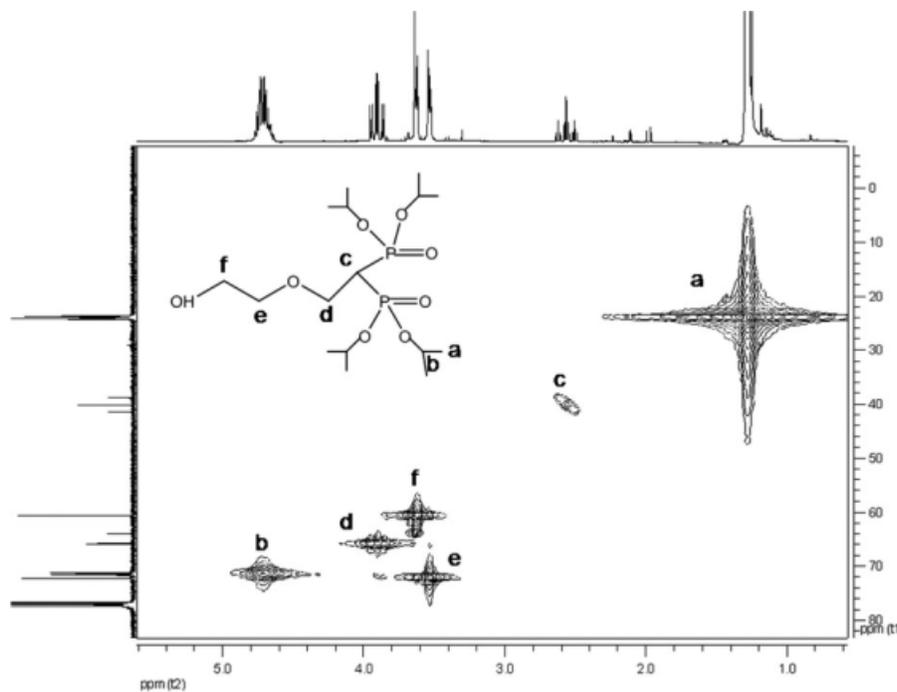
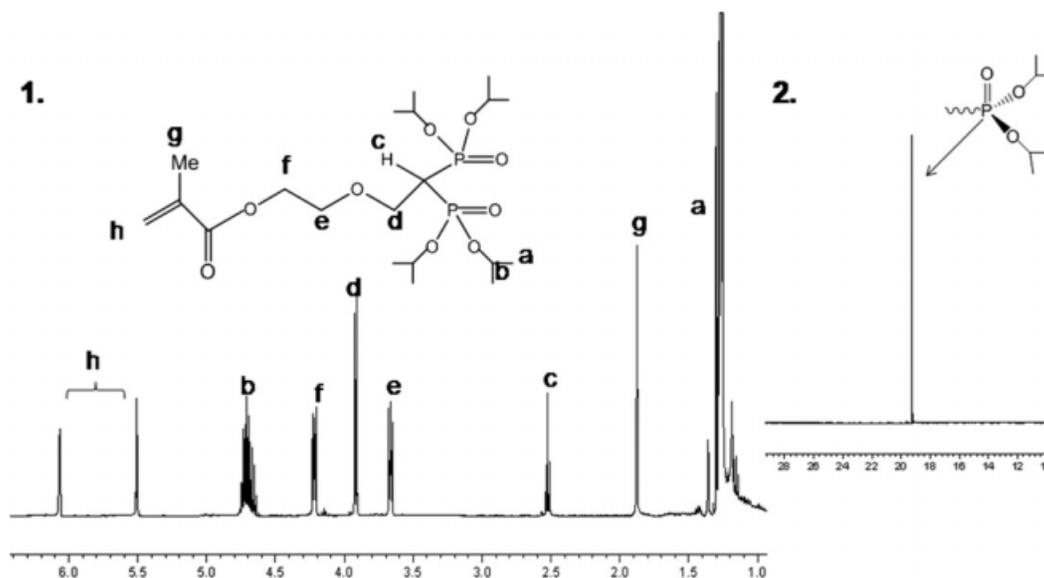**Figure 4.**   COSY NMR spectrum of 2-[2,2-bis(diisopropoxyphosphoryl)ethoxy]-methylmethacrylate (MAC$_3$P$_2$) precursor.

Figure 5. ^{31}P NMR and ^{1}H NMR of 2-[2,2-bis(diisopropoxyphosphoryl)ethoxy]-methylmethacrylate (MAC$_3$P$_2$) final product.

group, and in region **c** both the presence of the bisphosphonate group and of the ether bond in the β position. In addition, the ^{1}H-^{13}C HMQC spectrum indicates high purity of compound **3**. This hydroxy compound was then esterified in the presence of methacryloyl chloride (Fig. 2), leading to the corresponding bisphosphonate methacrylate MAC$_3$P$_2$, with a yield of 85%. The ^{1}H NMR spectrum of MAC$_3$P$_2$ (Fig. 5) confirms a successful esterification with methacryloyl chloride, as it is observed that the **f** signal corresponding to the methylene group, previously centered at 3.55 ppm for the hydroxy compound, is shifted to 4.3 ppm. The ^{31}P NMR spectrum (compound **2** in Fig. 5) indicate that the peak for the P—O—iPro centered at 19 ppm was shifted to 16.2 ppm for P—OH (Table 1) after hydrolysis of MAC$_3$P$_2$ in the presence

of BrSi(Me)$_3$. Table 1 also presents the chemical shift of MAC$_3$P at 29.2 ppm for the phosphonic group. This methacrylate monomer, bearing three methylene spacers and a single phosphonic group had been previously synthesized, and its efficiency as an adhesion and anticorrosion promoter will be assessed alongside that of the phosphonic forms of MAC$_3$P$_2$ and MAC$_3$NP$_2$.

Adhesion and Anticorrosion Characterization

As described in the experimental section, mixtures of the acrylates and the various phosphonic methacrylates were polymerized via UV photo-initiation, activated by Darocur 1173. In total, five different blends of coating were prepared, their exact compositions shown in Table 2. The first

Table 2. The Composistion of the Five Formulas that were Tested for Anticorrosion by the Salt-Spray Method

Formulation	Acrylates (w %)	MAC$_3$P (w %)	MAC$_3$NP$_2$ (w %)	MAC$_3$P$_2$ (w %)
1	88	/	/	/
2	85	3	/	/
3	86,5	/	1.5	/
4	85	/	3	/
5	87	/	/	1

In addition to the contents listed here, each formula contain 3% thiol, 6% darocur and 3% FC-430 (a fluoro-surfactant that helps to reduce the surface tension and decrease surface defects).
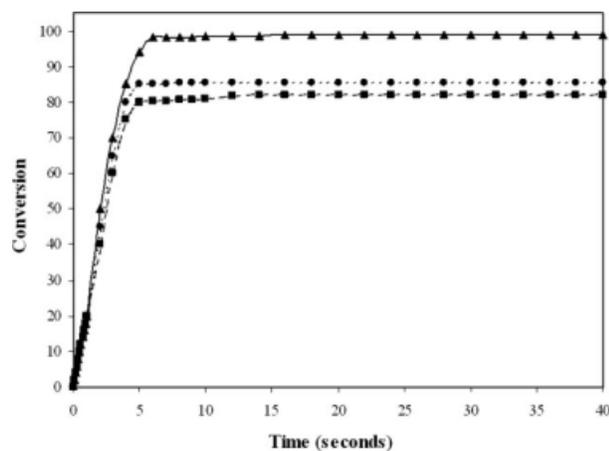
Figure 6. Real-time FTIR of conversion of acrylate monomer to polymer. Only the composition with 6% darocur and 3% thiol (▲) reached 100% conversion. The remaining compositions of 3% darocur with 3% thiol (◆) and that of 3% darocur (■) failed to reach complete conversion.

composition is a blank, composed only of acrylate (tripropyleneglycol-diacrylate and hexanediol-diacrylate) and photo-initiator, whereas the subsequent four compositions contain acrylates and various amounts of the phosphonic or bisphosphonic methacrylates with photoinitiator. A small amount (3% w.w) of mercaptan was added to each formulation, aiding reticulation of the coatings.

The conversion of free acrylate monomer (which makes up ca. 87% w.w of each formula) to polymer was monitored by way of real time FTIR. Figure 6 shows a comparison for three compositions, and it can readily be observed that the mixture containing a blend of darocur (6% w.w) and thiol reaches 100% conversion in a very short period of time. The other two, without thiol and with lower concentrations of darocur, fail to reach full conversion during the same time frame, thus 6% w.w photo-initiator and thiol were added to all the formulas.

The test which allows for the most direct comparison between the various compositions is the salt spray test; this is where the coating is spread onto a standardized alloy plate, and then subject to an intense standardized solution of salt spray, the details of which are outlined in the experimental section. This test allows immediate comparison as to the anticorrosive and thus adhesive abilities of each coating. Figure 7 shows a comparison between the results of the salt spray test, while some examples of the plates after being exposed to the test are shown in Figures 8 and 9.

Figure 8 shows progressive corrosion for coatings based on formula 4. The resistance to corrosion for all the five formulations are presented in Figure 7, and unsurprisingly the formula with no methacrylate exhibited the least resistance to corrosion, and thus is the least favorable in terms of adhesive ability. The formula with the highest resistance to corrosion, that which included MAC_3P_2, showed excellent resistance to corrosion up to 900 h (37.5 days). Figure 9 shows visual comparison of plates with coatings based on formula 2 (MAC_3P, at time = 700 h), formula 3 (MAC_3NP_2, at time = 700 h) and formula 5 (MAC_3P, at time = 900 h); formula 5 clearly shows excellent resistance to corrosion, at a time 200 h longer than the other two formulations.

From the empirical data presented, it is apparent that the presence of phosphonated methylmethacrylates is directly responsible for the excellent adhesion and anticorrosive properties, as the system formed without phosphonic additives shows very poor properties (formula 1 versus formula 5, for the most extreme example). There is also a distinct difference between the formulas containing phosphonated components; the system based on MAC_3P_2 (and at only 1% w.w concentration), having two phosphonic functional groups and no amine function, shows significantly better adhesion that the other three formulas. This could be readily described by the higher amount of phosphonic groups, however formula 2, based on
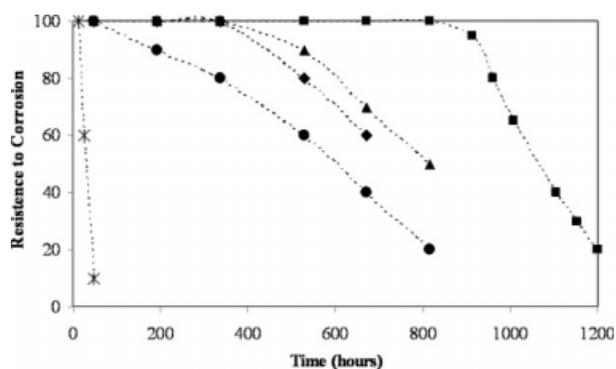

Figure 7. Graphical result of the resistance to corrosion after being subject to the salt spray test (0.5 mol/L NaCl in water at 35 °C; where, corresponding to Table 1, × = formula 1; ◆ = formula 2; ● = formula 3; ▲ = formula 4; ■ = formula 5). The resistance to corrosion is measured visually as a count out of 100 (each plate is divided into 10 × 10 squares), therefore 100 is equal to no apparent corrosion and 0 is equal to complete corrosion.
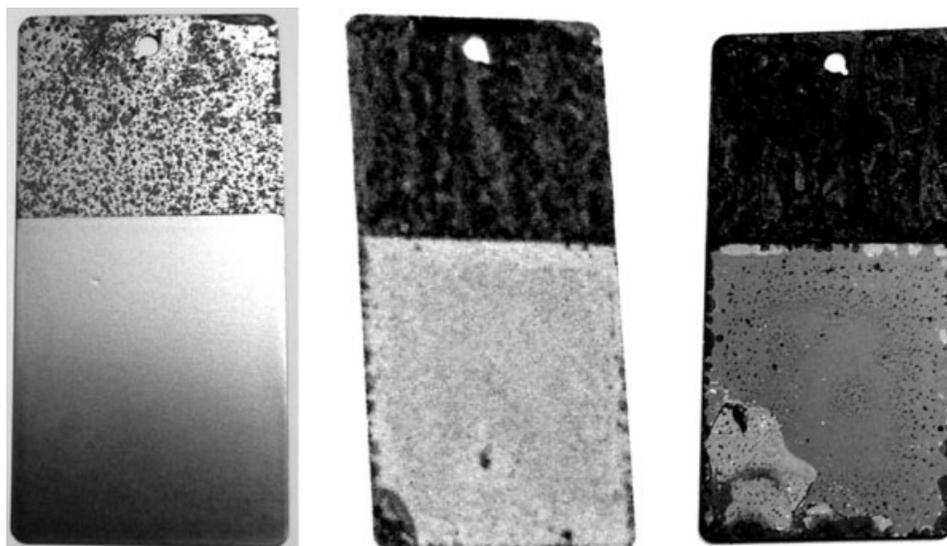
Figure 8. Q-plates coated with a coating based on formula 4 after being subject to the salt spray test (0.5 mol/L NaCl in water at 35 °C). The plates, from left to right, were reomved at 200, 500, and 700 h, respectively, and it can be observed that there is increased corrosion over this time. The picture is presented in high contrast black and white to best highlight corroded areas.

a monophosphonic methylmethacrylate (MAC$_3$P), was added at twice the concentration (relative molar ratio of phosphonic acid groups) than MAC$_3$P$_2$, yet failed to come close in terms of anticorrosion capabilities (Fig. 7). The two other for-

mulas, based on varying levels of the bisphosphonic MAC$_3$NP$_2$ (formulas 3 and 4), the N denoting the inclusion of an amine group; as discussed in the introduction, aminophosphonic acids are highly efficient at forming adhesive complexes
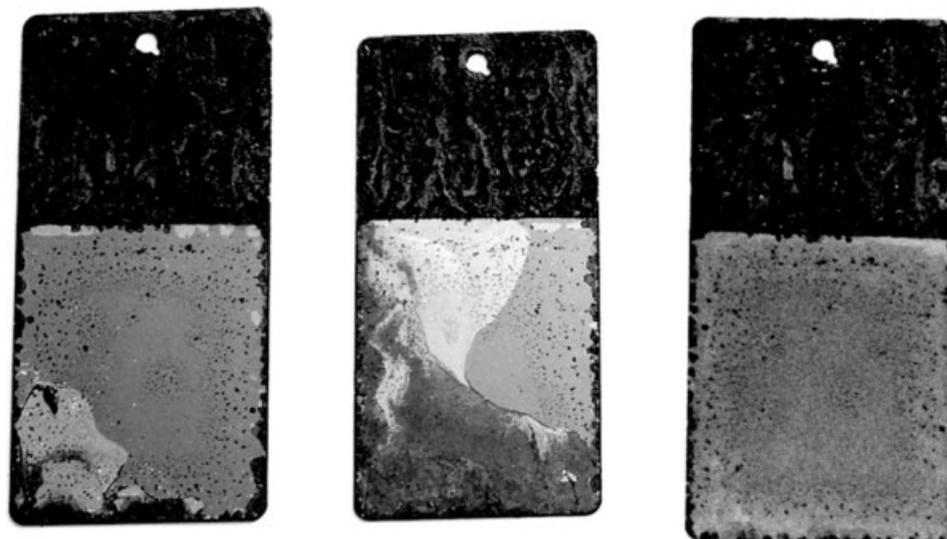

Figure 9. Q-plates coated with a coating based on various formulas after being subject to the salt spray test (0.5 mol/L NaCl in water at 35 °C). The plates, from left to right, are representative of formula 2 (700 h), formula 3 (700 h), and formula 5 (900 h) respectively, and it can be observed that the plate coated with formula 5 is still (relatively) corrosion free, even after 200 additional hours exposure. The picture is presented in high contrast black and white to best highlight corroded areas.
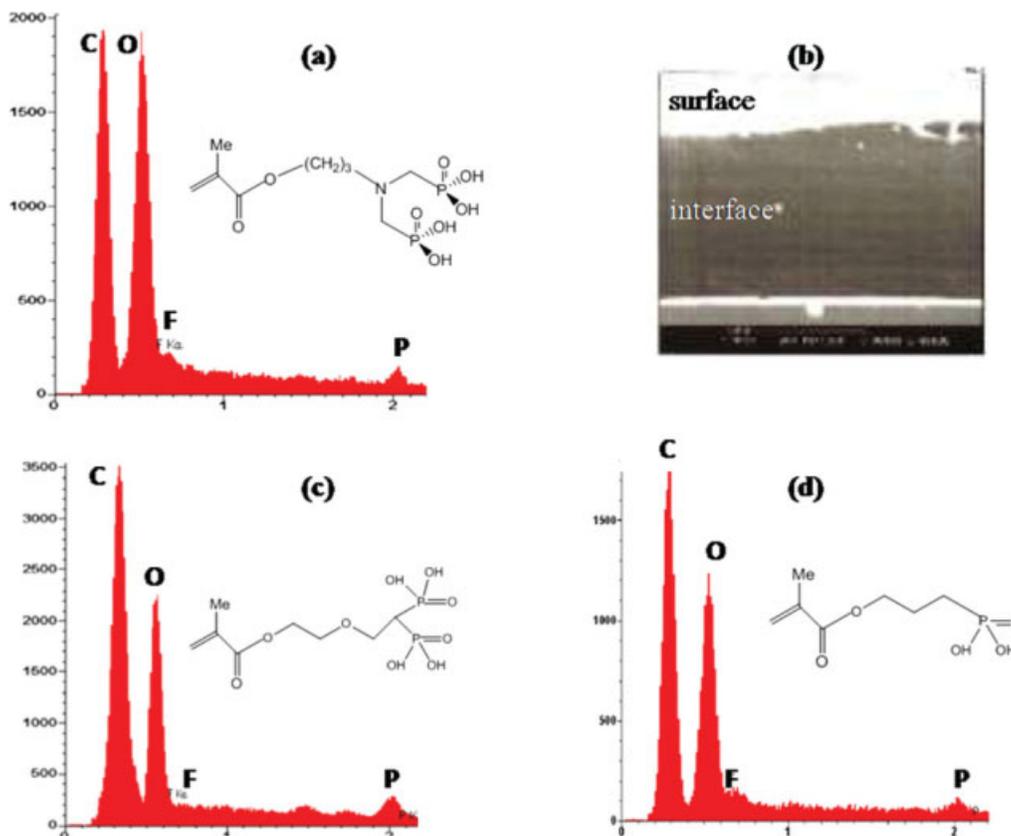
Figure 10. The three EDX spectra correspond to the elemental composition at the interface for MAC_2NP_2 (a), $MACP_2$ (c) and MACP (d). The image (b) corresponds to a cross section of the film coating; all EDX analysis were taken at the interface.

with calcium based substrates,[30,31] or forming micelles with calcium salts in aqueous medium,[32] as yet there have been no investigations into how they (aminophosphonic acid monomers) will adhere to metal or metal alloy surfaces. From Figure 7 it can be observed that the adhesion properties are similar to that of the formula with the mono-phosphonic methylmethacrylate additive (formula 4 versus formula 2), or in the case of formula 3 the adhesive properties are considerably worse. It is known that tertiary amine will form a quaternary ammonium complex when in an aqueous solution; thus an assumption could be made that the reason behind the reduction in adhesive properties for the aminophosphonic acid based formulas (formulas 3 and 4) is due to the formation of the ammonium complex. Therefore these monomers show little promise as adhesion promoters, but could prove to be efficient as flame retardants or in the field of biomedical science for bone restoration.

Perhaps the most intriguing result for this study is that unlike most anticorrosive coatings,

the ones presented here were composed without the use of additional barrier components, for example poly(VDF) which was used in a previous study on phosphonated methacrylates,[24] of poly(VC).[39] In the study concerning poly(VDF), the methacrylate monomers were MAC_1P, i.e.; based on only one carbon link, and they showed significantly less resistance to anticorrosion, despite being used in combination with poly(VDF). This phenomenon can be partially explained by an EDX study of the interface between the coating and the Q-Plate (Fig. 10); a cross section of the film interface(s) is shown in Figure 10(b), and each EDX, be it for MACP, MAC_2P_2 or MAC_2NP_2 based coating, shows a relatively high amount of the phosphorus element. The migration of phosphonated components to the interface has been studied previously,[39] and they were shown to behave unlike most polymers and coatings, where additives are thought to be evenly dispersed throughout the medium, and migrate preferentially to the interface. This is explained by the ability of phosphonic acids to form complexes with

the metal interface[25] which is thought to influence their migration, and also create partially segregated phosphorus rich nodes at the interface.

CONCLUSIONS

Two bisphosphonate methacrylate monomers with C_3 spacers, one incorporating aminophosphonate end group, have been successfully synthesized using efficient synthetic pathways resulting in high yield. These monomers have been hydrolyzed and mixed with acrylates and photo-sensitive initiator species to allow for UV curable surface coatings. These coatings were applied to iron-alloy Q-plates and then subject to the salt spray test, which is the most stressful test to assess the anticorrosive and adhesion properties of a coating. The results concerning the formulation based on $MAC_3P_2(OH)_4$ (bisphosphonic with a C_3 spacer and no amino group) were excellent, with little corrosion being observed after ca. 38 days. These results are unexpected as no halogenated polymer (e.g., poly(VDF) or poly(VC)) has been used, which are typical of anticorrosive formulations as they act as efficient gas barriers. This indicates that bisphosphonic functional groups show high capacity as adhesion promotors and could be further optimized for industrial applications.

REFERENCES AND NOTES

1. Quittmann, U.; Lecamp, L.; El Khatib, W.; Youssef, B.; Bunel, C. Macromol Chem Phys 2001, 202, 628–635.
2. Hwang, K.-Y.; Chen, H.-H.; Tu, A.-P. In U.S. Pat. Appl. Publ.; (Chang Chun Plastics Co., Ltd., Taiwan). USA, 2003, p 10.
3. Wan, I. Y.; Keifer, L. A.; McGrath, J. E.; Kashiwagi, T.; Polym Prepr (ACS, Division of Polymer Chemistry) 1995, 36, 491–492.
4. Zhang, Y.; Tebby, J. C.; Wheeler, J. W. Eur Polym J 1998, 35, 209–214.
5. Horrocks, A. R.; Zhang, S. Polymer 2001, 42, 8025–8033.
6. Fesman, G.; Lin, R. Y.; Rehder, R. A. In Eur. Pat. Appl.; (Stauffer Chemical Co., USA). Ep, 1985, p 14.
7. Ebdon, J. R.; Price, D.; Hunt, B. J.; Joseph, P.; Gao, F.; Milnes, G. J.; Cunliffe, L. K. Polym Degrad Stab 2000, 69, 267–277.
8. Zakikhani, M.; Davis, J.; In Eur Pat. Appl.; (Albright & Wilson Uk Limited, UK). Ep, 1997, p 10.
9. Okamoto, T.; Mori, H.; Matsuda, H.; In U.S.; (Okura Industrial Co., Japan). Us, 1984, p 8.
10. Herbst, W.; Ludwig, H.; Roehlitz, F.; Vilcsek, H.; (Metallgesellschaft A.-G.). De, 1965, p 3.
11. Moszner, N.; Zeuner, F.; Fischer, U. K.; Rheinberger, V. Macromol Chem Phys 1999, 200, 1062–1067.
12. Moszner, N.; Salz, U.; Zimmermann, J. Dent Mater 2005, 21, 895–910.
13. Salz, U.; Zimmermann, J.; Zeuner, F.; Moszner, N. Polym Prepr (ACS, Division of Polymer Chemistry) 2004, 45, 325–326.
14. Salz, U.; Zimmermann, J.; Zeuner, F.; Moszner, N. J Adhes Dent 2005, 7, 107–116.
15. Zeuner, F.; Moszner, N.; Volkel, T.; Vogel, K.; Rheinberger, V. PSS Relat Elem 1999, 144–146, 133–136.
16. Zeuner, F.; Moszner, N.; Drache, M.; Rheinberger, V. PSS Relat Elem 2002, 177, 2263.
17. Senhaji, O.; Robin, J. J.; Achchoubi, M.; Boutevin, B. Macromol Chem Phys 2004, 205, 1039–1050.
18. Jeanmaire, T.; Hervaud, Y.; David, G.; Boutevin, B. PSS Relat Elem 2008, 183, 2204–2213.
19. Boutevin, B.; Hamoui, B.; Parisi, J. P. J Appl Polym Sci 1994, 52, 449–456.
20. Boutevin, B.; Hamoui, B.; Parisi, J. P. Polym Bull (Berlin, Germany) 1993, 30, 243–248.
21. Panwar, P.; Singh, S.; Kumar, N.; Rawat, H.; Mishra, A. K. Bioorg Med Chem 2007, 15, 1138–1145.
22. Guenin, E.; Monteil, M.; Bouchemal, N.; Prange, T.; Lecouvey, M.; Eur J Org Chem 2007, 20, 3380–3391.
23. Benabdellah, M.; Dafali, A.; Hammouti, B.; Aouniti, A.; Rhomari, M.; Raada, A.; Senhaji, O.; Robin, J. J Chem Eng Commun 2007, 194, 1328–1341.
24. El Asri, Z.; Chougrani, K.; Negrell-Guirao, C.; David, G.; Boutevin, B.; Loubat, C. J Polym Sci Part A: Polym Chem 2008, 46, 4794–4803.
25. Bressy-Brondino, C.; Boutevin, B.; Hervaud, Y.; Gaboyard, M. J Appl Polym Sci 2002, 83, 2277–2287.
26. Chougrani, K.; Boutevin, B.; David, G. Eur Polym J 2008, 44, 1771–1781.
27. Baylis, E. K.; Campbell, C. D.; Dingwall, J. G. J Chem Soc, Perkin Trans 1 1972–1999, 1984, 2845–2853.
28. Kafarski, P.; Lejczak, B. PSS Relat Elem 1991, 63, 193–215.
29. Sheridan, R. P. J Chem Inf Comput Sci 2002, 42, 103–108.
30. Vepsalainen, J. J. Curr Med Chem 2002, 9, 1201–1208.
31. Geddes, A. D.; D'souza, S. M.; Ebetino, F. H.; Ibbotson, K. J Bone Mineral Res 1994, 8, 265–306.

32. Alfano, N. J.; Shenberger, D. M.; In U.S.; (Calgon Corp., USA). US, 1995, p 6. Cont.-in-part of U.S. Ser. No. 124, 920, abandoned.

33. Brondino, C.; Boutevin, B.; Parisi, J.-P.; Schryne-mackers, J. J Appl Polym Sci 1999, 72, 611–620.

34. Shida, A.; Sugimura, H.; Futsuhara, M.; Takai, O. Surf Coat Technol 2003, 169/170, 686–690.

35. Kabachnik, M. I.; Medved, T. Y. Doklady Akademii Nauk SSSR 1952, 83, 689–692.

36. Fields, E. K. J Am Chem Soc 1952, 74, 1528–1531.

37. Wu, J.; Sun, W.; Xia, H.-G.; Sun, X. Org Biomol Chem 2006, 4, 1663–1666.

38. Degenhardt, C. R.; Burdsall, D. C. J Org Chem 1986, 51, 3488–3490.

39. Rixens, B.; Severac, R.; Boutevin, B.; Lacroix-Desmazes, P. J Polym Sci Part A: Polym Chem 2005, 44, 13–24.