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Investigation of the electroactivity of polymethylthiophene film for the corrosion protection of mild steel

Abstract The protection mechanism of intrinsically conducting polymers (ICPs) is still under discussion. Most of the discussions concentrate on the effect of the redox behavior and electroactivity of ICPs on the corrosion protection. In the present paper it is shown that polymethylthiophene (PMT) films electropolymerized on mild steel, with 2-(3-thienyl)ethylphosphonic acid used as adhesion promoter, show the desired redox activity. The interaction between the PMT film and some conventional coatings, and the influence of the pH of electrolyte, were investigated. It was shown that the electroactivity of PMT film is lost by the interaction with coatings of high nucleophilicity and is markedly decreased by immersion in an aqueous solution of pH 11.

Keywords Corrosion protection · Electroactivity · Electropolymerization · Mild steel · Polymethylthiophene

Introduction

In the last decade, the corrosion protection of intrinsically conducting polymers (ICPs) has been intensively investigated [1, 2, 3, 4, 5, 6, 7]. Some recent results in the field of corrosion protection of mild steel with ICPs have been summarized [8, 9]. It was pointed out that the most discussed aspect of the protection by ICPs like polyaniline (PANi) or polypyrrole (PPy) is due to an anodic protection that reduces significantly the corrosion rate of steel. The mechanism of anodic protection was proposed

based on the shift of potential of the steel substrate to a value where the steel is in its passive state. It is assumed that the ICP is able to mediate the anodic current between the passivated steel surface and the oxygen reduction taking place on the ICP film [10, 11]. Therefore the galvanic coupling between ICP and steel is connected with the oxidized conductive form of ICP. During the coupling the ICP is reduced and its galvanic activity is lost, if the ICP cannot be reoxidized by oxygen reduction. Investigations by Kinlen et al. [10] have shown that the metal surface can also be protected when artificial pinholes were made down to bare steel. By using a scanning reference electrode technique, localized anodes in pinholes and delocalized cathodic regions over the PANi coating were observed. The galvanic activity was decreased after several days of immersion. This can be due to the passivation of the pinhole [9] or to the reduction of the ICP.

The galvanic activity strongly depends on the nature of the environment, the ratio of anodic and cathodic areas and the redox activity of the ICP. Especially the pH of an aqueous electrolyte near a corroding metal can be very high due to oxygen reduction to form hydroxide. If electroactive ICPs should provide corrosion protection, then their redox activity must be maintained at high pH values.

The redox activity of ICPs can also be influenced by the topcoat. In the present paper, we have investigated the interaction of several topcoats with ICPs and the influence of pH on the conductivity of ICPs. In the first case, PMT was deposited onto mild steel and then overcoated with some conventional clear topcoats. The influence of the pH was investigated by the conductivity of PMT and PPy films electrogenerated on a platinum electrode.

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Experimental

The mild steel St38 was polished with 600 grit paper and then etched in 2% H_2SO_4 and 30% H_2O_2. After drying, the PMT film was grown on the steel surface at room temperature. The first step was the chemical pretreatment with 10^{-3} M 2-(3-thienyl)ethylphosphonic

acid used as adhesion promoter. The following step was the electrochemical deposition of the polymer film. The PMT film was polymerized galvanostatically on the pretreated steel surface with a current density of 2.5 mA/cm² in 0.1 M methylthiophene in dichloromethane. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (NBu$_4$PF$_6$). The film thickness was about 1 μm. The synthetic details and the characterization of the adhesion promoter have been described elsewhere [12].

The PMT film on the mild steel substrate was topcoated with conventional clear coats with a thickness of about 20 μm, in order to observe directly the change of color connected with the reduction or the possible deactivation of the PMT film.

PMT and PPy films were prepared on a platinum electrode by electrochemical oxidation of methylthiophene (0.1 M) in dichloromethane containing 0.1 M NBu$_4$PF$_6$, and of pyrrole (0.1 M) in aqueous 0.1 M KNO$_3$, respectively, at a current density of 1 mA/cm² for 200 s.

The conductivity of PMT films on mild steel was measured by electrochemical impedance spectroscopy (EIS) at different potentials, using the IM5d impedance system of Zahner-Elektrik. A saturated (LiCl/EtOH) Ag/AgCl ($E = + 140$ mV vs. NHE) electrode was used as reference electrode for measurements in dichloromethane + 0.1 M NBu$_4$PF$_6$, free of monomer.

The conductivity of the PMT and PPy films on the Pt electrode was measured by EIS in aqueous 0.1 M LiClO$_4$ at different pH values. The saturated calomel electrode was used as reference electrode. The frequency range analyzed was 100 kHz to 0.1 Hz.

Results and discussion

Redox activity of PMT film on mild steel in an organic electrolyte

To obtain a better insight into the redox activity of PMT film formed on steel, the electrochemical behavior of the polymer film was measured in dichloromethane, which is considered as an acidic solvent (donor number DN = 4). Electroactive films were obtained in dichloromethane with 0.1 M NBu$_4$PF$_6$. The PMT film can be reduced and then reoxidized reversibly on mild steel, as shown by the cyclic voltammogram in Fig. 1. The cyclic voltammogram of PMT on mild steel has the same shape as observed with PMT on Pt [13].
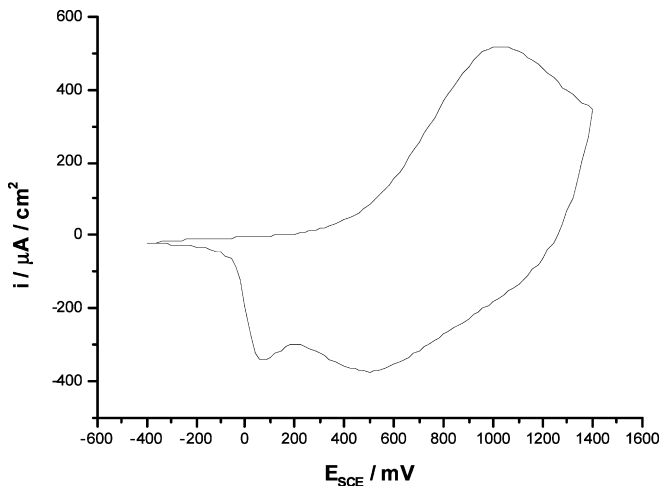
The electroactivity of PMT films on mild steel was also demonstrated by EIS measurements. The EIS was employed to determine the resistance and capacitance of PMT as a function of the applied potential. The impedance data were obtained at potentials between 1 V to −0.3 V. All measurements began at the open circuit potential $U_{OC} = 0.4$ V and films were allowed to equilibrate for 15 min at each potential before being measured. Figure 2 shows the impedance plots for a PMT film electrode in organic solution.

The experimental data can be described using the equivalent circuit shown in Fig. 3b. The Bode plot can be divided into three frequency sections, which are typical for the partial processes at the electrode (Fig. 3a). The high-frequency range (section I) of the system (Fig. 3a) is determined by the electrolyte resistance R_E and an artificial capacitance C_X, which is caused by the cell design. The medium-frequency range (section II) is determined by the resistance of the polymer film R_{PM}, which is a measure of the conductivity of the polymer and the polymer capacitance C_{PM}. Resistance R_{PM} and capacitance C_{PM} are related to the redox process of the polymer film. The low-frequency range (section III) can be attributed to the electrochemical reaction taking place at the steel/PMT interface.
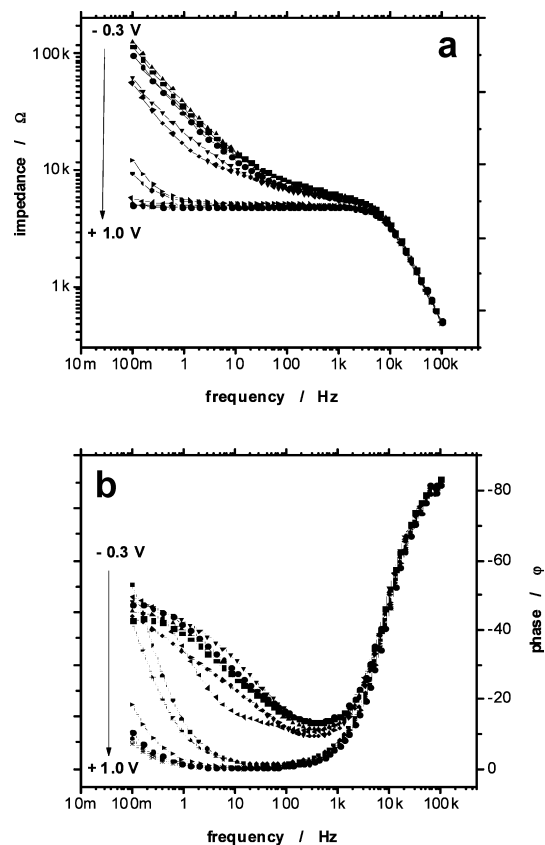

Fig. 1 Cyclic voltammogram of PMT on mild steel in 0.1 M NBu$_4$PF$_6$ in dichloromethane. Scan rate 10 mV/s

Fig. 2a, b Bode plots of a PMT film on steel in an organic electrolyte at different potentials. a Modulus of impedance; b phase angle

Fig. 3a Bode plot of a PMT film on steel at −200 mV. Measured data: *circles*, modulus of impedance; *triangles*, phase angle. Fitted data: *solid* and *dotted lines*. **b** Equivalent circuit: R_E, electrolyte resistance; C_X, artificial capacitance; R_{PM}, polymer resistance; C_{PM}, polymer capacitance; Z, impedance attributed to an electrochemical reaction taking place at the steel/polymer interface
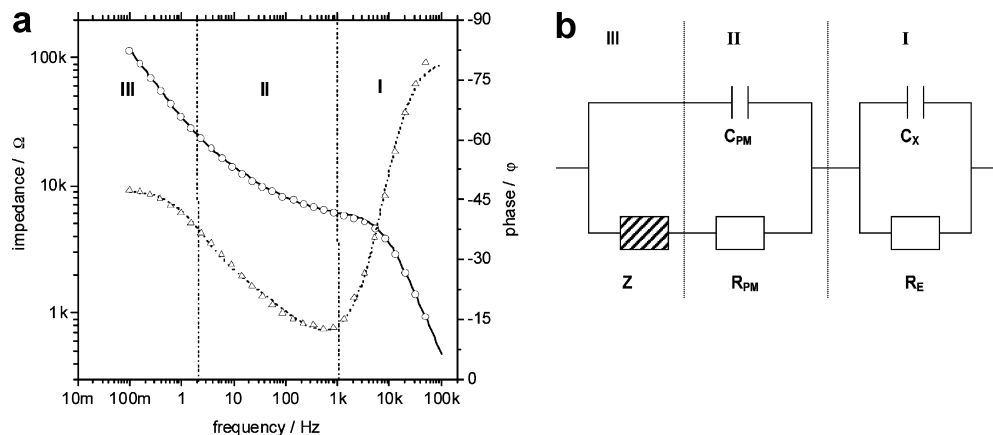
With this simple equivalent circuit the data can be fitted very well. The Bode plot shows the experimental (points) and the fitted data (lines), measured at −0.2 V. The EIS measurements reflect the reversible redox behavior of PMT on steel in organic media.

As can be seen in Fig. 4a, the polymer resistance increases from about 10 Ω to 100 kΩ during the reduction. After scanning back of the potential, the
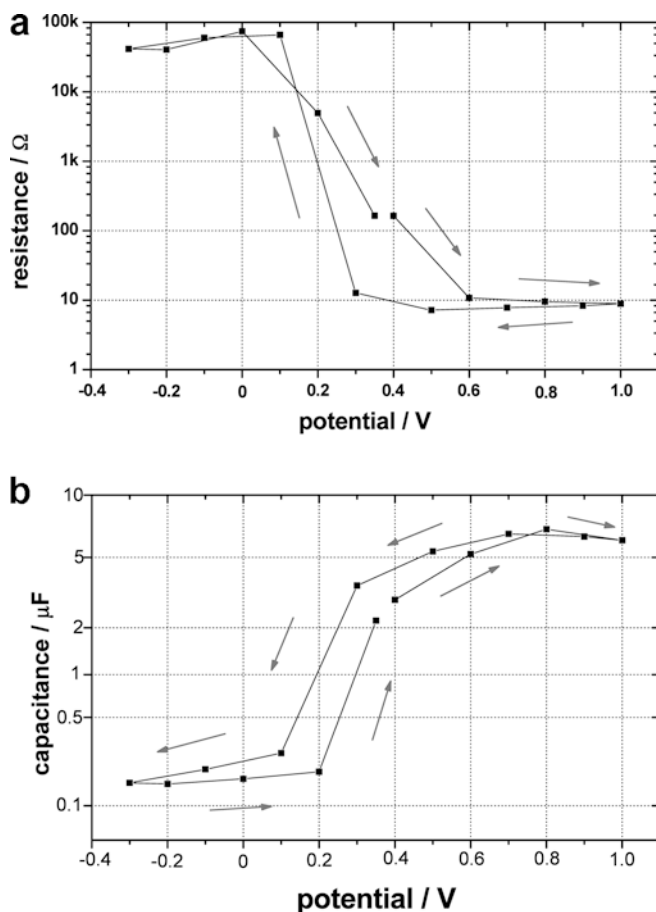

Fig. 4 Resistance (**a**) and capacitance (**b**) of PMT film on steel versus potential, in dichloromethane + 0.1 M NBu$_4$PF$_6$; monomer free

resistance decreases again and reaches the same value at the open circuit potential as measured at the beginning.

The potential dependence of the polymer capacitance also shows reversible behavior (Fig. 4b). The capacitance decreases at potentials more negative than the open circuit potential and corresponds to a space charge capacitance in the potential range from 0.2 V to −0.3 V [14]. In this potential range the polymer is in the reduced semiconducting state.
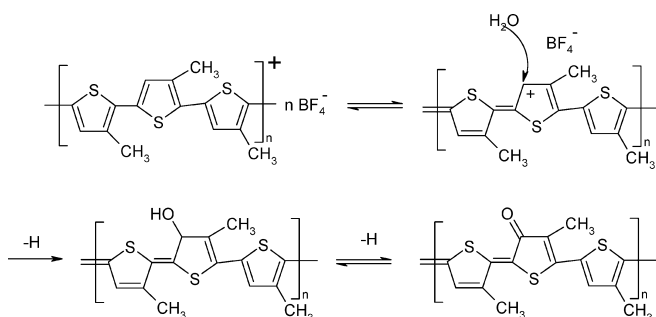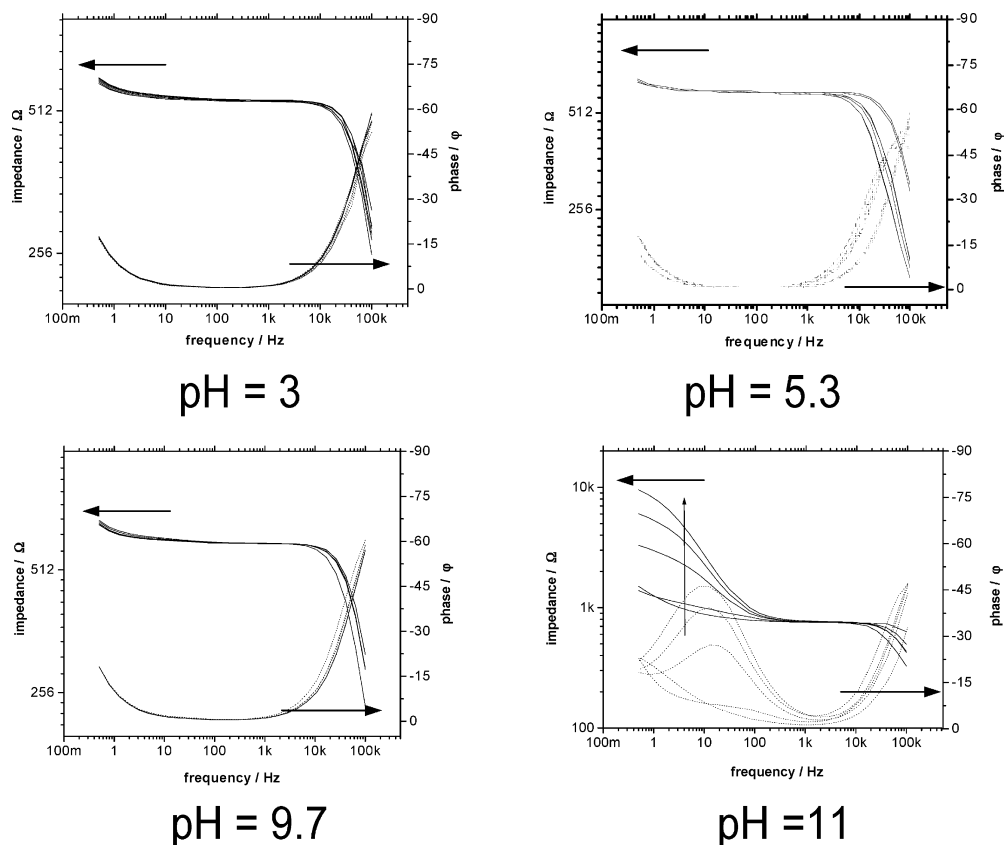
The influence of topcoat on the conductivity of a PMT film on mild steel

The thin PMT film itself cannot completely protect mild steel from corrosion, because the corrosion potential of PMT-coated steel is only 150 mV more positive than the potential of blank steel and still in the active range of iron dissolution [15]. Therefore, it is necessary to add a topcoat. We have investigated the compatibility between PMT film and topcoat. PMT films were overcoated with some conventional clear coating systems and the state of the PMT was assessed by the color of the film. An oxidized PMT film has a blue color, changing to red if the PMT is reduced.

As can be seen in Table 1, the electroactivity of the PMT film was lost by coating with many topcoats. It was only with a polyurethane-containing acidic hardener that the blue color of the PMT film on mild steel did not change. It was assumed that the electroactivity of the PMT film was lost by interaction with a topcoat containing nucleophilic groups like hydroxyl, amine, polyols and others. Investigations by Wang [16, 17] have shown that solvents have a great influence on the electroactivity and stability of ICPs. The polymers deactivate quickly in a solvent with strong nucleophilicity like acetonitrile and are more stable in nitromethane or propylene carbonate with weak nucleophilicity. The nucleophilicity of water depends on the pH value of the solution. Therefore, the waterborne coating at pH 11 deactivates PMT in a short time. A possible deactivation mechanism in the case of water attack is given in Scheme 1.

Table 1 Color of PMT film overcoated with clear coating systems

Clear coating system	PMT color
Epoxy 2K(ZD73-0000) with hardener	Red
Epoxy(ZD73-0000) without hardener	Red
Epoxy with acrylicacid as hardener	Red
Alkydal F26/60%in xylol (purchased from Bayer)	Light red
Alkyd	Red
Waterborne coating (pH 11) containing 1-methoxy-2-propylacetate, 1-methoxy-2-propanol, cyclohexanone	Red
Polyurethane 2K + hardener ZH62	Red
Polyurethanewithout hardener	Blue
Polyurethane + acrylicacid as hardener	Blue

Scheme 1

The formation of $C=O$ bonds in the aromatic ring disturbs the conjugated system of the polymer, with the result that the polymer is deactivated. The structure is irreversibly changed by the nucleophilic attack.

Influence of the pH of the electrolyte on the conductivity of PMT and PPy films on a Pt electrode

The influence of the pH of the aqueous electrolyte on the electroactivity of PMT film was also studied. If anodic protection is possible, the ICPs have also to be stable in solutions with the high pH values occurring near a corroding steel surface. Therefore the conductivity of PMT films on Pt was measured in 0.1 M $LiClO_4$ at pH values up to 11.

The EIS measurements in Fig. 5 show that the PMT film is stable until pH 9.7. However, its conductivity at pH 11 is lost in a short time. The resistance of the PMT film increases strongly at this pH value, as shown by the increase of impedance at low frequencies. After fitting the EIS data, the dependence of the PMT film resistance on pH was plotted in Fig. 6.

At lower pH (<9.7), the polymer is conductive. The resistance is low and does not change within 90 min. On the other hand, at pH 11 the resistance increases to 500 Ω and to 5000 Ω after 60 min and 120 min, respectively. It can be seen that the pH value has a strong influence on the conductivity of the PMT film. After 120 min at pH 11 the

Fig. 5 EIS measurements of PMT films on Pt in 0.1 M $LiClO_4$ at different pH values. Modulus of impedance and phase angle are indicated by the *horizontal arrows*

pH = 3

pH = 5.3

pH = 9.7

pH =11

Fig. 6 Resistance of a PMT film on Pt at pH = 5.3, 9.7, 11.0 and 2.0
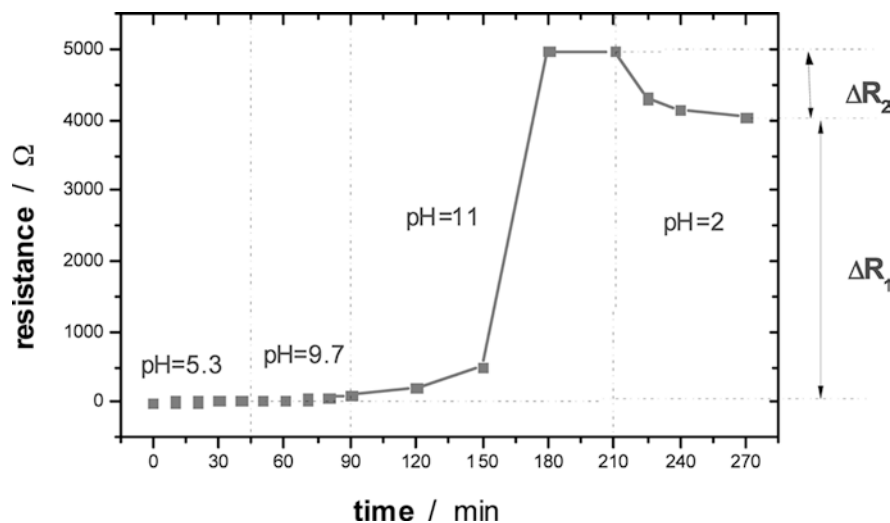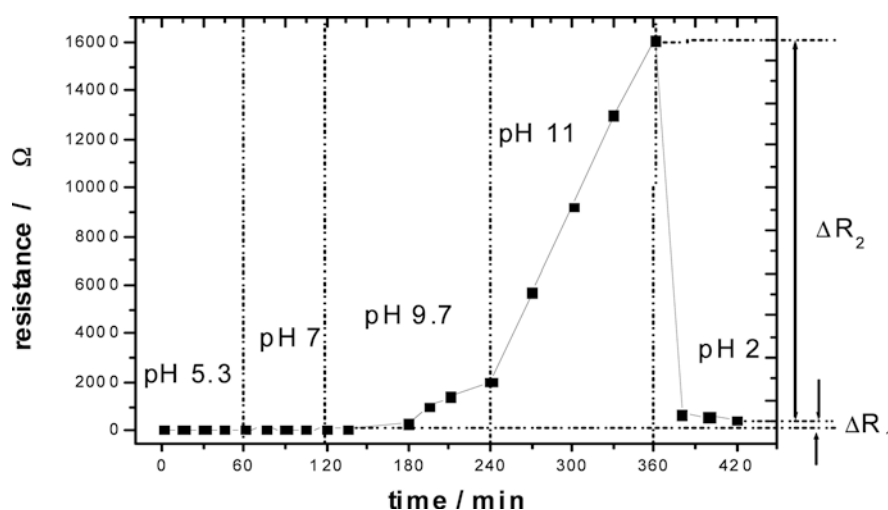

Fig. 7 Resistance of a PPy film on Pt at pH = 5.3, 7.0, 9.7, 11 and 2.0

PMT film was immersed in an acidic electrolyte (pH 2) in order to verify whether the PMT film becomes conductive again. At pH 2 the resistance decreases only slightly from 5000 Ω to 4060 Ω and then remains constant. The loss of PMT conductivity is irreversible. The PMT film cannot be reoxidized either by insertion of anions from the electrolyte or by oxygen reduction by air, as discussed in some reports for PANi [1, 2, 18].

For comparison, the EIS measurements were also carried out with a PPy film on Pt in 0.1 M LiClO$_4$ electrolyte at different pH values. It was observed that the PPy film was stable in solution until pH 7, but its conductivity at pH 9.7 was lost in a short time. After 120 min immersion in an electrolyte with pH 11 the PPy film was reimmersed in an acidic electrolyte at pH 2. In Fig. 7 it can be seen that, in contrast to PMT, PPy becomes conductive again.

The PPy film is also attacked by nucleophiles [19, 20]. According to Wernet and Wegner [21], PPy reacts with nucleophiles, as shown in Scheme 2. In contrast to PMT, this process is partially reversible by subsequent treatment with acids. The former counter ions (NO$_3^-$) are replaced by the anions from the acid (ClO$_4^-$).
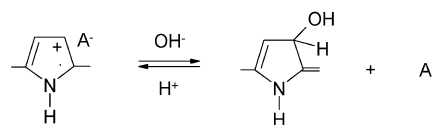
Scheme 2 Reaction of PPy in basic and acidic solutions

Conclusions

PMT films generated on mild steel show well-defined redox activity in organic media (dichloromethane + 0.1 M NBu$_4$PF$_6$). The films can be reduced and then reoxidized reversibly. However, the redox activity is lost if the PMT film is overcoated with conventional coating systems with strong nucleophilicity.

This was also observed with PMT films electrodeposited on Pt in aqueous solutions at different pH values. If the pH increases, the conductivity decreases. The loss of conductivity is irreversible with PMT films. If PMT is to provide anodic protection in small defects or pinholes of a coating system where the pH could be very high, the behavior of PMT in basic media has to be considered. An

active protection by PMT films as a primer layer can only be given in the case where the electronic conductivity of PMT is high enough for galvanic coupling.

By comparison of the change of conductivity of PMT and PPy films in acidic and basic solutions, it was shown that the redox activity of the polymer only remains if the conjugated structure of the polymer is not damaged.

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