Electropolymerization of pyrrole in the presence of fluorinated carboxylate and sulfonate salts

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Abstract

Electropolymerization of pyrrole in the presence of fluorinated mono- and bis-carboxylates and -sulfonates results in the formation of polymeric films having electrical conductivities in the range 0.8–50 S cm^{-1}. The conductivities, stabilities, optical spectra and morphological properties of selected films have been investigated.

Introduction

Polypyrrole (PPY) has been studied intensively since the discovery by Diaz *et al.* [1] that highly conducting films (100 S cm^{-1}) could be prepared by the electropolymerization of pyrrole. Conducting polypyrrole is of great interest because of its potential use as a charge-storage medium [2], in electrochromic displays [3], and in binding metal complexes which can act as electrocatalysts [4, 5] as well as biologically important molecules which can act as sensors [6]. Recently, these materials have become of added interest due to their non-linear optical properties [7, 8].

It has been recognized that the doping anion has an effect on the properties of the resulting polymer [9–13], but most studies have been concerned with more conventional anions such as ClO_4^-, PF_4^-, BF_4^-, NO_3^-, $RCOO^-$ and RSO_3^-. When fluorine is substituted for hydrogen in organic substances, improved thermal and chemical stability often results [14, 15]. Hence, it was of considerable interest to investigate the electropolymerization of pyrrole in the presence of fluorinated carboxylate and sulfonate salts, to determine in which cases polymerization would occur and the effects of these anions on the conductivities, morphologies and stabilities of the resulting films.

Experimental

Methods

Voltammetry and controlled potential electrolysis were carried out using an EG&G PARC model 173 potentiostat/galvanostat equipped with a model

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179 Digital Coulometer and a model 175 Universal Programmer. Glassy carbon and platinum discs (0.07 cm^2) and indium-doped tin oxide-coated glass (1.5 cm^2, Donnelly Corp.) were used as the working electrodes. The glassy carbon and platinum electrodes were polished with consecutively finer grades of alumina (Buehler Corp.) down to 0.05 μm. The ITO electrodes were washed with ethanol followed by acetone and thoroughly dried in a desiccator. The counter electrode was a large platinum spiral which was cleaned in a flame and washed with deionized water prior to use. A saturated calomel electrode was used as the reference in aqueous solution. A silver wire pseudoreference was used in organic media, and the potential was referred to the SCE at the end of each experiment. The electrochemical cell consisted of a three-electrode, two-compartment configuration based on a University of Southampton design [16] which incorporates a Luggin capillary to minimize ir drop. The solution was purged with argon and an argon atmosphere was maintained during the experiment.

Conductivity measurements were carried out by the four-point probe method; the thickness of the films was measured by electron microscopy of film samples encapsulated in epoxy resin and sectioned using a microtome. Estimates of the doping levels, which provide a partial analysis (PPY/dopant ratio), were made by coulometric measurements of the redox processes in a 0.1 mol dm^{-3} solution of the salt, the anion of which had been doped into the polymer during previous electropolymerization. The total charge passed during oxidation along with the weight of the film (Cahn microbalance) allowed calculation of the doping level in each case. Ultraviolet–visible spectra were recorded on a Hewlett-Packard model 8452A diode array spectrometer interfaced to a Zenith 286 computer. Scanning electron micrographs were taken on a Philips model 515 SEM. The films were sufficiently conducting to render sputter-coating with Pd unnecessary.

Electropolymerization was performed by cycling the system through a potential range (cyclic voltammetry, CV) or by controlled potential electrolysis (CPE). Solutions from 0.1–0.24 mol dm^{-3} in supporting electrolyte were prepared and scanned over a suitable potential range to establish the background current. If a sufficiently flat background was obtained, the solution was made 0.05 mol dm^{-3} in pyrrole, and electropolymerization was carried out by either the CV or CPE method.

Materials

Pyrrole (Aldrich, 99%) was doubly distilled in vacuum just prior to use. Heptafluorobutyric acid, pentafluorobenzoic acid (Aldrich), perfluoroglutaric acid (PCR, Inc.) and tetraethylammonium perfluorooctane sulfonate (Fluka) were used as received. Tetraethylammonium perfluorobutane 1,4-bis(sulfonate) was prepared from bis(1,4-fluorosulfuryl)perfluorobutane by hydrolysis in aqueous barium hydroxide, treatment with 6 M H_2SO_4 and, after filtration, titration of the resulting acid with TEAOH (Aldrich). The solution containing the product was dried, filtered and rotary-evaporated to yield hygroscopic crystals of the product (30% yield). The ^{19}F NMR spectrum of the product in DMSO-d_6 was in agreement with that found for the analogous potassium salt [17], and the ^1H NMR spectrum agreed closely with that reported for TEABr [18]. Acetonitrile (Fisher HPLC grade) was distilled from calcium hydride prior to use. Propylene carbonate (Aldrich, 99%) was used as withdrawn through a septum from bottles sealed under dry nitrogen. Water was first distilled and then passed through a Barnstead deionizer.

Results

A variety of fluorinated carboxylate and sulfonate salts was used as supporting electrolytes in the electropolymerization experiments. Salts of perfluorobutyrate, perfluorobenzoate, perfluorooctane sulfonate, perfluoroglutarate, and perfluorobutane 1,4-bis(sulfonate) gave well-defined nucleation loops for the first CV scan in both water and acetonitrile, but, in propylene carbonate, only solutions containing perfluorooctane sulfonate and perfluorobutane 1,4-bis(sulfonate) did so. Free-standing films could be grown in all cases in aqueous solution. The conductivities of the films grown from aqueous solution showed a correlation with the doping level (Table 1). $PPY^+\ {}^-SO_3(CF_2)_7CF_3$ grown in acetonitrile and in propylene carbonate gave onset potentials of 723 and 843 mV and conductivities of 0.8 and 2.1 S cm^{-1}, respectively. For the latter, the conductivity was measured before stretching (2.1 S cm^{-1}) and along the axis of stretch after stretching (about 10% elongation, 33.4 S cm^{-1}).

A study of the change in conductivity of polypyrrole heptafluorobutyrate with pH was carried out by electropolymerizing pyrrole in heptafluorobutyric acid solutions for which the pH had been adjusted by the addition of tetrabutylammonium hydroxide. Data: pH, σ (S cm^{-1}): 1.5, 6.2; 3.5, 7.2; 5.4, 11.0; 6.5, 6.7; 8.0, 4.0; 10.2, 1.8; 12.2, negligible. Electronic absorption spectra were obtained for samples of $PPY^+\ A^-$ in which $A^- = CF_3CF_2CF_2COO^-$, ${}^-OOC(CF_2)_3COO^-$, and $CF_3(CF_2)_7SO_3^-$ (Table 2).

The conductivities of two samples were measured after they were freshly prepared and again after they had been allowed to stand in the atmosphere. A fresh sample of $PPY^+\ {}^-OOCCF_2CF_2CF_3$, prepared in an aqueous solution, had a conductivity of 22 S cm^{-1} and one of 14 S cm^{-1} after 3 weeks. The

TABLE 1

Electrical parameters for selected electrolytes

Supporting electrolyte[a]	E_{mon} (mV SCE)	Conductivity (S cm^{-1})	Doping level
$CF_3CF_2CF_2COO^-$	720	50.0	0.30
${}^-OOC(CF_2)_3COO^-$	760	12.0	0.10
$O_3S(CF_2)_4SO_3^-$	650	10.3	0.05
$CF_3(CF_2)_7SO_3^-$	600	3.4	0.03

[a] All in aqueous solution.

TABLE 2

Spectral data for selected polypyrrole films

Film		UV–visible absorption bands (nm)					
$PPY^+\ {}^-OOC(CF_2)_2CF_3$		342	428	580			
$PPY^+\ ({}^-OOC)_2(CF_2)_3$		330	415	544			
$PPY^+\ {}^-O_3S(CF_2)_7CF_3$		338	422	570			
Literature data [33]							
$PPY^+\ ClO_4^-$	high	344	459			1239	
doping level	low	387		590	885		1771

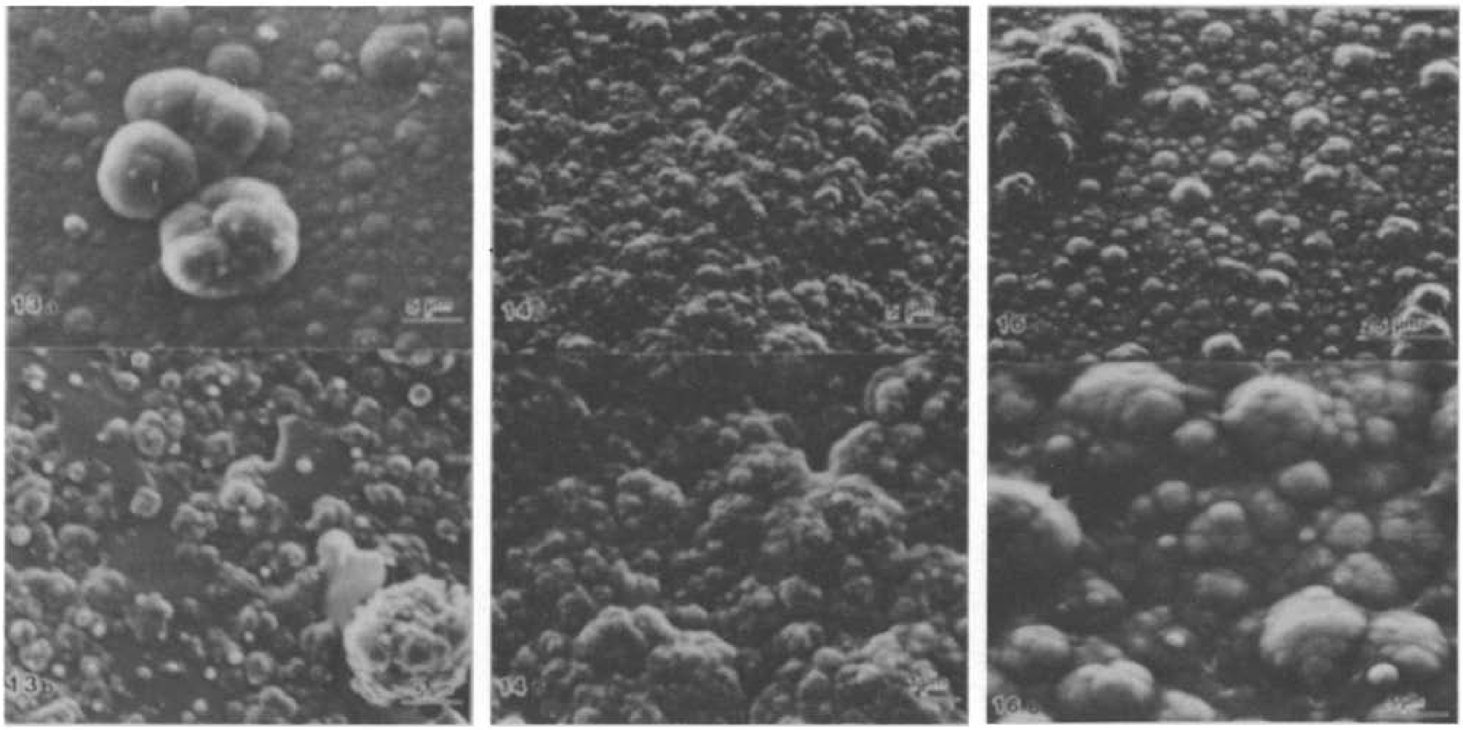

Fig. 1. Scanning electron micrographs of polypyrrole doped with perfluoroglutarate, perfluorooctane sulfonate and perfluorobutyrate. Conditions: 0.25 M pyrrole, 0.15 M supporting electrolyte (aqueous) -0.4–0.9 V, $v = 100$ mV s^{-1}. 13a: perfluorooctane sulfonate; -0.4–1.2 V, conductivity $= 0.8$ S cm^{-1}. 14a, b: perfluorooctane sulfonate; conductivity $= 3.4$ S cm^{-1}. 16a, b: perfluorobutyrate; conductivity $= 50$ S cm^{-1}.

conductivity of a fresh sample of $PPY^+\ {}^-SO_3(CF_2)_7CF_3$ was 5.4×10^{-2} S cm^{-1} and, after 3 weeks, 1.1×10^{-2} S cm^{-1}. The tensile strengths of two doped polymeric films were measured and the percentage elongation at break was also determined. A film of $PPY^+\ {}^-OOCCF_2CF_2CF_3$ had a tensile strength of 3.3 MPa and a 10% elongation at break. A sample of $PPY^+\ {}^-OOC(CF_2)_3COO^-$ had a tensile strength of 2.7 MPa and a 19% elongation at break. Samples of PPY^+A^- were prepared for SEM studies using the CV method, but with higher concentrations of pyrrole in the supporting electrolyte (Fig. 1).

Discussion

Previous workers have reported on the electropolymerization of pyrrole in the presence of triflate [10, 11, 19–21], perfluorobutane sulfonate [20] and perfluorooctane sulfonate [10, 11, 20, 21]. Recently, a report on the chemical polymerization of polyelectrolytes by triflic, trifluoroacetic, pentafluoropropionic, heptafluorobutyric and perfluorooctanoic acids has appeared [22]. Although work has been carried out on the electropolymerization of pyrrole in solutions containing alkyl sulfonates [23–26], alkane bis(sulfonates) [11] and aromatic mono-, bis- and tris-(sulfonates) [9, 27, 28], investigations concerning perfluorobutyrate, fluorinated bis(sulfonates) and fluorinated bis(carboxylates) have not been published to our knowledge. We have found that pyrrole could be electropolymerized in aqueous solution in the presence of the sodium and tetraethylammonium salts of perfluoroglutaric acid, $HOOC(CF_2)_3COOH$; the sodium salts of perfluorobutyric acid, $CF_3(CF_2)_2COOH$, and perfluorobenzoic acid, C_6F_5COOH; the tetraethylammonium salt of perfluorobutane 1,4-bis(sulfonic) acid, $HO_3S(CF_2)_4SO_3H$; and the tetraethylammonium salt of perfluorooctane sulfonic acid, $CF_3(CF_2)_7$-SO_3H. In all cases, free-standing films which could be peeled from the electrodes were grown. In acetonitrile solution which contained of the order of 1% water [29], free-standing films could be obtained only in the presence of sodium perfluorobenzoate and tetraethylammonium perfluorooctane sulfonate, although nucleation occurred in the presence of perfluoroglutaric acid and its tetraethylammonium and sodium salts, as well as in the presence of sodium perfluorobutyrate and tetraethylammonium perfluorobutane 1,4-bis(sulfonatc). In propylene carbonate which contained 1% water, a free-standing film was obtained using tetraethylammonium perfluorooctane sulfonate as a supporting electrolyte; no nucleation occurred using tetraethylammonium perfluorobutyrate or tetraethylammonium perfluorobutane 1,4-bis(sulfonate). It appears that, in those cases in which nucleation occurs but thick films do not form, that the film becomes insulating probably due to overoxidation during the electrochemical polymerization process [30].

It has been recognized for some time that the supporting electrolyte has an influence on the conductivity of the resulting film [13, 31], and the conductivities of the films described in the present work show these effects. Measurement of the potential at which pyrrole is oxidized in aqueous solution indicates that the process is more facile in the presence of fluorinated sulfonates than with fluorinated carboxylates. Once formed, polypyrrole films doped with fluorinated carboxylate anions exhibited moderately higher conductivities than those doped with fluorinated sulfonate anions, but all had conductivities in the range usually found for conducting polypyrrole [32]. It was observed that the perfluorobutyrate-doped polypyrrole had consistently higher conductivities (11–50 S cm^{-1}) than reported earlier for aqueous trifluoroacetate-doped PPY (1–1.3 S cm^{-1}) [10]. Generally, it has been observed that the greater the nucleophilicity of the anion dopant, the lower the quality of the resulting polypyrrole film [32]. However, the small difference between the nucleophilicity of trifluoroacetate and perfluorobutyrate does not explain the difference in conductivity. It is possible that this difference results from the greater ordering effect of the larger perfluorobutyrate anion.

The doping levels measured coulometrically for perfluorobutyrate- and perfluoroglutarate-doped polypyrrole were consistent with the conductivity measurements, 50 and 12 S cm^{-1}, respectively. In general, the bis(carboxylate)- and bis(sulfonate)-doped polypyrrole films exhibited lower conductivities than shown by films doped with univalent anions. This has also been observed in the case of aromatic sulfonates and was interpreted in terms of the localization of the charges on the polymer chain by the multivalent anion [27].

The optical spectra were also consistent with the conductivities and doping levels. Table 2 lists the transitions observed for $PPY^+\ ^-OOCCF_2CF_2CF_3$, $PPY^+\ ^-OOC(CF_2)_3COO^-$ and $PPY^+\ ^-SO_3(CF_2)_7CF_3$. The bandgap transitions are 342, 330 and 338 nm, respectively, and it is clear that these absorptions are in the region associated with higher doping when compared with the absorption reported for highly doped $PPY^+\ ClO_4^-$ at 344 nm versus that for a lower doping level at 387 nm [33]. The absorptions at 428, 415 and 422 nm are the high-energy components of the bipolaron transition; the low-energy components occur outside the visible region in the near-infrared. Bands in the region 544–580 nm may be associated with residual polaron transitions, since none of the films is doped to 33%. The suspected polaron band is weakest for $PPY^+\ ^-OOC(CF_2)_2CF_3$ which is the species determined to have the highest doping level and, therefore, the lowest residual polaron level.

We also observed that the conductivities of the $PPY^+\ ^-OOC(CF_2)_2CF_3$ films were dependent upon the pH of the electrolyte. The conductivities ranged from 6.2 S cm^{-1} at low pH (1.5) to 11 S cm^{-1} at a pH value of 5.4. At a pH value of 8 and higher, the conductivities fell rapidly due to reaction of the pyrrole radical cation with the very nucleophilic hydroxide ion. Inganas *et al.* [34] found a decrease of over four orders of magnitude in the conductivity when $PPY^+\ ClO_4^-$ or $PPY^+\ BF_4^-$ were treated with strong base. The decrease in conductivity at the lowest pH could possibly be explained by repression of the dissociation of the parent acid, which results in a lower effective concentration of the anion in the supporting electrolyte. However, Warren and Anderson [10] found that, for simple inorganic and organic anions, the conductivity of polypyrrole was higher when it was formed in strongly acidic solution. Given that two protons are lost per pyrrole unit during the polymerization process, the acid concentration near the electrode must be quite high in any case, and the pH dependence below a pH value of 7 is difficult to understand.

Although the perfluorobutyrate-doped polypyrrole has good conductivity, it does not possess high stability under ambient conditions in the laboratory. There was a 36% decrease in conductivity over a period of 3 weeks. The perfluorooctane sulfonate-doped polypyrrole was even less stable and lost 80% of its conductivity over the same period. A strong synergistic effect of oxygen and water vapor on polymer degradation has been reported [35]; anions are lost from the film in this process. Since the fluorinated anions are stable and not easily removed from the film, the changes responsible for the loss in conductivity may be associated with oxidation of the pyrrole rings in polypyrrole in humid air [36].

The tensile strength of perfluorobutyrate-doped polypyrrole was 3.3 MPa, while for perfluoroglutarate-doped polypyrrole it was 2.7 MPa. Elongations at break were 10% and 19%. These data indicate that the films are not very strong but are reasonably ductile. Qian *et al.* [37] found that tosylate-doped polypyrrole, prepared in aqueous solution, had a tensile strength of 23 MPa and an elongation at break of 3%. Tosylate-doped films, prepared in organic solvents such as acetonitrile, have been found to have tensile strengths as high as 69 MPa and elongations at break from 15–60% [38].

When examined by SEM all films showed the globular structure characteristic of these materials, which has been interpreted as resulting from nucleation and three-dimensional hemispherical growth [28, 38, 39]. There is some correlation between surface smoothness and conductivity, presumably because a smoother surface indicates a higher degree of order in the film. This effect can be observed in Fig. 1. Although these globular surfaces have been observed for $PPY^+\ {}^-OOCF_3$ and $PPY^+\ {}^-OSO_2CF_3$ as well as a variety of other anions [19, 40–44], morphologies described as dendritic or porous have been reported [45, 46]. We have observed the formation of tubules at higher electropolymerization potentials in the $PPY^+\ {}^-OOC(CF_2)_2CF_3$ system [47], and others have also reported this phenomenon [48–50].

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