Novel protective coatings for steel based on a combination of self-assembled monolayers and conducting polymers

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Abstract
Investigations on the development of a new primer system for iron or carbon steel have led to first results. Several special phosphonic acids with thiophene derivatives as head groups have been synthesized. They are able to 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 to a 2-dimensional conducting polymer layer.

Keywords
coating, primer, self-assembled monolayer, conducting polymer, corrosion protection

Introduction
The investigation of Self-Assembling organic Monolayers (SAM) on metal surfaces has come into the focus of surface technology in the last few years. While the formation of organic coatings with a well defined thickness in the nanometer range is generally quite expensive, by self-organisation highly qualitative monomolecular films can nowadays be obtained in a rather simple and cost-effective manner.

The aim of the investigations presented here is therefore the development of a new primeer system for iron or carbon steel based on the method of self-organisation of an organic monolayer adsorbed onto the passivated metal surface. The organic molecules used for this purpose consist of a thiophene head group and a phosphoric acid anchor group, which are connected via an alkyl chain. By dipping the passivated substrate into a solution of these specific molecules covalent bondings are formed between the phosphoric acid group and the metal oxide in the passive layer. In this way a highly oriented and densely packed monomolecular film can be built up, which is terminated to air by the thiophene head groups. By the following oxidation a 2-dimensional network of polymerised thiophene rings is formed. The coating process is shown schematically in Figure 1.
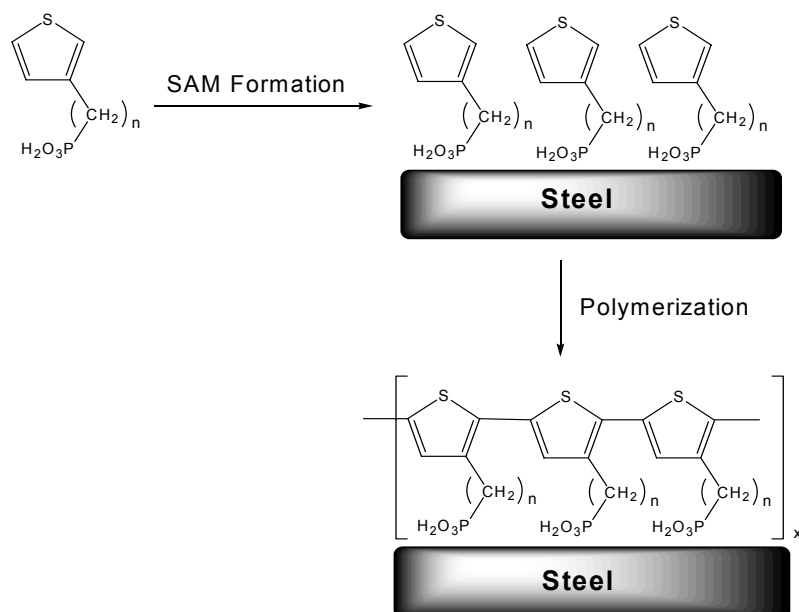
Fig.. 1: *Formation of a new primer system for iron and carbon steel*

Numerous investigations with oxidised surfaces of iron, titanium, zinc and aluminium (but not with SiO_2) have shown the formation of stable bonds between phosphonic acid anchor groups and the passive layers of these metals [1-7]. In these investigations also corrosion inhibiting effects could be observed. The structure of phosphonate monolayers was investigated in more detail on TiO_2 surfaces [8-9]. It was revealed that the structure shown in Fig. 2 is built by the formation of covalent bondings. Similar structures may be assumed also for passivated iron.
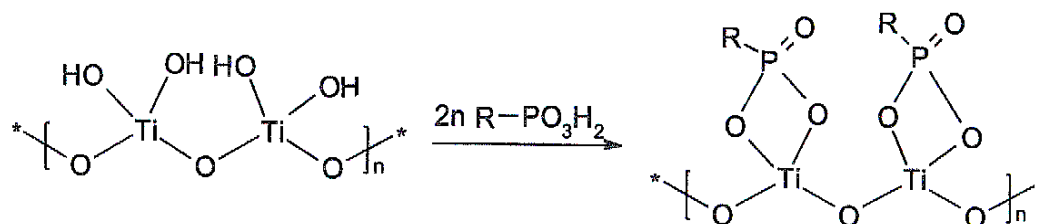

Fig. 2 : *Formation of bondings between phosphonic acids and a TiO_2 surface*

Electropolymerisation of SAM head groups
The electropolymerisation of head groups of self-assembled monolayers on gold surfaces has first been described by Willicut and McCarley [10] as well as by Mekhalif et. al. [11]. Willicut and McCarley investigated SAMs of ω-(N-pyrrolyl)-alkanthioles on Gold. The electropolymerisation could be confirmed by cyclic voltammetry. Recently at the University of Dresden SAMs of thiophenyl-alkyl-phosphonic acids (e.g. thiophene hexane phosphonic acid THPS, see Fig. 3) have been investigated on aluminium and iron with the aim to improve the adhesion of coatings from conducting polymers [1,5]. However, in these investigations no polymerisation of the SAM head groups was carried out, but after SAM formation a further

film of a conducting polymer (thiophene derivative) was electrochemically deposited from a solution of the monomer.

Experimental details

For the investigations described here phosphonic acids as shown in Fig. 3 have been synthesized in order to obtain an optimised bonding to the passivated iron and to allow a cross-linking of the thiophene head groups. Further details about the syntheses have been described elsewhere [12]. Before SAM formation the iron (steel) surfaces were treated in the following way: First of all iron samples (0.35 cm^2) were mechanically grinded, cleaned with distilled water and degreased with ethanole in an ultrasonic bath. Afterwards the surface was passivated by a treatment with 10 % HNO$_3$ for 4 minutes at 30^0 C. Due to the etching effect of the nitric acid a roughening of the iron surface occurs. Besides the described chemical passivation also an electrochemical passivation by anodic polarisation in a solution of 0.1 M KNO$_3$ or 0.1 M Na$_2$HPO$_3$ was tested.

The formation of monolayers (SAM) was achieved by dipping the substrate into a 10^{-3} M solution of the phosphonic acids mentioned above (Fig. 3) together with 10 - 50 % ethanole at pH 3.6 - 4.4. The bath temperature was 40-50 ^{0}C. Under these conditions the formation of the monolayers was nearly complete after only about 1 minute. For further investigations the samples were rinsed with ethanole and water and dried in a nitrogen stream.
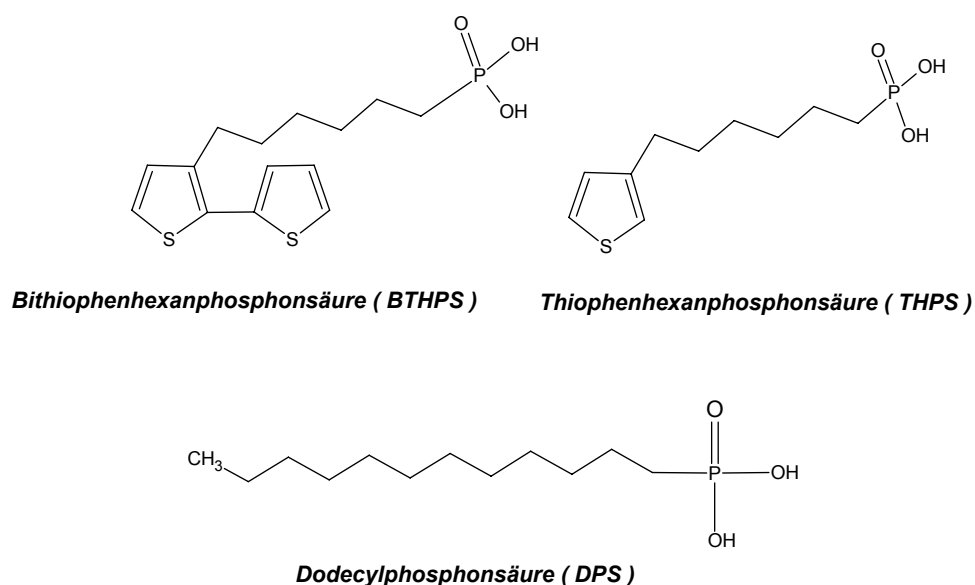

Bithiophenhexanphosphonsäure (BTHPS)   Thiophenhexanphosphonsäure (THPS)

Dodecylphosphonsäure (DPS)

Fig. 3 : *Structures of the phosphonic acids used in this study for SAM formation on passivated iron surfaces*

Results and Discussion

Contact angle measurements

A first hint on a successful SAM formation is given by contact angle measurements. Fig. 4 shows the contact angle measurement of water on passivated iron. The very low contact angle of 18.5° shows that the passivated iron surface is very hydrophilic.
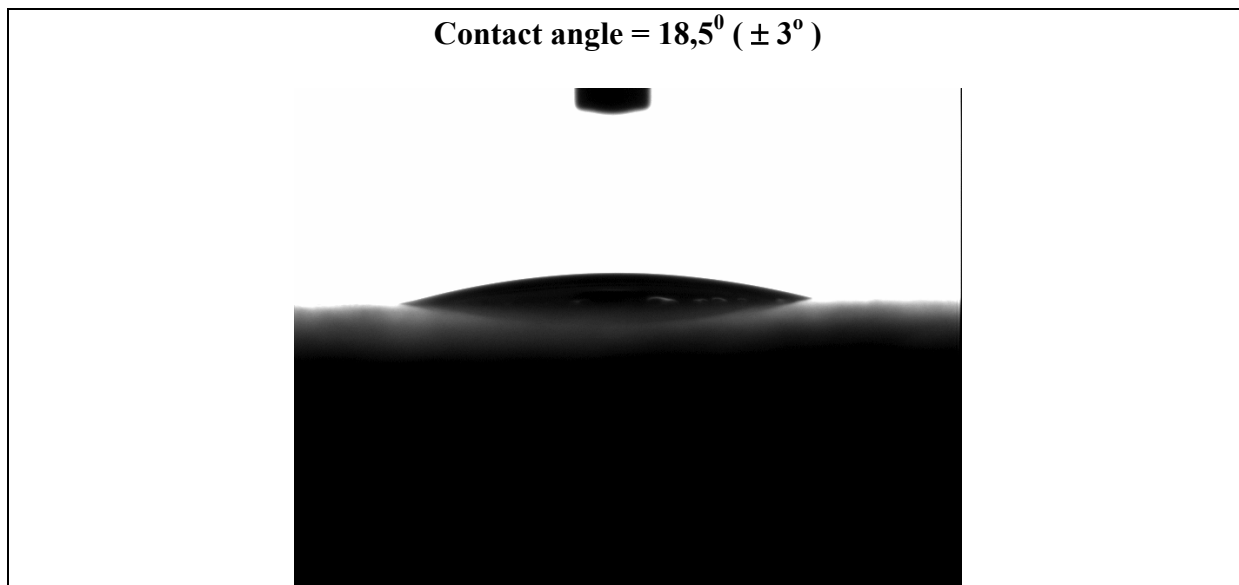
Contact angle = 18,5^0 (± 3°)

Fig. 4 : *Contact angle measurement of water on passivated iron*

By dipping into the thiophene solution the iron surface is becoming very hydrophobic as Fig. 5 shows for two samples treated with different molecules. Contact angles of 120° and 150° can be observed here respectively.
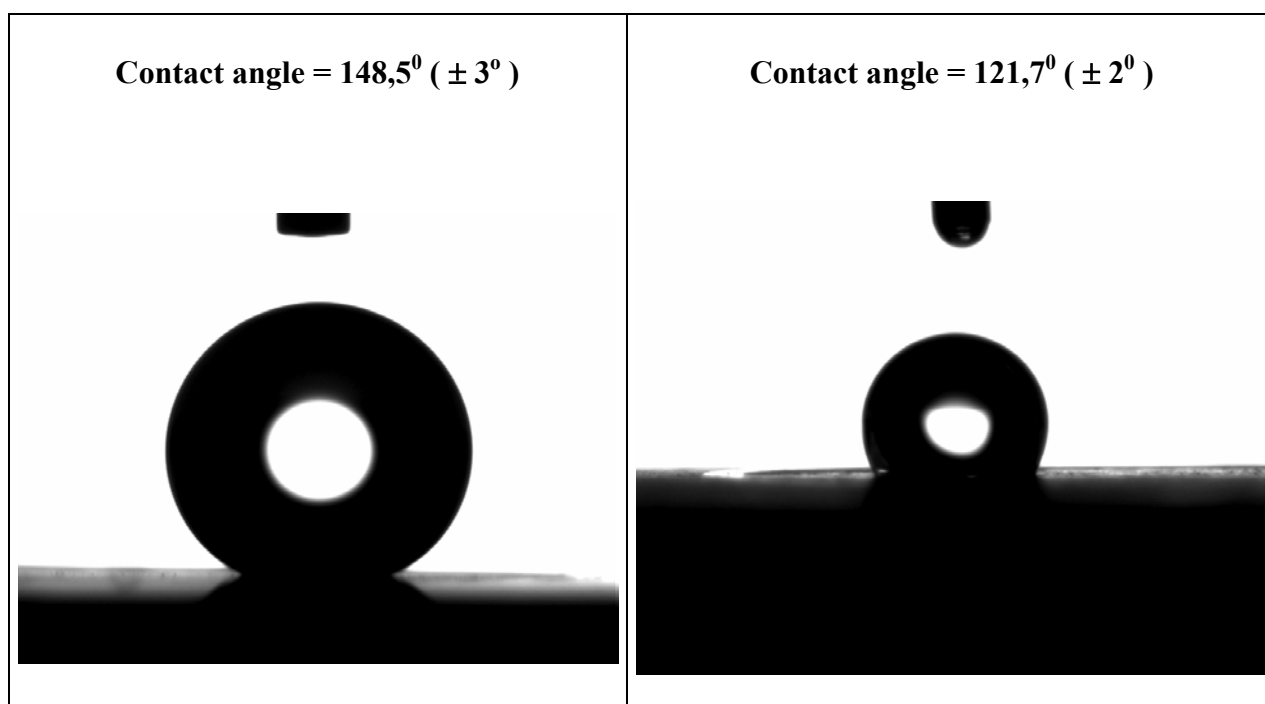

Contact angle = 148,5^0 (± 3°)

Contact angle = 121,7^0 (± 2^0)

Fig. 5 : *Contact angle measurement with water on passivated iron after SAM formation by dodecyl-phosphonic acid (left) and bithiophene-hexane-phosphonic acid (right)*

Current density – potential curves

As a further method to investigate SAM formation current density – potential curves have been measured using a rotating disc electrode (0,35 cm^2) as part of a 3-electrode cell in an aerated 0.1 M NaClO$_4$ solution. Starting from the open circuit potential the electrode was polarised with a constant rate of 50 mV min^{-1} up to about 900 mV vs. Ag/AgCl. It could be observed that by SAM formation the current density in the passive range is decreased to about 10% compared to the passivated iron (Fig. 6).
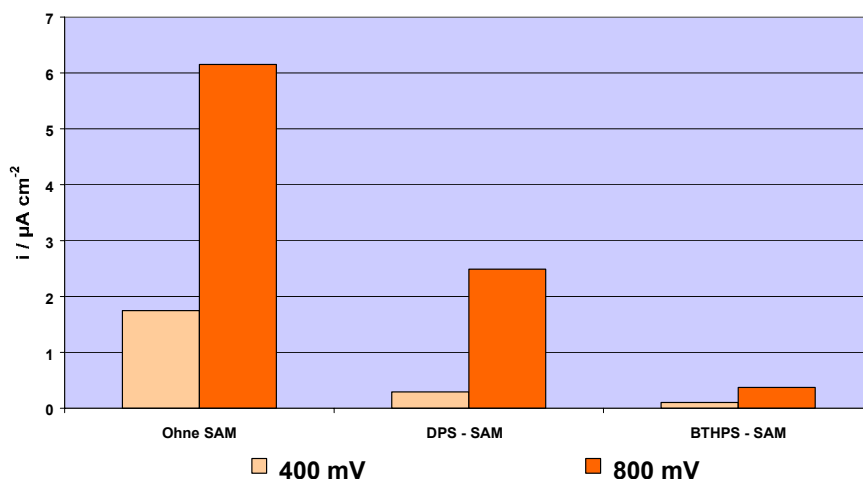

Fig. 6 : *Current density in the passive range of iron in 0.1 M NaClO$_4$ before and after dipping into phosphonic acid solution at 400 and 800 mV respectively*

Electropolymerisation of the thiophene head groups

After successful SAM formation on the passivated iron surface could be derived from the experiments as described above experiments were carried out to prove that electropolymerisation of the head groups of the adsorbed monolayer is possible. For this purpose cyclic voltammograms were recorded in propylene carbonate with 0.1 M NBu$_4$ClO$_4$ with a scan rate of 50 mV s^{-1} in the potential range of 0 V up to +1.4 V. Fig. 7a and 7b show such voltammograms as recorded after SAM formation with bithiophene-hexane-phosphonic acid (BTHPS).

In Fig. 7a several cycles are shown in which polarisation has been carried out only up to +1.3 V. In this potential range no electropolymerisation of the BTHPS monolayer can occur, yet, so that only iron dissolution in the passive and transpassive range (>1 V) is taking place. After increasing the anodic potential border up to +1.4 V polymerisation of the bithiophene head groups is starting and a 2-dimensional polymer network is formed. This can very clearly be derived from the increased reversible oxidation and reduction currents in the potential range between 0.6 V and 1.4 V. After 10 to 20 cycles a stationary state is reached so that in every further cycle the formed 2-dimensional polymer is nearly reversibly electrochemically oxidised and reduced according to the following scheme:
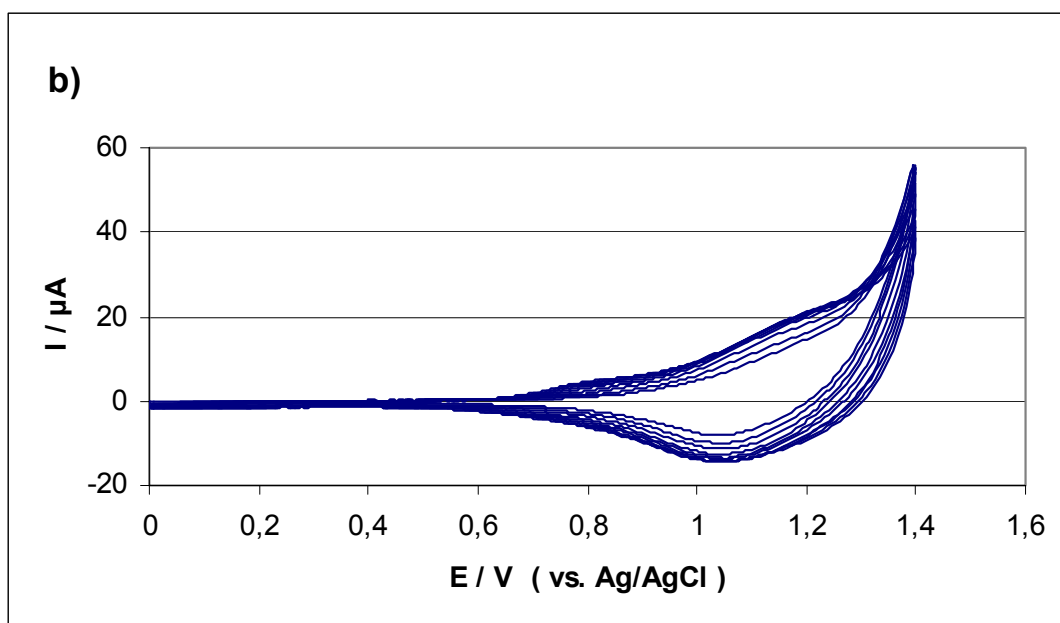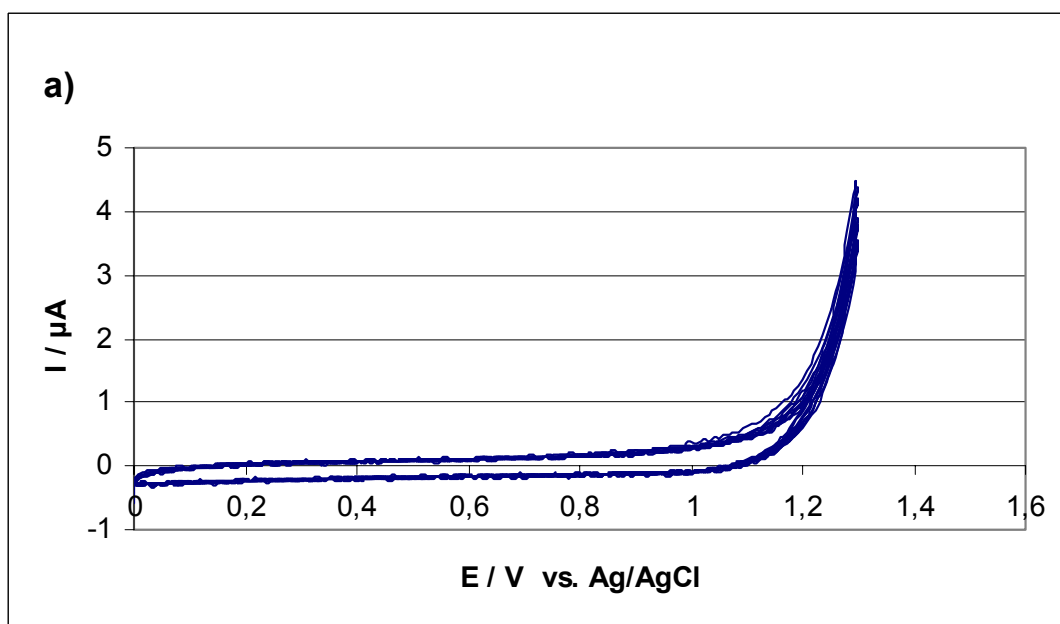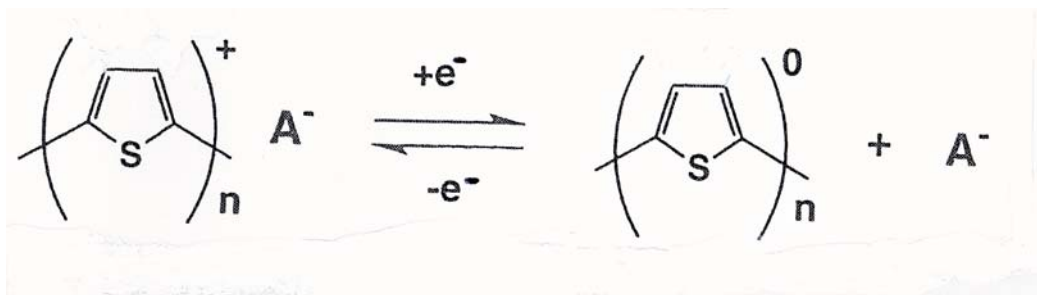
Fig. 7 *Cyclic voltammograms of passivated iron after SAM formation by dipping into bithiophene-hexane-phosphonic acid solution. Electrolyte: propylene carbonate + 0.1 N NBu₄ClO₄ (aerated); potential scan rate: |dE/dt| = 50 mV s⁻¹, RDE rotation frequency: 1000 min⁻¹ ; anodic reversal potential (a) 1,3 V and (b) 1,4 V.*

Similar experiments were also carried out with dodecylphosphonic acid (DPS) and thiophene-hexane-phosphonic acid (THPS), however, for both compounds so far no electropolymerisation could be obtained up to +1.7 V.

Conclusions

The results shown in this paper are a first step towards the development of a new primer system for iron and steel surfaces. Investigations have shown so far that by self-organisation monolayers of organic molecules with monomer head groups can be obtained on passivated iron surfaces in a quite fast and simple way. By anodic polarisation these head groups can be cross-linked to a 2-dimensional conducting polymer. Such polymeric layers do not only offer a good corrosion protection but should also be able to be beneficial as adhesion promoters for further organic coatings. Investigations about the adhesion of top-coats on the new primer layer as well as about their corrosion protection properties (as single layers or in the a coating system) are carried out in the progress of this project. Furthermore the formation procedure of the new primer layers is being optimised towards more simplicity, e.g. by the synthesis of phosphonic acids with head groups which are polymerisable in a water-based solution under rather mild conditions.

References

1. H.-J. Adler, E. Jähne, F. Simon (Institut für Polymerforschung Dresden e.V.) , Final report of Sonderforschungsbereich 287 / Part B1 .
   The report is available at http://www.chm.tu-dresden.de/sfb/b/b1/b1.htm as a PDF file (in German).
2. I. Mäge, E. Jähne, A. Henke, H.-J. Adler, C. Bram, C. Jung, M.Stratmann,
   Macromol. Symp. **1997**, *126,* 7.
3. E. Kalman, *Electrochim. Acta* **2001**, *46,* 3607.
4. I. Felhösi, Z. Keresztes, E. Kalman, Proc. 2001 Joint International Meeting,
   San Francisco, 2-7 September, **2001** (Abstract Nr. 499).
5. a) U. Rammelt, P.T. Nguyen, W. Plieth, Korrosionsschutzeigenschaften
      dünner Polymethylthiophenfilme auf Eisen, GDCh-Monographie, **2000**,
      Bd. *21,* 275-283 ; (ISBN : 3-924763-90-9) .
      TU Dresden (Institut für Physikalische und Elektrochemie).
   b) U.Rammelt, W. Plieth, P.T. Nguyen, H.-J. Adler, E. Jähne, D. Ferse
      Verfahren zur Erzeugung von Schichten aus leitfähigem Polymer auf
      Metalloberflächen ,
      Patent **DE10040993 A** (Offenlegung am 07.03.2002)
6. I. Felhösi, J. Telegdi, K. Papp, E. Kalman, A. Stahl, J. Bognar,
   Macromol. Symp. **2002**, *187,* 306.
7. I. Felhösi, J. Telegdi, G. Palinkas, E. Kalman,
   Electrochim Acta **2002**, *47,* 2335.

8. Dissertation Michael Wedel : „Synthese von Porphyrin- und Chlorinderivaten zur Immobilisierung auf Elektrodenoberflächen und Darstellung von Porphyrin-Fulleren-Dyaden" (Bremen 2000) , S. 76 .

9. Y. Chen, W. Liu, C. Ye, L. Yu, S. Qi, *Materials Research Bull.* **2001**, *36,* 2605.

10. a) R. J. Willicut, R. L. McCarley, *J. Am. Chem. Soc. 116* (1994) 10823.
    b) R. J. Willicut, R. L. McCarley, *Adv. Mater.* **1995**, *7,* 759.

11. Z. Mekhalif, A. Lazarescu, L. Hevesi, J. – J. Pireaux, J. Delhalle, *J. Mater. Chem.* **1998**, *8* 545.

12. U. Harm, R. Bürgler, W. Fürbeth, K.-M. Mangold, K. Jüttner*, Macromol. Symp. **2002**, *187,* 65.