Properties of polypyrroles treated with base and acid

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The conductivity of different polypyrrole salt films has been varied by treatment with NaOH and H_2SO_4. With NaOH, conductivities smaller than that of the initial sample can be obtained whereas an H_2SO_4 treatment leaves the conductivity nearly unchanged. Both procedures result in an increase in the long-term stability of the conductivity at least at 80°C and 140°C. Using elemental analysis and energy dispersive X-ray spectroscopy it was shown that the chemical treatments cause ion exchange processes which are almost completely reversible. The properties of the polypyrrole salt film such as conductivity, weight, thickness, and oxygen permeability are closely related to the counterions

(Keywords: polypyrrole; conductivity; base and acid treatment; ageing; ion exchange)

INTRODUCTION

The long-term stability of the electrical conductivity of polypyrroles is a crucial property from an application point of view. Recently it has been shown that the conductivity and the ageing behaviour of polypyrroles can be altered by treatment with acid or base[1]. These findings are not only interesting for the application of polypyrrole as a conducting material but, moreover, they throw some light on the influence of counterions on the conductivity. As a continuation of the studies reported in ref. 1 this paper gives more detailed results on how polypyrrole can be modified and describes the experiments which contribute to a greater understanding of the underlying processes involved.

EXPERIMENTAL

The polypyrrole films were obtained in the usual way by electrochemical polymerization. In the case of the phenylsulphonate acting as counterion the corresponding tetrabutylammonium salt in acetonitrile was used as the supporting electrolyte; the polypyrrole with ClO_4^- as counterion has been prepared from a solution of $LiClO_4$ in propylene carbonate. The films were washed and dried *in vacuo*. From elemental analysis one counterion per three pyrrole rings has been found in the case of the two polypyrrole phenylsulphonates and one counterion per four pyrrole rings for polypyrrole perchlorate (*Table 1*).

After the treatment with acid or base the samples were washed in water and dried again. This procedure almost completely removes any residual acid or base from the films. For the treatment with NaOH this conclusion can be drawn from the negligible amount of sodium found by the elemental analysis given in *Table 2*.

The conductivity measurements were carried out using the four-probe technique. During ageing at higher temperatures the samples were permanently contacted in order to avoid any mechanical damage of the thin films by the repeated attachment of the measuring gauge. The heating was achieved by blowing temperature-controlled air over the samples.

The energy dispersive X-ray experiments were performed on films which were embedded in epoxy resin and then cut. The lateral resolution of the applied method lies at around 0.5 μm.

SODIUM HYDROXYDE AQUEOUS SOLUTION TREATMENT

The exposure of a poly(pyrrole phenylsulphonate) film of 30 μm thickness to a 2% solution of sodium hydroxide in water leads to a decrease of conductivity as *Figure 1* demonstrates. Within 15 min a change by a factor of 2000 is observed. At higher exposure times the conductivity decrease levels off. The change in conductivity is accompanied by a loss of weight which reaches 40% after an exposure time of 240 min (cf. *Figure 1*).

This process does not only depend on time but is strongly influenced by the concentration of the base and the film thickness. In *Figure 2* the results of treatments at different NaOH concentrations are given for a poly(pyrrole phenylsulphonate) film of 90 μm thickness. This sample has the same initial composition as the thinner 30 μm film (cf. *Figure 1*, *Table 1*). If one compares the conductivities as a function of the time of exposure to

Table 1 Elemental analysis of nitrogen and anions of two polypyrrole salts

Sample	Weight [%]			Molar ratio	
	N	S	Cl	S/N	Cl/N
PPy phenylsulphonate ($d = 30$ μm)	11.7	8.5	–	0.32	–
PPy phenylsulphonate ($d = 90$ μm)	11.7	8.7	–	0.33	–
PPy perchlorate ($d = 20$ μm)	14.0	–	9.1	–	0.26

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Table 2 Elemental analysis of poly(pyrrole phenylsulphonate) films treated with base and acid

Sample	Weight [%]	
	S	Na
PPy phenylsulphonate ($d=30\,\mu$m)	8.5	–
treated 15 min with 2% NaOH	3.0	0.60
treated 120 min with 2% NaOH	–	0.24
treated 240 min with 2% NaOH	0.8	–
treated 15 min with 10% H_2SO_4	11.4	–
treated 240 min with 10% H_2SO_4	6.4	–
PPy phenylsulphonate ($d=90\,\mu$m)	8.7	–
treated 15 min with 2% NaOH	7.1	0.29
treated 120 min with 2% NaOH	–	0.91
treated 240 min with 2% NaOH	3.1	–
treated 15 min with 10% H_2SO_4	11.4	–
treated 240 min with 10% H_2SO_4	7.9	–

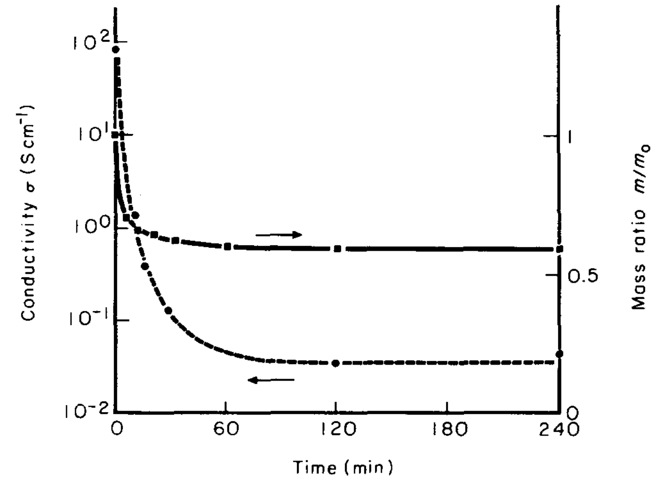

Figure 1 Influence of the treatment by a 2% aqueous NaOH solution on the conductivity and the weight of a $30\,\mu$m polypyrrole phenylsulphonate film. m describes the mass of the film after base treatment for a time t, m_0 is the initial sample mass

the 2% NaOH solution, a much smaller decrease in conductivity is found for the thicker film.

The influence of the concentration of NaOH on the conductivity change shows a surprising feature. Whereas the stronger decrease in conductivity by the 10% NaOH compared with the 2% NaOH is to be expected because of the higher ion concentration this conclusion does not explain the totally unchanged conductivity of the polypyrrole if it is exposed to a 50% NaOH solution. In ref. 1 detailed results on the concentration dependence of the conductivity decrease of polypyrroles by NaOH treatment are given. According to these measurements the conductivity, after an exposure of 240 min, runs through a broad minimum as a function of the concentration of NaOH.

An insight into the effects of the NaOH treatment is obtained from an investigation of the distribution of the phenylsulphonate ions across the sample thickness (*Figure 3*). The measurements were obtained by energy dispersive X-ray spectroscopy (EDX). The initial sample shows a homogeneous sulphur distribution across its thickness of around $30\,\mu$m. From this result it can be concluded that the phenylsulphonate moiety is homogeneously distributed in the sample at least within the resolution of the experiment. The exposure to a 2% NaOH solution leads to an obvious depletion of the sulphur-containing species, which becomes more pronounced the longer the treatment lasts.

The depletion of sulphur implies a removal of the phenylsulphonate ions by the base treatment. Because of the electroneutrality principle another anion must replace the phenylsulphonate within the polypyrrole. There is some indication for a replacement of the phenylsulphonate by hydroxide, which covalently binds to pyrrole (see later). These covalent bonds shorten the conjugation length, which results in a decrease of the conductivity.

The exposure of polypyrrole to a base does not only effect a decrease of the conductivity but also influences the ageing behaviour significantly. *Figure 4* shows the time dependence of the conductivity at a temperature of 140°C for poly(pyrrole phenylsulphonate) films and its modification by NaOH treatment over 240 min at various concentrations. The relatively high temperature has been chosen in order to avoid an unreasonably long duration of the experiment. While the conductivity of the initial film has dropped by nearly two decades during the ageing over 100 days the conductivity of the samples treated with 1%, 2%, 5%, and 20% NaOH has hardly altered. It is remarkable that the exposure of the film to 0.1% NaOH,

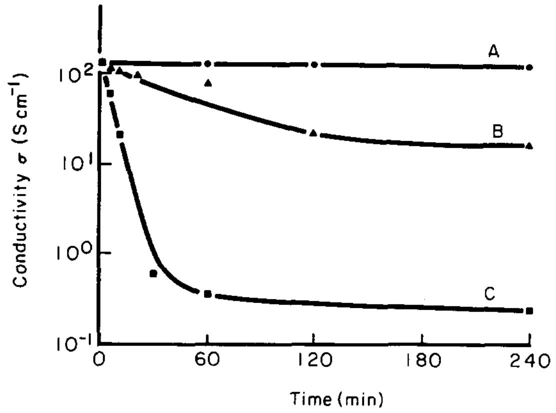

Figure 2 Conductivity change of a poly(pyrrole phenylsulphonate) film treated with aqueous NaOH solutions of various concentrations. Film thickness is $90\,\mu$m: A, treated with 50% NaOH; B, 2% NaOH; C, 10% NaOH

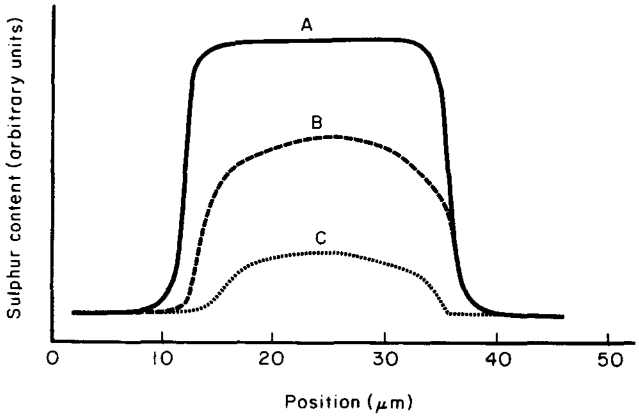

Figure 3 Sulphur distribution within poly(pyrrole phenylsulphonate) films treated by a 2% aqueous NaOH solution for different times. Film thicknesses around $30\,\mu$m. A, initial sample; B, treated for 120 min; C, treated for 240 min

which reduces the conductivity only slightly, improves the stability quite significantly. A similar influence of the NaOH treatment on the ageing behaviour is observed at 80°C.

SULPHURIC ACID TREATMENT

The exposure of a poly(pyrrole phenylsulphonate) film of 30 μm thickness to 10% sulphuric acid influences the conductivity. As shown in *Figure 5* the conductivity first increases as a function of exposure time, runs through a maximum and finally reaches a plateau value only slightly lower than the conductivity of the initial sample. Besides the conductivity change, the acid treatment results in a 30% weight loss of the sample which occurs mainly during the first 30 min of the treatment. This loss in weight is slightly smaller than in the case of the exposure to NaOH. The decrease in mass indicates an exchange of the phenylsulphonate by sulphate or hydrogen sulphate ions. This conclusion is supported by the EDX spectra in *Figure 6*. On the one hand the sulphur content has dropped only slightly because of the acid treatment; on the other a shrinkage of the sample can be observed (cf. next section of this paper) besides the decrease in mass. The sulphur distribution of both samples is found to be homogeneous across their thickness.

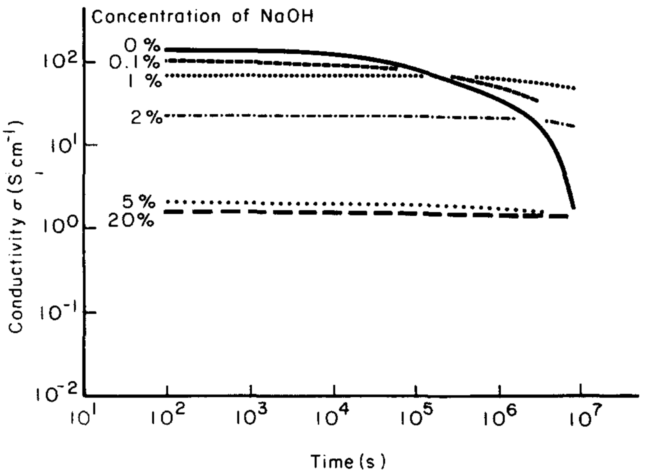

Figure 4 Ageing behaviour with regard to conductivity of poly(pyrrole phenylsulphonate) films exposed to NaOH solution of different concentrations. Film thickness: 90 μm. Ageing temperature: 140°C. Time of exposure: 240 min

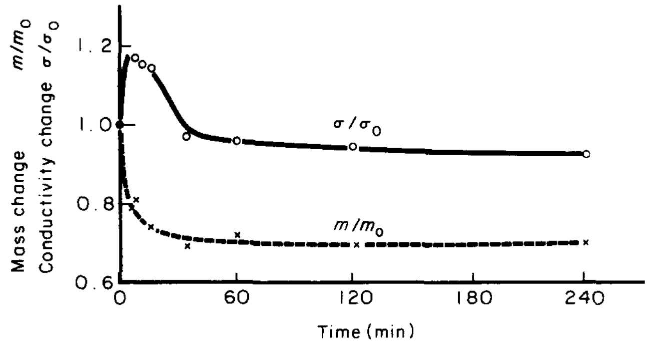

Figure 5 Conductivity and mass change of poly(pyrrole phenylsulphonate) film exposed to 10% H_2SO_4. σ_0 and m_0 are the initial conductivity and mass, respectively, σ and m are the corresponding quantities after a treatment for a time t

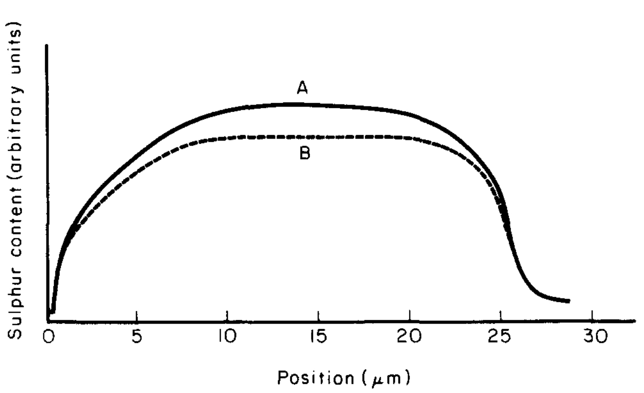

Figure 6 Sulphur distribution within a poly(pyrrole phenylsulphonate) film of thickness 30 μm before and after treatment with sulphuric acid (EDX measurements): A, initial sample; B, sample treated with 10% H_2SO_4 for 240 min

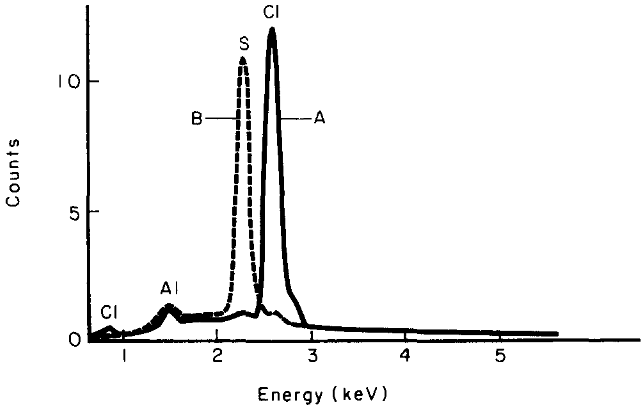

Figure 7 Ion exchange in a poly(pyrrole perchlorate) film of 20 μm thickness by treatment with sulphuric acid as measured by EDX: A, initial sample; B, sample treated with 10% H_2SO_4 for 240 min

An ion exchange due to the treatment with sulphuric acid can clearly be seen in experiments using poly(pyrrole perchlorate) (*Figure 7*). After an exposure of this sample to 10% H_2SO_4 for 240 min, the distinct Cl-peak of the initial film has almost completely disappeared. Perchlorate is replaced by a sulphur-containing counterion as the pronounced sulphur peak indicates.

The treatment with sulphuric acid improves the stability with regard to the conductivity of the two different polypyrrole salts remarkably as the ageing behaviour at 140°C in *Figure 8* demonstrates. In the case of the poly(pyrrole perchlorate) the conductivity becomes distinctly higher owing to the exposure to sulphuric acid. For poly(pyrrole phenylsulphonate) a slight decrease in conductivity is observed (cf. *Figure 5*). The improvements of the stabilities are comparable if one takes the smaller film thickness of the poly(pyrrole perchlorate) into account.

ALTERNATING TREATMENT WITH BASE AND ACID

The conductivity decrease of a poly(pyrrole phenylsulphonate) film by base treatment is reversed following exposure to sulphuric acid, as can be concluded from the results shown in *Figure 9*. The electrical conductivity, which has become smaller by more than three decades after treatment with 10% NaOH for 4 h, nearly reaches its initial value after exposure of the film to 10% sulphuric acid for the same time period. The alternating treatments with base and acid result in a cyclic behaviour for the

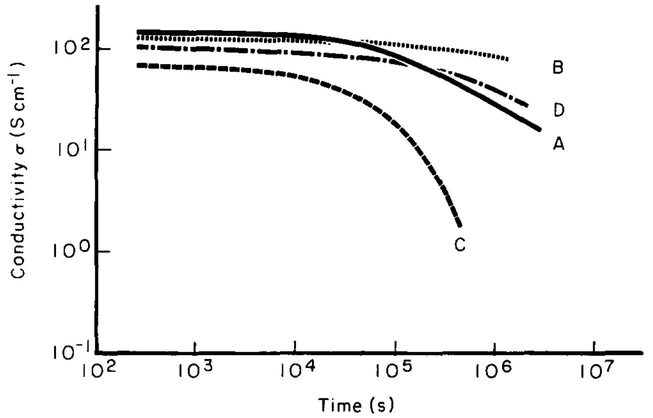

Figure 8 Change of ageing behaviour of two polypyrrole films with different counterions after treatment with sulphuric acid. Ageing temperature: 140°C. Treatment: 240 min. A, poly(pyrrole phenylsulphonate) (30 μm); B, poly(pyrrole phenylsulphonate) treated by 10% H_2SO_4; C, poly(pyrrole perchlorate) (20 μm); D, poly(pyrrole perchlorate) treated by 10% H_2SO_4

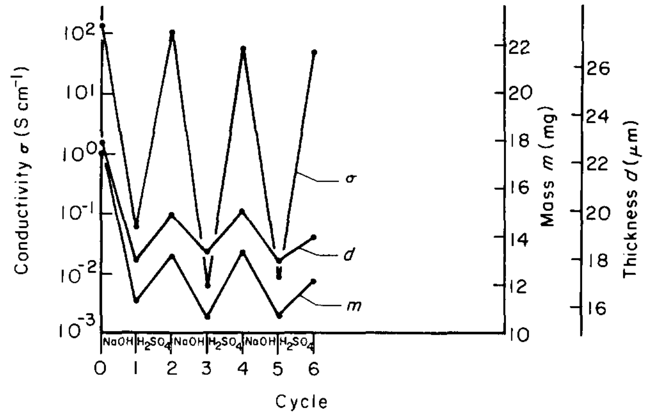

Figure 9 Changes in conductivity, mass, and thickness of a poly(pyrrole phenylsulphonate) film of 30 μm thickness by alternating exposures to aqueous sodium hydroxide and sulphuric acid

conductivity. A similar effect has been observed with polypyrrole using NaOH and HCl[2].

The maximum conductivity slightly decreases with the number of cycles. Parallel to the change in conductivity a cyclic variation of the mass and the thickness of the film is observed (*Figure 9*). This result indicates the exchange of anions if one assumes a constant degree of oxidation. The mass and the thickness of the film exposed to sulphuric acid after the first base treatment do not reach the initial value of the unmodified polypyrrole film.

A qualititatively similar behaviour is found after treatment for only 10 min with base and acid and, as expected, the effects are less pronounced.

Besides the rise in conductivity of a NaOH-treated polypyrrole film following exposure to sulphuric acid, a stabilizing effect is also observed. Four hours as well as the fourteen hours exposure of the previously NaOH-treated polypyrrole to aqueous sulphuric acid increases the long-term stability at 140°C significantly. Whereas the conductivity of the initial sample has decreased by a factor of two after 40 h the comparable ageing of the film modified with NaOH and then for 14 h with H_2SO_4 takes about 100 days. After that time the other polypyrrole film exposed for 4 h to H_2SO_4 has lost only 30% of its initial conductivity. These findings correspond to the stabilizing effect observed with polypyrrole which has been treated with H_2SO_4 alone (cf. *Figure 8*).

The EDX spectra show that the sulphur content, after the NaOH- and H_2SO_4-treatments of the film, is very close to that of the initial sample. This finding of a nearly unchanged sulphur content together with the observed loss of weight confirms the assumption that the phenylsulphonate is replaced by HSO_4^- and not by SO_4^{2-} which could compensate two positive charges of the polypyrrole resulting in a distinctly lower sulphur content.

ION EXCHANGE KINETICS RESULTS

From the sulphur distribution measured by EDX an interesting insight into the ion exchange kinetics can be obtained. According to *Figure 10* the sulphur concentration after a 10 min NaOH-treatment has almost decreased homogeneously over the sample thickness. The following exposure of 10 min to sulphuric acid fills only the area close to the film surfaces with sulphur containing ions whereas the sulphur content in the centre of the sample remains almost unchanged. This result leads us to the conclusion that the anions of the phenylsulphonate diffuse faster out of the film than the ions of the sulphuric acid into it. Because of the smaller size of the latter this finding seems to be reasonable only if one assumes a change of morphology of the polypyrrole induced by the ion exchange.

The role of diffusion processes in the ion exchange becomes clearer from the results shown in *Figures 11* and

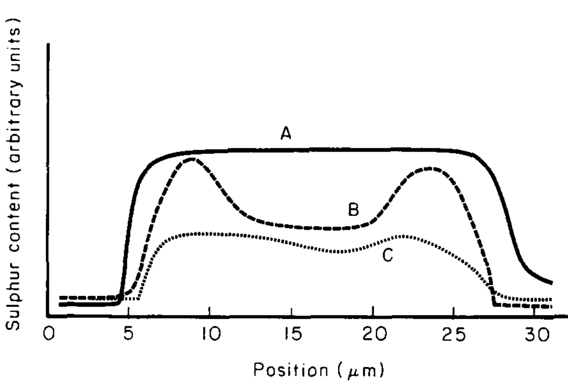

Figure 10 Sulphur distribution of poly(pyrrole phenylsulphonate) films of thickness ~30 μm after different short treatments with NaOH and H_2SO_4 (EDX measurements): A, initial sample; B, sample treated with 10% NaOH and 10% H_2SO_4 for 10 min each; C, sample treated with 10% NaOH for 10 min

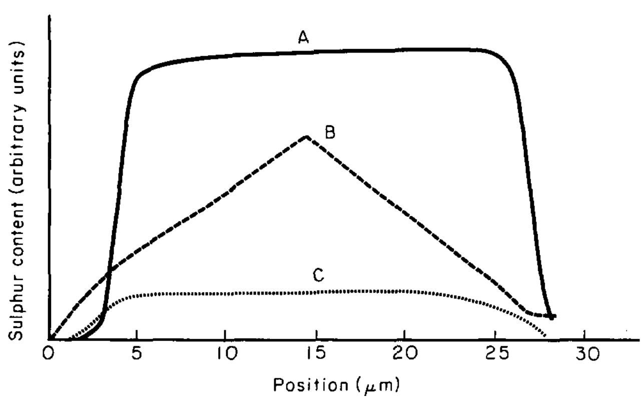

Figure 11 Sulphur distribution as a function of the exposure time to NaOH for a thin poly(pyrrole phenylsulphonate) film (thickness ~30 μm): A, initial sample; B, sample treated with 2% NaOH for 15 min; C, sample treated with 2% NaOH for 240 min

12. They represent the sulphur distribution of two polypyrrole films of different thicknesses treated in the same way with 2% NaOH. Whereas the sulphur content of the thinner film has homogeneously decreased after the base treatment for 240 min (cf. *Figure 11*), the original sulphur content is found to be almost unchanged in the centre of the thicker sample (*Figure 12*). After a treatment of 15 min the base has attacked only the outer layers. In the case of the thinner film this time is sufficiently long to remove any sulphur containing ions from the centre of the film also.

DISCUSSION

Change of conductivity

The main feature of the base and acid treatments is the ion exchange, which has to be regarded as the reason for the change in conductivity. The elemental analysis confirms the removal of the phenylsulphonate or perchlorate anions by the NaOH treatment (*Tables 2* and *3*). From the 8.5 wt% sulphur of the untreated sample only 0.8% is found after a 240 min exposure of the 30 μm film to 2% NaOH. The 90 μm film treated under the same conditions contains 3.1% sulphur and the sodium content is negligible. In the case of the 20 μm poly(pyrrole perchlorate) film a negligible amount of chlorine is found after a 120 min NaOH treatment (*Table 3*). The exposure of the original film to 10% sulphuric acid for 240 min results in a decrease in the chlorine content from 9.1 to 0.5% while the sulphur content increases up to 6.8%. Once again only traces of sodium could be detected analytically. This result clearly confirms the EDX findings that ClO_4^- is exchanged by a sulphur-containing ion from the sulphuric acid. From a weight balance it seems probable that ClO_4^- is replaced by HSO_4^-.

For NaOH treatment the insertion of OH^- can be assumed as the process of retaining the electroneutrality of the sample. Infra-red studies, however, give no indication for such a reaction. A simple calculation which starts from the assumption of an exchange of the phenylsulphonate by OH^- shows that the measured weight loss of the initial polypyrrole, by its exposure to NaOH as given in *Figure 9*, can quantitatively be described. Our hypothesis is that OH^- forms covalent bonds with polypyrrole. This reaction decreases the conjugation length and following from that the conductivity becomes lower. This explanation is in contrast with the assumption of a deprotonation of the NH bonds in alkaline solutions postulated in ref. 2. Exposing polypyrrole to sulphuric acid results in an exchange of ions only. No covalent bonding occurs and the conductivity remains almost unchanged.

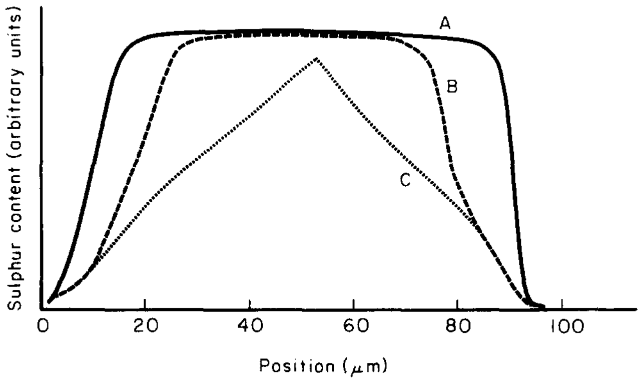

Figure 12 Sulphur distribution as a function of the exposure time to NaOH for a thick poly(pyrrole phenylsulphonate) film (thickness ~90 μm): A, initial sample; B, sample treated with 2% NaOH for 15 min; C, sample treated with 2% NaOH for 240 min

Table 3 Elemental analysis of a poly(pyrrole perchlorate) film treated with base and acid

Sample	Weight [%]		
	S	Na	Cl
PPy perchlorate ($d = 20$ μm)	<0.4	–	9.1
treated 15 min with 2% NaOH	–	<0.10	3.2
treated 120 min with 2% NaOH	–	0.42	<0.5
treated 240 min with 2% NaOH	<0.5	–	–
treated 15 min with 10% H_2SO_4	1.8	–	6.3
treated 120 min with 10% H_2SO_4	6.2	–	0.9
treated 240 min with 10% H_2SO_4	6.8	–	0.5

In the special case of the alternating conductivity change by base and acid treatments (cf. *Figure 9*) one has to assume that the reaction which leads to covalent bonds between polypyrrole and OH^- can be reversed in an acidic medium. The electroneutrality is maintained by the insertion of anions from the acid and the conjugation length is restored, leading to an increase in conductivity.

This process does not seem to be completely reversible, however, as can be concluded from the slightly decreased maximum values of the conductivity after the repeated treatment with sulphuric acid (cf. *Figure 9*). This result gives some hint to a small irreversible part of the reaction between polypyrrole and OH^- which gradually decreases the conjugation length.

Improvement of stability

The most surprising feature of the base and acid treatment is the remarkable improvement of the ageing behaviour measured at 80°C and 140°C. In the case of the polypyrrole films with a lowered conductivity these findings could be explained by assuming a blocking along the chain of all the sites which could react with oxygen and water from the air by the OH^--anions from the base. Such an argument does not hold, however, for the ion exchange with sulphuric acid, which leaves the conductivity nearly unchanged. The measured decrease in sample thickness shown in *Figure 9* gives rise to the idea that a change in morphology and, following from that, a decrease of the permeability of oxygen and water vapour, could be the reasons for the improved stability.

The results of the measurements of the permeabilities of oxygen and water vapour are given in *Tables 4* and *5* for three polypyrroles. Sample A is the untreated poly(pyrrole phenylsulphonate) film, sample B has been exposed for 240 min to a 10% sulphuric acid, and sample C for the same time to a 10% solution of NaOH in water. As can be seen from the data the permeability of oxygen is remarkably reduced by these treatments. Nearly independent of temperature in the range between 23°C and 80°C, the permeability is found to have decreased by a factor of two for the poly(pyrrole phenylsulphonate) treated with H_2SO_4 and by a factor of three for the sample exposed to NaOH.

The permeability of water vapour shows a different behaviour compared with the permeability of oxygen (cf. *Table 5*). For the sample treated with NaOH the

Table 4 Permeability for oxygen of differently treated polypyrrole salt films

	O_2-permeability $\left(\frac{cm^3 \cdot 100\,\mu m}{m2\,dbar}\right)$		
T[°C]	A	B	C
23	18	8	6
40	54	26	19
60	272	160	97
80	1186	681	367

A: initial sample
B: treated with 10% H_2SO_4 for 240 min
C: treated with 10% NaOH for 240min

Table 5 Permeability for water vapour of differently treated polypyrrole salt films

	H_2O-permeability $\left(\frac{cm^3 \cdot 100\,\mu m}{m^2\,dbar}\right)$		
T[°C]	A	B	C
23	39	58	24
40	76	107	47
60	277	344	139
80	664	801	275

A: initial sample
B: treated with 10% H_2SO_4 for 240 min
C: treated with 10% NaOH for 240min

permeability is half of the value of the initial polypyrrole film. According to *Table 5* the treatment with H_2SO_4 even increases the permeability of the water vapour by about 25%.

For the discussion of the influence of the acid and base treatment on the ageing measurements of polypyrrole at 80°C and 140°C the permeability of oxygen is of stronger relevance than that of water vapour because of the low humidity of air at these elevated temperatures. Taking this into account the improvement in stability of poly(pyrrole phenysulphonate) films treated with H_2SO_4 or NaOH can be understood from the permeability data for oxygen, at least on a qualitative basis. Even the slightly higher stability of the base-treated polypyrrole film in comparison with the film exposed to sulphuric acid (cf. *Figure 4* and *Figure 8*) can be related qualitatively to its somewhat lower permeability.

The different changes for the permeabilities of oxygen and water vapour by the NaOH- and the H_2SO_4-treatments suggest an experiment from which an insight into the role of humidity and oxygen for the ageing process of polypyrrole could be expected. Because of the small variation of the permeability of water vapour by the H_2SO_4 treatment this modification should hardly influence the ageing behaviour at a high humidity if water is mainly responsible for the decrease in conductivity. Experiments of this nature are under way.

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