

Phosphonic acid-containing polysulfones as anticorrosive layers

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ABSTRACT: As a part of research work to elaborate polymeric materials for metal corrosion protection, we have developed a new family of phosphonic acid-containing polymers. The synthesis and the characterization of polysulfones bearing alkyl phosphonate ester side groups are first described. These polymers are synthesized by direct polycondensation of a phosphonate ester-containing bisphenol by aromatic nucleophilic substitution. The physicochemical properties of the resulting polymers are described. Acidic hydrolysis of phosphonate esters results in the formation of phosphonic acid groups. A series of phosphonic acid-containing polysulfones is therefore obtained and characterized. A preliminary evaluation of the anticorrosive properties of these polymers is described. In 0.25M Na₂SO₄ solution, the corrosion rate of a polymer-coated mild steel sample is much lower than of the free metal substrate. These results suggest that phosphonic acid-containing polysulfones might be interesting as anticorrosive coatings. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, *132*, 41890.

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INTRODUCTION

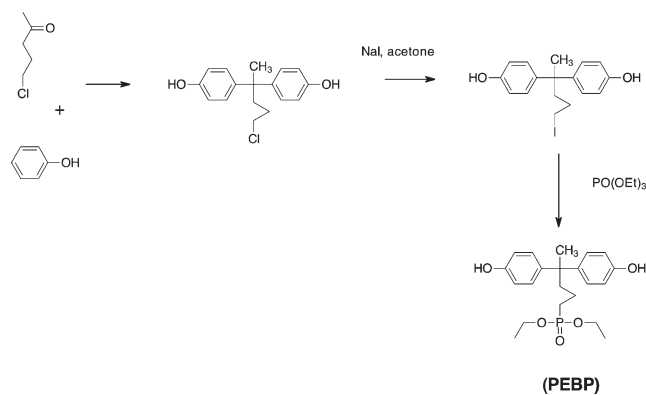
Increasing concern regarding the detrimental effects of mild steel corrosion has prompted industrial and academic material chemists to design new efficient coatings. Different approaches are currently described using a sacrificial layer, with small organic molecules, macromolecules, or inorganic coatings (sol-gel processed oxide films) that isolates the metal from the aggressive environment, etc. In this context, the development of high-performance polymer coatings appears very promising. Conductive polymers (polyaniline,¹ polypyrrole²) have been extensively studied because they induce steel passivation, due to their oxidizing properties. Other organic polymers have emerged as promising candidates, such as epoxy resins, polyimide-block-polyurea,³ polysulfones, etc. The addition of passivation inhibitors such as metallic nanoparticles⁴ and clay nanocomposite^{5,6} has also been reported recently to enhance their protecting effect. Notwithstanding recent advances, the main problems encountered with these systems are related with the presence of defects and porosity of the coating, and of a fair metal-coating interfacial adhesion. The coating delamination is

highly detrimental to the metal protection as the coating rapidly loses its barrier properties toward the underlying surface and therefore becomes ineffective.

Organophosphorus compounds have been widely studied to inhibit carbon steel corrosion. Compared to the well-known and well-used phosphates, phosphonates are very promising as they are less sensitive to hydrolysis.⁷ Different phosphonic acid-containing compounds have been successfully used as corrosion inhibitors.^{8–10} In addition to their anticorrosive properties, phosphonic acid groups are known to strongly enhance adhesion on metallic substrates. Jaehne *et al.*¹¹ developed a strategy by forming a thin layer of bifunctional molecules onto metal surfaces, with one phosphonic acid group designed to react with metal oxides and the second functional group to polymerize. In this approach, delamination tests were performed, and a beneficial effect was clearly shown in the presence of the phosphonic acid adhesion promoter. Even better results were obtained after polymerization of the second functional group, thus forming a thin polymer film at the metal surface. This result suggests that great advantages should be expected with

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Scheme 1. Three-step synthesis of phosphonate ester-containing bisphenol (PEBP).

phosphonic acid-containing polymers as thin anticorrosive coatings. In this respect, most recent works concern the synthesis of acrylate or methacrylate polymers.^{12–14} Concerning the development of phosphonic acid-containing high-performance polymers, very little work has been reported.¹⁵ Moreover, to the best of our knowledge, such polymers have not been tested as anti-corrosion coatings.

The present work concerns the synthesis and characterization of a series of polysulfones bearing alkyl phosphonate ester or alkyl phosphonic acid side chains. Their chemical structures were confirmed by NMR analysis, and their thermal properties were investigated. Electrochemical analyses show an improvement of the corrosion resistance of the mild steel substrates coated with these polymers.

EXPERIMENTAL

Materials

4,4'-Difluorodiphenylsulfone and bisphenol A (Aldrich) were purified by crystallization. All other chemicals (dimethyl sulfoxide (DMSO), potassium carbonate (K_2CO_3), *N*-methylpyrrolidone (NMP), $ISiMe_3$, HCl, NaCl, and Na_2SO_4) were commercially available and used as received. Mild steel samples (8 cm × 8 cm) were obtained from SMG (Société Métallurgique de Grenoble).

p-(4-(Diethoxyphosphonyl)-1-(*p*-hydroxyphenyl)-1-methylbutyl)phenol (PEBP) was synthesized in three steps, as described in Scheme 1. Experimental details will be reported elsewhere (to be published). ^{31}P NMR (400 MHz, DMSO- d_6 , δ): 31.78; 1H NMR (400 MHz, DMSO- d_6 , δ): 1.17 (*t*, $J = 1.8$ Hz, 3H, H^{11}), 1.28–1.30 (*m*, 2H, H^3), 1.48 (*s*, 3H, H^5), 1.60–1.68 (*m*, 2H, H^1), 3.86–3.96 (*m*, 4H, H^{10}), 6.63 (*d*, $J = 8$ Hz, 4H, H^8), 6.93 (*d*, $J = 8$ Hz, 4H, H^7), 9.2 (OH); ^{13}C NMR (400 MHz, DMSO- d_6 , δ): 16.1 (C^{11}), 17.6 (C^3), 24.7 (*d*, C^1), 27.4 (C^5), 42.3 (C^2), 44.1 (C^4), 60.6 (C^{10}), 114.5 (C^8), 127.6 (C^7), 139.6 (C^6), 154.8 (C^9).

Synthesis of Polymers

Synthesis of Phosphonate Ester-Containing Polysulfones. Typical procedure for the synthesis of PEPS4. About 0.6 g (1.53 mmol) of *p*-(4-(diethoxyphosphonyl)-1-(*p*-hydroxyphenyl)-1-methylbutyl)phenol (PEBP), 1.003 g (3.95 mmol) of 4,4'-difluorodiphenylsulfone, 0.5517 g (2.42 mmol) of bisphenol A and 1.19 g

(8.68 mmol) of potassium carbonate were added to 6.4 mL of DMSO and heated at 80°C for 48 h, in a two-necked reactor equipped with a nitrogen inlet and a mechanical stirrer. After cooling, the mixture was poured into water. The white fibrous polymer was cut into pieces, collected by filtration, washed with water and dried under vacuum at 80°C for 4 h.

Synthesis of phosphonic acid-containing polysulfones (PAPS) by acidic hydrolysis. Method I. PEPS (as fibers or as thin membranes) were suspended in 37% HCl and refluxed for 24 h. The reaction was monitored by ^{31}P NMR. Samples were dissolved in NMP, and nuclear magnetic resonance (NMR) experiments were performed with a coaxial tube containing DMSO- d_6 . Upon completion of the reaction, the polymers were filtered and thoroughly rinsed with hot water and dried under vacuum at 80°C.

Method II. PEPS were dissolved in NMP (20 wt %). A large excess (5.2 eq/phosphonate ester groups) of iodotrimethylsilyl ($ISiMe_3$) was added dropwise to the homogeneous solution. Direct ^{31}P NMR analyses of the reaction mixture using a coaxial tube filled with DMSO- d_6 were achieved to monitor the hydrolysis of the phosphonate ester groups. At the end of the reaction, the resulting polymer was precipitated in methanol, filtered, and dried under vacuum at 80°C.

The experimental proportion of phosphonate esters incorporated (x) was evaluated by 1H NMR (Figure 2), according to the following eq. (1):

$$x = 2 \times \frac{\int_{2.17\text{ppm}} (H_b)}{\int_{7.85\text{ppm}} (H_{g+g'})} \quad (1)$$

with $\int_{2.17\text{ppm}} (H_b)$ corresponding to the integral of protons b (at 2.17 ppm) and $\int_{7.85\text{ppm}} (H_{g+g'})$ corresponding to the integral of protons g and g' (at 7.85 ppm).

The amount of phosphonate ester groups present in each sample (expressed in milli equivalent of phosphonate groups per gram of dry polymer) was determined according to the following eq. (2):

$$\text{meq } P/g = \frac{x}{xM_x + yM_y} \times 1000 \quad (2)$$

M_x : mean of the molecular weights of the structural units (PEBP and difluorodiphenylsulfone). M_y : mean of molecular weights of the structural units (bisphenol A and difluorodiphenylsulfone).

Film Preparation

Thin self-standing films of PEPS were prepared by casting onto a glass substrate, a 20 wt % polymer solution in NMP. The films thus obtained were dried under nitrogen at 50°C overnight and then successively treated 1 h at 80°C, 120°C, 150°C, and 180°C. Membranes were peeled off by immersion in water.

General Procedure for the Preparation of PAPS-Coated Metal Sample

The mild steel sample surface (8 cm × 8 cm) was initially mechanically polished with silicon carbide (PRESI SiC) abrasive paper from P80 down to P1200, with a PRESI-Mecatech 334

automatic polisher. The samples were then rinsed with ethanol and dried in hot air. Samples were kept dry to prevent the surface oxidation before the polymer coating. A phosphonic acid-containing polysulfone thin layer (PAPS obtained by dealkylation in the presence of ISiMe_3) was then deposited on the treated surface sample by casting a 20 wt % NMP polymer solution. The solvent was evaporated under nitrogen at 50°C overnight and 1 h at 80°C, 120°C, 150°C, and 180°C.

Methods

^1H , ^{13}C , and ^{31}P nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer operating at the following frequencies of 400.16 MHz for ^1H , 100.63 MHz for ^{13}C , and 161.99 MHz for ^{31}P . Tetramethylsilane was used as the internal standard for ^1H , whereas 85% H_3PO_4 was used as the reference for ^{31}P analyses. Thermogravimetric analyses (TGA) were performed under air at a heating rate of 10°C min^{-1} using a TA Instruments model 950 thermogravimetric analyzer. Polymer glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) with a Mettler-Toledo DSC822e equipment. Analyses were performed under nitrogen, at a heating rate of 5°C min^{-1} . Reported values were obtained from a second heat scan. Thermomechanical analyses (TMA) were performed on a TA Instruments model Q400, under nitrogen, at a heating rate of 5°C min^{-1} and in the penetration mode.

Molecular weights were determined by size exclusion chromatography on a system equipped with an AGILENT G1310A pump and a differential refractive index detector (Wyatt optilab -rEX 25°C and 658 nm). DMF containing 0.05M LiBr was used as eluent. SEC analyses were performed on two PLgel Mixed D columns thermostated at 70°C. Molecular weights (denoted $M_{n(\text{PS})}$ and $M_{w(\text{PS})}$) were determined from a polystyrene calibration curve.

The water uptake (W_{uptake}) measurements were performed at room temperature and at 90°C. The self-standing membrane samples were previously dried at 100°C under vacuum for one day. The preweighted dried films (W_{dry}) were immersed in deionized water for 3 h, slightly wiped and then weighted (W_{swollen}). A second measurement was repeated 3 h later and the reported values correspond to an average uptake. The water uptake was calculated from eq. (3):

$$W_{\text{uptake}}(\%) = \frac{W_{\text{swollen}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (3)$$

Electrochemical characterizations were performed with a conventional thermostated ($T = 22^\circ\text{C}$) three-electrode electrochemical cell. The nature of the reference electrode (either saturated sulfate or calomel electrode) was chosen according to the electrolyte used (0.6M NaCl or 0.25M Na_2SO_4). The coated sample was used as working electrode (4.9 cm^2). A detailed description of the experimental device is provided in Supporting Information Figure S1. All measurements were made using a GAMRY 600 Potentiostat/Galvanostat/ZRA. The following five-step procedure was used and repeated successively 10 times:

1. Open circuit potential (OCP) (i.e., the corrosion potential of the mild steel covered by different coatings) was recorded for 3600 sec.

2. Linear polarization resistance (LPR) measurements were performed by varying the potential of the electrode from -0.02 V versus OCP to $+0.02$ V versus OCP, at 0.04 mV s^{-1} . The resulting current was measured.
3. Two hours waiting was applied before the next step.
4. Electrochemical impedance spectroscopy (EIS) was recorded at immersion potential (OCP) by applying a 10 mV sinusoidal potential within a frequency range of 100 kHz to 1 mHz, with a 10 mV perturbation.
5. Two hours waiting was applied before repeating the procedure.

RESULTS AND DISCUSSION

Synthesis and Physicochemical Characterization of PEPS and PAPS

A phosphonate ester-containing bisphenol (PEBP) was synthesized in three steps, according to Scheme 1. Experimental details will be described elsewhere. ^1H NMR characterization of polymer-grade PEBP is presented in Figure 1.

This monomer was incorporated in poly(ether sulfone) structures by aromatic nucleophilic substitution (Scheme 2). Typically, the polymerization reaction was performed by condensation of the different monomers (PEBP, bisphenol A and 4,4'-difluorodiphenylsulfone) in a polar aprotic solvent (DMSO), in the presence of K_2CO_3 , at 80°C. At the end of the polymerization reaction, the polymers are isolated in their phosphonate ester form (PEPS) by precipitation in water. As reported in Table I, high-molecular-weight polymers were obtained in such mild conditions. A typical SEC chromatogram and its polystyrene calibration curve are available in Supporting Information Figure S2. In addition, the absence of visible chain ends in the polymer proton NMR spectra (Figure 2) confirms the synthesis of high-molecular-weight macromolecules. This is due to the high reactivity of difluorodiphenylsulfone compared to the commonly used dichlorodiphenylsulfone that requires higher polymerization temperatures.

According to this procedure, the proportion of phosphonate ester groups incorporated in the polymer chains is controlled by the quantity of the phosphonate ester precursor involved in the polymerization reaction. In this way, a series of functionalized polysulfones was prepared by varying the degree of the phosphonate ester monomer (Table I). Their chemical structures were confirmed by ^1H NMR. Some typical spectra are reported in Figure 2.

The ratio of phosphonate ester monomer incorporated in the polymer chain (x) was determined by ^1H NMR using eq. (1) (see the Experimental section). As reported in Table I, the experimental values determined from this relation are in good agreement with the theoretical values based on the quantities of monomer used for the polymerization reactions. Moreover, less than 4% of hemiphosphonate ($\text{PO}(\text{OEt})(\text{OK})$ groups at 19 ppm) are formed with these polymerization conditions, as shown in ^{31}P NMR spectra (Figure 3).

The very small amount of hemiphosphonate group may be ascribed to a partial dealkylation due to the effect of K_2CO_3 during the polycondensation reaction.

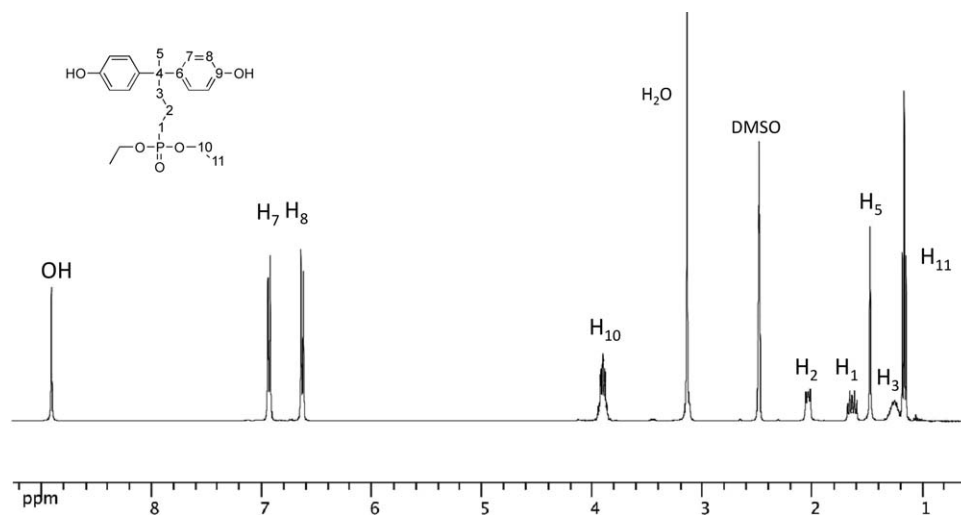
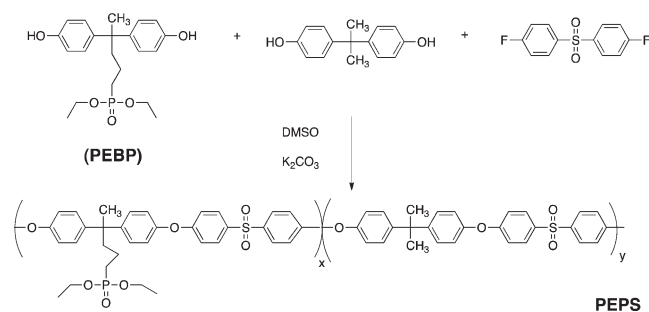


Figure 1. ^1H spectrum (DMSO- d_6 , 80°C) of PEBP.

The thermograms of these polymers (Supporting Information Figure S3) obtained by TGA analysis under air account for a good thermo-oxidative stability. Whatever the phosphonate ester content, a first weight loss (from 5.3 wt % to 12.3 wt %)

is observed between 250°C and 350°C. Such a thermal behavior has been already reported by different authors^{16,17} and is ascribed to a decomposition of the ethyl groups of the phosphonated ester into the free acid and ethylene, as well as a possible formation of anhydride groups from two phosphonic acids. The degradation of the polymer backbone (attributed to C–P bond cleavage) is observed at much higher temperatures (> 380°C). The PEPS polymers were found soluble in some aprotic solvents (DMSO, DMF, NMP). Tough and flexible thin films (around 40 microns thick) were elaborated from a 20 wt % solution in NMP, by a conventional solvent casting method.



Scheme 2. Synthesis of PEPS.

As mentioned in Table I, the glass transition temperature of the polymers decreases as the proportion of phosphonate ester alkyl groups grafted on the polymer chain increases. This behavior is typical of a plasticizing effect of the alkyl side chains. Such results have already been observed with polystyrene-co-vinylphosphonate¹⁸ and phosphonated polysulfones¹⁹.

Table I. Physicochemical Characterizations of PEPS

Entry	PEBP (mol %) theo	PEBP (mol %) exp ^a	PO(OEt) ₂ (mol %) ^b	PO(OEt)(OK) (mol %) ^b	$M_{n(\text{PS})}$ (g mol ⁻¹) ^c	$M_{w(\text{PS})}$ (g mol ⁻¹) ^c	PDI	T_g (°C) ^d	T_g (°C) ^e	$T_{5\% \text{ deg}}$ (°C) ^f
PEPS0	0	0	-	-	-	-	-	181	190	453
PEPS1	5	5	>99	<1	-	-	-	172	185	451
PEPS2	10	9	>99	<1	47,900	169,700	3.4	172	184	446
PEPS3	20	20	>99	<1	32,500	129,600	3.9	156	-	366
PEPS4	39	34	97.5	2.5	46,500	124,800	2.7	148	159	349
PEPS5	55	51	97	3	35,100	77,300	2.2	130	145	332
PEPS6	67	61	96.5	3.5	36,000	94,500	2.6	125	141	336
PEPS7	86	81	96.5	3.5	34,300	77,300	2.2	114	133	324
PEPS8	100	98	98.5	1.5	30,400	77,900	2.5	98	123	351

^aFrom ^1H NMR.

^bFrom ^{31}P NMR.

^cSEC calibrated with polystyrene standards, PDI: polydispersity index; -: undetermined.

^dDetermined by DSC.

^eDetermined by TMA.

^fTemperature of 5% weight loss, determined by TGA under air.

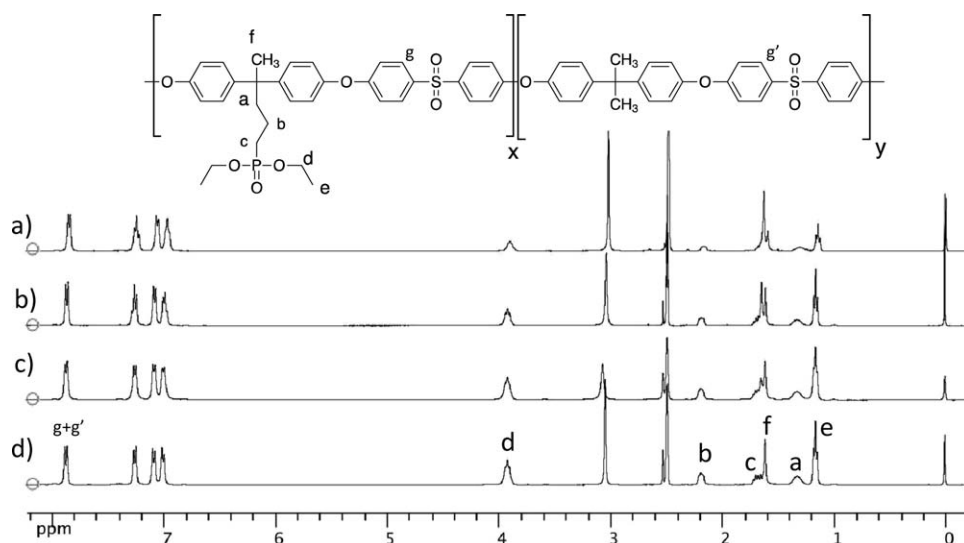


Figure 2. ^1H NMR spectra (DMSO- d_6 , 80°C) of (a) PEPS5, (b) PEPS6, (c) PEPS7, and (d) PEPS8.

The phosphonic acid-containing polymers (PAPS) are obtained after a subsequent acidic hydrolysis of the ethylphosphonate groups, either by refluxing the polymer in concentrated hydrochloric acid solution for 24 h or in the presence of iodo trimethylsilane (ISiMe₃) (Scheme 3).

Phosphonate ester-containing polymers were first refluxed in concentrated HCl (37%). The efficiency of this acidic hydrolysis was monitored by ^{31}P NMR. The ^{31}P NMR spectra of PEPS show a unique peak at 31.4 ppm, which is assigned to the phosphorus nucleus of diphosphonate ester groups (PO(OEt)₂). During the hydrolysis process, this peak progressively disappears, while two new peaks appear at 27.7 ppm and 26.4 ppm which were respectively assigned to the hemiphosphonic acid groups (PO(OEt)(OH)) and to the diphosphonic acid groups (PO(OH)₂). The dealkylation was quasi-complete after 24-h

reaction. As shown in Figure 4, ^1H NMR confirms also the disappearance of the ethyl groups in the aliphatic region. In addition, the experimental conditions of the hydrolysis do not induce any modification on the polymer chain as shown in the aromatic part of the spectrum.

When the hydrolysis was performed in the presence of ISiMe₃, small amount of hemiphosphonate groups was possibly present (Table II). This might be attributed to a polymer fraction partly precipitated in the reaction mixture.

Polymers containing high proportions of phosphonic acid groups are often reported to be fairly soluble in polar aprotic solvents,²⁰ and the addition of some mineral acid is usually used to help preventing the formation of strong ionic clusters. In contrast, the polymers synthesized in this work were readily

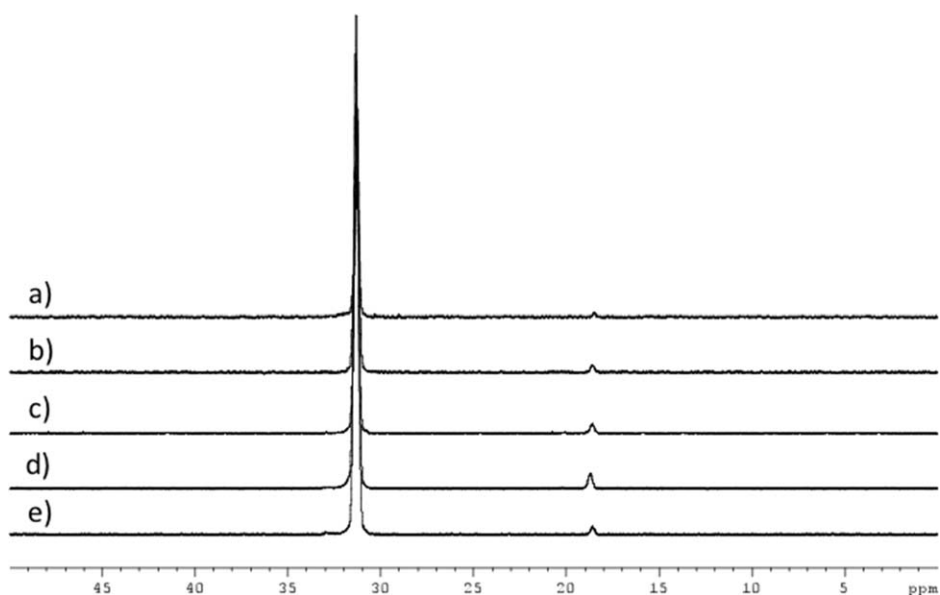
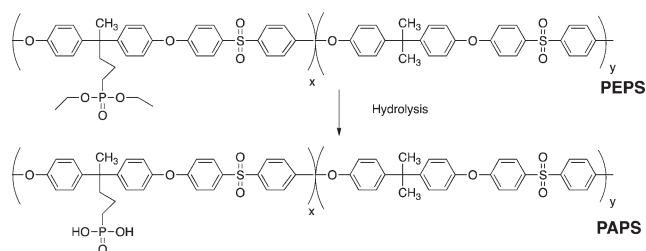


Figure 3. ^{31}P NMR spectra (DMSO- d_6 , 80°C) of (a) PEPS4, (b) PEPS5, (c) PEPS6, (d) PEPS7, (e) PEPS8.



Scheme 3. Acidic hydrolysis of PEPS.

soluble in NMP (20 wt %). However, this good solubility was not very helpful to prepare films from polymer solution casting method because the adhesion of films on the glass substrate was so strong, they cannot be peeled off. As a consequence, the polymers were routinely cast in their phosphonate ester form, and the dealkylation reaction was performed on the films. In this case, it is worth noting that the toughness of the films was not affected during the drastic dealkylation. All films obtained were opaque. This opacity is likely due to the formation of some porosity during the hydrolysis treatment.

The T_g of PAPS determined from DSC analyses are reported in Table II. The T_g values are rather high ($>200^\circ\text{C}$) and increase with the phosphonic acid-containing monomer units incorporated in polymer chains. These results are in agreement with those reported by Meng *et al.*²¹ These authors ascribe this effect to strong ionic interactions between the phosphonic acid functions. A similar interpretation was reported by Wu *et al.*,¹⁸ who suggest that "intermolecular hydrogen bonding and strong dipole associations act as physical cross-link and restrict the mobility of the polymer backbone." However, it is well accepted that upon heating at temperatures higher than 180°C , the condensation of phosphonic acid groups may result in the formation of anhydrides bridges which could also contribute to the

high T_g values. This means that the accurate T_g measurement of the free phosphonic acid-containing polymers above 200°C is impossible. This is confirmed when the T_g of polymers is determined after a third heat scan (Table II). In these particular cases, it is more reasonable to consider that T_g corresponds to a polymer partially crosslinked via phosphonic anhydride bond formation. All polymers are highly thermostable with a starting decomposition temperature above 350°C (Supporting Information Figure S4). Increasing amounts of functional monomer into the polymer chains slightly lowers the onset of degradation temperature as well as the temperature corresponding to 5% weight loss.

The water uptake of PAPS films was determined at room temperature and at 90°C . As reported in Table II, excepted for the polymer based on 100% of PEBP (PAPS8), it appears that the incorporation of phosphonic acid functions into the polysulfone backbone does not increase the water uptake drastically.

Evaluation of the Anticorrosive Properties of PAPS

The presence of chlorine ions is well known to induce localized corrosion. Therefore, the use of iodotrimethylsilane was preferred to synthesize PAPS. All these polymers were directly coated onto pre-polished mild steel samples from polymer solutions. After solvent evaporation, transparent thin films were obtained. Based on their transparency, it is reasonable to consider that these coatings do not present any macroscopic porosity. It is worth noting that these coatings have a very good adhesion to the metal and cannot be unstuck, unless by dissolution in a solvent.

Electrochemical measurements were performed in two different media to evaluate the anticorrosive properties of the polymer coatings in a fairly aggressive 0.25M Na_2SO_4 solution and in a much more corrosive 0.6M NaCl solution. Depending on the

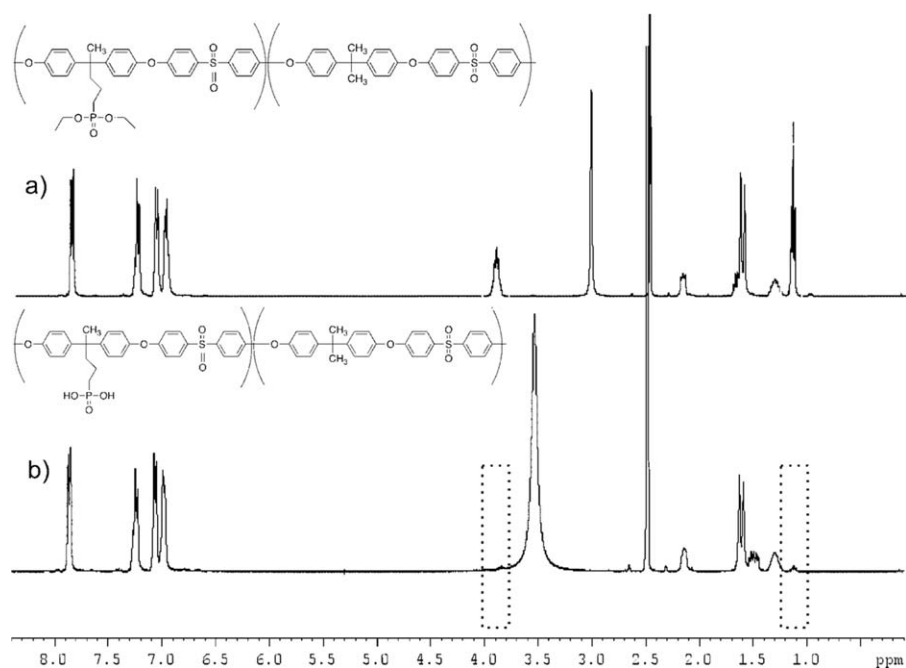


Figure 4. Typical ^1H NMR spectra ($\text{DMSO}-d_6$, 80°C) of (a) PEPS (b) PAPS.

Table II. Physicochemical Characterizations of PAPS

Entry	PEBP (mol %)	PO(OEt)(OH) (%) ^a	PO(OH) ₂ (%) ^a	T _g (°C) ^b	T _g (°C) ^c	W _{uptake} ^e (%)		
						T _{amb}	90°C	T _{5% deg} (°C)
PAPS1	5	-	100	183	178	<5	<5	437
PAPS2	10	-	100	178	183	<5	<5	433
PAPS3	20	-	100	-	194	<5	<5	432
PAPS4	39	9	91	204	222 ^d	5	5	437
PAPS5	55	7.6	92.3	219	220	10	6	427
PAPS6	67	6	94	221	241 ^d	8	6	394
PAPS7	86	4.8	95.2	239	>250	7	7	380
PAPS8	100	5.4	94.6	-	>250	28	44	378

^aDetermined by ³¹P NMR.^bDetermined by DSC.^cDetermined by TMA.^dAfter a third heat scan.^eWater uptake.

electrolyte solution, the corrosion appeared differently with the NaCl solution a pitting corrosion (with some additional cracks) was observed while a whole surface corrosion was identified with the Na₂SO₄ solution.

As shown in Figure 5, for all polymer coatings, the open circuit potential reaches quickly a constant value. Considering that no macroscopic pinholes were observed on the surface of the different polymer coatings, these results could be accounted by the presence of a nanoporosity.²² Indeed, in these conditions, the electrolyte could easily attain the substrate and bring about a whole surface corrosion. On the other hand, the fact that the OCP remains relatively stable during the experimental test periods suggests that no great modification of the substrate or degradation of the polymer coating occurred. Indeed, the OCP or corrosion potential of the steel increased from -800 mV to at least -400 mV when coated with PAPS. The proportion of phosphonic acid groups present on the polymer chains seems however to have a strong influence on the OCP value as shown

in Figure 6 (the OCP of samples coated with PAPS0, PAPS1, and PAPS2 are around -300 mV/ECS, whereas OCP of samples coated with PAPS5 and PAPS7 are around +200 mV/ECS. The highest corrosion potential was obtained with PAPS5 (+0.18 V/ECS) (Figure 5).

As to the polarization resistances measured by EIS and reported in Figure 7, the values are in good agreement with those determined from LPR measurements. As expected, the lowest polarization resistance (i.e., the higher corrosion rate) is observed for the sample without coating (5×10^{-4} MΩ). Conversely, the presence of polysulfone coatings significantly reduces the corrosion rate, at least by a factor of 1000. However, depending on the proportion of phosphonic acid groups present on the polymer backbone, some differences were observed. For the polymers containing up to 20% of phosphonic acid groups, the polarization resistance increases significantly (i.e. the corrosion rate decreases) until to reach a maximum value of 5500 MΩ. On the other hand, this resistance decreases (around 1 MΩ) with the coatings based on the polymers having more phosphonic acid groups (55% and 85%). These results suggest that the PAPS containing 20% of phosphonic acid groups offers, in the used test conditions, the better corrosion protection for the mild steel samples.

Considering the evolution of R_p versus the time of ageing, a similar trend is observed for all coatings. In the early part of the tests, R_p slightly decreases and then remains at a relative constant value. Such phenomenon has already been observed by Delimi *et al.*²³ on carbon steel-coated fluoropolymer thin films. As it is mentioned by these authors, one of the key factors for corrosion stability is the adhesion stability of metal/polymer interface which depends on the water present at the interface. So it seems reasonable to consider in our case that the effectiveness of PAPS polymers as corrosion protective layers is depending on the compromise between water uptake and adhesion properties which are related to the extent of phosphonic acid groups bounded on the polymer chains. In this connection, the PAPS with 20% of phosphonic acid groups offers this good compromise.

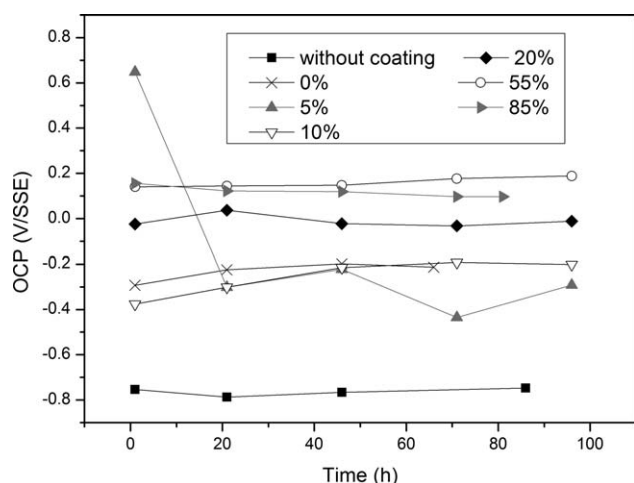


Figure 5. Open-circuit potential (OCP) as function of time for PAPS-coated mild steel samples, in 0.25M Na₂SO₄.

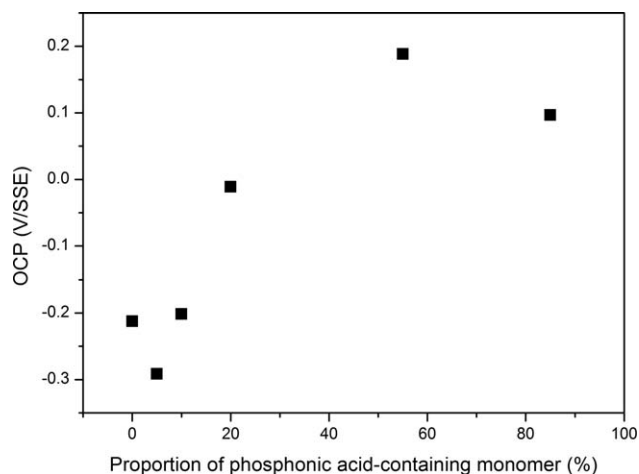


Figure 6. Corrosion potential at open circuit voltage (OCV), with the 0.25M Na₂SO₄ electrolyte for different phosphonic acid-containing polymers.

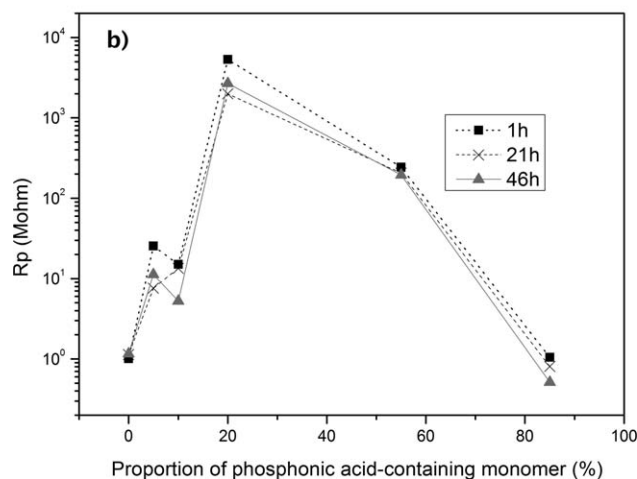
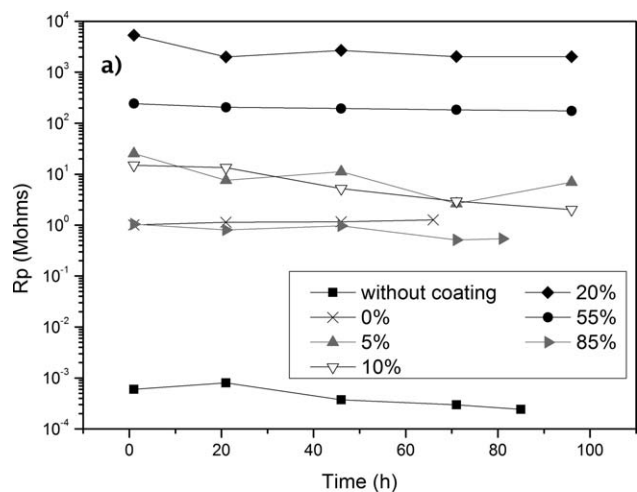


Figure 7. R_p of different phosphonic acid-containing coatings measured by EIS, in 0.25M Na₂SO₄. (a) The polarization resistance as a function of ageing time. (b) Variation of R_p as a function of the extent of phosphonic acid groups bonded along the PAPS chains.

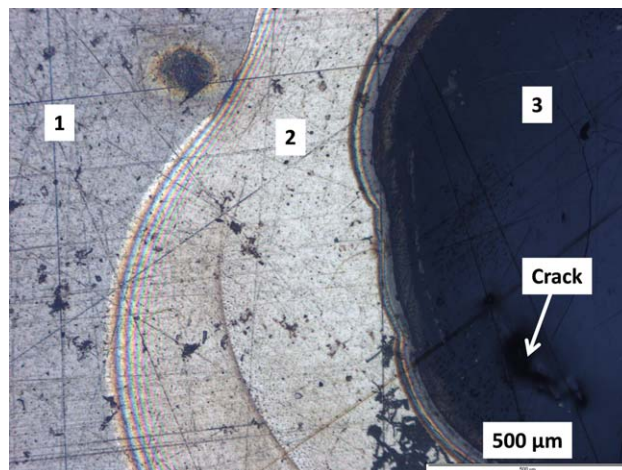


Figure 8. Picture of the surface coating based on PAPS3 after corrosion tests in 0.6M NaCl solution. (1) Coating zone with small corrosion spots; (2) unstuck coating around the pits; (3) pits with cracks. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Different results were obtained when performing the experiments in the presence of more corrosive NaCl solution. In this case, corrosion comes along with the appearance of pits (Figure 8).

Even though pitting corrosion is unpredictable, a general trend of the R_p evolution was determined by liner polarization resistance (LPR) measurements. As illustrated in Figure 9, the polarization resistance profiles are different from those observed with the Na₂SO₄ electrolyte.

The PAPS with 10% of phosphonic acid groups clearly appears to be the best protective coating. Its initial polarization resistance is closed to 1600 MΩ, whereas the R_p of the other polymers are lower than 700 MΩ. However, in all cases, a sharp drop of the initial R_p is measured in the first 10 h. One plausible explanation is the apparition of pits that could induce some cracks in the coating and therefore favor the metal corrosion as illustrated in Figure 8. Based on the results reported here, it is

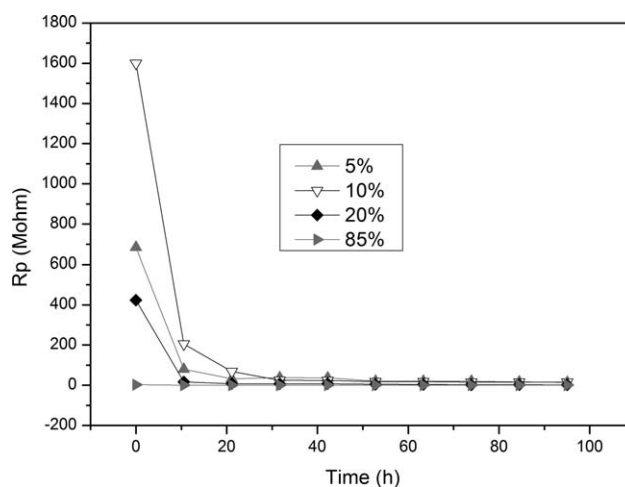


Figure 9. R_p evolution versus time measured by LPR in 0.6M NaCl solution.

clear that no structure properties relationship can be established. However, one can consider that the diffusion of the electrolytes used in this work through the PAPS coatings are different and consequently lead to different corrosion processes. On the other hand, it could be hazardous to compare our results to those reported in literature because the systems are quite different (test conditions, nature of the electrolyte). Having said that, the R_p values are relatively high compared to those generally mentioned in literature and obtained with experimental conditions less aggressive than those we used.^{14,22,24}

CONCLUSIONS

New phosphonate ester and phosphonic acid-containing polysulfones were successfully synthesized with high molecular weights. All the polymers have a good thermal stability, show 5% weight loss up to 380°C and form tough thin films with a strong adhesion on mild steel substrate. Tested in two different electrolytes, PAPS show interesting anti-corrosion properties. Among the different polymer coatings tested, the one based on the 20% phosphonic acid-containing polysulfone appears as the most promising candidate.

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