Poly(MMA)-*b*-poly(monophosphonic acrylate) Diblock Copolymers Obtained by ATRP and Used as Additives for Anticorrosive Coatings

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ABSTRACT: Atom transfer radical polymerization (ATRP) of dimethyl(methacryloyloxy)methyl phosphonate (MAC_1P) was investigated in toluene, in the presence of methyl 2-bromoisobutyrate as the initiator, and using different metal and ligand systems. Polymerization proceeded with very low monomer conversion, which was attributed to the ability of phosphorus to complex the copper ions, removing copper ions from original ligand, and then stopping the MAC_1P polymerization. Poly(MMA)-*b*-poly(phosphonate acrylate) diblock copolymer structure was efficiently obtained by the ATRP process, based on a four-step reaction. Poly(MMA)-*b*-poly(*tert*-butyl acrylate) diblock copolymer was first obtained by ATRP, then the *tert*-butyl groups were removed and phosphonate functions were incorporated by esterification reaction, using 4-dimethylaminopyridine as the catalyst. This new diblock copolymer was used as an additive for anticorrosive coating; however, no improvement (using the salt spray test technique) was observed comparatively with the statistical copolymer with the same acid content. This study enhanced that the acid content of phosphonic additives is the main parameter, unlike their structuration, to increase the resistance to corrosion. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2213–2220, 2009

Key words: adhesion; atom transfer radical polymerization; block copolymers; coatings

INTRODUCTION

Commercial anticorrosion polymer compounds are generally formed from Sipomer® or Phosmer® monomers, which are phosphate-type (meth)acrylates, and can be readily polymerized by emulsion polymerization or solution polymerization.[1,2] Polymers with some phosphonate functionality have long been established as excellent adhesives and anticorrosion compounds,[3–10] however there has been very little investigation on the use of phosphonate-type methacrylates for the same purpose.[1,2] Dimethyl(2-methacryloyloxyethyl)phosphonate (MAC_2P) has been successfully copolymerized in its acidic form with methyl methacrylate (MMA), to be used as an additive with polyvinylidenefluoride [poly(VDF)].[11,12] 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,[11] but the phosphonic component remained soluble in the poly(VDF) matrix inhibiting water penetration and thus corrosion. More recently, dimethyl(methacryloyloxy)methyl phosphonate (MAC_1P; the synthesis of which requires nonhazardous and low cost reagents) was also copolymerized with MMA, leading to statistical copolymers.[13] The anticorrosive behavior of these copolymers was evaluated using the salt spray test (well-established as the best standard to measure the adhesion and anticorrosive properties of a surface coating),[14] with only 30% of the metallic surface corroded after 300 h. These adhesion and anticorrosive properties should be enhanced by favoring the migration of phosphonic groups towards the metallic surface. Gradient copolymers (used as additives in the poly(VDF) matrix) increase migration of the phosphonic groups, as previously demonstrated by the work of Rixens et al.[15] Compared with the gradient copolymers, diblock copolymers should be better candidates to favor migration of phosphonic groups and promote better adhesion and anticorrosive properties.

The current study has two aims, the first involving the synthesis of novel phosphonate (meth)acrylate diblock copolymers. The second aim is to test these new diblock copolymers as additives for the adhesion and anticorrosive properties of metals. Living/controlled radical polymerization (CRP) allows obtaining block copolymers. However, CRP of

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phosphonate monomers seems to be much challenging, which can be probably ascribed to two reasons; the first one is the limited commercial availability of phosphonate-containing vinyl monomers. Indeed, dimethylvinyl phosphonate and vinyl phosphonic acid, the only available phosphonate monomers, were polymerized using a degenerative transfer (DT) process [namely Iodine Transfer Polymerization (ITP)], but were not sufficiently activated to give an efficient CRP.[16] The second reason is related to the peculiar behavior of the phosphonate monomers during a CRP process. Recently, MAC_1P was polymerized using two different DT processes: reversible addition fragmentation transfer (RAFT) and ITP, and authors observed an unexpected behavior (for both processes) when referring to MMA, from which CRP based on DT is well-established. Relatively poor controlled polymerization was observed with limited monomer conversion, partially explained by a radical deactivation attributed to the phosphonate group.[17]

Other CRP techniques can be used to reach phosphonate diblock copolymers. Noteworthy, Huang and Matyjaszewski[18] have performed atom transfer radical polymerization (ATRP) of dimethyl(1-ethoxycarbonyl)vinyl phosphate (DECVP), a phosphate-type monomer, leading to a relatively good control of the polymerization, despite limited monomer conversion (about 60%). To synthesize poly(MMA)-*b*-poly(phosphonate methacrylate), ATRP of MAC_1P was first investigated in this article. As MAC_1P ATRP was unefficient (see ATRP of MAC_1P of Results and Discussion), another synthetic strategy was used to synthesize phosphonate diblock copolymers. These copolymers were then tested as additives for anticorrosion properties.

EXPERIMENTAL SECTION

Materials

Ethyl 2-bromoisobutyrate (EBriBu), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), 2,2′-bipyridine (Bpy), CuCl, CuBr, $Cu(Cl)_2$, $Cu(Br)_2$, dicyclocarbodimide (DCCI), and 4-dimethylaminopyridine (DMAP) were purchased from Aldrich (Lyon, France) and used without further purification. MMA and *tert*-butyl acrylate were vacuum-distilled. 2,2′-Azobisisobutylonitrile (98%, Fluka, Geneva, Switzerland) was recrystallized in methanol before use.

Measurements

The chemical structure of the products was determined by ^{1}H-NMR, ^{31}P-NMR, and ^{13}C-NMR (Bruker

AC 400 MHz) at room temperature in $CDCl_3$ solutions. Abbreviations s, d, t, q, and m stand for singlet, doublet, triplet, quadruplet, and multiplet, respectively. The INVGATE procedure with a delay, D1 of 10 s was used to quantify the final yield. Elemental analysis was also performed by the Service Central d'Analyses (Vernaison, France). Steric Exclusoin Chromatography (SEC) analyses were performed using a Spectra-Physics apparatus, equipped with a set of PLgel (5 mm) MIXED-C columns, from Polymer Laboratories. The eluent was tetrahydrofuran at a flow rate of 0.8 mL min^{-1}. The calibration curve was established using PMMA standards from Polymer Laboratories. Infrared (FT-IR) spectra are recorded on a Nicolet 510P FT-IR spectrometer with a band accuracy of ± 2 cm^{-1}.

MAC_1P ATRP

The synthesis of dimethyl(methacryloyloxy)methyl phosphonate (MAC_1P) was described in a previous paper.[13] A typical ATRP was carried out as follows: to a 10 mL dried Schlenk flask, MAC_1P, 1 g (4.8 mmol), EBriBu, 0.0087 g (0.048 mmol), and toluene (1 mL) were added. After three freeze-pump-thaw cycles, HMDETA, 0.011 g (0.048 mmol) and Cu(I)Cl, 4.8 mg (0.048 mmol) were added under N_2. After stirring for 10 min at room temperature, the flask was placed in a thermostated oil bath at 70°C. Samples were taken to analyze the monomer conversion by ^{1}H-NMR, and molecular weight by SEC, at different time intervals during the polymerization. The polymerization was stopped by cooling the flask to room temperature and opening the flask to air.

Synthesis of bromo-terminated poly(MMA) macroinitiator

The procedure that was used for the synthesis of Poly(MAC_1P)-Br was utilized for the ATRP of MMA with the following ratio: [MMA] : [EBrIB] : [CuBr] : [PMDETA] = 200 : 1 : 1 : 1.

Poly(MMA)-Br was obtained with 88% conversion having an M_n of 18,200 g/mol (PDI = 1.1).

Synthesis of poly(MMA)-*b*-poly(tBuA) diblock copolymer

The same procedure that was used for the synthesis of Poly(MAC_1P)-Br was utilized for the ATRP of tBuA in benzonitrile with the following ratio: [tBuA] : [PMMA-Br] : [CuCl] : [PMDETA] = 20 : 1 : 1 : 1. Poly(MMA)-*b*-poly(tBuA) was obtained with 90% conversion having M_n of 21,300 g/mol (PDI = 1.1).
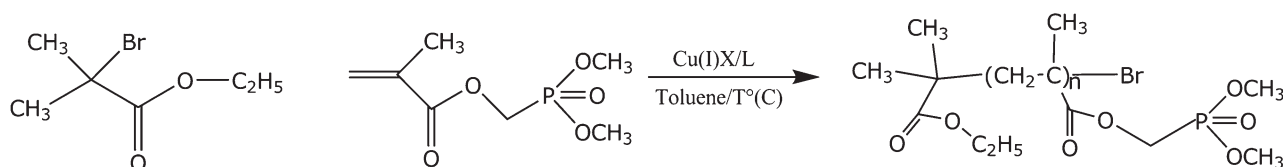
Figure 1 ATRP of MAC$_1$P in toluene.

Hydrolysis of *tert*-butyl group from poly(MMA)-*b*-poly(tBuA) diblock copolymer

In a 50 mL round bottom flask, Poly(MMA)-*b*-poly-(tBuA), 1 g (6.63 10^{-3} mmol) was dissolved in 5 mL of dichloromethane. Then, trifluoroacetic acid (TFA), 7.5 mg (6.63.10^{-2} mmol) was added at 0°C, and the mixture was stirred at room temperature overnight until completion of *tert*-butyl hydrolysis (evidenced by the disappearance of the peak at 1.4 ppm, characterizing the *tert*-butyl groups), leading to Poly-(MMA)-*b*-poly(AA) diblock copolymer.

Synthesis of poly(MMA)-*b*-poly(phosphonic acrylate) diblock copolymer

In a 50 mL round bottom flask, Poly(MMA)-*b*-poly-(AA), 1 g (6.63 10^{-3} mmol) and hydroxymethyl dimethylphosphonate (its synthesis was described in a previous paper[13]), 1.4 g (0.01 mol) were dissolved in 5 mL of dichloromethane. Then DCCI, 2.27 g (0.01 mol) and DMAP, 0.12 g (0.001 mol) were added drop wise into the solution at 0°C. The mixture was stirred at room temperature overnight, and the block copolymer was purified by methanol precipitation. Finally, Poly(MMA)-*b*-poly(phosphonic acrylate) was obtained by hydrolysis of the phosphonate groups in the presence of NaBr, as already described by El Asri et al.[13]

Anticorrosive properties of poly(VDF) and copolymers blends

Preparation of blends

PVDF SOLEF 1010/1001 (9% w : w) was first dissolved with *N*-methyl pyrrolidone (90% w : w) at room temperature. To this solution, diblock copolymer (1% w : w) was added in a dropwise manner. The solution was deposited onto galvanized steel plates using a BarCoater (120 µm Braive instruments). After the removal of solvents (heating to 190°C), the thickness of the films was measured with Byko-test 7500 apparatus and was about 10 µm.

Anticorrosive test

The salt spray test (DIN 50021) was used to evaluate the anticorrosive properties of the diblock copoly-mers. A solution containing 0.5 mol/L of NaCl in purified water was dispersed on the coatings using a Ascott S120T salt spray machine, at a constant temperature of 35°C. At regular intervals (ca. every 50 h) plates were removed from the machine and visually assessed for corrosion. 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 and adhesive test methods.

Determination of acid value

The phosphonic acid groups bring adhesive and anticorrosive properties, so the titration of these functions was necessary. Acid value (*Ia*) was defined as the amount of potassium hydroxide necessary to neutralize 1 gram of copolymers. The copolymer was dissolved into dimethylformamide (7 g/L), 10 mL of this solution was titrated with a KOH/EtOH solution (N/10). The values used to calculate *Ia* were the molecular weight of KOH (M_{KOH}, 56 g/mol), the concentration of KOH (C_{KOH}), the volume at equilibrium (V_{KOH}), and the weight of copolymer titrated (m_{copo}).

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

RESULTS AND DISCUSSION

Atom transfer radical polymerization of MAC$_1$P

Firstly, ATRP of dimethyl(methacryloyloxy)methyl phosphonate (MAC$_1$P) was investigated in toluene, using ethyl 2-bromoisobutyrate (EBriBu) as the initiator (Fig. 1). To our knowledge, ATRP was only studied on DECVP, i.e., a phosphate monomer where the phosphate substituent is situated in α-position of the radicals, which can therefore stabilize them during the ATRP process. In the case of MAC$_1$P, the phosphonate group is linked to the ester substituent (the latter having an electron-

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TABLE I
Results for ATRP of MAC$_1$P ([MAC$_1$P]$_0$ = 1 mol/L) in Toluene Initiated with Ethyl 2-bromoisobutyrate (EBriBu),
PMDETA = N,N,N',N'',N''-Pentamethyldiethylenetriamine, HMTETA = 1,1,4,7,10,10-Hexamethyltriethylenetetramine,
and Bpy = 2,2′-Bipyridine

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Entry	[EBriBu]$_0$/[M]$_0$/[Cu(I)X]$_0$/ [L]$_0$/[Cu(II)X$_2$]$_0$	X	L	T (°C)	Time (h)	Conv. (%)	M_n (g/mol) exp	theor
1	1/200/1/1	Br	PMDETA	100	6	0	/	/
2	1/100/1/1	Br	PMDETA	100	6	24	4900	500
3	1/100/1/1/0,2	Br	PMDETA	100	6	18	3700	300
4	1/100/1/1/0,1	Cl	PMDETA	70	10	15	2600	300
5	1/100/1/1/0,1	Cl	HMTETA	70	10	/	/	/
6	1/100/1/1/0,1	Cl	Bpy	70	10	10	2000	/
7	1/100/1/1/0,1	Cl	PMDETA	100	6	20	4500	500
8	1/100/1/1/0,1	Cl	PMDETA	100	20	22	4600	500

withdrawing effect). It is also difficult to predict whether the radicals will be stabilized or not during ATRP. Hence, several experiments have been performed and the results are shown in Table I, where several metal and ligand systems have been used at two different temperatures (70 and 100°C). From entries 1 to 8, where CuBr was replaced by CuCl, and where three different ligands (PMDETA, HMTETA, and Bipyridine) were used, MAC$_1$P ATRP always proceeds with low monomer conversions, leading to very low experimental molecular weights (two monomer units were only introduced into poly-(MAC$_1$P)). Even an increase in the reaction time (Entry 8) does not improve the polymerization rate (only 22% monomer conversion). This set of experiments clearly indicate unsuccessfull ATRP for MAC$_1$P. This behavior could be due to high termination rate at the beginning of the polymerization. Cu(II)Cl$_2$ (Entries 4–8) or Cu(II)Br$_2$ (Entry 3) were added (about 10 mol % of Cu(I)Cl) to decrease termination reactions, but no improvement was observed. The second explanation refers to the ability of the phosphorus to complex the copper ions, removing it from original ligand, which then stops the MAC$_1$P polymerization. This behavior requires more investigation, especially because it is in contradiction with the study of Huang et al., where successull CRP is obtained despite the presence of a phosphate substituent.

The aim of this study is the synthesis of poly-(MMA)-b-poly(phosphonate (meth)acrylate) diblock copolymers using ATRP. Unsuccessfull CRP of MAC$_1$P, either by DT (previous study)[17] or by ATRP (this study), shows that MAC$_1$P is not promising to obtain diblock copolymers. Consequently, another strategy based on a four-step reaction using ATRP was proposed to efficiently synthesize such diblock copolymers, to be used as additives for anticorrosion properties.

Synthesis of poly(MMA)-b-poly(phosphonate (meth)acrylate) diblock copolymers

Poly(MMA)-b-poly(phosphonate (meth)acrylate) diblock copolymer structure can be efficiently obtained by ATRP process, based on a four-step reaction (Fig. 2). First, poly(MMA)-b-poly($tert$-butyl acrylate), a true diblock copolymer, was obtained by the ATRP of MMA [Fig. 2(a)] followed by the ATRP of $tert$-butyl acrylate, using PMMA-Br as the macroinitiator [Fig. 2(b)]. Such diblock copolymer has already been designed by other authors,[19–21] and can be easily characterized by the linear evolution of the molecular weight (M_n) over the monomer conversion route. PMMA-Br macroinitiator was synthesized with an M_n of 18,200 g/mol (PDI = 1.1), and extented with $tert$-butyl acrylate. The true diblock copolymer is demonstrated by the absence of a tail in the low molecular weight region, as well as by an increase of the molecular weight value (Fig. 3) showed by the SEC analysis. The poly-(MMA)-b-poly($tert$-butyl acrylate) diblock copolymer shows an M_n of 21,300 g/mol, corresponding to approximatively 15 $tert$-butyl acrylate units. $Tert$-butyl substituents of poly(MMA)-b-poly($tert$-butyl acrylate) diblock copolymer were cleaved using TFA at 0°C to give the corresponding poly(MMA)-b-poly (acrylic acid) diblock copolymer [Fig. 2(c)]. The cleavage occured quantitatively, according to ^{1}H-NMR analysis (Fig. 4), where the peak attributed to the $tert$-butyl substituent (δ = 1.5 ppm) totally disappeared (upper spectrum). The acid groups of poly(MMA)-b-poly(acrylic acid) diblock copolymer then reacted, through a condensation reaction with dimethyl-α-hydroxymethyl-phosphonate (HOC$_1$P) [Fig. 2(d)], the synthesis of which was well-described and characterized elsewhere.[13] This condensation reaction was performed at 0°C quantatively, thanks to the use of DMAP catalyst (10 mol % of HOC$_1$P).
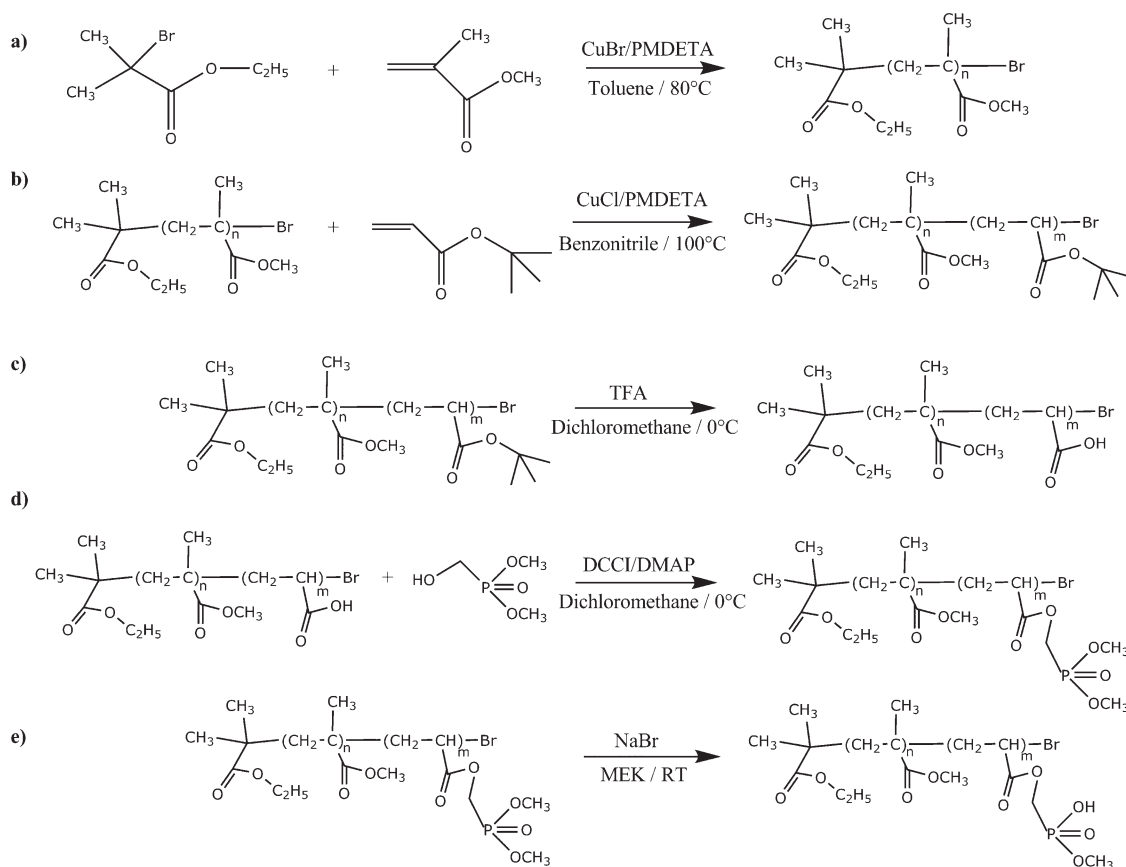
Figure 2 Five-step synthesis of the poly(MMA)-*b*-poly(monophosphonic acrylate) diblock copolymer.

^{1}H-NMR (Fig. 5) of the poly(MMA)-*b*-poly (phosphonate acrylate) diblock copolymer especially shows the peaks of the methylene substituent (δ = 3.9 ppm) and the methyl groups of the phosphonate (δ = 3.8 ppm), with an intensity ratio of about 1/3. ^{31}P-NMR shows only one peak (δ = 26 ppm), which was downshifted when compared with that of HOC_1P (δ = 28 ppm).

Based on the ATRP followed by a chemical modification, poly(MMA)-*b*-poly(phosphonate acrylate) is the first true phosphonate diblock copolymer, which possess about 200 MMA units (allowing for p(VDF)

compatibility) and about 15 phosphonate units (enabling for metal adhesion). To be efficient as additives, the phosphonate substituent of the diblock copolymer must be replaced with the corresponding methyl phosphonic hemi-ACID [Fig. 2(e)].[11–13] Such cleavage was done using NaBr reagent[13] and was evidenced by the ^{31}P-NMR analysis, where only one peak is observed (high-field shifted to δ = 18 ppm). Finally, poly(MMA)-*b*-poly(monophosphonic acrylate) diblock copolymer was synthesized with approximatively 7 mol % of monophosphonic group (compared with MMA), corresponding to an acid
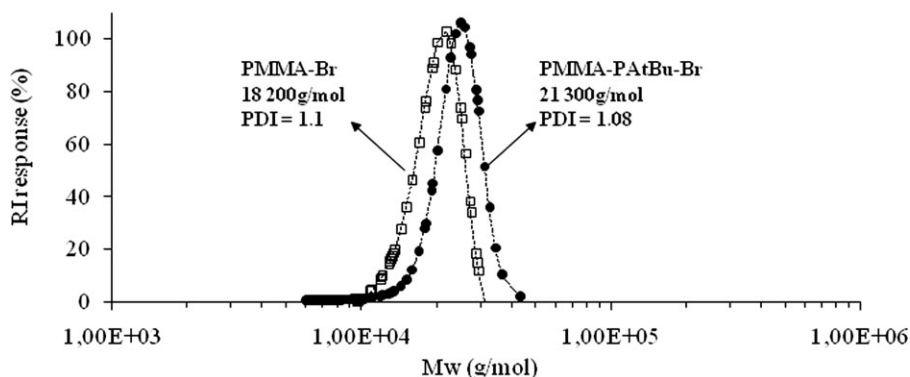

Figure 3 GPC traces of the PMMA-Br macroinitiator and poly(MMA)-*b*-poly(*tert*-butyl acrylate) diblock copolymer.
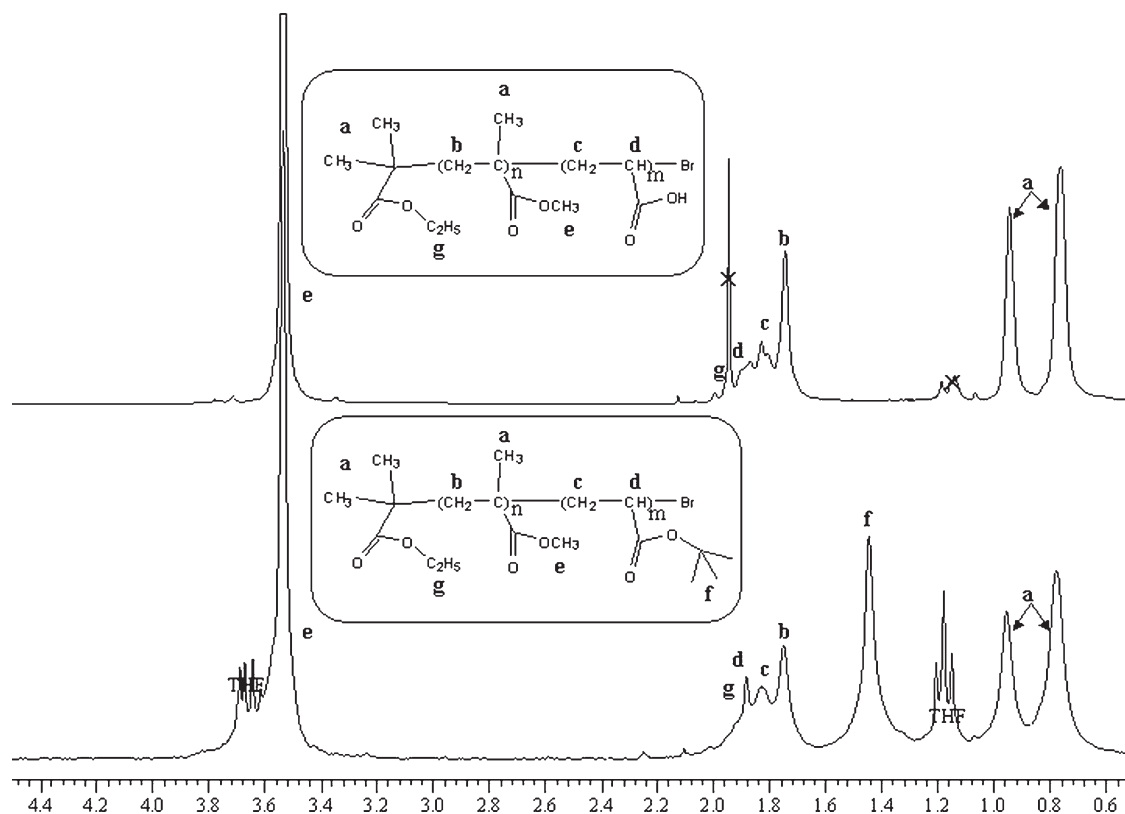
Figure 4 ^{1}H-NMR (CDCl$_3$) of the poly(MMA)-*b*-poly(*tert*-butyl acrylate) (lower spectrum) and poly(MMA)-*b*-poly(acrylic acid) (upper spectrum) diblock copolymers.
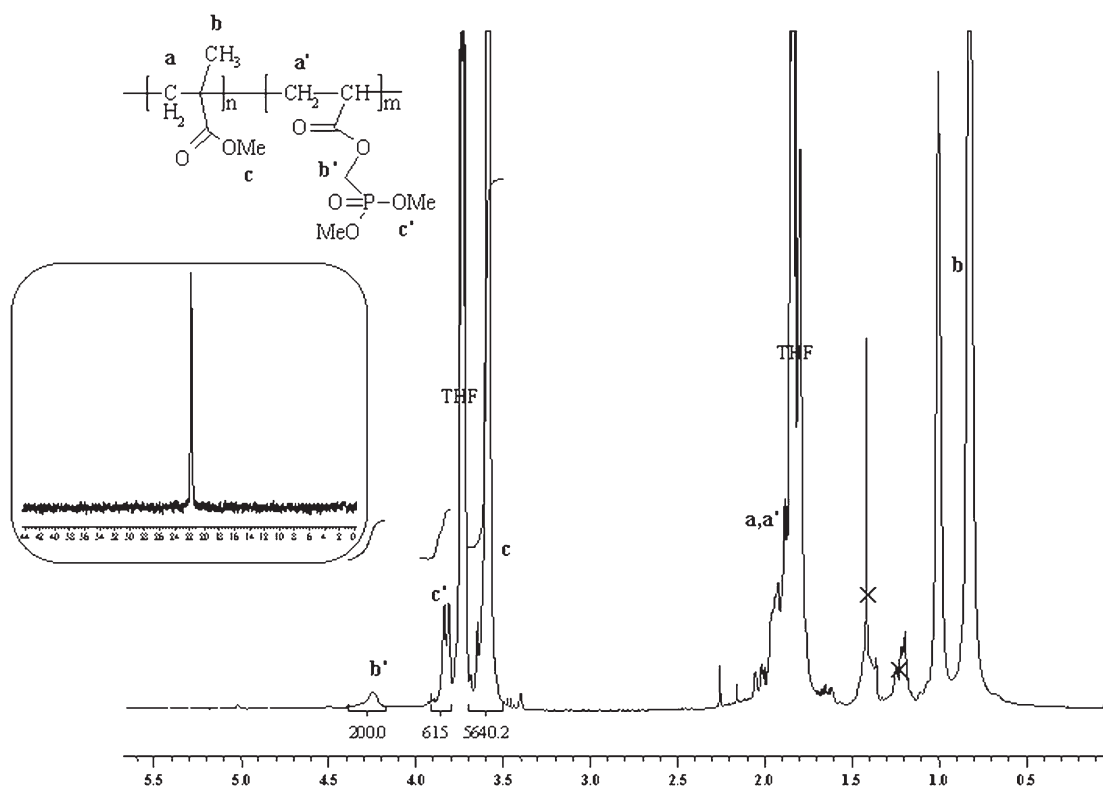

Figure 5 ^{31}P (inset) and ^{1}H-NMR (CDCl$_3$) of the poly(MMA)-*b*-poly(phosphonate acrylate) diblock copolymer.

TABLE II
Anticorrosive Properties of Poly(VDF) Blended with Hemi-Phosphonic Statistical and Diblock Copolymers Additives (10% w : w Compared to Poly(VDF)); (●) = MMA Unit and (Ⓟ) = Hemiphosphonic Acid Unit

Blends (weight %)	Structure of the monophosphonic additive	Ia of blend (mg KOH/g)	% of corroded surface (after 14 days)	Ref
Virgin poly(VDF)	/	0	100 (after 2 days)	/
Poly(VDF) ●●Ⓟ●●ⓅⓅ●●●Ⓟ●	Statistical copolymer	4.6	40	13
Poly(VDF) ●●●●●ⓅⓅⓅⓅ	Diblock copolymer	2.7	48	Our work

value (Ia) of about 2.7 mg KOH/g (calculated from KOH titration).

Adhesion and anticorrosion characterization

To protect the galvanized stell-plate against corrosion, single-coat system was prepared consisting of a blend of poly(VDF) (inhibiting water penetration) with poly(MMA)-b-poly(monophosphonic acrylate) diblock copolymer with 10 weight % (compared with poly(VDF)). Similar blends were already made[11,13] of poly(VDF) with statistical monophosphonic methacrylate copolymers, using the same weight %. Table II shows the characteristics of both blends, i.e., acid value and weight % of the additive. Anticorrosive properties of virgin poly(VDF) was also determinated without any additive to be compared with the blends. Anticorrosive behavior of these systems can be evaluated using the salt spray test, which is the best standard to measure the anticorrosive properties of a surface coating.[14] Figure 6 shows an almost linear trend for the evolution of corrosion as a function of time, when diblock copolymer is used as additive. As expected, virgin poly-(VDF) alone is not able to prevent the metal from corrosion, as the surface is almost completely corroded only after 48 h. Figure 6 also shows high improvement when poly(VDF) is blended with the poly(MMA)-b-poly(phosphonate methacrylate) diblock copolymer additive, although the statistical copolymer seems to afford better adhesion towards the metallic surface, and hence better anticorrosion properties. Table II gives the content of the corroded surface after being subjected 14 days to the salt spray test, as well as the acid content of the additive. The blend made of diblock copolymer additive and poly(VDF) brings high efficiency towards corrosion [compared to virgin poly(VDF)], as about 50% of the metallic surface is corroded after being submitted 14 days to the salt spray test. But, comparatively to the blend made of statistical copolymer additive and poly(VDF), no improvement is clearly observed (40% of corroded surface after 14 days). Two main differences arise from

these two blends, the first one being the monophosphonic additive structure and the second one being the acid value, Ia. To be highly efficient against corrosion, the additive must ensure high adhesion at the interface between the metal and the poly(VDF) matrix. Promoting adhesion induces migration of the phosphonic group at the metal surface. This migration occurs when phase seggregation is obtained, i.e., phosphonic acid nodules into a PMMA matrix.[15] Noteworthy, segregation is favored both by the structure of the copolymer and the content of phosphonic acid units. The anticorrosion tests shown in Table II prove that the acid content into the copolymers is the main parameter that controls phase segregation, from which high adhesion towards metal should be obtained.

Noteworthy, Rixens et al.[15] showed that about 15 monophosphonic units incorporated into the gradient copolymer were sufficient, compared with approximately 100 vinylidene chloride (VDC) units, to create phase segregation and consequently migration of phosphonic units. Poly(MMA)-b-poly (monophosphonic acrylate) diblock copolymers synthesized herein show a similar MMA and monophosphonic molar ratio as that of the VDC and monophosphonic molar ratio (VDC and MMA been both hydrophobic, allowing phase segregation with
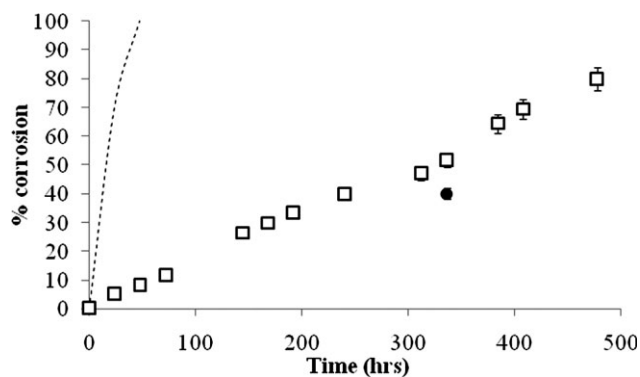

Figure 6 Graphical result of the corrosion after being subjected to the salt spray test (0.5 mol/L NaCl in water at 35°C) where (---) = virgin poly(VDF), (□) = diblock copolymer, and (●) = statistical copolymer.

phosphonic units), which make them good candidates to promote migration towards the metallic surface. However, if phase segregation is required, higher phosphonic content will therefore increase the adhesion and anticorrosive properties; it will be then necessary to more efficiently tune the content of phosphonic group, i.e., increasing the size of the *tert*-butyl acrylate block. This is the focus of a coming work, still in progress.

CONCLUSION

This study first underlines the inhibiting effect of the phosphorus atom that complex the copper ions during the ATRP process, which proceeds with poor monomer conversion. To overcome phosphorus complexation, phosphonate diblock copolymer structure is obtained using a four step reaction, based on the modification of poly(MMA)-*b*-poly(*tert*-butyl acrylate) diblock copolymer. The newly hydrolysed poly (MMA)-*b*-poly(phosphonic acrylate) diblock copolymer, with about 15 phosphonic repeating units, were used as additives in poly(VDF) coatings to protect steel against corrosion. High resistance towards corrosion was observed (about 40% of the surface was corroded after 14 days); however, no real improvement was obtained compared to poly(MMA) additives in which the phosphonic groups are statistically attached to the poly(MMA) backbone. Although better resistance to corrosion will be probably brought by additives containing higher phosphonic content, poly(MMA)-*b*-poly(phosphonic acrylate) being the first real phosphonate diblock copolymer, may be used for other applications such as flame retardant.

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