

Electrochemical codeposition of polypyrrole with polyacrylates

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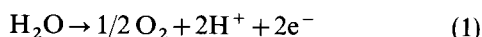
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It is possible to electrodeposit polypyrrole layers at Pt or Fe from aqueous solutions in the presence of partially neutralized polyacrylates. The galvanostatic electrocoatings are performed at $j=0.1-2 \text{ mA cm}^{-2}$. The polyanion is inserted in the polypyrrole at a relatively low stoichiometry ($y=0.05$). The protons, liberated in the anodic process, may lead to an additional electrocoagulation of the polyacrylate itself, yielding a sandwich structure. The doped polypyrrole layer, which adheres excellently, is fabricated exclusively, if the current density is held below the critical value for electrocoagulation, and/or the liquid flow rate is held above the critical value. The polypyrrole chain is in an overoxidized state.

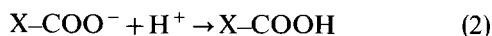
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INTRODUCTION

Twenty-five years ago, electrodeposition of paint was introduced into industrial practice to provide the first polymer layer on steel surfaces (as in motor car bodies) for an effective corrosion protection¹⁻³. The mechanism of this electrochemical process can be briefly described in terms of an electrocoagulation. With regard to the anode, water electrolysis injects protons into the diffusion layer:



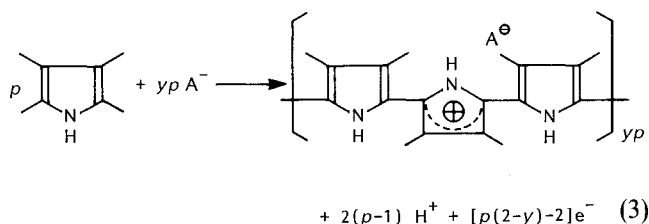
Polymer anions, which make up the waterborne polymer, are transported, mainly by electrophoresis, into this acid region, where they are converted to the insoluble acid form:



X denotes a section of the polymer carrying one free anionic carboxylate group. This mechanism, originally suggested by Beal⁴, was later confirmed by Beck by electrodeposition at the rotating disc electrode⁵⁻⁷. The polymer layer is a poor ionic conductor in the wet state. After stoving, it becomes practically an insulator. In 1979, the anionic paints were nearly totally substituted by cationic systems due to their improved corrosion protection qualities.

More recently, quite another type of electrocoating was introduced. Aromatic and heteroaromatic monomers, dissolved in the electrolyte, can be converted at an inert anode to a polymer with conjugated double bonds along the backbone. The polymer forms a film at the electrode surface. The most important example is polypyrrole, which was subject to large research efforts in the last years⁸⁻¹¹. As it is shown in equation (3), the anodic coupling proceeds in the α, α' position and every third (or fourth) ring unit in the polymer is further oxidized to the

radical cation. The positive charge is compensated by an anion A^- , which is inserted into the solid.



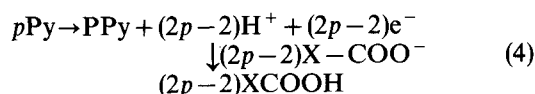
In equation (3) p is the degree of polymerization and y is the degree of insertion. In the example shown, y is 0.33. The four C-H bonds in the monomer and the remaining two C-H bonds in the polymer are marked separately.

The oxidative 'doping' process, running in parallel at the potential of electrodeposition, dramatically increases the electronic conductivity. This important effect was found for the first time with chemically synthesized polyacetylene^{12,13}. The principle seems to be a general one, cf. ref. 14, and it is analogous to the formation of graphite intercalation compounds, cf. ref. 15. In spite of many interesting practical aspects of these new materials, no large industrial application as in batteries, electrochromic displays, electrocatalysis or corrosion protection has been reported up to now.

We found that the aforementioned two important principles for the electrocoating of suitable electrodes can be combined. In the following, this will be demonstrated for the system polypyrrole/polyacrylate. The protons liberated by the electropolymerization process described by equation (3) act in the same way as those protons, which are generated through water electrolysis according to equation (1). The fact that a solid is produced rather than a gas should facilitate the electrocoagulation. In this way, a codeposition should occur, if both polyacrylates and pyrrole (in aqueous solution) are converted at the anode. The overall process, neglecting the doping, can be

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written as follows:



The pyrrole monomer is denoted by Py. One important consequence is the doping of the polypyrrole by the polyacrylate anion itself due to the fact that no other kind of anions are present in the system. Under special conditions, the formation of polyacrylate doped polypyrrole can even be studied separately.

EXPERIMENTAL

All experiments were performed in aqueous solutions, made from distilled water. The temperature was 20°C, if not stated otherwise. Pyrrole (Janßen) was freshly distilled under nitrogen. Its usual concentration was 0.1 M. Two different polyacrylates were employed. The model polyacrylate MA had the composition (mole%) 10% acrylic acid, 45% acrylic acid n-butylester and 45% acrylic acid t-butylester. Luhydran E33, commercially available, is from the polyacrylate type. Solubilization in water was performed with the help of the addition of triethylamine up to 81% degree of neutralization for MA and 143% for E33. The pH was 8.8 and 9.2, respectively. A strong stirring machine was used to homogenize the 10% aqueous acrylate systems to give an opaque white dispersion.

The rotating disc electrodes were made from platinum or iron (99.99%) with an area of 0.5 and 0.2 cm², respectively. They were surrounded by a coaxial polypropylene shaft. The rotator was from Pine Instruments Co. (Grove City, Pennsylvania, USA). A constant current source (Philips) and a potential/time recorder completed the measuring unit. A larger iron disc (10.8 cm²), made from carbon steel St 37, was also used. For the electrodeposition onto larger metal panels made from iron or stainless steel (V2A), a simple flow cell with slowly circulating electrolyte was employed, resembling the cell published elsewhere¹⁶. Figure 1 shows this cell, which had a longer extension in the flow direction, schematically. As a constant current source, a Philips power supply PE 1527 (150 V/3 A) was available. The electrodeposited polypyrrole layers were rinsed with methanol, then with acetone. They were finally dried at 50°C. In case of the sandwich coatings or the pure polyacrylate electrodeposits, rinsing was performed with distilled water and drying at 110°C.

I.r.r.a.s. spectra were measured as described by Molt¹⁷. Potentials were determined versus the saturated calomel electrode, and they are denoted as U_K .

RESULTS

Codeposition at the rotating disc electrode

Electrodeposition was performed under galvanostatic conditions. Figure 2 shows four typical potential/time curves at platinum for two current densities and two electrolytes. Both contained the polyacrylate E33. The rotation speed is indicated at each curve. Its basic curve was in the vicinity of the so called critical rotation speed n^* , see below. The basic curve (dashed line) showed the same features as reported earlier⁵⁻⁷. The small voltage

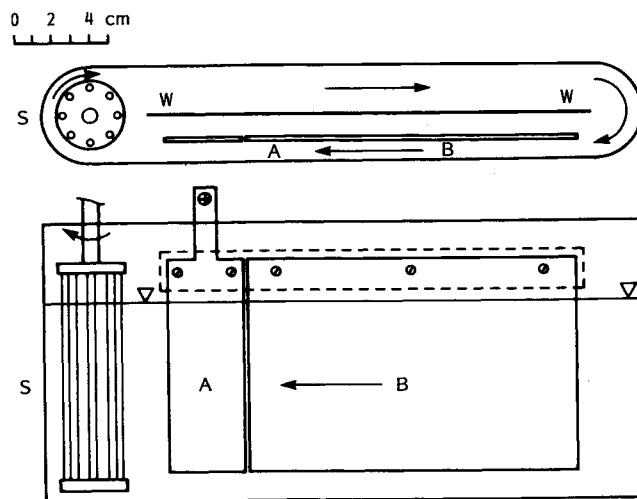


Figure 1 Flow cell for the anodic electrodeposition of polypyrrole/polyacrylates. A, Working electrode; B, non-polarized plate; S, grid stirrer, 550 rpm; W, wall for flow orientation; ←, flow direction, 20 cm s⁻¹

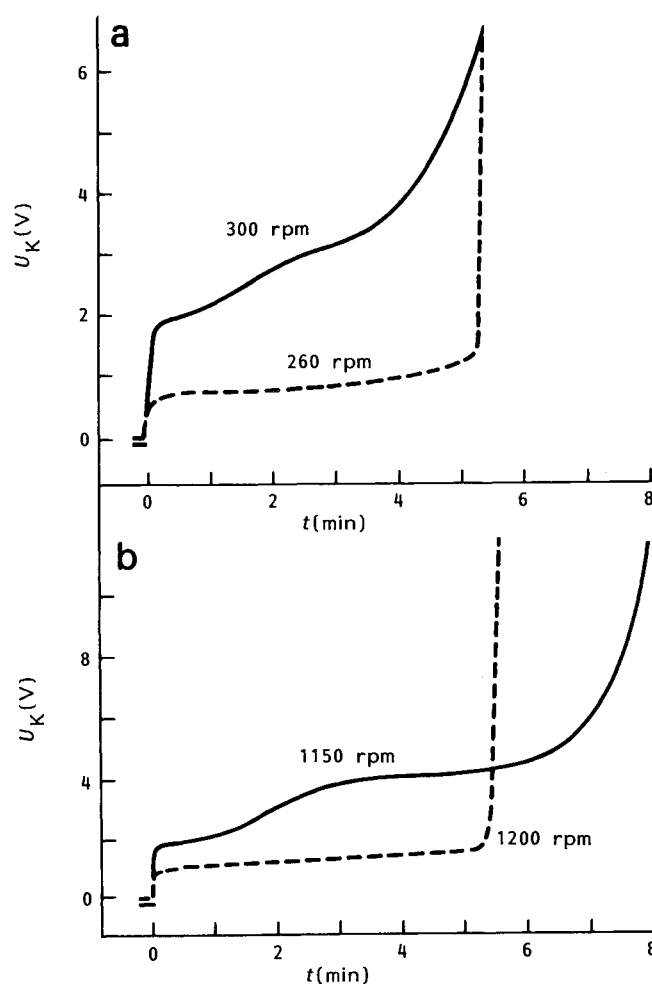


Figure 2 Potential time curves for the galvanostatic deposition of polyacrylate E33 alone (---) and for codeposition E33/polypyrrole (—) at the rotating Pt-disc electrode. Rotation speed is indicated at the curves. The current densities are: A, $j=1 \text{ mA cm}^{-2}$; B, $j=2 \text{ mA cm}^{-2}$

drop at the beginning of the experiment is interpreted as iR in the electrolyte. After an induction period, the voltage rose steeply, indicating the formation of a coherent polyacrylate film. The induction period is due to

a colloid chemical nucleation and phase formation process. It is short at low rotation speeds, but it rapidly rises on approaching the critical rotation speed; n^* is defined for that n , where no electrodeposition occurs within 5–10 min.

An addition of 0.1 M pyrrole leads to the curves drawn as full lines. Two changes can be recognized, namely an enhanced voltage drop (in two stages) along the induction period and a less pronounced transition to the steep voltage rise on film formation. The electrodeposited wet film is white in case of the basic curve. It is greyish black for the codeposition. Leaching with acetone rapidly removes the white film but the black film seems to be insoluble.

As it is shown in Figure 3, a plot of n^* versus j^2 gives a straight line in both cases, with an approximate coincidence. It must be stated that reproducibility of n^* in the presence of pyrrole was not perfect.

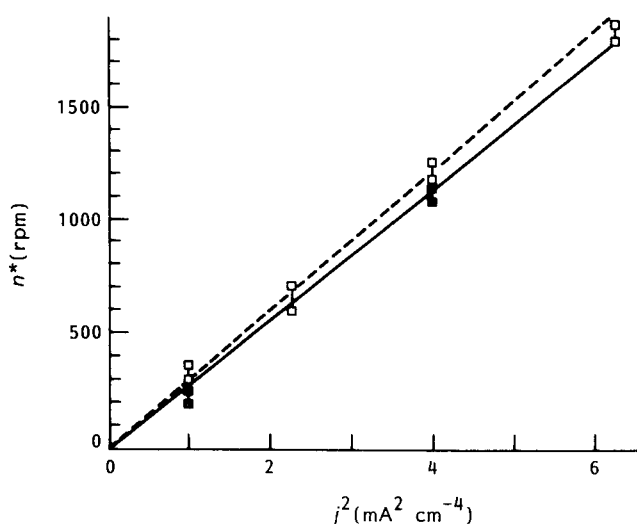


Figure 3 A plot of critical rotation speed n^* versus the square of current density j for the galvanostatic (co)deposition at a rotating Pt disc electrode; ---, 10% E33 alone; —, 10% E33 + 0.1 M pyrrole

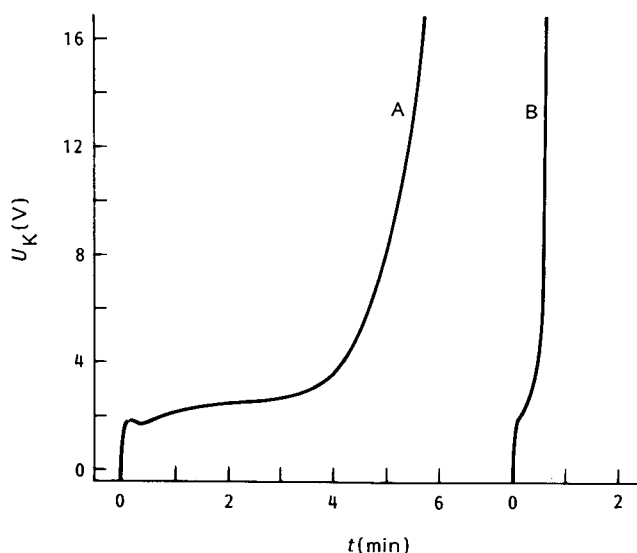


Figure 4 Potential/time curves for the galvanostatic codeposition of polypyrrole/polyacrylate E33 at two current densities; A, $j = 1 \text{ mA cm}^{-2}$; B, $j = 2 \text{ mA cm}^{-2}$; at a rotating iron-disc electrode, 300 rpm

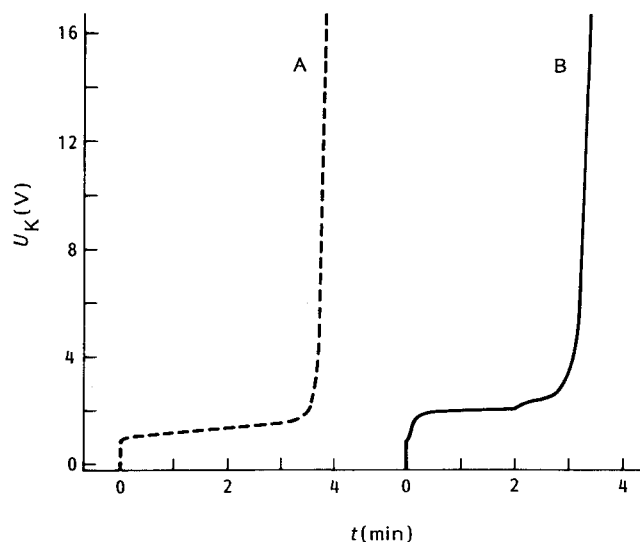


Figure 5 Potential/time curves for the galvanostatic (co)deposition of polypyrrole/polyacrylate MA at the rotating Pt-disc electrode, $j = 2.5 \text{ mA cm}^{-2}$, 500 rpm; A, polyacrylate MA alone; B, polyacrylate MA/polypyrrole

Table 1 Induction periods τ (min) for the codeposition of polyacrylate E22 with 0.1 M pyrrole at two different base metals

j (mA cm^{-2})	n (min^{-1})	τ at Pt	τ at Fe
1	100	1.6	1.4
1	300	5.8	5.9
2	300	0.45	0.60
2	1100	1.7	1.3

The same U_K/t and n^*/j^2 behaviour could be found for the other acrylate resin MA and for the other base metal iron. Figures 4 and 5 give two additional examples for the voltage/time behaviour of the acrylate E33 at the iron disc in the presence of 0.1 M pyrrole and for the model acrylate MA at platinum, respectively. Table 1 demonstrates with some selected induction periods that there is a strong analogy between the two base metal electrodes.

Galvanostatic codeposition at $j = 1\text{--}2 \text{ mA cm}^{-2}$

Electrocoating of sheets ($A = 42 \text{ cm}^2$), made from Pt or Fe (St 37) was performed at current densities of 1 and 2 mA cm^{-2} , well above the so-called critical current density j^* (refs. 7 and 18). The sheets were arranged in parallel between two counter electrodes of the same size in a glass cylinder. The acrylate resin E33 was used. Figures 6 and 7 and Table 2 show clearly that the voltage is rising up to about 120 V with the acrylate alone, but only to about 70–90 V in the presence of additional 0.1 M pyrrole. In the latter case, a brown to black coating was found with both Pt and Fe anodes. On leaching with acetone after drying at 110°C , removal of the polymer layer was quantitative only after several days, while in the absence of pyrrole, it dissolved rapidly. Normally, at 110°C no crosslinking reactions can proceed. Table 2 summarizes the electrochemical equivalents m_e , which were determined by this method; m_e is in the order of 20 mg C^{-1} and does not depend significantly on the current density, the presence of pyrrole or on stirring.

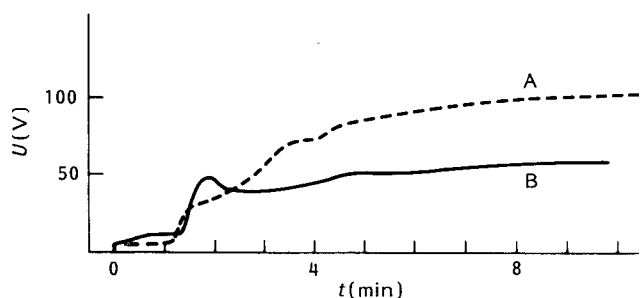


Figure 6 Voltage/time curves for the galvanostatic (co)deposition of polypyrrole/polyacrylate at Pt-sheets, $j = 1 \text{ mA cm}^{-2}$; A, polyacrylate E33 alone; B, polyacrylate E33/polypyrrole

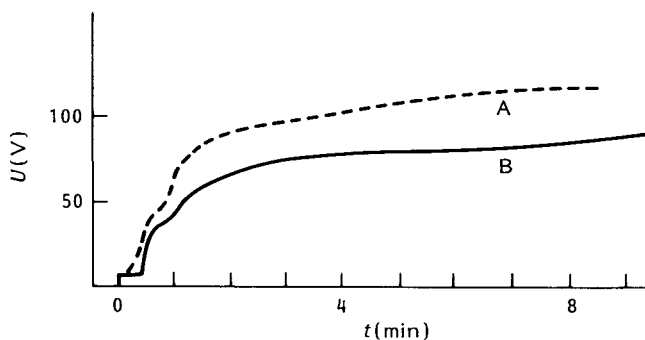


Figure 7 Voltage/time curves for the galvanostatic (co)deposition of polypyrrole/polyacrylate at Fe-sheets, $j = 2 \text{ mA cm}^{-2}$; A, polyacrylate E33 alone; B, polyacrylate E33/polypyrrole

Table 2 Electrochemical equivalent for the electrodeposition of polyacrylate E22 at a constant current density j

Anode	j (mA cm^{-2})	Slow stirring	0.1 M pyrrole	m_e (mg C^{-1})
Pt	1	—	—	24
	1	+	—	24.5
	2	—	—	24
	2	+	—	23
	1	—	+	17
	1	+	+	21
	2	—	+	21
	2	+	+	21
Fe	1	—	—	25
	1	+	—	24.5
	2	—	—	27
	2	+	—	23
	1	—	+	18
	1	+	+	21
	2	—	+	29
	2	+	+	23

Table 3 Electrodeposition of polypyrrole doped with polyacrylate, in the flow cell. Concentrations: polyacrylate, 10 wt%; pyrrole, 0.1 M. Area of stainless steel electrode: 66 cm^2 , $T = 20^\circ\text{C}$

No.	Acrylate	j (mA cm^{-2})	t (min)	U/V	Q/C	Δm (mg)	γ (%) ⁴	Footnote
1	E33	0.125	19.3	3.9	9.5	1.8	9.4	
2	E33	0.25	8.7	7.9	8.6	1.8	10.5	
3	E33	0.125	310	10	153	30.9	10.0	
4	E33	0.125	138	10	68	43.0	31.6	1
5	E33	0.125	210	5.2	103.5	40.4	19.5	2
6	E33	0.25	30	8.4	29.6	12.9	19.5	2
7	E33	0.25	40	10.5	39.4	18.1	23.0	1, 2
8	MA	0.125	40/800	10/35	19.7/394	42.1	106/5.3	3
9	MA	0.125	37.5	9.4	18.5	3.8	10.2	1, 2
10	MA	0.10	52.5	10	20.7	10.1	24.3	1, 2

¹ Temperature: 50°C

² Concentration of pyrrole: 1 M

³ Long term experiment with continuous increase of voltage: 10 V after 40 min

⁴ γ = current efficiency, cf. Figure 9 and equation (3)

Galvanostatic codeposition at $j = 0.125\text{--}0.25 \text{ mA cm}^{-2}$

Electrocoating of rectangular plates ($A = 66 \text{ cm}^2$), made from stainless steel, was performed in the flow cell already described in Figure 1. Flow rate of the bath was 20 cm s^{-1} . Electrode length parallel to liquid flow was 4 cm. A coplanar, but nonpolarized plate was arranged upstream, providing a roughly constant thickness of diffusion layer at the electrode. The current density was 0.125 or 0.25 mA cm^{-2} . The relatively strong convection and a current density below the critical current density^{7,18} efficiently prevented the acrylate resin from being electrocoagulated. Thus it was possible to study the electrodeposition of polypyrrole separately. It was found that the voltage remained low (4–8 V) under these conditions. Table 3 summarizes the experimental results in terms of current density, time of deposition, average voltage, charge, mass of the electrodeposit and current efficiency γ , calculated under the assumption $y = 0.250$ (cf. refs. 11 and 21).

The thin polymer layers were greyish black with an extremely strong adherence at the stainless steel electrode in case of the very thin layers with a nominal thickness¹¹ of 30–100 nm. Thicker layers, especially those deposited at 50°C , had a somewhat lessened adherence. Δm was determined after an extended leaching of the layer with acetone. Table 3 shows that current efficiency is only in the range of 10–30%. The long term experiment No. 8 leads to about 100% current efficiency. However, it is not clear if the electrocoagulate, indicated by the continuous voltage rise up to 35 V, was quantitatively removed.

In addition, we employed large rotating disc electrodes to perform these types of measurements. However, the results were less reliable, which may be partially due to the relatively small electrode area of about 10 cm^2 .

NON-ELECTROCHEMICAL RESULTS

Some of the electrodeposited polypyrrole layers deposited at $j = 0.125\text{--}0.25 \text{ mA cm}^{-2}$ were mechanically removed from the stainless steel substrate for elemental analysis. In Table 4, the results are compared with some theoretical compositions.

A good fit between theoretical and experimental findings, at least for the acrylate E33/polypyrrole system No. 1, is obtained for the theoretical composition No. 7, corresponding to the normal stoichiometry with small inorganic anions. However, the experimental value for nitrogen remains much too high and experimental

hydrogen is too low. Even under the assumption of a very low degree of insertion ($y=0.1$, cf. No. 9), this high N value cannot be attained and the oxygen becomes too low. However, a nearly total match can be achieved with the theoretical composition No. 12, which assumes a very low degree of insertion ($y=0.05$) and one oxygen per monomer unit. Oxygen was repeatedly found in polypyrrole (cf. ref. 10). Some nitrogen found in the polyacrylate alone (No. 3) is indicative for the codeposition of amine cations. However, this effect would lead to a maximum composition $\text{CH}_{1.75}\text{N}_{0.013}\text{O}_{0.28}$. Therefore, it must be concluded that additional amine molecules are absorbed in the polymer.

I.r.r.a.s. spectra of these polypyrrole films adhering at the substrate were measured. Figure 8 shows some of the results. A strong carbonyl band was found in the following range of wave numbers: $\nu=1703\text{--}1719\text{ cm}^{-1}$. The polyacrylates alone show two carbonyl bands:

Polyacrylate	Band 1	Band 2
E33:	1692 cm^{-1}	1740 cm^{-1}
MA:	1702 cm^{-1}	1752 cm^{-1}

The second band is stronger than the first one. This is to be expected because the polymer contains two types of carbonyl groups, the carboxylic group, which lies theoretically at 1695 cm^{-1} , and the ester group; a saturated ester absorbs at $1735\text{--}1750\text{ cm}^{-1}$.

The experimental findings can be rationalized in two ways:

1. The carbonyl band is an over-oxidation band of polypyrrole, which is at $1717\text{--}1720\text{ cm}^{-1}$ (ref. 19). However, elemental analysis totally contradicts this view. H is too high and N is too low.

2. The vibrations of the carboxylate group in the inserted polymer anion is sterically hindered. As a matter of fact, the characteristic bands of inorganic anions as ClO_4^- or BF_4^- cannot be found in doped polypyrrole^{20,21}. This may be due to the steric hindrance of the anion oscillations. In this case, the presence of only one carbonyl band should be a strong argument for the presence of inserted polyacrylate anions.

DISCUSSION

Codeposition as a sandwich

Galvanostatic codeposition at $1\text{--}2\text{ mA cm}^{-2}$ and weak convection must lead to a sandwich structure.

Table 4 Elemental analysis for polyacrylate doped polypyrrole, cf. Figure 9

No.	System	C	H	N	O
1	Polypyrrole/E33, average of 3 samples (No. 3, 4, 5) from Table 3	1	1.2	0.16	0.28*
2	Polypyrrole/MA, one sample (No. 8) from Table 3	1	1.5	0.15	0.68*
3	Polyacrylate alone	1	1.68	0.035	0.23*
4	Polypyrrole alone ¹¹	1	0.86...0.98	0.24	—
5	Theoretical composition for MA	1	1.68	—	0.30
6	Theoretical composition for PPy	1	0.75	0.25	—
7	Theoretical composition for $(\text{C}_4\text{H}_3\text{N})_x=3[\text{C}_{20}\text{H}_{30}(\text{COO})_{10}(\text{C}_4\text{H}_9)_9]$	1	1.54	0.04	0.26
8	As No. 7, $x=4$	1	1.50	0.05	0.24
9	As No. 7, $x=10$	1	1.33	0.09	0.19
10	Theoretical composition for $(\text{C}_4\text{H}_3\text{NO})_x=4[\text{C}_{20}\text{H}_{30}(\text{COO})_{10}(\text{C}_4\text{H}_9)_9]$	1	1.50	0.05	0.29
11	As No. 10, $x=10$	1	1.33	0.09	0.28
12	As No. 10, $x=20$	1	1.17	0.14	0.27

* Calculated from $100 - (\text{C} + \text{H} + \text{N})\%$

Polypyrrole doped with polyacrylate anions provides the first layer at the substrate. The protons generated in the course of the electrodeposition according to equation (3), electrocoagulate the polyacrylate, cf. equation (2), after the transition time τ . The former layer has a specific conductivity for electrons in the order of 1 S cm^{-1} but the latter is a poor ionic conductor ($\kappa=10^{-8}\text{ S cm}^{-1}$) and thickness growth of polyacrylate layer is indicated by a strong voltage rise. Our experiments at the rotating disc

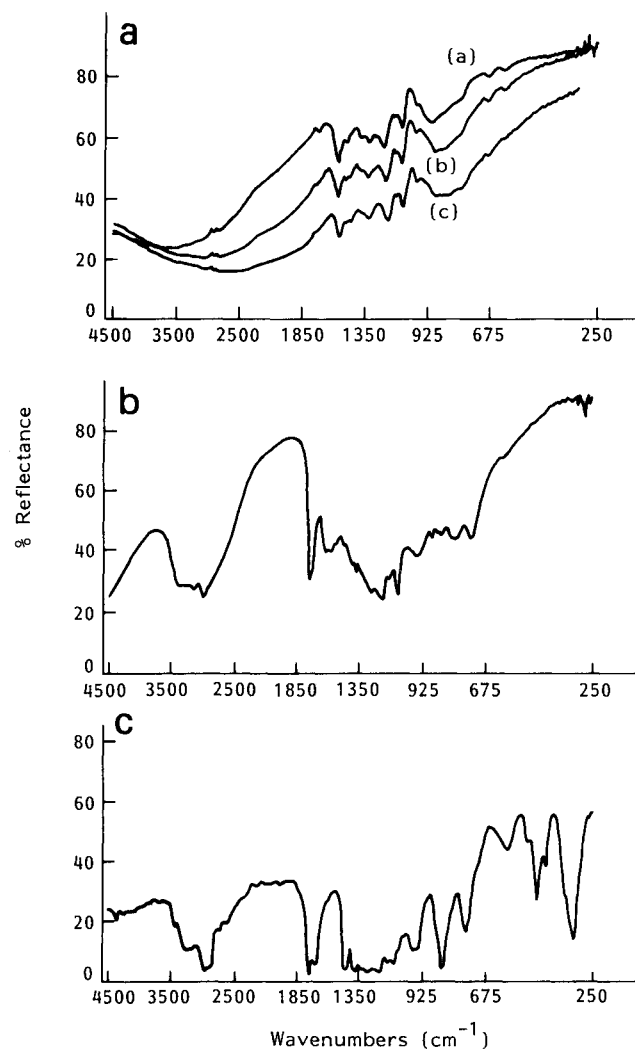


Figure 8 I.r.r.a.s. spectra, 85° . A, Polypyrrole, doped with three various anions (a, ethylsulphate; b, p-toluene sulphonate; c, tetrafluoroborate). B, Codeposition of polypyrrole/polyacrylate MA; C, Polyacrylate alone (E33; transmission)

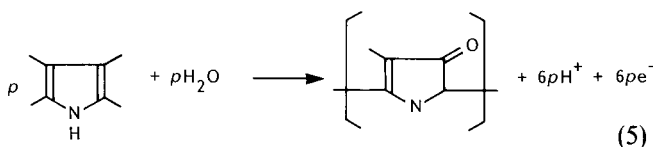
electrode and the preparative electrodepositions at 1–2 mA cm⁻² strongly support this view.

The further course of the potential/time curve, which is characterized by the presence of space charges in the polarized polymer, is also influenced by the pyrrole, cf. *Figures 6 and 7*. The anodic polypyrrole formation may even be possible by permeation of the monomer through the swollen polyacrylate film. A percolated polyvinylchloride/polypyrrole structure was fabricated at the anode, starting from a swollen PVC layer on Pt^{22–26}. Similar composites with polypyrrole are known with Nafion^{27–27}, Nucleopore^{31,32} and polyester³³. The potential/time curve shows lower voltages in our case in comparison to the system free of pyrrole. This indicates the improved conductivity. Another mechanism for the codeposition of polypyrrole in the polyacrylate film would be a chemical one: oxygen, generated according to equation (1) from water transported through the polyacrylate film, polymerizes the incoming pyrrole molecule to yield the polypyrrole in the film.

Codeposition as pure polyacrylate doped polypyrrole

The results of galvanostatic codeposition at $j=0.125$ – 0.25 mA cm⁻² show clearly that at low current densities (below the critical one for electrodeposition of paint) and/or at strong convection^{7,18}, the electrodeposition of pure polyacrylate doped polypyrrole is realized as a thin, strongly adhering, greyish black layer. The electrocoagulation of the polyacrylate itself is effectively inhibited. The voltage remains at a low level in the course of the experiment. As it is shown in *Figures 6 and 7*, even at higher current densities, the voltage remains low in the course of the induction period τ . Experiments where the substrate was removed from the electrolyte at the end of τ revealed a thin polypyrrole layer. The current efficiencies were the same as in the flow cell at low current densities.

The only anionic species in the system is the polyacrylate. Thus, it must act as the counterion in the polypyrrole, whose structure is shown in *Figure 9* by analogy with the commonly doped polypyrrole with small inorganic anions like BF₄⁻ or ClO₄⁻. However, the real degree of insertion y seems to be much lower than 0.33, which is anticipated in *Figure 9*. As it is pointed out previously, y seems to be as low as 0.05 and the polypyrrole backbone must contain additional oxygen. The low current efficiencies of 10–30%, which were found for these electrodeposits (cf. *Table 3*), are calculated on the basis of the structure in *Figure 9*. If one assumes the anodic formation of carbonyls at the pyrrole rings in the 3 position, the theoretical charge triples and the current efficiency becomes nearly quantitative:



Low molecular weight carboxylates cannot be inserted in polypyrrole, as shown by Warren and Anderson³⁴. On the other hand, the tendency to insert polyanions as polystyrene sulphonates is very pronounced due to the strong electrostatic interaction³⁵. This may also assist the insertion in our case. Moreover, the significant improvement in current efficiency at 50°C (*Table 3*) and

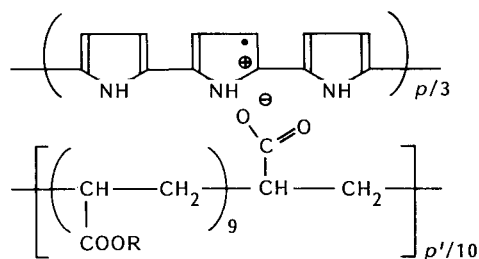


Figure 9 First approach for a structure of the polypyrrole/polyacrylate codeposit

the high over-voltage, ca. 1 V, in comparison to the insertion of small anions shows clearly that the insertion of the polymer is a process with electrical *and* thermal activation.

It was possible to electrodeposit this polypyrrole at iron from the aqueous electrolyte. The current efficiencies were the same at Pt and at Fe. If an attempt is made to create a polypyrrole layer from 0.1 M pyrrole and 0.1 M NEt₃H⁺BF₄⁻ in aqueous solution (containing the same cation as in the polyacrylate bath), only Pt can be electrocoated. Iron dissolves anodically. We found that aqueous nitrate is the only example from more than 20 electrolytes with low molecular weight anions, from which iron could be electrocoated²¹.

Contrary to the common inorganic anions, the polyacrylate does not interfere negatively with an iron substrate if the layer is used as an (inter)layer for corrosion protection. Although good adherence on iron is a problem for PPy/NO₃⁻ layers from aqueous electrolytes, we found with the thin PPy/polyacrylate film a deposit with an extremely good adherence. Because this parameter is very important in corrosion protection of metals^{36,37}, the new layers should be useful in this field.

ACKNOWLEDGEMENTS

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