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Novel Protective Coatings for Steel Based on a Combination of Self-Assembled Monolayers and Conducting Polymers

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Summary : Investigations for a new primer system for iron or low alloyed steel have led to first results. Several special phosphonic acids with thiophene derivatives as head groups have been synthesized. They form stable self-assembled monolayers (SAMs) on passivated iron by dipping the substrates into aqueous phosphonic acid solutions. SAM formation was validated by current potential curves and also by contact angle measurements, which showed an intensive hydrophobisation of the iron surface after the dipping process. Finally cyclovoltammetric (CV) experiments after SAM formation indicated the successful polymerisation of the immobilised thiophene derivatives.

Introduction

Several corrosion protection layers with conducting polymers for steel and other metals have been developed during the last few years.[1-3] Barrier or inhibitor effects, anodic protection or the mediation of oxygen reduction are proposed mechanisms for the anticorrosive effects observed with conducting polymers. [1]

Self-assembled monolayers (SAMs) heve been well known for more than a decade. Examples are thiols or other sulfur compounds on gold or silver which could become important for many potential applications, e.g. surface hydrophobisation, chemical or biological sensoring and catalytical or optical devices. SAMs of phosphonic acids or phosphonates on passivated iron (also on Ti / TiO_2 or Al / Al_2O_3) have also been investigated in detail in the last years. [4-7] These investigations have shown that the phosphonic acid group is one of the best anchor groups for building stable SAMs on passivated iron. This was the starting point for the development of a new primer system for iron or low alloyed steel, which basically consists in SAM formation of special phosphonic acids on iron followed by polymerisation of the head groups to polythiophene chains. The new primer system promises to combine anticorrosive

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effects (for example anodic corrosion protection) with improved adhesiveness for several top coats. After first investigations the practical application of the primer system appears to be feasible because the required SAM formation on passivated iron and later electropolymerisation of the head groups was achieved. Clearly, further investigations will have to be made before this process will be of industrial interest. Fig. 1 shows the procedure for the planned primer system.

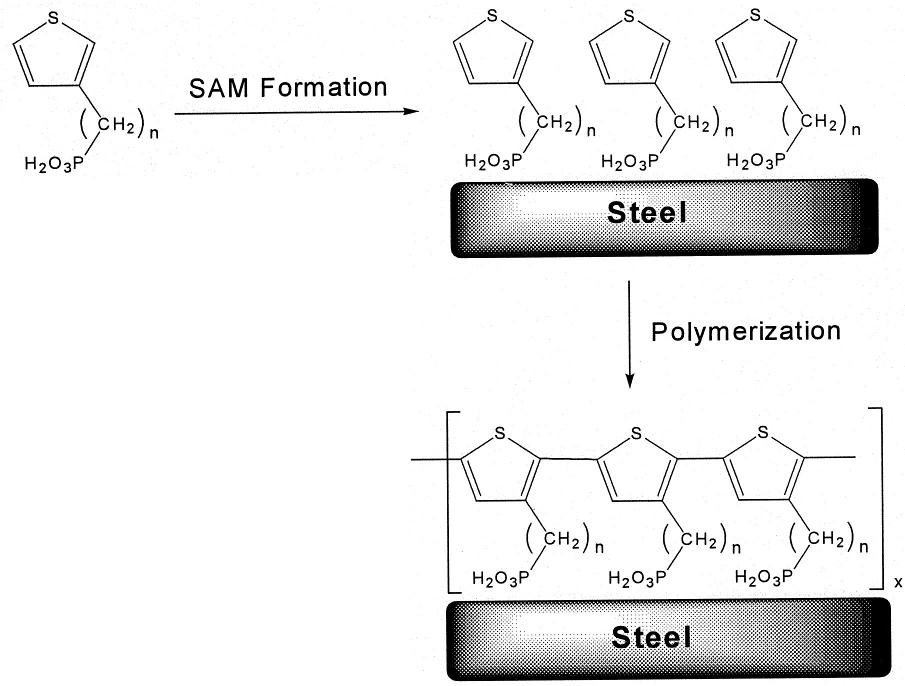
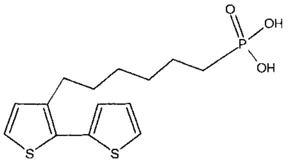


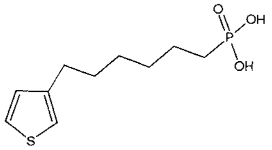
Figure 1 . Scheme of the procedure for the new primer system.

Synthesis of the phosphonic acids required

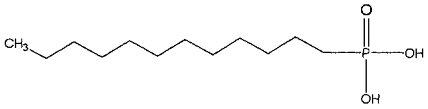
An overview of the structures of the synthesised phosphonic acids is given in Fig. 2.



Bithienylhexanephosphonic acid (BTHPA) 7



Thienylhexanephosphonic acid (THPA) 6



Dodecylphosphonic acid (DPA) 5

Figure 2. Overview of synthesized phosphonic acids used to date.

Synthesis of 6-(3-Thienyl)hexyl bromide 3 (the precursor of THPA 6) was carried out by a method published by Bäuerle et. al. [8] . The reaction sequence is quite similar to the one of the corresponding 6-(3-Bithienyl)hexyl bromide 4 , which is shown below.

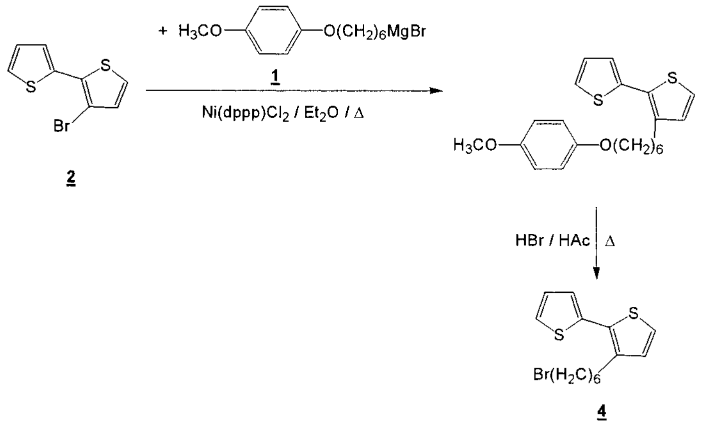


Figure 3. Synthetic route for preparing 6-(3-Bithienyl)hexyl bromide 4 .

3-bromo-2,2'-bithiophene 2 was prepared by a coupling reaction with 2-thienylmagnesiumbromide and 2,3-dibromothiophene according to literature descriptions.[9-10] Dodecylphosphonic acid (DPA) 5 was synthesized from 1-bromododecane and triethylphosphite by a standard procedure of the Arbuzov reaction. [11-12]

Thienylhexanephosphonic acid (THPA) 6 and Bithienylhexanephosphonic acid (BTHPA) 7 were prepared from the corresponding hexyl bromides 3 and 4 by a special variant of the Arbuzov reaction.[4+11] Instead of triethyl phosphite this method uses tris-trimethylsilyl phosphite as the agent, which allows more moderate reaction conditions.

p-Methoxyphenoxyhexylbromide 1

Into a 500 ml round bottom flask was placed 200 ml [1.30 mol] 1,6-dibromohexane (Merck) in 150 ml methanol. At 80^0 C under N_2 and with stirring was added dropwise a solution (over 1 h), which was prepared from 40.0 g [0.322 mol] p-methoxyphenol and 17.74 g [0.320 mol] KOH in 100 ml methanol. The reaction mixture was further stirred for 2 h at this temperature before it was allowed to reach room temperature. After removal of the methanol by evaporation, the resulting liquid was decanted from solid impurities and 100 ml chloroform and 200 ml cooled 5 % KOH was added to the oily liquid before extracting. The organic layer was washed with 200 ml 1 % $NaHCO_3$ solution and dried over sodium sulfate. After filtering through a 2 cm Na_2SO_4 layer, the chloroform and later the dibromhexane was removed by vacuum distillation. Recrystallisation of the residue from 400 ml 99 % methanol yielded 59.4 g [64.9 %] 1 as colourless crystals of melting point (mp) 52 - 54^0 C.

MS (relative intensity) : m/z = 286 (55 %) $[M^+]$ and m/z = 288 (57 %) $[M^+]$;
m/z = 124 (100 %) $[C_7H_8O_2]^+$

3-Bromo-2,2'-bithiophene 2

A Grignard solution of 9.8 ml [102.8 mmol] 2-bromothiophene and 4.0 g [164.5 mmol] Mg in 150 ml ether was prepared (finally refluxing for 45 minutes unter N_2). This Grignard solution was added dropwise under N_2 (over 1 h) to a stirred and cooled (about -5^0 C) suspension of 640 mg [0.78 mmol] $Pd(dppf)Cl_2$ / CH_2Cl_2 –Komplex (Aldrich) { dppf = 1,1'-Bis-diphenylphosphino-ferrocene }, 10.0 ml [88.2 mmol] 2,3-dibromothiophene (from Lancaster synthesis) and 100 ml dry diethyl ether. After stirring at 0^{0} C for 3 h, 10 ml methanol was added (to end the reaction) and the mixture was filtered through a 3 cm Na_2SO_4 / silicagel double layer. After further eluating the layer with 30 ml dry diethyl etherthe solvent of the combined solutions was rotary evaporated. The residual oily liquid was purified by silica gel chromatography with hexane / CCl_4 (98:2) as the solvent to yield 19.0 g [87.9 %] 2 as slightly green oil.

Thin layer chromatography (DC) on silica gel 60 plates (Machery & Nagel) with hexane showed a pure product with a retention factor $R_f = 0.33$.

^{1}H-NMR [$CDCl_3$; 250 MHz] : δ_1 = [6.99 ppm ; d ; ^{3}J=6.2 Hz ; H-4 or H-5]

δ_2 = [7.05 ppm ; dd ; all ^{3}J=6.2 Hz ; H-4']; δ_3 = [7.15 ppm ; d ; ^{3}J=6.2 Hz ; H-4 or H-5]

δ_4 = [7.32 ppm ; dd ; ^{3}J=6.2 Hz and ^{4}J=1.25 Hz; H-5'/3']; δ_5 = [7.40 ppm ; dd ; ^{3}J=6.2 Hz and ^{4}J=1.25 Hz; H-3'/5']

6-(3-Bithienyl)hexylbromide 4

A solution of 4.30 g [0.015 mol] methoxyphenoxyhexyl bromide 1 in 40 ml dry diethyl ether was added slowly over 1 h under N_2 and with stirring to 0.52 g [0.021 mol] Mg (iodine etched) at 40^{0} C and the mixture was refluxed for 5 h before it was allowed to reach room temperature. The Grignard solution was slowly transferred (over 1 h) via a double needle to an ice cooled suspension of 2.50 g [0.010 mol] 3-bromothiophene (Merck) and 50 mg [0.092 mmol] Ni(dppp)Cl_2 {dppp = 1.3-bis(diphenylphosphino)propane } (Aldrich) . After slowly coming to room temperature, the reaction mixture was refluxed for 20 h under N_2 . After an addition of ice, 200 ml 1M HCl and 50 ml diethyl ether, the mixture was extracted and the organic phase was washed with 1 % NaCl solution and with $NaHCO_3$ solution. Drying over Na_2SO_4 , filtration through a 2 cm Na_2SO_4 / silica gel double layer and cold evaporation of the solvent led to a partly cristalline colourless product of the 3-methoxyphenoxyhexyl-bithiophene as intermediate, which seemed to be almost pure in thin layer chromatography on silica gel with CH_2Cl_2 as solvent ($R_f = 0.64$).

Without further purification, a solution, which was obtained by slowly mixing 13.6 ml [0.12 mol] 47 % HBr and 18.7 ml [0.20 mol] acetic anhydride (cooling necessary !) was added. The reaction mixture was stirred at 100^{0} C for 20 h under N_2. Then 100 ml ice water, 200 ml 5 %

NaCl solution was added and after two-fold extraction with 100 ml diethyl ether, the combined organic phases were washed twice with 1 % NaCl solution and with 1% $NaHCO_3$ solution. After drying over Na_2SO_4 , hexane was added until hydrochinone precipitated. This suspension was filtered through a 2 cm Na_2SO_4 / silica gel double layer and the diethyl etherwas cold rotary evaporated. The residue was immediately purified by silica gel chromatography with cyclohexane to yield 1.80 g [5.47 mmol] (83 %) Bithienylhexyl bromide 4 as slightly yellow oil.

Thin layer chromatography on silica gel with cyclohexane indicated a pure compound with $R_f = 0.18$.

MS : ***m/z = 328*** (100 %) [M^+] and ***m/z = 330*** (92 %) [M^+] .

^{1}H-NMR [250 MHz ; $CDCl_3$] : δ_1 = 1.42 ppm [m ; 4H ; H-4''/5''] ; δ_2 = 1.68 ppm [m ; 2H ; H-3'']; δ_3 = 1.82 ppm [m ; 2 H ; H-2'']; δ_4 = 2.75 ppm [t ; ^{3}J=7.6 Hz ; 2H ; H-1'']; δ_5 = 3.37 ppm [t ; ^{3}J=6.9 Hz ; 2H ; H-6'']; δ_6 = 6.92 ppm [d ; ^{3}J=5.1 Hz ; 1H ; H-4]; δ_7 = 7.08 ppm [m ; 4H ; H-3'/4']; δ_8 = 7.17 ppm [d ; ^{3}J=5.2 Hz ; 1H ; H-5]; δ_9 = 7.29 ppm [dd ; ^{3}J=5.0 Hz ; ^{4}J=1.3 Hz; 1H ; H-5']

6-(3-Bithienyl)hexanephosphonic acid (BTHPA) 7

A mixture of 2.01 g [6.11 mmol] Bithienylhexyl bromide 4 and 2.09 g [7.00 mmol] tris-trimethylsilylphosphite (Aldrich) was heated under argon (after removal of oxygen by using an ultrasonic bath) at 150^0 C for 4 h. Later 10 ml 80 % methanol were added at room temperature and the mixture was stirred for 15 h.

After the addition of 100 ml 1 M NaOH it was extracted twice with 50 ml tert. butylmethyl ether and the aquous layer was then acidified by adding 200 ml 5 M H_2SO_4. After twice extraction of this aquous solution with a mixture of 50 ml tert. butylmethylether / pentane (3 : 1) the combined organic phases were dried over Na_2SO_4 and this solution was filtered through a 2 cm Na_2SO_4 layer. Rotary evaporation of the solvents yielded 1.82 g [90.2 %] BTHPA 7 as a colourless highly viscous oil.

MS : m/z = 330.2 (100 %) [M^+].

^{1}H-NMR [250 MHz ; $CDCl_3$] : δ_1 = 1.35 ppm [m ; 4H ; H-4''/5''] ; δ_2 = 1.65 ppm [m ; 6H ;

H-2''/3''/6'']; δ_3 = 2.72 ppm [t ; ^3J=7.9 Hz ; 2H ; H-1''] ; δ_4 = 6.89 ppm [d ; ^3J=5.2 Hz ; 1H ; H-4]; δ_5 = 7.05 ppm [m ; 2H ; H-3'/4'] ; δ_6 = 7.13 ppm [d ; ^3J=5.2 Hz ; 1H ; H-5]; δ_7 = 7.27 ppm [dd ; ^3J=5.0 Hz ; ^4J=1.3 Hz; 1H ; H-5']; δ_8 = 9.70 ppm [s (breit) ; 2H ; $-PO_3H_2$]

Dodecylphosphonic acid (DPA) 5

A mixture of 23.9 ml [0.10 mol] 1- bromododecane (Merck) and 18.9 ml [0.11 mol] triethyl phosphite (Aldrich) was heated (after removal of oxygen in an ultrasonic bath) under argon for 4 h at 160-190^0 C with continuous removal of the ethylbromide formed.

Now 100 ml 40 % HBr was added at room temperature and the mixture was refluxed under stirring for 3h (oil bath temperature about 140^0 C) with evaporation the hydrobromic acid at the end. On reaching room temperature a colourless solid was obtained, which was washed with pentane, recrystallised from hexane and from 0.1 M H_2SO_4 . Now 300 ml 0.1 M H_2SO_4 and 250 ml diethyl ether were added and after extraction the organic phase was dried over Na_2SO_4 .

Rotary evaporation of the solvent and new recrystallisation from hexane yielded 14.45 g [57.7 %] dodecylphosphonic acid 5 as colourless plates of a melting point (mp) 98-99^0 C .

Lit. [13] **:** mp = 100.5-101.5^0 C (from hexane).

SAM formation of the phosphonic acids on iron

The first step in the formation of self-assembled monolayers (SAMs) of the new primer system with phosphonic acids is the passivation of the iron surface. Different methods of iron passivation have been described in the literature.[4-7] After several attempts with different passivation methods, a treatment with 10% HNO_3 (4 minutes at 25^0 C) [2] after grinding (paper with grain size 600) and degreasing with ethanol proved to be most effective.

SAM formation on the passivated iron was investigated after dipping the disc electrodes (armco iron) for 15 h in a 10^{-3} M aqueous solution of the sodium salts (1 : 1 - mixture of mono- and disodium salt) of the different phosphonic acids (pH 7.8 – 8.5). Before starting the electrochemical and contact angle measurements, the treated samples were stored dust-free in dry atmosphere to allow an optimal SAM orientation.

The anodic polarisation curves of the treated samples showed a significant decrease in current densities compared with those of untreated passivated iron (see Table 1). Contact angle measurements also impressively indicated the sucessful SAM formation of the phosphonic acids. The dipping process converts the hydrophilic surface of the passivated iron into a strong hydrophobic surface (see Table 1).

Table 1 shows the anodic current densities of the passivated iron disc electrodes (A = 0.35 cm^2) at 800 mV vs. Ag/AgCl in aerated 0.1 M $NaClO_4$ at a rotation rate of 1000 rpm before and after treatment with **DPA 5** and **BTHPA 7** solution.

Additionally the contact angles with water were specified. The values noted were the median of 4 - 8 measurements.

Table 1. Effect of phosphonic acid treatment of passivated iron, observed with the anodic current density and contact angle values.

	Passivated iron (untreated)	**Passivated iron with DPA 5 treatment**	Passivated iron with **BTHPA 7** treatment
Anodic Current density at +800 mV vs. Ag/AgCl	**6,14 µA / cm^2**	**2,56 µA / cm^2**	**0,37 µA / cm^2**
Contact angle (water)	**$18.5^0 \pm 4^0$**	**148.5^0 ($\pm 3^0$)**	**121.2^0 ($\pm 2^0$)**

For comparison, the contact angle of unpassivated armco iron (after grinding and degreasing with ethanol as described) was **51.4^0 ($\pm 4^0$).**

Electropolymerisation of immobilised bithiophene head groups on iron

Willicut & McCarley [14-15] described the electropolymerisation of pyrrol head groups after immobilisation of N-pyrrolyl-alkanethiols on a gold surface in propylene carbonate.

Now similar cyclovoltammetric experiments were carried out to electropolymerise the bithiophene head groups after SAM formation on passivated iron with **BTHPA 7** solution.

Anodic switching with potentials below 1.3 V (vs. Ag/AgCl) did not show any signs of electropolymerisation (see Fig. 4). After several further CV cycles with an increased switching potential of 1.4 V, where oxidation peaks appeared, reversable oxidation and reduction peaks could now be observed (see Fig. 5). They are characteristic for the formation of conducting polymers, e.g. polybithiophene.

Analogous experiments (anodic polarisations in CV cycles up to 1.7 V vs. Ag/AgCl) with thiophene head groups (iron samples, treated with **THPA** 6) gave no indication of a polymerisation process. This can be explained by the higher oxidation potential of thiophene (head group) compared to bithiophene.

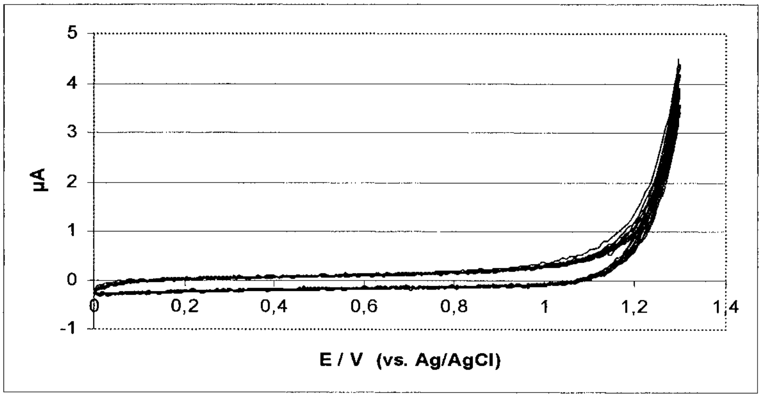


Figure 4. Cyclovoltammogramm of HNO_3 passivated armco iron after BTHPA 7 treatment in propylene carbonate / 0.1 M NBu_4ClO_4 (50 mV s^{-1} ; 1000 rpm rotation). CV cycles 1 – 5 with low maximum potential of 1.3 V .

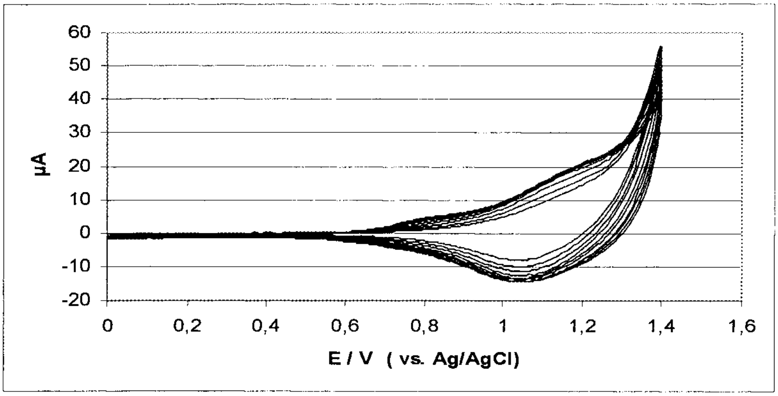


Figure 5. The electrode and system used above (Fig. 4) after 10 further CV cycles with a maximum potential of 1.4 V. The CV cycles 15 - 24 are shown with the increased maximum potential of 1.4 V vs. Ag/AgCl (50 mV s^{-1} ; 1000 rpm).

Discussion

Experimental results of both SAM formation of special phosphonic acids on passivated iron and of experiments to electropolymerise the bithiophene head groups of corresponding monolayers show that the new primer system planned (see Fig. 1) is feasible. Evidently, many further investigations are necessary before this new procedure will be of industrial interest. Furthermore direct structural information of the SAM's before and after polymerisation will be acquired by special surface analytical techniques, suchas AFM or XPS investigations.

The influence of other iron passivation methods with less surface roughness and more durable passivation layer on SAM formation and subsequent electropolymerisation will be studied in further experiments. Further phosphonic acids with bithiophene or other probably polymerisable head groups are also in development.

References

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