Water-soluble self-doped 3-substituted polypyrroles

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micrographs in Figure 10 support the conclusion that pillaring results in the formation of galleries who’s volume contributes mostly to the porosity of the material. Second, another argument is provided by data concerning the alkylammonium intercalates (used for indirect-exchange processes). Indeed, these products exhibit high order along the swelling axis, as evidenced by the strong 0/k, reflections, and it is easy to show that the area covered by the intercalated alkylammoniums is very close to the theoretically calculated area available to the Al pillars (from \(Q^0/Q^4\) ratios: cf. supra). By use of the experimentally observed degrees of exchange \((2z \approx 0.3 \text{ in } (\text{RNH}_2)_2H_2\text{SiO}_2\cdot y\text{H}_2\text{O})\) and assuming that the alkylammonium chains oriented perpendicular to the layers covering an area of 25 \(Å^2\), the surface area available for intercalation in the silicate network would be \(~345 \text{ m}^2/\text{g}\). This value is close to those reported in Table VI. In addition, we have shown that, by using ethylammonium fluoride intercalates (where some of the gallery silanols are replaced with fluoride), the amount of Si–O–AlIV and of nonframework aluminum is dramatically reduced. Thus, there are clear indications that pillaring occurs to a large extent in the interlayer gallery.


Conclusion

KHSiO, and its intercalation products have been exchanged with solutions containing Al polyhydroxy polymers.

During the exchange process, three competing reactions may happen, namely, (1) hydrolysis of the solid with partial delamination and, in unfavorable cases, amorphization; (2) condensation of hydrolyzed layers with siloxane bridge formation; (3) pillaring by aluminum polymer cations.

In spite of this competition, Al pillaring is most probably extensive enough that high surface areas can be obtained without noticeable destruction of the lattice; an alternate explanation in terms of bulk amorphization cannot be definitely ruled out, but there exist considerable indirect evidence to make this explanation rather unlikely.

These high surface area products are stable at least until 300 °C for most exchange products, and preliminary work on ethylammonium fluoride intercalation-mediated ACH exchange indicates that they could be stable up to 500 °C. The intercalation process seems to proceed through initial grafting of A1IV in the interlayer gallery, followed by charge compensation by Al-containing polymers.

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Water-Soluble Self-Doped 3-Substituted Polypyrroles

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The preparation of sodium salts of 3-alkylsulfonate pyrroles with various lengths of the alkyl chain (propyl-, butyl-, and hexylsulfonate) and their electrochemical polymerization to poly(3-alkylsulfonate pyrroles) are described. The low oxidation potential of the monomers allows a direct oxidative electrochemical polymerization, without additional conduction salts. The experimental conditions provide, for the first time, solid evidence of the existence of self-doped conducting polypyrroles. The polymers are characterized by spectroscopy (FTIR, UV–vis–NIR, ESR, 'H NMR in D2O solution), X-ray diffraction, cyclic voltammetry, and elemental analyses. The covalently attached sulfonate groups act as counterions for the charged backbone. The charge carriers are mainly spinless bipolarons. The conductivities are in the range \(0.5–10^{-3} \text{ S/cm}\), the lower value referring to the hexyl chain. Indications are given for deviations from planarity of the main chain. The substituted polypyrroles are water soluble in the self-doped state. 'H NMR spectra of the aqueous solutions of self-doped polymers are discussed.

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Introduction

Extended conjugated polymers can, in general, be transformed into conducting materials by doping. In the doping procedure, a reduction (to n-type doping) or oxidation (to p-type doping) yields highly charged polymer backbones. The charges are neutralized by counterions. In all traditional conducting polymers the counterions are absent in the neutral polymer and have to be injected into the polymer to provide doping. The doping process is often reversible, and the counterions or other neutralizing ions can move in and out many times. In self-doped conducting polymers, however, the counterions are covalently attached to the polymer backbone. The concept of self-dope of conducting polymers has been introduced by Patil et al. In contradistinction with other doped polymers, dedoping of these self-doped polymers cannot be obtained by out-diffusion of the counterions but should be performed by in-diffusion of foreign cations. Moreover, the polymers in the self-doped state proved to be slightly soluble in water.

The first-reported self-doped polymers were poly(3-alkylsulfonate thiophenes) 1a,b, obtained by hydrolysis of...
polysulfonate thiophene) methyl esters. The latter were prepared by electrochemical polymerization of the corresponding monomeric thiophenes. Since the synthesis of the doped polymers was performed in the presence of "foreign" conducting salts, various experiments and arguments were put forward to prove self-doping, including cyclic voltammetry experiments combined with pH measurements in organic solvents.

Using a 3'-propylsulfonate 2,2':5',2'-terthienyl, we were able to polymerize the potassium salt of this monomer directly by electrochemical oxidation without the interference of foreign ions. In this case, the monomer itself also acts as the conduction salt during the electrochemical polymerization, resulting in solid evidence for self-dope. The self-doped poly(3'-propylsulfonate 2,2':5',2'-terthienyl) (2) is soluble in water. However, the stability of the aqueous solutions proved to be unsatisfactory. Stable solutions of self-doped polymers are required to prepare conducting films from these solutions.

The reduction potential of doped polypyrroles is higher than that of the doped polythiophenes. Therefore, soluble conducting polypyrroles are expected to be more stable with respect to dedoping than the corresponding polythiophenes, and recently a few approaches to self-doped polypyrroles have been presented. Attempts to arrive at N-substituted polypyrroles were successful in the case of copolymers of pyrrole and N-alkylsulfonate pyrroles and recently for the homopolymers as well.

However, in most of these cases too no solid proof of self-doping was presented, because foreign conducting salts were present during the electrochemical synthesis and were recovered in the polymers. Moreover, it is well-known that N-substituted polypyrroles show very modest conductivities. The self-doped N-substituted polypyrroles are no exception to this rule. For that reason it is of profound interest to study poly(3-alkylsulfonate pyrroles) as more ionic monomers. The electrochemical polymerization used for 3'-propylsulfonate 2,2':5',2'-terthienyl, we were able to polymerize the potassium salt of this monomer in aqueous solutions proved to be unsatisfactory. Stable solutions of self-doped polymers are required to prepare conducting films from these solutions.

In this paper we report on the synthesis of sodium salts of 3-alkylsulfonate pyrroles with various lengths of the alkyl side chain and describe the polymerization of these ionic monomers. The electrochemical polymerization used will afford "purely" self-doped conducting polypyrroles. The polymers are characterized in detail by using a variety of techniques. A short preliminary note on this subject has been published.

**Experimental Section**

**Apparatus.** All electrochemical work was carried out by using a Wenking Potentiostat POS 73. X-ray diffraction patterns were obtained with the aid of a Philips automatic diffraction unit PW 1730 using Cu Kα radiation, starting with θ = 2°. IR spectra were recorded on a Bruker IFS 45 FTIR spectrometer. NIR–vis–UV spectra were recorded on a Beckman Acta MIV spectrophotometer, while the UV–vis were recorded on a Varian Supercans 3. H NMR spectra were recorded at 60 MHz with a Perkin Elmer R-24B, at 80 MHz with a Bruker WP 80 S, at 300 MHz on a Varian VXR300, and at 500 MHz on a Varian VXR500 spectrometer. The spectra of the polymers were recorded by using D₂O as solvent with solvent suppression of the remaining H₂O. 13C NMR spectra were recorded at 20.13 MHz on a Bruker WP 80 SY. ESR spectra were recorded on a Bruker ESR spectrometer ER 220D SR. SEM photographs were taken on a Philips 525.
gammated zinc is added (from 240 g of fine powder zinc and 20 g of HgCl₂, prepared as described in ref 15), followed by 400 mL of concentrated HCl. The mixture is heated under gentle reflux with good stirring for 2.5 h (in such a way that the foaming is not too excessive). During this heating period another 150 mL of concentrated HCl is added in 50-mL portions, each time after most of the foaming has stopped. The progress of the reaction can easily be followed by HNMR. After cooling, the layers are separated, and the water layer is extracted with toluene; the combined organic layers are washed with water, dried, and evaporated to yield 86 g of 8 as an oil that tends to darken on standing; ¹H NMR (CDCl₃) δ 1.5–1.9 (m, 4H), 2.05 (t, 2H), 2.5 (t, 2H), 6.1 (m, 1H), 6.8 (br s, 1H), 7.0 (m, 1H), 7.2–7.5 (m, 5H).

4-(3-Pyrrolyl)butanesulfonic Acid, Sodium Salt (11). A mixture of 17.6 g (59.2 mmol) of the crude hydrochloride 8, 175 mL of water, 70 mL of ethanol, 17.5 g of Na₂SO₃, 2 g of tetrabutylammonium bromide (the necessity of adding this phase-transfer catalyst was not explored), and 2.6 g of NaOH is heated under reflux for 18 h. To this mixture 17.6 g of NaOH is added, and an additional 1.5 h of heating under reflux is followed by the addition of 150 mL of brine. The cooled reaction mixture is extracted twice with CHCl₃. The organic layer is washed with some water, and the combined aqueous layers are evaporated. The residue is boiled with 200 mL of water and then allowed to cool to room temperature. The resulting paste is filtered with suction, and the solid is washed twice with 25 mL of brine. The filtrate, which by ¹H NMR contains benzenesulfonic acid only, is discarded. The still-wet solid is boiled with 250 mL of 96% ethanol and 10 mL of 2-chloroethanol to give a neutral suspension. This suspension is filtered while hot, and the hot solid is boiled with 100 mL of 96% ethanol and filtered while hot, and the solvent of the combined filtrates is evaporated completely. The residue is then treated with 250 mL of 90% ethanol, boiled, and filtered while hot. Again the filtrate is evaporated completely. The residue is heated with 150 mL of 96% ethanol and 5 mL of water. After cooling to room temperature, the solution is filtered to remove some colored impurities, and the filtrate is then cooled to −15 °C. The crystalline product is filtered with suction and washed with 96% ethanol and acetone to give 3.0 g of 11. The filtrates are evaporated, and the residue is recrystallized from 75 mL of 96% ethanol and 1 mL of water. After this cools to −15 °C, another 2.57 g of product is obtained. A total yield of 40% is obtained on the basis of N-(phenylsulfonyl)pyrrole (5.57 g, 24.76 mmol). The material is hygroscopic and therefore contains traces of water. No melting point could be detected due to decomposition; ¹H NMR (D₂O) δ 1.4–1.7 (m, 4H), 2.3 (t, 2H), 2.8 (t, 2H), 5.9 (m, 1H), 6.45 (br s, 1H), 6.6 (m, 1H); ¹³C NMR (D₂O/CH₃OH) δ 24.3 (t), 28.1 (t), 29.9 (t), 51.3 (t), 107.8 (d), 115.9 (d), 115.7 (d), 123.6 (d); static SIMS (negative ion spectrum) 202.5 (M) +.

1-(Phenylsulfonyl)-3-pyrrolyl)-3-chloropropane (4). This compound is obtained in a way identical with that described for 5 from 55.8 g of AlCl₃ (0.440 mol), 56 g of 3-chloropropionyl chloride (0.457 mol), and 68.3 g of N-(phenylsulfonyl)pyrrole (0.330 mol) in 500 mL of CH₂Cl₂. The crude product is obtained as an oil that solidifies on standing and is used as such in the next step; mp 52–54 °C (from CH₂Cl₂); ¹H NMR (CDCl₃) δ 1.1–2.0 (m, 6H), 2.7 (t, 2H), 3.3 (t, 2H), 6.6 (m, 1H), 7.1 (br s, 1H), 7.2–8.0 (m, 6H); exact mass 383.016 (calc 383.019).

1-(Phenylsulfonyl)-3-pyrrolyl)-6-bromo-1-hexanone (6). A mixture of 6-bromohexanoic acid (0.132 mol) and 30 mL of thionyl chloride is heated under gentle reflux. The crude acid chloride, obtained after filtration, is converted to 6 by using the procedure described for 5 using 18.5 g of AlCl₃ (0.139 mol) and 27.0 g of N-(phenylsulfonyl)pyrrole (0.130 mol) in 200 mL of CH₂Cl₂. The crude product, being an oil that solidifies on standing, is used as such in the next step; mp 52–54 °C (from CH₂Cl₂); ¹H NMR (CDCl₃) δ 1.5–2.2 (m, 2H), 2.2–2.9 (m, 2H), 5.9 (m, 1H), 6.45 (br s, 1H), 6.6 (m, 1H); ¹³C NMR (CD₂Cl₂/CH₃OH) δ 25.0 (t), 25.7 (t), 50.8 (t), 107.4 (d), 115.8 (d), 118.6 (d), 122.4 (s); static SIMS (negative ion spectrum) 182.5 (M) +.

1-(Phenylsulfonyl)-3-pyrrolyl)-6-bromohexane (9). Clemmensen reduction of the crude 6 as described for 5 affords 41.5 g of an oil (which tends to darken on standing) which is pure by ¹H NMR. It is used as such in the next step; ¹H NMR (CDCl₃) δ 1.2–1.6 (m, 8H), 2.3 (t, 2H), 5.9 (t, 2H), 6.0 (m, 1H), 6.7 (br s, 1H), 6.9 (m, 1H), 7.1–7.8 (m, 5H).

1-(Phenylsulfonyl)-3-pyrrolyl)-6-hexane-1-sulfonic Acid, Sodium Salt (12). To a mixture of 30 g of the crude bromide 9, obtained above, 30 g of Na₂SO₃, 3.5 g of tetrabutylammonium bromide, 6.5 g of NaI, and 200 mL of water at ca. 70 °C is added 180 mL of 96% ethanol over 90 min. The suspension is heated under reflux for 20 h, 20 g of NaOH is added, and the mixture is heated under reflux for 90 min, while allowing part of the ethanol to distill off. To the cooled residue 150 mL of brine is added, and the mixture is extracted with 2 × 150 mL of chloroform. The organic layers are washed with 100 mL of water, and the aqueous layers are evaporated. The residue is recrystallized from 250 mL of water, and the precipitate that is formed on cooling is filtered with suction and washed with 50 mL of brine (according to ¹H NMR spectroscopy the filtrate contains sodium benzenesulfonate only). The still-wet solid is boiled with 200 mL of ethanol and 10 mL of 2-chloroethanol and filtered while hot. The filtrate is completely evaporated, and the residue is boiled with 100 mL of 96% ethanol and 5 mL of water and filtered while hot. The filtrate is cooled to room temperature, filtered again (and washed with some absolute ethanol), and then evaporated, giving a slightly colored product. According to ¹H NMR the filtrate contains a mixture of sodium benzenesulfonate and 12 (ca. 1:2 ratio); no attempt was made to isolate more 12 from this filtrate; yield 7.65 g (30.24 mmol, 36% based on N-(phenylsulfonyl)pyrrole); ¹H
NMR (D$_2$O) δ 1.0–1.9 (m, 8 H), 2.3 (t, 2 H), 2.7 (m, 2 H), 5.9 (m, 1 H), 6.45 (br s, 1 H); 6.6 (m, 1 H); static SIMS (negative ion spectrum) 230.

Polymerizations. Electrochemical polymerizations were carried out in acetonitrile (Merck, pa) as received. Pure nitrogen (<2 ppm O$_2$) was always bubbled through the solutions before and during the reactions, and magnetic stirring was applied. Before use, Pt electrodes were scrubbed with fine sandpaper, etched in 1 M HCl in water, rinsed with water, and dried. ITO glass electrodes were used as received. In a typical one-compartment experiment two Pt electrodes (wetted surface 3 × 1.5 cm$^2$) are put into a 150-mL glass beaker 1 cm apart, and a standard calomel electrode with saturated KCl in water (SCE) is placed such that its tip just faces the edge of the working electrode. The beaker is filled with a suspension, partly solution, of the monomer. After an adaptation time of about 5 min, the wanted potential (typically 1.4 V, SCE) is slowly applied to the working electrode, and the current (about 0.5–1 mA) is monitored.

After about 80% of the theoretically needed integrated current has passed through the cell, the electrodes are removed from the solution, rinsed with pure acetonitrile, and dried. The yield of polymer is determined by weighing the working electrode before and after the deposition of the polymer. In general one needs about 2.5 electrons per molecule of monomer for the polymerization reaction (for a doping level of 2.5 holes per ring the theoretical value is 2.25 electrons). In a number of experiments we added a conduction salt (0.05 M solution in acetonitrile of NaBF$_4$, JanusChemics 99%, or 0.03 M solution of NaBP$_4$, Riedel deHaen, pure). With the same voltage the current increased up to a factor of 5.

The polymeric layers formed in this way are rather incoherent, especially when the thickness exceeds 1 μm. More coherent films are obtained if the procedure above is carried out in an ultrasonic field or in a two-compartment cell. In the latter the counter-electrode was put in a department filled with the conduction salt solution in acetonitrile, separated by a glass frit from the monomeric solution/suspension in acetonitrile.

The chemical polymerizations of 10–12 using FeCl$_3$ were performed analogous to the Armes' method for pyrrole.\(^\text{18}\)

Chemical Element Analysis. The elements C, H, N, and S were determined by standard organic element analysis methods, using a separate burning method for S. O was determined by a pyrolysis method (as CO). Na and Fe were determined after a wet destruction method by flame atomic absorption and ICP emission spectroscopy, respectively. Cl was determined titrimetrically after a Schoniger destruction. The same methods applied to the monomers yielded a total amount retraced of 95–99%. For the polymers, however, we always got results adding up to about 95–98% at most. The reason for this is not clear. A second method was carried out in which the samples were washed carefully; only a bit of chlorine and traces of other elements were detected, adding up to at most 0.5%. For this reason the results of the analyses are still somewhat doubtful. The estimated maximum relative error in the individual determinations is at most 3%, except for O and H, where it may amount to 5%. As we set the carbon content as a standard, this means that differences between observed and calculated values for O and H should be larger than 6% to be significant, while for the other elements at 4% level is appropriate.

ESR Measurements. ESR spectra of several samples were determined with the use of a Bruker ESR spectrometer ER 220D SR. Integrated intensities were measured relative to a standard of DPPH (FlukaChem, prakt). As a double check, some polypyrrole samples were measured as well. As usual, the results of the number of spins for the same compounds are reproducible only within about a factor of 2.

Resistance. The resistivity was measured by a four-probe method. Film thickness was measured with DEKTAK 3000. By variation of the applied voltage, the Ohmic behavior of the resistivity was checked, and its electronic character was verified


\(^{\text{17}}\) Tourillon, G., in ref 1, p. 296.


Results

Synthesis of Pyrrole Monomers. The basis of our route toward the desired pyrrole monomers involves acylation in the 3-position of pyrrole with a suitable ω-halo acid chloride, followed by a Clemmensen reduction to give 3-(ω-haloalkyl)pyrrole, which is subsequently converted to the required sulfonated alkylypyrrole. Access to pyrroles acylated in the 3-position is possible by first protecting pyrrole as the N-(phenylsulfonyl) derivative with benzenesulfon chloride under phase-transfer conditions, followed by acylation under Friedel–Crafts reaction conditions and deprotection with base. Several 3-acylpyrroles have been obtained by using this technique.\(^\text{13,14}\) Conversion to the corresponding 3-alkylpyrroles is best accomplished using the Clemmensen reduction on the N-protected acylylpyrrole followed by deprotection.\(^\text{14,15}\)

Our route to 3-alkylsulfonate pyrroles is sketched in Scheme I. N-(Phenylsulfonyl)pyrrole (3) is readily acylated with 3-chloropropionyl chloride, 4-chlorobutryl chloride, and 6-bromohexanoyl chloride by using AlCl$_3$ in CH$_2$Cl$_2$. The stable, protected, acylpyrroles 4–6 are then reduced by the Clemmensen reduction to the corresponding protected 3-(ω-haloalkyl)pyrroles 7–9.

As expected, the preparation and purification of the sulfonated alkylpyrroles presented some problems in our planned route. Reaction of 7–9 with Na$_2$SO$_3$ in the presence of Bu$_4$NBr\(^\text{16}\) and NaI under specific conditions for each compound gives the N-protected sulfonated alkylypyrrole, which is deprotected without previous isolation with NaOH to give a mixture of the desired sodium 3-alkylsulfonate pyrrole, sodium benzenesulfonate, and other salts. Isolation and purification of the compounds 11 and 12 is possible due to their lower solubility in water as compared with sodium benzenesulfonate and the other salts. However, the homologue with the propylene group, 10, could not be treated in this way because its solubility
in water is almost equal to that of sodium benzenesulfonate. Therefore, the disturbing presence of another sulfonate in the final reaction mixture was circumvented by first deprotecting the intermediate 7 by heating a solution with a base in an alcohol. During this reaction part of the chloride is replaced by an alkoxy group, and the best procedure found with respect to rate of alcoholysis and deprotection is refluxing for 1.5 h in ethanol. The resulting mixture of the deprotected pyrroles 13 and 14 can be readily transformed into the desired 3-propylene (sodium sulfonate) pyrrole, which can now be purified. Attempts to circumvent this complication by protecting pyrrole with two other sulfonyl halides, viz., 4-chlorobenzenesulfonyl chloride and methanesulfonyl chloride, were not completely successful. Applying to these protected pyrroles the same reaction sequence as outlined above resulted in a mixture of 10 and other salts. In spite of a slightly higher (lower) solubility in water of sodium methanesulfonate (sodium 4-chlorobenzenesulfonate) as compared with that of sodium benzenesulfonate, a complete separation via crystallization proved to be still impossible.

**Synthesis of Polymers.** In the majority of cases we prepared the polymers 15–17 by electrochemical oxidation (Scheme II). The sodium 3-alkylsulfonate pyrrole 10, 11, or 12 is dissolved in acetonitrile to give a saturated solution (about 0.5 g/L), and excess of the solid monomer is suspended. No additional conduction salt has to be added for the electrochemical polymerization process, as the monomer itself also acts as the conduction salt. During polymerization the monomer dissolves gradually, and the polymer forms an insoluble bluish-black layer on the anode. If the reaction is carried out until completion, we are left with a clear and colorless liquid phase. However, since the yield of polymer with respect to the current passed through the cell decreases in the final stages (probably due to side reactions), we normally stopped the polymerization at an earlier stage.

Elemental analysis of the polymers proved to be rather difficult. In spite of extensive searches for possible errors in the procedures, only 95–98% of the total composition could be recovered. Therefore, we compare only relative quantities, and the results are given in Table I (more details are given in the Experimental Section). In general, the data observed are in good agreement with those calculated for the elements C, H, N, O, and S. The data show further that only a limited number of sodium ions are present in the polymer.

The oxidation potentials of the monomers 10 and 11, determined from the potentiodynamic i–V curve in saturated solutions of monomer in acetonitrile with Pt electrodes, are around 0.65 V vs SCE, while for 12 a somewhat higher value (0.7 V vs SCE) is observed. These values are similar to the value found for pyrrole itself (0.8 V vs SCE). The polymerization has to be carried out at potentials below 1.7 V vs SCE. If higher polymerization potentials were used, we obtained evidence from elemental analysis that a proportion of the sulfonate groups is split off, giving rise to a water-insoluble polymer that is probably slightly cross-linked.

During the polymerization process the polymers formed are in the doped state (see below), just as in the case of polypyrrole. In a one-compartment cell the state of doping of the polymer deposited on the anode decreases gradually during the process, resulting in slightly inhomogeneous films. The electrochemical polymerization reaction is preferentially carried out in a two-compartment cell, leading to more homogeneous films.

The electrochemical polymerization can also be carried out in solutions of the monomers in water. At low monomer concentrations no polymer is deposited on the anode, but the aqueous solution darkens. The polymer formed remains in solution and, in view of the UV–vis–NIR spectra, is largely in the undoped form. At high concentrations of 11, polymer 16 is formed at the anode as an incoherent film. With all spectroscopic analyses used, it proves to be similar to samples of 16 prepared in acetonitrile.

To increase the current density during the electrochemical polymerization reaction, we sometimes added sodium or tetrabutylammonium boron tetrafluoride (0.03, 0.05 M, respectively) as a conduction salt. Element analysis showed that the polymers prepared by adding a conduction salt contain only minor concentrations (<1% by weight) of BF₄⁻ ions.

Another way of polymerizing 10–12 is via a chemical route using FeCl₃ as oxidant. This method is known to be successful for pyrrole. In our case the polymers formed precipitate from the aqueous reaction mixture. Elemental analysis (Table I) showed that substantial amounts of Fe, about one ion to three pyrrole rings, are present in these polymers. As we did not yet determine the valency and the specific role of Fe in these polymers, most experiments discussed in this paper are carried out

**Table I. Elemental Analysis of the Monomers and Polymers**

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<td>14.6</td>
<td>5.5</td>
<td>0.02</td>
<td>0.07 Cl, 0.34 Fe</td>
</tr>
<tr>
<td>17, obs</td>
<td>10</td>
<td>1.04</td>
<td>1.01</td>
<td>15.8</td>
<td>4.8</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>17, calc</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>15.35</td>
<td>3.45</td>
<td>0.30</td>
<td>0.25 hole/ring</td>
</tr>
</tbody>
</table>

*The carbon content is used as reference. † Polymers prepared by oxidation with FeCl₃.
with the polymers made electrochemically.

We have characterized the self-doped polymers in detail. FTIR spectra show the normal peaks for heavily doped wavelengths, indicating the presence of quasi-free charge carriers. Also observed are a very large and broad peak around 1,190 and 1050 cm⁻¹ of SO₃⁻ carriers. The exact shape of the absorption curves differs somewhat from one sample to another, but the overall shape is always retained. Upon dedoping the spectra change considerably.

Representative spectra of the three (propyl-, butyl- and hexylsulfonate) substituted poly(pyrrrole) show (Figure 2) that the low-energy parts differ from each other and also from the published spectra of unsubstituted poly(pyrrrole). As the latter spectra have been interpreted in detail as being due to the presence of bipolarons, the nature of the charge carriers in the present polymers might be significantly different. Dedoping the samples, leading to partially undoped polymers (see also the section on electrochemical properties), induces marked changes in the spectra (Figure 3), but again no close correspondence with partially undoped poly(pyrrrole) is observed.

To determine the spin state of the charge carriers, we performed a number of ESR measurements on samples with various degrees of doping. All samples show neat resonances with Lorentzian line shapes, line widths between 0.6 and 1.2 G, and a g value of 2.0027. The g factor is the same as found for poly(pyrrrole). For unsubstituted poly(pyrrrole) both a narrow (0.3-0.4 G) and a broad line (2.8 G) have been reported. We find only a single broad line (3 G) in our samples of poly(pyrrrole), which has a non-Lorentzian shape. A quantitative evaluation of the intensities of the ESR lines of the doped substituted pyrrrole polymers leads to an average concentration of the order of 1 uncompensated spin per 200 rings (Table II). This concentration is similar to that found unsubstituted poly(pyrrrole) (or slightly higher). Our data for the latter agree with literature values, which are between 200 and 800.

Electrical Conductivity of the Polymers. The electrical conductivity of all samples is significantly higher than the N-substituted self-doped polymers but much lower than that of poly(pyrrrole) with about the same level.

| Table III. Conductivities of the Self-Doped Poly(pyrrrole)  
<table>
<thead>
<tr>
<th>sample</th>
<th>15</th>
<th>16</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td>pressed bar</td>
<td>0.05</td>
<td>0.5</td>
<td>0.002</td>
</tr>
<tr>
<td>film from electrode</td>
<td>0.01</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>film from water</td>
<td>0.01</td>
<td>10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>pressed bar</td>
<td>0.002</td>
<td>0.003</td>
<td>0.001</td>
</tr>
</tbody>
</table>

* Data from samples prepared with additional conduction salt (Bu₄NBF₄) are denoted with an asterisk.
Figure 2. Characteristic NIR-vis-UV absorption spectra of doped thin films of poly(3-alkylsulfonate pyrroles) with propyl (15, n = 3), butyl (16, n = 4), and hexyl (17, n = 6), respectively, on ITO glass electrodes. The origins of the curves of n = 3 and n = 4 have been shifted upward. Note the differences between the spectra of the various polymers at the low-energy side.

of doping. The data are summarized in Table III. The presence of severe cracks in the as-grown films is probably the reason their conductivity is not higher than that of the pressed bars. The conductivities found for the chemically prepared samples are lower than the same polymers made electrochemically. In all samples, the conductivity could not be increased by exposing the samples to iodine vapor.

The lower conductivity of 17 may be significant, because the near-IR spectra of this polymer differ most from those of polypyrrole. As the conductivities measured are not in the metallic range, one expects and finds a strong increase of resistivity with decreasing temperature. This aspect was not analyzed in detail.

Electrochemical Properties of the Solid Polymer.
Thin layers (20–50 nm) of polymer as prepared electrochemically on Pt or ITO glass electrodes are in a self-doped state, viz., the polypyrrole chain is positively charged and the charge is compensated for by sulfonate ions missing a counterion (Na⁺ or H⁺). No redox reaction can be detected when the film is subjected to cyclic changing potentials in contact with a 0.05 M N(C₄H₉)₄BF₄ solution in acetonitrile. However, when a potential of -0.6 V vs SCE is applied for a long time, the polymer gradually bleaches, indicating dedoping (see UV spectra in Figure 3). The process takes about 1 h, which means that the diffusion of the tetrabutylammonium ions into the polymer is very slow. In nearly saturated NaBF₄ solution in acetonitrile the diffusion of the much smaller cations is faster, and we see a very slight response to the alternating potential. If a trace of acid (final solution 0.5 mM HNO₃) is added, we find a gradually improving redox reaction (see UV spectra in Figure 3). After some 50 cycles the response becomes stationary for at least 100 cycles. The cyclovoltammogram of such a pretreated sample is shown in Figure 5.

Figure 3. NIR-vis-UV spectra of thin films of poly(3-hexylsulfonate pyrrole) 17 on ITO glass electrode for various degrees of doping. Doping increases gradually in going from a through e. For each curve the origin is indicated.

Figure 4. Response of a virgin thin film of poly(3-butylsulfonate pyrrole) 16 on a Pt electrode to a cyclic electrical potential.

The difference between oxidation and reduction wave (+0.05 vs -0.08 V vs SCE) is small, and the values are only slightly higher than those reported for polypyrrole itself (-0.11 vs -0.28 V). Although we have reproduced the voltammograms shown several times, we do not always get the same shape. Shapes like that in Figure 6 are sometimes found as well. The exact behavior is clearly a sensitive function of the way the samples are prepared, while others have stressed the sensitivity to traces of water.²²

The propylene and the butylene compounds show a very similar electrochemical behavior, whereas the hexylene compound never showed more than a minor voltammetric response.

**Aqueous Solutions of the Self-Doped Polymers.** The sulfonate side groups give the polymers a polyelectrolytic character. Therefore they are soluble in water, although only to a very limited extent (order of magnitude 0.1–0.5 g/L). The solubility increases with increasing length of the side chains. The electrochemically prepared polymers have a greater solubility than the chemically prepared ones. If we start with a doped deposit on the electrode, the aqueous solution also shows the UV-vis spectrum of a doped polymer, albeit the level of doping has decreased a bit by going into solution (see Figure 7, curves a and b). Such a solution of doped polymer is stable; even after several weeks hardly any changes in the spectrum of the polymer can be detected. If the deposit of polymer is dedoped before going into solution, the solution has the same spectrum as the solid (Figure 7, curves c and d).

Although the solubility in water is low, it is sufficient to measure an $^1$H NMR spectrum of the polymer in D$_2$O solutions (Figure 8). The spectra exhibit broad resonances in the aliphatic region, due to the CH$_2$ chain. The methylene group adjacent to the pyrrole ring is shifted about 0.5 ppm downfield with respect to the monomer, due to the charged polypyrrole backbone. The aromatic region of the spectrum is markedly dependent on the way the polymer is prepared. In many cases the aromatic resonances have vanished, while at least the 4-H atom of the pyrrole ring should be present. In other cases a very broad resonance is observed at 7–8 ppm.

Recording the spectra at different magnetic fields (80, 300, and 500 MHz) shows that this broadening is due to inhomogeneous line broadening. No clearcut relation between level of doping and the appearance and intensity of the aromatic resonances was found. However, the hexyl-chain-substituted 17 showed most often a detectable resonance in the aromatic region.

**Discussion**

The success of the electrochemical polymerization of the pyrroles 10–12 without using an additional conduction salt provides firm evidence that the resulting polymer is really...
self-doped. It represents the first example in which a monomer with one sulfonate group per ring has been polymerized as an ionic species.7 Other self-doped polymers are either copolymers of pyrroles made in the presence of additional conduction salts or the poly(3-alkylsulfonate) thiophenes 1a,b made by Wudl et al.3 using an indirect route. Recently, copolymers of pyrrole and N-substituted self-doped polypyrroles have been made without the addition of additional electrolytes, leading to similar results as described here, with the difference that they exhibit low conductivity relative to the N-substitution.8

During the polymerization of 10–12 most of the sodium ions are removed from the sulfonate groups. This follows from elemental analyses. Charge compensation of these groups in the polymer is mainly by the positive charge of the polypyrrole backbone and by hydronium ions. The sodium ion is probably lost during the first step in the polymerization, in which a zwitterionic pyrrole radical cation is formed. The loss of sodium is comparable with the nearly complete replacement of potassium by hydronium ions in the case poly(3-propylsulfonate 2,2'-5',5''-terthiényl) 2.5.8 A smaller replacement of the alkali ions in 15–17 is to be expected, as their side chains outnumber those of 2 by a factor of 3. A replacement of sodium ions by hydronium ions was also found in the reversible dedoping of 1a,b, and in the N-substituted self-doped polypyrroles.5,8 The addition of excess “foreign” conduction salts in the electrochemical polymerization process does not result in a substantial incorporation of foreign ions in the polymer. Evidently, self-doping is preferred in these substituted polypyrroles, as is expected in view of the polymerization mechanism via the zwitterionic radical cation. The electrochemical polymerization of solutions in water depends on the concentration of the monomer. At low concentrations the polymer formed remains in solution, while at concentrated solutions it is partly deposited on the anode. Apparently, deposition can be obtained due to saturation effects. The electrochemical activity of 15–17 on Pt or ITO glass electrodes not only depends on the electrolytic medium but also is very dependent on the way of preparation of the polymers. In these polymers the rate-determining step in the reversible doping–dedoping process is the inter-diffusion of cations, rather than the out-diffusion of foreign “dopant” counterions. The difference in the rate of inter-diffusion of large cations like tetrabutylammonium ions (slow) and smaller sodium ions (faster) is striking. Cyclic voltammograms of good quality could be obtained only in slightly acid solutions after prolonged cycling. This ion-popping has been seen in other self-doped polymers, too.3,4,8 The electrochemical response in other solvents has not yet been studied. Probably the diffusion of cations in and out of the self-doped polymeric films can be accelerated by choosing a solvent that swells the polymer. However, more detailed experiments, including chronocoulometry, should be performed to come to more definite conclusions with respect to this ion diffusion.

The polymers 15–17 have also been prepared by means of oxidative coupling using FeCl₃. These samples show the composition including iron. Similarly to other reports, it is expected that at least part of the iron is present as ferrous ions. The concentration of Cl is low; hence, no important doping by foreign ions like FeCl₄⁻ is present. The solubility in water is somewhat lower than that of polymers prepared electrochemically. Moreover, the conductivity is lower too and could not be increased by I₂ treatment. The lower conductivity can be due to a variety of differences in the materials made either chemically or electrochemically, i.e., morphology, chain length, or degree of doping. Therefore, the FeCl₃ samples were not investigated as thoroughly as polymer prepared electrochemically.

All samples were X-ray amorphous. Amorphous structures are found quite generally in polypyrroles, the main exception being polypyrroles doped by sulfonic acids with rather long alkyl chains, where an X-ray diffraction peak at low angle was taken as evidence of ordered stacking of parallel main chains separated by the dopant molecules.4,24 Elemental analyses show that the sulfonate groups are completely retained during the electrochemical synthesis ([S]/[N] ≈ 1). Only if too high voltages are applied are the samples low in sulfonate content. At these conditions an electrochemical side reaction analogous to the Kolbe decarboxylation can take place, yielding a cross-linked polymer by radical dimerization and SO₃ elimination. In spite of working under nitrogen flush, all samples have oxygen in excess. Part of it is present as H₂O, but some oxygen must be bound in a different way.

The conductivities found for the self-doped polypyrroles are lower than we expected. In part this is due to the failure to make films of good quality. However, we presume that other reasons for the relatively high values of the resistivity are operative. A possible explanation might be a less regular structure of these polymers as compared with polypyrrole itself. Both the overlap between the various chains and the conjugation along the chains will be lowered by deviations from planarity. The absorption spectra of our polymers give indeed hints in this direction (see below)

The intensive absorptions in the NIR region of the spectra of the as-grown sulfonate-substituted polypyrroles point to a doping level of the main chain that is comparable with that of simple as-grown polypyrrole, viz. about one charge per four rings. The accuracy of the elemental analyses, however, did not allow an independent check of this degree of doping. The number of free spins, as measured by ESR, amounts to only a few percent of the doping level. Hence most charge carriers form spin-compensated states, probably bipolarons, just as in regular polypyrrole. However, the low-energy parts of the electronic spectra of the three self-doped polypyrroles differ from each other and from that of regular polypyrrole. Similar differences are also present when comparing partially dedoped samples of the four polymers. The spectra of polypyrrole have been explained in detail with the use of a bipolaron model.20 If one uses the same model for our self-doped polypyrroles, we must assume that the polarons will adopt different configurations. These may be related to larger deviations from planarity of the conjugated chains in our samples. The irregularity of such deviations explains in a natural way the occurrence of many peaks in the electronic spectra of the self-doped polypyrroles. Moreover, the ESR data suggest a trend toward an increase in the number of free spins with increasing lengths of the side chains. The latter is in agreement with the conductivity data that also show a lower conductivity for 17. These trends are easily understood if one allows for the proposed increasing deviations from planarity of the main chains for longer side chains. A similar trend is found for poly(3-alkylpyrroles).12a

Moreover, the decrease of the transition temperature of alkyl-substituted polythiophenes to a less conjugated state with increasing length of the side chains has been assigned to a similar deviation from planarity. Apparently, the steric hindrance of a substituent at the 3-positions of polypyrrole or polythiophene is not negligible.

One of the aspects of self-doped polypyrroles not yet fully understood is the dependence of properties on the way of preparation. All electrochemical variables such as voltage, current density, conduction salt, solvent, electrode material, and type of cell influence the morphology, conductivity, and solubility of the polymers. This dependence is best reflected in the NMR spectra of the aqueous solutions of the self-doped polypyrroles. $^1H$ NMR data of the polymers in $D_2O$ confirm the charged backbones. However, although the H atom attached directly to the pyrrole ring is found as a broad peak shifted downfield by about 1 ppm, its intensity is always too low and sometimes even vanishingly small. Since no clear differences are observed in the electronic spectra and, hence, in the level of doping, a more detailed study of this dependence will be necessary.

Conclusions

3-Substituted pyrroles are made by a three-step synthesis from $N$-(phenylsulfonyl)pyrrole. A tedious purification of the sodium salts of these monomers for self-doped polypyrroles has been adopted. The low oxidation potential of these monomers allows a direct oxidative electrochemical polymerization. The possibility of performing this polymerization without the addition of another conduction salt is a direct proof of the self-doped state of the polymer formed. The polymers 15 and 16 formed on Pt or ITO glass electrodes show neat cyclic voltammograms when these polymers are in contact with acetonitrile solutions containing protons. On the other hand, polymer 17 shows only a minor electrochemical response. From elemental analyses it is clear that the polymers contain an excess of oxygen, partly as water. X-ray analysis shows that the polymers are amorphous. ESR data show that only one spin per 150-300 rings is present, and the charge carriers are mainly bipolarons. From UV–vis–NIR spectra it is clear that the doping level is comparable to plain polypyrrole but that the polarons must have different configurations. This is ascribed to less planar conjugated chains in the substituted polypyrroles. The polymers are sparingly soluble in water. UV–vis–NIR spectra of such stable solutions indicate that the chains remain largely self-doped. The conductivity of the polymers ranges from $10^{-4}$ to 0.5 $S/cm$. The low values may partly be due to the deviations from planarity of the conjugated backbones. Since the self-doped polymers are water soluble, it is possible to record $^1H$ NMR spectra of aqueous solutions. This makes research to the molecular origin of conductivity in polymers feasible.

Acknowledgment. Thanks are due to L. W. van Horsen and I. Rotte (Philips Research) for their assistance during many of the experiments and to W. H. Kruizinga (University of Groningen) for recording the high-field $^1H$ NMR spectra. The analytical departments of both laboratories are gratefully acknowledged.

Influence of Oxygen Partial Pressure on the Synthesis of Ba$_2$YCuxO$_7$ from a Novel Oxalate Precursor

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An oxalate precursor precipitate is prepared by reacting carbonate, hydroxide, and/or oxides with oxalic acid in a heated aqueous solution. By this approach, there are no extraneous anions or cations introduced by the starting salts or created during the reaction since the products are only water and carbon dioxide. Specific solubility differences may be compensated by recycling the filtrate. The thermal conversion of the resulting coarse crystalline precipitate to the desired oxide product is studied by thermomorphological techniques and X-ray diffraction. The oxygen content and, hence, the defect structure of the product depend upon the partial pressure of oxygen and the temperature. Consequently, the kinetics of the final stage of the reaction, eq 1, are influenced by the value of $x$.

Introduction

There has been an enormous interest generated in cuprate systems having various layered structures because a number of them have exhibited confirmed superconductivity at temperatures as high as 125 K. There have been problems associated with the stability, reproducibility, fabrication, and strength of the material as well as several crucial electrical properties, e.g., the critical current ($J_c$), critical field ($H_c$), and high-frequency ac conductivity. Many of these difficulties can be associated with the phase purity, microstructure, grain boundary effects, etc. Consequently, numerous synthetic approaches have been utilized in an effort to obtain optimum properties in the final sintered ceramic or film. Besides the conventional ceramic methods, most of the more modern "chemical" approaches, e.g., sol–gel, coprecipitation, spray roasting or drying, freeze-drying, pyrolysis of organometallics, etc., have been utilized with varying degrees of success. Two of the most successful aqueous coprecipitation techniques produce a fine hydroxide–carbonate mixture or more coarse crystalline oxalate precipitate. In terms of fil-
