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 $0k0$ 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^3/Q^4 ratios: cf. supra). By use of the experimentally observed degrees of exchange ($2z \simeq 0.3$ in $(RNH_3^+)_{2z}H_{2(1-x'-z)}Si_2O_{5-x'}\cdot yH_2O$) and assuming that the alkylammonium chains oriented perpendicular to the layers covering an area of 25 Å^2,[23] the surface area available for intercalation in the silicate network would be ~345 m^2/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–Al^{IV} and of nonframework aluminum is dramatically reduced. Thus, there are clear indications that pillaring occurs to a large extent in the interlayer gallery.

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Conclusion

$KHSi_2O_5$ 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 Al^{IV} 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, ^{1}H NMR in D_2O 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 $0.5–10^{-3}$ 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. ^{1}H NMR spectra of the aqueous solutions of self-doped polymers are discussed.

Introduction

Extended conjugated polymers can, in general, be transformed into conducting materials by doping.[1] 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.[2] In contradistinction with other doped polymers, dedoping of these self-doped polymers cannot be obtained by outdiffusion 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.[3]

The first-reported self-doped polymers were poly(3-alkylsulfonate thiophenes) **1a,b**, obtained by hydrolysis of

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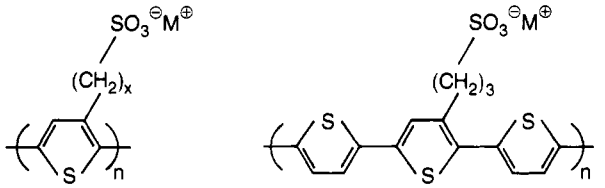

1a x=2
1b x=4

2

poly(3-alkylsulfonate thiophene) methyl esters.[3] 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.[4]

Using a 3′-propylsulfonate 2,2′:5′,5″-terthienyl, we were able to polymerize the potassium salt of this monomer directly by electrochemical oxidation without the interference of foreign ions.[5,6] In this case, the monomer itself also acts as the conduction salt during the electrochemical polymerization, resulting in solid evidence for self-dope.[7] The self-doped poly(3′-propylsulfonate 2,2′:5′,5″-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.[8-10] 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.[8,9]

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.[11] The self-doped N-substituted polypyrroles are no exception to this rule.[8,9] For that reason it is of profound interest to study poly(3-alkylsulfonate pyrroles) as more stable self-doped polymers. It is only recently that 3-substituted pyrroles have come to be studied in relation with conducting polymers. Both alkyl- and acyl-substituted pyrroles are susceptible to electrochemical oxidation, yielding polymers with conductivities in the range 0.01–10 S/cm.[12]

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.[5]

Experimental Section

Apparatus. All electrochemical work was carried out by using a Wenking Potentioscan 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 $\theta = 2°$. 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 Superscan 3. ^{1}H NMR spectra were recorded at 60 MHz with a Perkin Elmer R-24B, at 80 MHz with a Bruker WP 80 SY, 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 D_2O as solvent with solvent suppression of the remaining H_2O. ^{13}C 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.

1-(Phenylsulfonyl)pyrrole (3).[13] To a well-stirred mixture of 750 g of NaOH in 900 mL of water, 160 g of pyrrole (2.388 mol), 800 mL of CH_2Cl_2, and 70 g of tetrabutylammonium hydrogen sulfate is added a solution of 600 g of benzenesulfonyl chloride in 300 mL of CH_2Cl_2 at such a rate that the mixture refluxes gently (some external cooling is necessary, although gentle reflux ought to be maintained). During the addition a thick paste is formed, which becomes thinner toward the end of the addition. After this stirs overnight, 3 L of water is added and the mixture is extracted with three times 1 L of $CHCl_3$. The organic layers are washed with water (two times 2 L), dried, and evaporated. Methanol is added to the residue, and the mixture is stirred for a few minutes. The product is suction-filtered and washed with methanol to give 270.3 g of 1-(phenylsulfonyl)pyrrole. Evaporation of the filtrates and addition of methanol to the residue gave an additional 89.0 g. The total yield of **3** is 359.3 g (1.736 mol, 73%).

1-[1-(Phenylsulfonyl)-3-pyrrolyl]-4-chloro-1-butanone (5).[14] A solution of 56 g of 4-chlorobutyryl chloride (0.397 mol) in 50 mL of CH_2Cl_2 is added over 20 min, cooling with water bath, to a stirred mixture of powdered $AlCl_3$ (50.5 g, 0.380 mol) in 250 mL of CH_2Cl_2. After continued stirring for 45 min a clear solution results. Then 62.1 g of **3** (0.30 mol) in 200 mL of CH_2Cl_2 is added over 30 min, while cooling with the water bath is continued. After stirring for 1 h, the solution is poured on 1 L of water. After shaking, the organic layer is separated, and the water layer is extracted with 500 mL of $CHCl_3$. The combined organic layers are washed successively with 20 g of NaOH in 750 mL of water and with 750 mL of water. To the turbid organic layer, methanol is added until two clear layers result. The lower layer is dried and evaporated to yield crude **5** that is pure by ^{1}H NMR; ^{1}H NMR ($CDCl_3$) δ 1.7–2.3 (m, 2 H), 2.8 (t, 2 H), 3.45 (t, 2 H), 6.5 (m, 1 H), 7.0 (m, 1 H), 7.2–8.0 (m, 6 H).

1-[1-(Phenylsulfonyl)-3-pyrrolyl]-4-chlorobutane (8). Crude **5**, as obtained in the reaction described above, is dissolved in 400 mL of toluene and 160 mL of water, and 240 g of amal-

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gamated zinc is added (from 240 g of fine powder zinc and 20 g of $HgCl_2$, 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 reduction can easily be followed by ^1H NMR. 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 ($CDCl_3$) δ 1.5–1.9 (m, 4 H), 2.35 (t, 2 H), 3.5 (t, 2 H), 6.1 (m, 1 H), 6.8 (br s, 1 H), 7.0 (m, 1 H), 7.2–7.9 (m, 5 H).

4-(3-Pyrrolyl)butanesulfonic Acid, Sodium Salt (11). A mixture of 17.6 g (59.2 mmol) of the crude halide **8**, 175 mL of water, 70 mL of ethanol, 17.5 g of Na_2SO_3, 2 g of tetrabutylammonium bromide (the necessity of adding this phase-transfer catalyst was not explored), and 2.6 g of NaI 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 $CHCl_3$. 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, the solid is boiled with 100 mL of 90% 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 3 mL of water to give a solution. 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 3.00 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 (D_2O) δ 1.4–1.7 (m, 4 H), 2.3 (t, 2 H), 2.8 (t, 2 H), 5.9 (m, 1 H), 6.45 (br s, 1 H), 6.6 (m, 1 H); ^{13}C NMR (D_2O/CH_3OH) δ 24.3 (t), 26.1 (t), 29.9 (t), 51.3 (t), 107.8 (d), 115.9 (d), 118.7 (d), 123.6 (s); static SIMS (negative ion spectrum) 202.

1-[1-(Phenylsulfonyl)-3-pyrrolyl]-3-chloro-1-propanone (4). This compound is obtained in a way identical with that described for **5** from 58.5 g of $AlCl_3$ (0.440 mol), 58 g of 3-chloropropionyl chloride (0.457 mol), and 68.3 g of *N*-(phenylsulfonyl)pyrrole (0.330 mol) in 500 mL of CH_2Cl_2. The crude product is obtained as an oil that solidifies on standing and is used as such in the next step; mp 75–78 °C (from methanol); exact mass 297.020 (calcd 297.022); ^1H NMR ($CDCl_3$) δ 3.15 (t, 2 H), 3.7 (t, 2 H), 6.6 (m, 1 H), 7.05 (m, 1 H), 7.3–8.0 (m, 6 H).

1-[1-(Phenylsulfonyl)-3-pyrrolyl]-3-chloropropane (7). Clemmensen reduction of the crude **4** as described for **8** affords 91.4 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 ($CDCl_3$) δ 2.0 (m, 2 H), 2.5 (t, 2 H), 3.4 (t, 2 H), 6.1 (m, 1 H), 6.9 (br s, 1 H), 7.1 (m, 1 H), 7.3–8.0 (m, 5 H).

3-(3-Pyrrolyl)propane-1-sulfonic Acid, Sodium Salt (10). A mixture of 30 g of crude chloride **7**, 150 mL of 96% ethanol, and 30 g of KOH is warmed. During this process 75 mL of water is added over 5 min. The mixture is then heated under reflux for 90 min. After cooling, 200 mL of water is added, and the mixture is extracted with 2 × 150 mL of $CHCl_3$. The organic layers are washed with water, dried, and evaporated. The residue consists of a mixture of 3-(3-pyrrolyl)-1-chloropropane (**13**) and 3-(3-pyrrolyl)-1-ethoxypropane (**14**, the ratio of **13**:**14** is ca. 2:1 by ^1H NMR). This mixture is warmed up with 22 g of Na_2SO_3, 2 g of tetrabutylammonium bromide, 6 g of NaI, and 280 mL of water. When most of the solids have dissolved, 105 mL of 96% ethanol is added over 15 min. The mixture is then heated under reflux for 18 h. After this cools, 150 mL of brine is added, and the mixture is extracted with 2 × 100 mL of $CHCl_3$. The organic layers are washed with 50 mL of water. Drying, evaporation, and Kugelrohr distillation give fairly pure **14**: ^1H NMR ($CDCl_3$) δ 1.2 (t, 3 H), 1.5–2.2 (m, 2 H), 2.5 (t, 2 H), 3.2–3.6 (m, 4 H), 5.9 (m, 1 H), 6.3 (br s, 1 H), 6.4 (m, 1 H). The aqueous layers are evaporated, and the not completely dry residue is boiled with 200 mL of absolute ethanol and with 200 mL of 96% ethanol, respectively. Filtration while hot gives residue A. The filtrates are evaporated completely, and the residue boiled with 150 mL of absolute ethanol and filtered while hot, giving residue B. From the filtrate, a gellike precipitate is formed on cooling, which is sucked off, washed with 96% ethanol (giving filtrate C), stirred with acetone, and sucked off to give 2.69 g of slightly colored product. Residue A is boiled for 30 min with 200 mL of 96% ethanol and filtered while hot. The filtrate is combined with residue B and filtrate C, and this mixture is evaporated completely. The residue is boiled with 150 mL of absolute ethanol and filtered while hot. On cooling, 1.74 g of product is obtained after washing with ethanol and stirring with acetone. The filtrates are evaporated, and the residue is boiled with 150 mL of absolute ethanol and filtered while hot. The filtrate is evaporated, and the residue is recrystallized from 100 mL of absolute ethanol to give after cooling to 0 °C another 1.16 g of pure product. The total yield of **10** is 5.59 g (26.5 mmol, 24% based on *N*-(phenylsulfonyl)-pyrrole. No melting point could be detected due to decomposition; ^1H NMR (D_2O) δ 1.5–2.2 (m, 2 H), 2.2–2.9 (m, 2 H), 5.9 (m, 1 H), 6.45 (br s, 1 H), 6.6 (m, 1 H); ^{13}C NMR (D_2O/CH_3OH) 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) 188.

1-[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 evaporation, is converted to **6** by using the procedure described for **5** using 18.5 g of $AlCl_3$ (0.139 mol) and 27.0 g of *N*-(phenylsulfonyl)pyrrole (0.130 mol) in 200 mL of CH_2Cl_2. The crude product, being an oil that solidifies on standing, is used as such in the next step; mp 52–54 °C (from CH_3OH); ^1H NMR ($CDCl_3$) δ 1.1–2.0 (m, 6 H), 2.7 (t, 2 H), 3.3 (t, 2 H), 6.6 (m, 1 H), 7.1 (br s, 1 H), 7.2–8.0 (m, 6 H); exact mass 383.016 (calcd 383.019).

1-[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 ($CDCl_3$) δ 1.0–2.0 (m, 8 H), 2.3 (t, 2 H), 3.2 (t, 2 H), 6.0 (m, 1 H), 6.7 (br s, 1 H), 6.9 (m, 1 H), 7.2–7.8 (m, 5 H).

6-(3-Pyrrolyl)hexane-1-sulfonic Acid, Sodium Salt (12). To a mixture of 30 g of the crude bromide **9**, obtained above, 30 g of Na_2SO_3, 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 cooled to −15 °C to give the 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

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NMR (D_2O) 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 20–200 mg 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 0.25 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 $(C_4H_9)_4NBF_4$, Jansen Chimica 99%, or 0.03 M solution of $NaBF_4$, 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 counterelectrode 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.

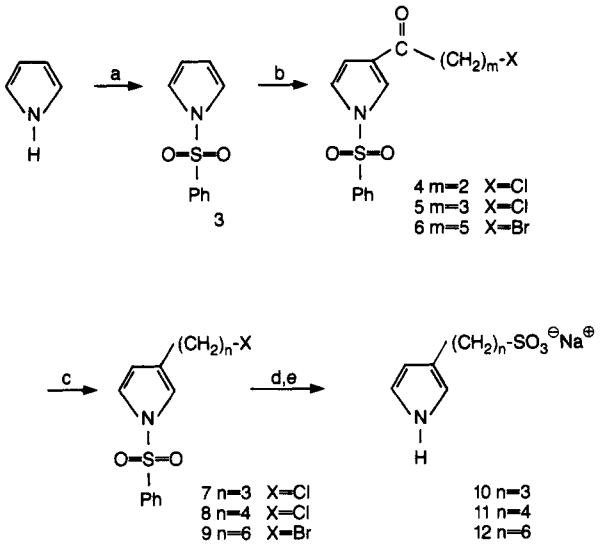
The chemical polymerizations of **10–12** using $FeCl_3$ were performed analogous to the Armes' method for pyrrole.[18]

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 98–99%. For the polymers, however, we always got results adding up to about 95–98% at most. The reason for this is not clear. A search for other elements present in the samples was unsuccessful; 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.

Resistivity. 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 by showing that exposing some samples to dc electric fields for a long time changed the resistance by only a few percent. The polymers were measured in various shapes: pressed bars (20 × 5 × 1 mm^3) formed at 700 MPa, more or less coherent films scraped from the electrodes (thickness of 0.5–2 μm), and films from evaporated water solutions on prefabricated gold electrodes on alumina.

Scheme I[a]



[a] (a) $PhSO_2Cl$, PTC, H_2O, CH_2Cl_2; (b) $X(CH_2)_mCOCl$, $AlCl_3$–CH_2Cl_2; (c) (Hg)Zn, HCl, toluene; (d) H_2O, EtOH, Na_2SO_3, PTC, NaI; (e) NaOH.

Results

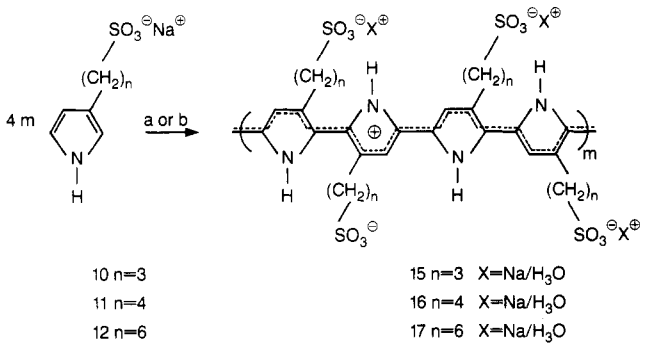
Synthesis of Pyrrole Monomers. The basis of our route toward the desired pyrrole monomers involves acylation in the 3-position of pyrrole with a suitable ω-halo acid chloride, followed by a Clemmensen reduction to give 3-(ω-haloalkyl)pyrrole, which is subsequently converted to the required sulfonated alkylpyrrole. Access to pyrroles acylated in the 3-position is possible by first protecting pyrrole as the *N*-(phenylsulfonyl) derivative with benzenesulfonyl 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.[13,14] Conversion to the corresponding 3-alkylpyrroles is best accomplished using the Clemmensen reduction on the N-protected acylpyrrole followed by deprotection.[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-chlorobutyryl chloride, and 6-bromohexanoyl chloride by using $AlCl_3$ in CH_2Cl_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_2SO_3 in the presence of Bu_4NBr[16] and NaI under specific conditions for each compound gives the N-protected sulfonated alkylpyrrole, 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

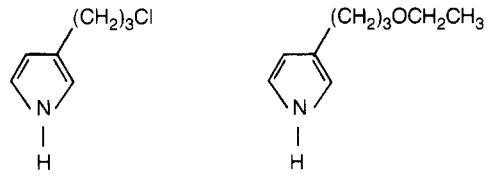
(16) Lantzsch, R.; Marhold, A.; Lehment, K. F., Ger. Off. 2545644, (*Chem. Abstr.* **1977**, *87*, 38874).
(17) Tourillon, G., in ref 1, p 296.
(18) (a) Armes, P. J. *Synth. Met.* **1987**, *20*, 365. (b) Bocchi, V.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1986**, 148.

Scheme II[a]



[a] (a) CH_3CN, 1.4 V, electrochemically; (b) $FeCl_3$, H_2O. X is either Na or H_3O; see text.

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



13 14

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,

Table I. Elemental Analysis of the Monomers and Polymers[a]

compd	C	N	S	H	O	Na	comment
10, obs	7	0.95	1.03	10.7	3.9	1.02	0.02 Cl
10, calc	7	1	1	11	3.5	1	$+0.5H_2O$
11, obs	8	0.96	1.00	13.6	4.0	1.05	0.06 Cl
11, calc	8	1	1	14	4	1	$+H_2O$
12, obs	9	0.93	1.04	17.8	4.1	1.02	
12, calc	9	1	1	18	4	1	$+H_2O$
15, obs	7	0.98	1.01	10.0	4.0	0.17	
15, calc	7	1	1	9.8	3.6	0.15	0.25 hole/ring
15, obs[b]	7	0.96	1.03	12.5	5.4	0.04	0.07 Cl, 0.33 Fe
16, obs	8	0.98	1.00	12.4	4.9	0.27	
16, calc	8	1	1	11.35	3.45	0.30	0.25 hole/ring
16, obs[b]	8	0.97	1.04	14.6	5.5	0.02	0.07 Cl, 0.34Fe
17, obs	10	1.04	1.01	15.8	4.8	0.29	
17, calc	10	1	1	15.35	3.45	0.30	0.25 hole/ring

[a] The carbon content is used as reference. [b] Polymers prepared by oxidation with $FeCl_3$.

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).[17] 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. Elemental analysis showed that the polymers prepared by adding a conduction salt contain only minor concentrations (<1% by weight) of BF_4^- ions.

Another way of polymerizing **10–12** is via a chemical route using $FeCl_3$ as oxidant. This method is known to be successful for pyrrole.[18] 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

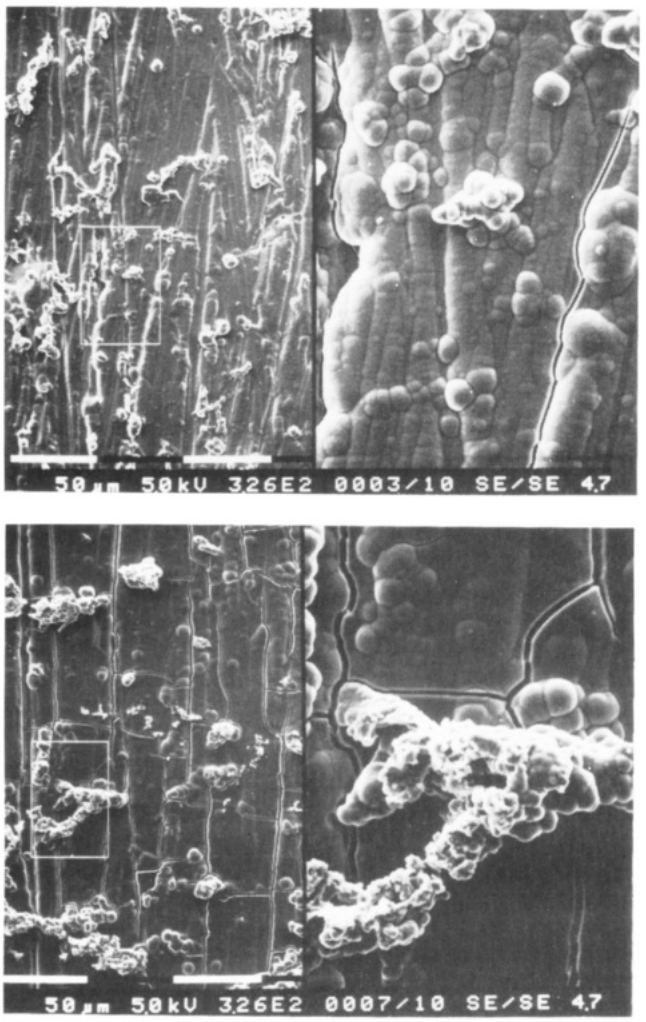


Figure 1. SEM photographs of the surface of a film of **16**, grown on a Pt electrode in a one-compartment cell; film thickness of about 100 nm (top) and about 1 μm (bottom).

with the polymers made electrochemically.

We have characterized the self-doped polymers in detail. FTIR spectra show the normal peaks for heavily doped polypyrrole and the increase in absorption at longer wavelengths, indicating the presence of quasi-free charge carriers. Also observed are a very large and broad peak at 3460 cm^{-1} due to NH, H_2O, and possibly to NOH, the broad and split peaks around 1190 and 1050 cm^{-1} of SO_3^- groups, and faint peaks around 2950 cm^{-1} of the methylene groups in the side chains.

Morphology of the Films. The morphology of the films produced is markedly dependent on the polymerization conditions. When the electrochemical polymerization is performed in a one-compartment cell the films are rather incoherent. SEM pictures (see Figure 1) show that these films are disfigured by severe cracks. In thin films (100 nm) isolated cracks are observed only, but in thick films (>1 μm) they form a network dividing the polymer film into small islands. More coherent films are obtained if the polymerization is carried out in an ultrasonic bath. Similar coherent films are obtained by using a two-compartment cell.

X-ray diffraction data taken of a number of samples indicated that all substituted polypyrroles were amorphous.

State of Doping of the Solid Polymers. UV–vis–NIR spectra of thin films of the polymers on ITO glass electrodes show large absorption peaks in the NIR, indicating a highly doped polypyrrole skeleton. 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 polypyrroles show (Figure 2) that the low-energy parts differ from each other and also from the published spectra of unsubstituted polypyrrole.[19] As the latter spectra have been interpreted in detail as being due to the presence of bipolarons,[20] 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 polypyrrole 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 polypyrrole.[18] For unsubstituted polypyrrole both a narrow (0.3–0.4 G) and a broad line (2.8 G) have been reported.[21] We find only a single broad line (3 G) in our samples of polypyrrole, which has a non-Lorentzian shape.

A quantitative evaluation of the intensities of the ESR lines of the doped substituted polypyrroles 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 polypyrrole (or slightly higher). Our data for the latter agree with literature values, which are between 200 and 800.[21]

Electrical Conductivity of the Polymers. The electrical conductivity of all samples is significantly higher than the N-substituted self-doped polymers[8,9] but much lower than that of polypyrrole with about the same level

Table II. Number of Monomeric Unit/Spins As Determined by ESR

compd	data[a]	av
14	141, 231*, 340, 412*	240
15	166, 185*, 252*, 384	210
16	136, 154	145
polypyrrole	240*, 554*	335

[a] Data from samples prepared with additional conduction salt (Bu_4NBF_4) are denoted with an asterisk.

Table III. Conductivities of the Self-Doped Polypyrroles[a]

sample	15	16	17
pressed bar[b]	0.05	0.5	0.002
film from electrode[c]	0.01	0.05	
film from water[d]		0.01	10^{-5}
pressed bar[e]	0.002	0.003	0.001

[a] Best conductivities (S/cm) measured for the various polymers. For other samples the conductivity was lower by up to 2 orders of magnitude. [b] Electrochemically prepared polymers measured as pressed bars. [c] Electrochemically prepared polymers measured as free-standing film obtained from the electrode. [d] Measured on a film obtained from an aqueous solution after carefull evaporation of the water. [e] Chemically prepared polymers measured as pressed bars.

(19) Yakushi, K.; Lauchlan, L. J.; Clarke, T. C.; Street, G. B. *J. Chem. Phys.* **1983**, *73*, 4774.

(20) Bredas, J. L.; Scott, J. C.; Yakushi, K.; Street, G. B. *Phys. Rev. B* **1984**, *30*, 1023.

(21) (a) Scott, J. C.; Pfluger, P.; Krounbi, M. T.; Street, G. B. *Phys. Rev. B* **1983**, *28*, 2140. (b) Devreux, F.; Genoud, F.; Nechtschein, M.; Travers, J. P.; Bidan, G. *J. Phys. (Paris)* **1983**, *C3*, 621.

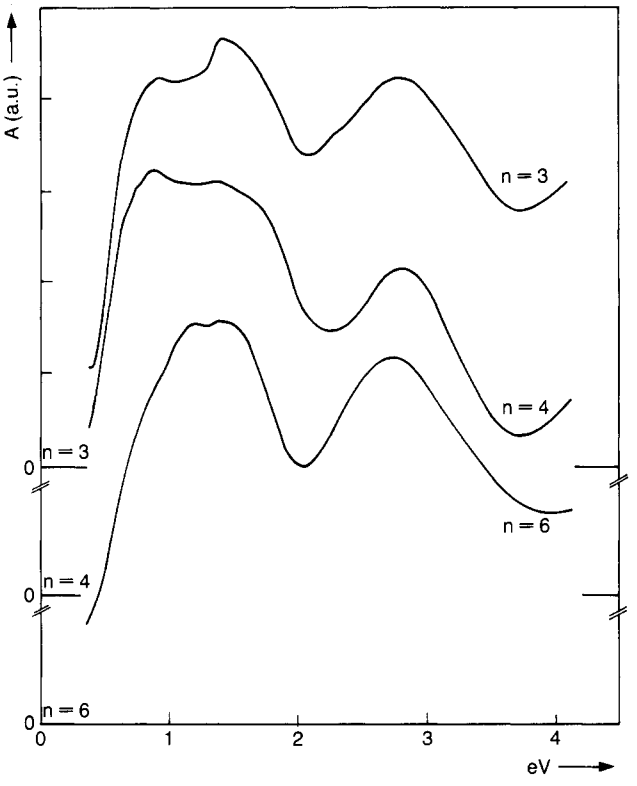


Figure 2. Characteristic NIR–vis–UV absorption spectra of doped thin films of poly(3-alkylsulfonate pyrroles) with propyl (**15**, n = 3), butyl (**16**, n = 4), and hexyl (**17**, n = 6), respectively, on ITO glass electrodes. The origins of the curves of n = 3 and n = 4 have been shifted upward. Note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

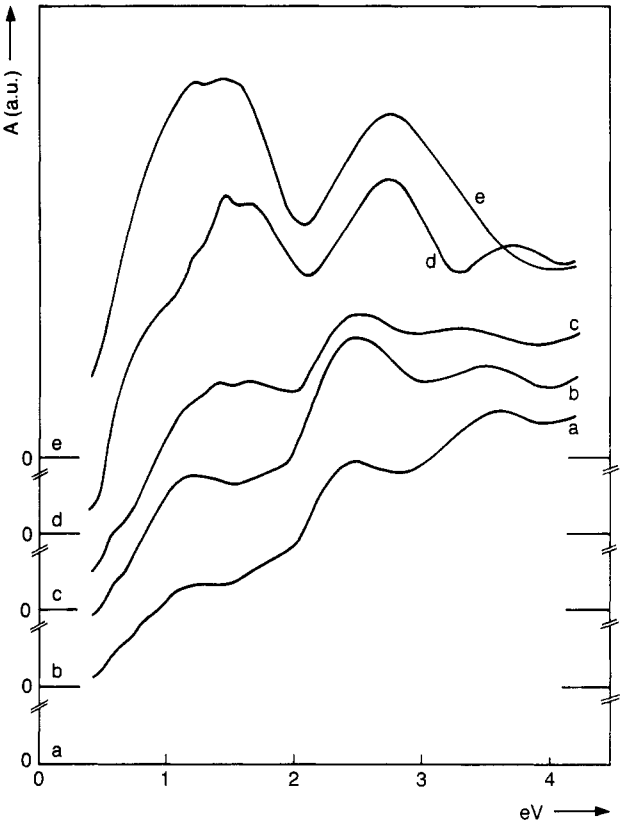


Figure 3. NIR–vis–UV spectra of thin films of poly(3-hexylsulfonate pyrrole) **17** on ITO glass electrode for various degrees of doping. Doping increases gradually in going from a through e. For each curve the origin is indicated.

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 $N(C_4H_9)_4BF_4$ 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 $NaBF_4$ 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 HNO_3) is added, we find a gradually improving redox reaction (see Figure 4). 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.

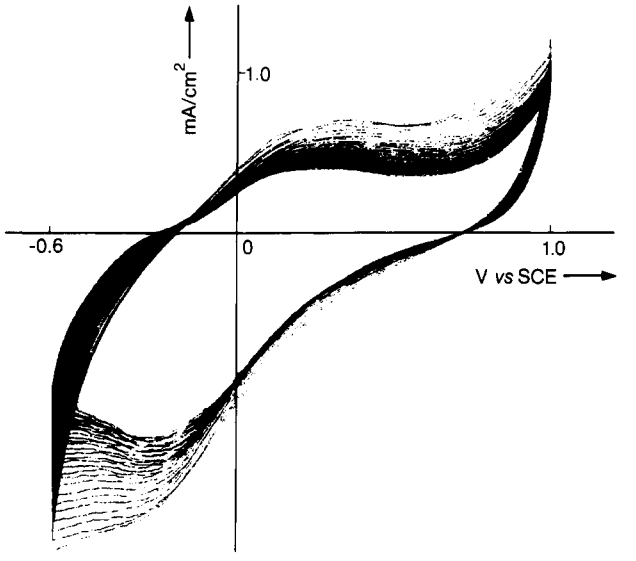


Figure 4. Response of a virgin thin film of poly(3-butylsulfonate pyrrole) **16** on a Pt electrode to a cyclic electrical potential.

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).[22] 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.[9]

(22) Diaz, A. F.; Castillo, J. I.; Logan, J. A.; Lee, W. Y. *J. Electroanal. Chem.* **1981**, *129*, 115.

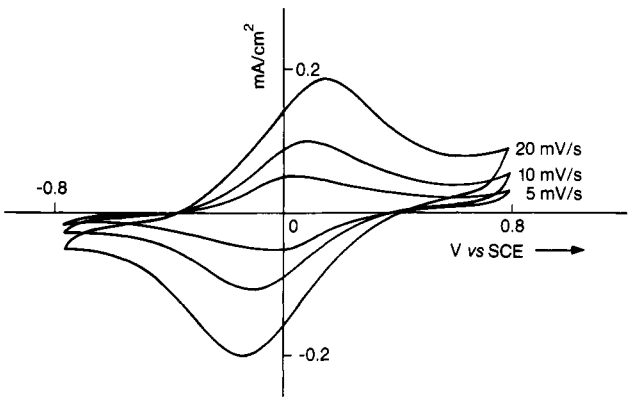


Figure 5. Reversible voltammogram finally obtained from the thin film of Figure 4 after some 100 cycles.

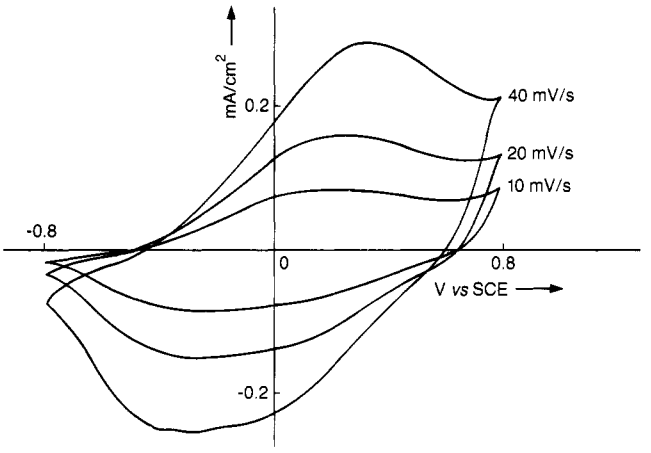


Figure 6. Deformed voltammogram obtained from a different film of the same polymer as in Figure 4.

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 ^1H NMR spectrum of the polymer in D_2O 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

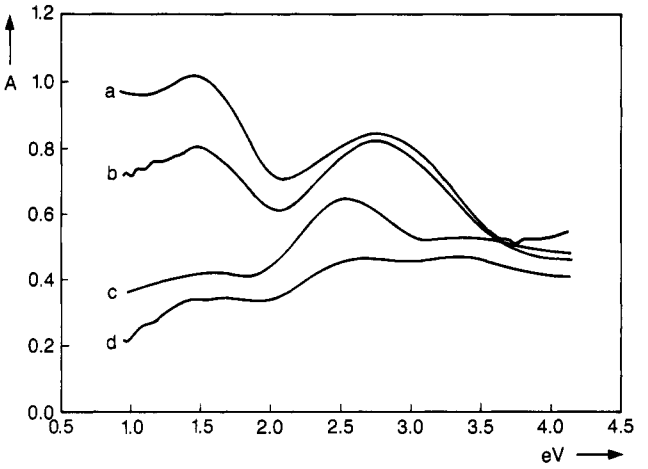


Figure 7. Absorption spectra of poly(3-butylsulfonate pyrrole) **16**: (a) as a heavily doped film on ITO glass electrode; (b) the same film of a dissolved in water; (c) as purposely dedoped film on ITO glass electrode; (d) the same film of c dissolved in water.

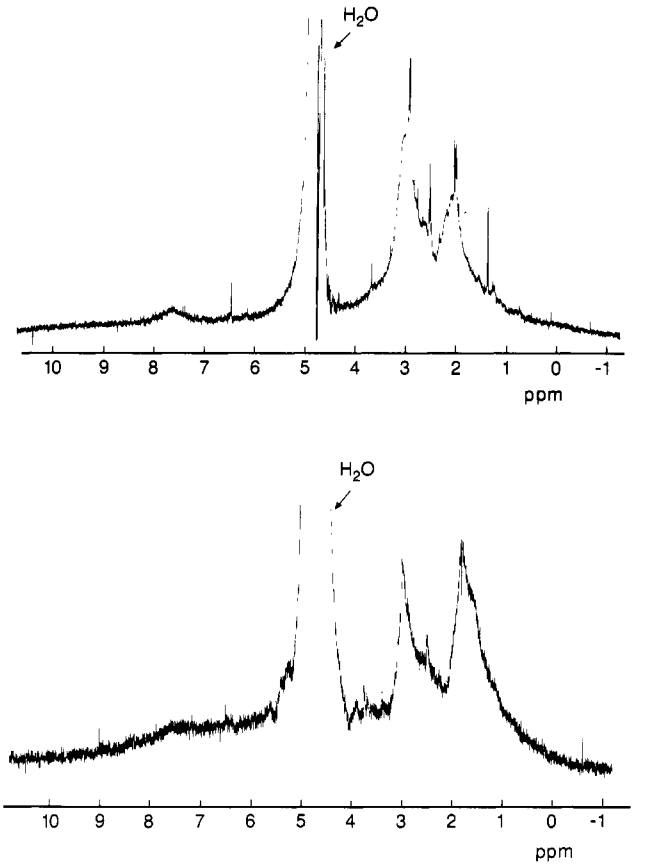


Figure 8. The 500-MHz ^1H NMR spectra of **15** (top) and **16** (bottom), recorded in D_2O by using solvent suppression.

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[8] 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 conductivities due to the N-substitution.[9]

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″-terthienyl) **2**.[5,6] 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**[3,4] and in the N-substituted self-doped polypyrroles.[8,9] 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 in-diffusion of cations, rather than the out-diffusion of foreign "dopant" counterions. The difference in the rate of in-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.[3,4,9] 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 $FeCl_3$. These samples show the composition including iron. Similarly to other reports,[23] 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 $FeCl_4^-$ 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 I_2 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 $FeCl_3$ 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.[24] Elemental analyses show that the sulfonate groups are completely retained during the electrochemical synthesis ($[S]/[N] \simeq 1$). 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,[25] yielding a cross-linked polymer by radical dimerization and SO_3 elimination. In spite of working under nitrogen flush, all samples have oxygen in excess. Part of it is present as H_2O, 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).[12e]

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Moreover, the decrease of the transition temperature of alkyl-substituted polythiophenes to a less conjugated state with increasing length of the side chains[26] has been asigned 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. ^{1}H 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^{-3} 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 ^{1}H NMR spectra of aqueous solutions. This makes research to the molecular origin of conductivity in polymers feasible.

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Influence of Oxygen Partial Pressure on the Synthesis of $Ba_2YCu_3O_7$ 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 thermoanalytical 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[1] or more coarse crystalline oxalate precipitate.[2,3] In terms of fil-

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