

Bulk electropolymerization of alkyppyroles

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New larger-scale (10 g monomer in 500 cm³) methods for the electropolymerization of alkyppyroles in quantity have been developed. These methods offer the advantage of electropolymerization with fractionation in a single step. Galvanostatic, potentiostatic and potentiodynamic methods have been considered. 3-Octadecylpyrrole was electrochemically synthesized in dichloromethane. The use of other solvent systems, namely dichloromethane/acetonitrile, carbon tetrachloride/dichloromethane or tetrahydrofuran/acetonitrile mixtures, has also been considered. Furthermore, the new copolymer of 3-octadecylpyrrole with pyrrole was successfully grown in dichloromethane/acetonitrile medium. The investigations were extended to 3-octylpyrrole, which was successfully electropolymerized. The products are conductive, some are electroactive and many can be dissolved in common organic media. The solubilities (some in excess of 50% by weight) of these polymers and their conductivities (as high as 31.4 S cm⁻¹) are reported. The yields and conductivities are dependent upon the solvent system and electrolyte used for electrosynthesis. The solvent system used for electrosynthesis also affected the solubility of the polymers produced. For cast films, the electroactivity depended not only upon the polymer but also upon the casting solvent. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

In the quest for more processable conducting polymers, numerous workers have been interested in the preparation and polymerization of 3-alkylpyrroles^{1–10}. The major advantage of alkylated polypyrroles is their enhanced solubility in common organic solvents and thus they lend themselves to further processing. In general, these workers^{1–10} were electrodepositing the polymers on the small scale and then dissolving them in organic solvents. Solubility data, however, are scarcely reported. Furthermore, some of the solvent systems used, for example acetonitrile, could only solubilize low quantities (1 mmol in 50 cm³) of monomers^{1,2}. High solubility of both the monomer and the polymer is of particular interest to us in our pursuit of novel conducting polymer membranes^{11–14} and chromatographic stationary phases^{15–22}.

Our applications^{11–20} require large quantities of poly(3-octadecylpyrrole) (PODP) (I) and poly(3-octylpyrrole) (POP) (II). Thus we have developed different, more efficient and larger-scale electropolymerization processes that we now report. In particular, our systems have the advantage of combining electrosynthesis and fractionation in a single step. Detailed new data, such as solubilities, are also reported.

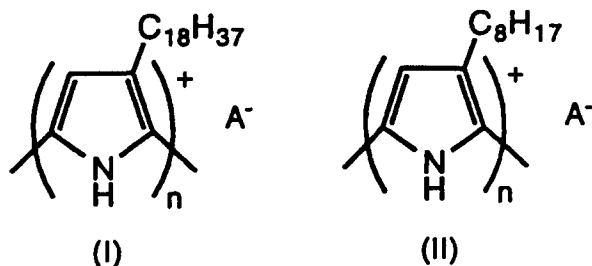
EXPERIMENTAL

Reagents

Tetrabutylammonium perchlorate (TBAP) (Fluka, Purum), tetrabutylammonium *p*-toluenesulfonate (TBAPTS) (Aldrich, 99%), *p*-toluenesulfonic acid monohydrate (pTS.H) (Sigma, 99%), dichloromethane (Mallinckrodt, AR), carbon tetrachloride (M & B, Proanalysis), acetonitrile (Mallinckrodt, AR) and tetrahydrofuran (BDH, Hipersolv) were used as received. Pyrrole (Sigma), however, was used only after redistillation.

Instrumentation

Electrochemical polymerizations were performed in a three-electrode cell where the working electrode was a Pt disc (0.017 cm², BAS), glassy carbon (GC) disc (0.07 cm², BAS) or Pt plate (50 × 70 × 0.4 mm³, Engelhard). The auxiliary electrode was a Pt mesh or reticulated vitreous carbon (ERG) sheet, and the reference electrode was Ag/AgCl (3 M NaCl, BAS) or Ag/Ag⁺ in a salt bridge.

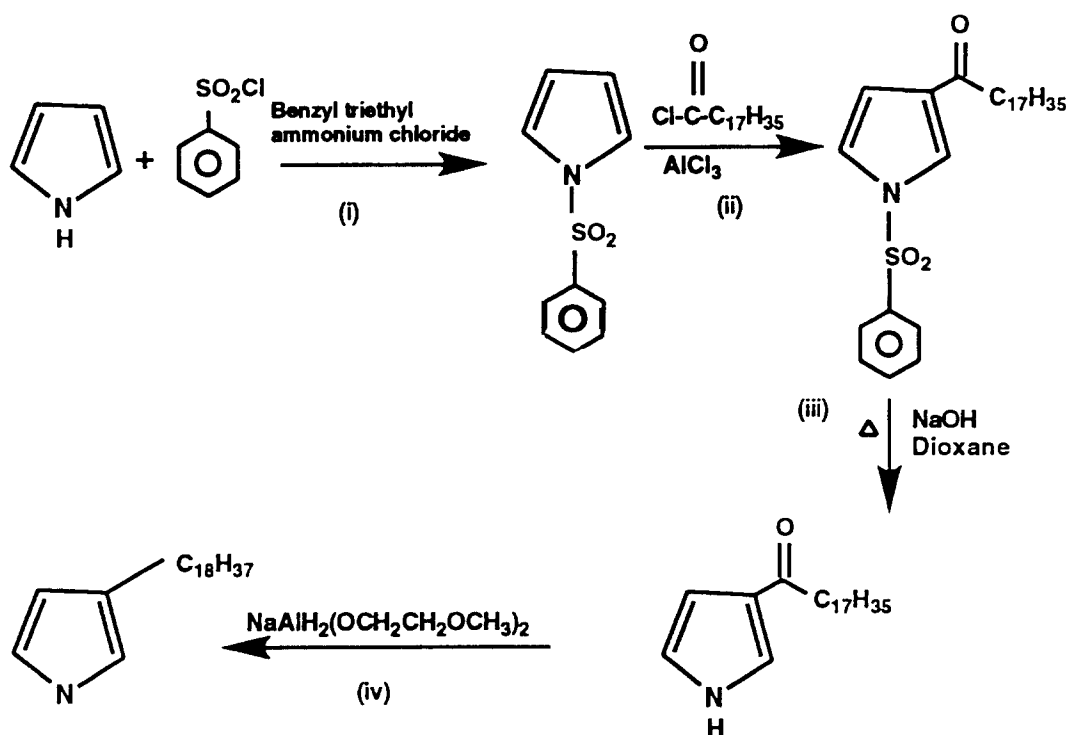


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For small-area working electrodes, potentiodynamic or potentiostatic growth was achieved by use of a BAS CV27 Voltammograph or BAS 100A Electrochemical Analyser, whereas galvanostatic growth was achieved by use of an in-house designed and constructed galvanostat. When large-area working electrodes were used, galvanostatic or potentiostatic growth was achieved by use of the PAR 173, and potentiodynamic growth by use of the PAR 173 in conjunction with a PAR 175.

Procedures

3-Octadecylpyrrole (ODP) was synthesized in four steps according to *Scheme 1*.



Scheme 1

- (i) the preparation of phenylsulfonylpyrrole by the reaction of pyrrole with phenylsulfonyl chloride in a phase-transfer medium²³;
- (ii) The Friedel-Crafts acylation²⁴ of stearoyl chloride with phenylsulfonylpyrrole;
- (iii) the removal of the phenylsulfonyl group by subsequent alkaline hydrolysis for 3 h under reflux instead of the 24 h reported previously²⁴; and
- (iv) the reduction of the ketone by using Red-Al to obtain the desired product (characterized by n.m.r., i.r. and fast-atom-bombardment mass spectrometry (f.a.b.m.s.)).

The synthesis of 3-octylpyrrole (OP) was similar to *Scheme 1* except that in step (ii) the Friedel-Crafts acylation used octanoyl chloride with phenylsulfonylpyrrole.

Potentiodynamic growth was carried out at 100 mV s^{-1} using a Pt disc working electrode in CH_2Cl_2 containing ODP (0.1 M) and TBAP (0.1 M), or OP (0.1 M) and TBAP (0.1 M) in acetonitrile. Galvanostatic electropolymerization, however, was performed at a current density of $1\text{--}2 \text{ mA cm}^{-2}$. The solution systems

considered are summarized in *Tables 1* and *2*. Typically, bulk electropolymerization was performed on 10 g of monomer in 500 cm^3 of solvent.

Electrochemical copolymerization of ODP with pyrrole (Py) was achieved using potentiodynamic conditions (scanning at 100 mV s^{-1} between 0.0 V and 3.0 V), and potentiostatic conditions at 3.0 V or 5.0 V. The monomer solution used consisted of ODP (0.1 M)/Py (0.1 M)/pTS.H (0.1 M) in CH_2Cl_2 (70%)/ CH_3CN (30%) solvent system.

The polymers electrodeposited on the Pt plate under stationary conditions were rinsed with the solvent used in polymerization, scraped off with a plastic spatula, and

stored for further processing and studies. Copolymers could be stripped off as stand-alone films.

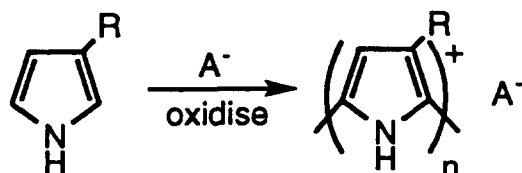
The soluble fractions of the electrosynthesized polymers and copolymers were recovered from the liquor using the following procedure. The solvent was evaporated off, and the residue polymer was ground with CH_3CN in a mortar and pestle to dissolve excess electrolyte. The polymer was filtered off and rinsed thoroughly with CH_3CN before drying and storage for further studies and processing. The yield of the soluble fractions can be increased by conducting the electrosynthesis in stirred solutions. Samples of poly(3-octadecylpyrrole) (PODP), poly(3-octylpyrrole) (POP) and copolymers were sent to the Australian National University for elemental analysis.

Solubility tests were conducted at 25°C by making up saturated solutions of the polymers in CH_2Cl_2 , CCl_4 or xylene and filtering off the residue. Accurate volumes (1.00 cm^3) of the saturated solutions were pipetted into pre-weighed vials and placed in the oven at 80°C to dry. The samples were then cooled in a desiccator and weighed. The drying and weighing procedure was repeated to constant weight.

Conductivity measurements using the four-point probe were made on films cast from xylene and stand-alone films. The thicknesses of the films were measured by use of a digital micrometer gauge. The electroactivity of these polymers and copolymers was investigated using cyclic voltammetry (c.v.). The films were electro-deposited or films were cast from solution onto a Pt disc electrode. The test solutions used were pTS.H (0.1 M) or TBAP (0.1 M) or TBAPTS (0.1 M) in acetonitrile, and NaNO_3 (0.1 M) in deionized water.

RESULTS AND DISCUSSION

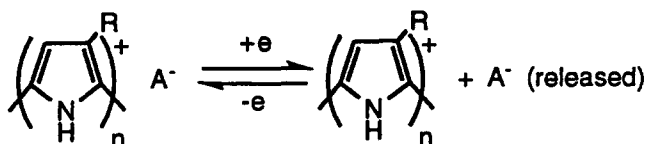
Initially the polymerization of ODP from CH_2Cl_2 (TBAP) was considered using several electrochemical techniques. Dichloromethane was used in preference to acetonitrile since the monomer is only sparingly soluble in the latter solvent. OP, however, was miscible with acetonitrile, and initial studies for this monomer were conducted in this medium. The polymerization is expected to occur at anodic potentials as the monomer is oxidized according to:



where $\text{R} = \text{C}_8\text{H}_{17}$ or $\text{C}_{18}\text{H}_{37}$.

Potentiodynamic polymerization

Cyclic voltammograms recorded indicated that the monomer was oxidized at approximately +0.90 V (first scan) for ODP and +0.72 V (first scan) for OP. Subsequent scans (Figure 1) show additional responses due to polymer oxidation/reduction. These responses labelled A/B are attributed to the redox processes described in the equation:



The magnitude of these responses continued to increase with the number of potential scans as more polymer was generated at positive potentials.

Galvanostatic polymerization

PODP- ClO_4 was successfully electrosynthesized using current densities in the range 0.5 to 2 mA cm^{-2} . The polymers can be electrodeposited directly onto the electrode substrate from still solutions. A typical chronopotentiogram obtained in still solutions is shown in Figure 2, where the potential attained continued to decrease from 1.23 V at the initial spike to

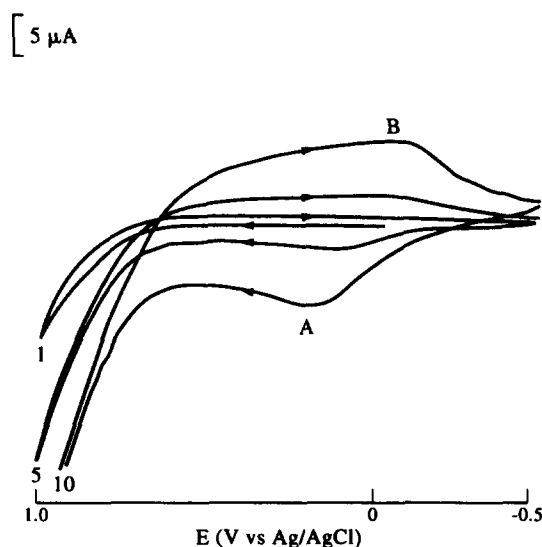


Figure 1 Potentiodynamic electropolymerization of ODP. Substrate: Pt disc electrode. Monomer solution: ODP (0.1 M) in TBAP (0.1 M)/ CH_2Cl_2 . Scan rate: 100 mV s^{-1}

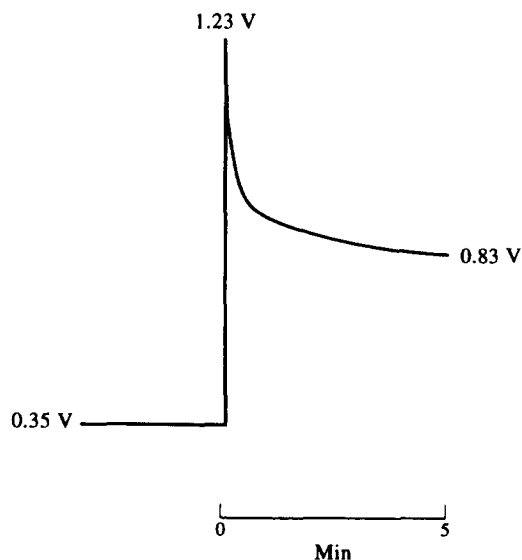


Figure 2 Chronopotentiogram of galvanostatic electropolymerization of ODP. Substrate: Pt disc electrode. Monomer solution: ODP (0.1 M) in TBAP (0.1 M)/ CH_2Cl_2 . Current density = 2 mA cm^{-2}

a final value of 0.83 V at the end. This is an indication that the polymer being grown is conductive.

It was found that the ODP monomer was also soluble in CCl_4 and tetrahydrofuran (THF), but the conductivities of these solutions (even containing supporting electrolyte) were much lower than when CH_2Cl_2 was used. Thus the use of CH_2Cl_2 , $\text{CH}_2\text{Cl}_2/\text{CCl}_4$, $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ or $\text{THF}/\text{CH}_3\text{CN}$ as solvent systems was considered with galvanostatic polymerization. It was found that with all these solvent systems polymer growth was possible (Table 1). In all cases polymer was deposited on the anode and some polymer product was evident in solution. This was not surprising since conducting polymer formation is known to occur in solution with subsequent deposition of the material onto the electrode surface²⁵. Since PODP is more soluble than other pyrroles, some solution-soluble fraction would be expected. The solvent used can influence the yield of

Table 1 Galvanostatic growth of PODP^a

Monomer solution	Weight of polymer (g) electrosynthesized per gram of ODP monomer		
	Deposited	In liquor	Total
ODP (0.1 M)/TBAP (0.1 M)/CH ₂ Cl ₂	0.11	0.96	1.07
ODP (0.1 M)/TBAP (0.1 M)/THF	0.18	0.88	1.06
ODP (0.1 M)/TBAP (0.1 M)/CH ₂ Cl ₂ (70%)/CH ₃ CN (30%)	0.16	0.40	0.56
ODP (0.1 M)/TBAP (0.1 M)/THF (90%)/CH ₃ CN (10%)	0.40	0.26	0.66
ODP (0.1 M)/TBAP (0.1 M)/CCl ₄ (80%)/CH ₂ Cl ₂ (20%)	0.25	0.64	0.89
ODP (0.1 M)/TBAP (0.1 M)/TBApTS (0.025 M)/CH ₂ Cl ₂ (20%)/CCl ₄ (80%)	0.07	0.96	1.03
ODP (0.1 M)/pTS.H (0.1 M)/CH ₂ Cl ₂ (70%)/CH ₃ CN (30%)	0.08	1.08	1.16
ODP (0.1 M)/pTS.H (0.1 M)/THF (90%)/CH ₃ CN (10%)	0.16	1.20	1.36

^a Notes: Pt plate dimensions = 6 × 5 cm²; current density = 2 mA cm⁻²; time = 24 h; monomer solution = 10 g monomer per 500 cm³ solvent; dep = deposited on electrode substrate; liq = recovered from the liquor

Table 2 Galvanostatic growth of POP^a

Monomer solution	Weight of polymer (g) electrosynthesized per gram of OP monomer		
	Deposited	In liquor	Total
OP (0.1 M)/pTS.H (0.1 M)/CH ₃ CN (75%)/CH ₂ Cl ₂ (25%)	0.1	0.76	0.86
OP (0.1 M)/TBAP (0.1 M)/TBApTS (0.025 M)/CH ₃ CN (75%)/CH ₂ Cl ₂ (25%)	0.3	0.3	0.6
OP (0.1 M)/TBAP (0.1 M)/TBApTS (0.025 M)/CCl ₄ (80%)/CH ₂ Cl ₂ (20%)	0.8	0.97	1.77

^a Notes: Pt plate dimensions = 6 × 5 cm²; current density = 1 mA cm⁻²; time = 24 h; monomer solution = 10 g monomer per 500 cm³ solvent; dep = deposited on electrode substrate; liq = recovered from the liquor

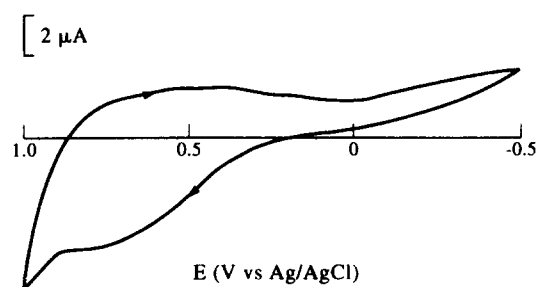


Figure 3 Electroactivity of PODP-pTS. Electrode: Pt/PODP-pTS. Test solution: pTS.H (0.2 M)/CH₃CN. Scan rate: 20 mV s⁻¹

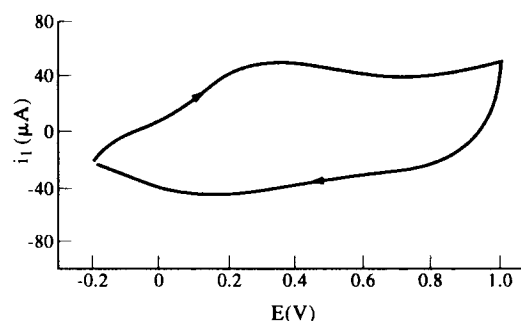


Figure 5 Electroactivity of POP-pTS. Electrode: Pt/POP-pTS. Test solution: TBAP (0.1 M)/CH₃CN. Scan rate: 100 mV s⁻¹

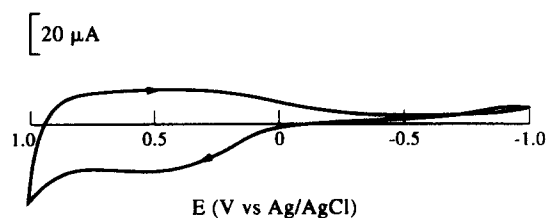


Figure 4 Electroactivity of PODP/PPy-pTS copolymer. Electrode: Pt/PODP/PPy-pTS. Test solution: TBAP (0.1 M)/CH₃CN. Scan rate: 20 mV s⁻¹

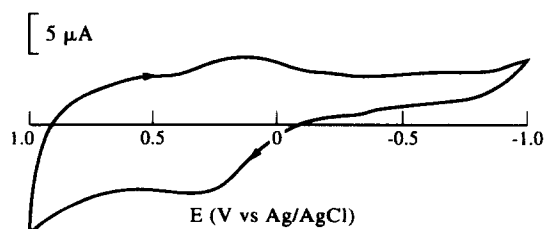


Figure 6 Electroactivity of cast PODP-ClO₄. Electrode: Pt/PODP-ClO₄. Casting solvent: CH₂Cl₂. Test solution: TBAP (0.1 M)/CH₃CN. Scan rate: 20 mV s⁻¹

both the electrodeposited fraction on a larger plate electrode and the amount of soluble product (*Table 1*). In the case of TBAP electrolyte, the solvent system used had a marked effect upon the yield of the polymer. For example, a total of 1.07 g of polymer per gram of monomer was obtained in CH₂Cl₂ medium as compared

with a total of 0.56 g of polymer per gram of monomer from CH₂Cl₂ (70%)/CH₃CN (30%). The other effect due to the solvent system was on the ratio of the weight of deposited polymer to the weight of dissolved polymer

Table 3 Solubility data at 25°C for PODP^a

Polymer	Solubility (g dm ⁻³)		
	In CH ₂ Cl ₂	In CCl ₄	In xylene
PODP-ClO ₄ electrodeposited from CH ₂ Cl ₂ recovered from CH ₂ Cl ₂ liquor	36 140	52.5 355	57 353
PODP-ClO ₄ electrodeposited from THF recovered from THF liquor	3.5 86	13.5 497	30.5 226
PODP-ClO ₄ electrodeposited from CH ₂ Cl ₂ /CH ₃ CN medium recovered from CH ₂ Cl ₂ /CH ₃ CN liquor	4 72	0 93	0 45
PODP-ClO ₄ electrodeposited from THF/CH ₃ CN medium recovered from THF/CH ₃ CN liquor	5 681	1 680	0 350
PODP-ClO ₄ electrodeposited from CCl ₄ /CH ₂ Cl ₂ medium recovered from CCl ₄ /CH ₂ Cl ₂ liquor	10 88	5 133	1 66
PODP-ClO ₄ /pTS electrodeposited from CCl ₄ (80%)/CH ₂ Cl ₂ (20%) medium recovered from the liquor	64 236	42 138	56 314
PODP-pTS electrodeposited from CH ₂ Cl ₂ /CH ₃ CN medium recovered from the liquor	40 440	34 323	51 384
PODP-pTS electrodeposited from THF/CH ₃ CN medium recovered from the liquor	8 626	8 388	7 501

^a Conditions: current density = 2 mA cm⁻²; polymerization time = 24 h

Table 4 Solubility data at 25°C for the copolymer of ODP with pyrrole^a

Copolymer	Solubility (g dm ⁻³)		
	In CH ₂ Cl ₂	In CCl ₄	In xylene
PODP/PPy-pTS electrodeposited at 3.0 V recovered from the liquor	n.t. 164	n.t. 67	6 77.5

^a Notes: n.t. = not tested; current density = 2 mA cm⁻²; polymerization time = 24 h

in the liquor (1.54 for THF (90%)/CH₃CN (10%) compared with 0.11 for CH₂Cl₂). TBApTS and pTS.H were also considered for use as electrolytes. The effect of the electrolyte is demonstrated by comparing the ratio of the weight of deposited polymer to dissolved polymer. For example, the ratio was 0.13 for PODP-pTS whereas it was 1.54 for PODP-ClO₄ in the case where THF

(90%)/CH₃CN (10%) was used as the solvent system. This is probably due to the higher solubility of pTS⁻ (an organic anion) as compared with that of ClO₄⁻ (an inorganic anion).

The galvanostatic approach was also employed for the large-scale synthesis of POP. In this case the solvent systems used were CH₃CN (75%)/CH₂Cl₂ (25%) and CCl₄ (80%)/CH₂Cl₂ (20%) (one of the successful systems already used for ODP). Once again, a deposited fraction and a fraction recovered from the liquor were obtained. The yields are given in Table 2.

Electroactivity

The polymers, in the form of as-electrodeposited samples on Pt disc electrodes, were tested for electroactivity in the supporting electrolyte of growth as well as in two other test solutions. The electroactivity was found to be dependent on the supporting electrolyte/solvent

Table 5 Solubility data at 25°C for POP^a

Polymer	Solubility (g dm ⁻³)		
	In CH ₂ Cl ₂	In CCl ₄	In xylene
POP-ClO ₄ /pTS electrodeposited from CH ₃ CN/CH ₂ Cl ₂ recovered from CH ₃ CN/CH ₂ Cl ₂ liquor	10 423	10 196	1.4 227
POP-ClO ₄ /pTS electrodeposited from CCl ₄ /CH ₂ Cl ₂ recovered from CCl ₄ /CH ₂ Cl ₂ liquor	6 377	11 460	3 386
POP-pTS recovered from CH ₃ CN/CH ₂ Cl ₂ liquor	329	153	185

^a Conditions: current density = 2 mA cm⁻²; polymerization time = 24 h

systems used for testing. Thus the most well defined cyclic voltammograms are now discussed. No change in the cyclic voltammograms was observed when cycled for 3–10 cycles.

Figure 3 shows the electroactivity of PODP-pTS polymer in pTS.H (0.2 M)/CH₃CN. The peaks are

broad with peak potentials $E_{p(a)}$ of +0.78 V and $E_{p(c)}$ of +0.36 V. The PODP/PPy-pTS copolymer was also electroactive (Figure 4), but in this case the best test solution was TBAP (0.1 M)/CH₃CN. Once again, the peaks were broad and the peak potentials were +0.53 V ($E_{p(a)}$) and +0.44 V ($E_{p(c)}$). Poly(3-octylpyrrole) was also

Table 6 Conductivity data of PODP and POP polymers

Polymer	Method of preparation	Thickness (μm)	Conductivity (Scm^{-1})
PODP-ClO ₄ /pTS	Electrodeposited galvanostatically from ODP (0.1 M)/TBAP (0.1 M)/TBApTS (0.025 M)/CCl ₄ (80%)/CH ₂ Cl ₂ (20%) and cast by solvent evaporation from xylene at 70°C	24.3 \pm 0.6	30.3 \pm 4.4
PODP-ClO ₄ /pTS	Electrodeposited galvanostatically from ODP (0.1 M)/TBAP (0.1 M)/pTS.H (0.1 M)/CH ₂ Cl ₂ (70%)/CH ₃ CN (30%) and cast by solvent evaporation from xylene at 70°C	179 \pm 1	0.4 \pm 0.1
POP-pTS	Electrodeposited galvanostatically from OP (0.1 M)/pTS.H (0.1 M)/CH ₃ CN (75%)/CH ₂ Cl ₂ (25%)	37 \pm 1	2.4 $\times 10^{-4}$ \pm 2 $\times 10^{-5}$
POP-ClO ₄ /pTS	Electrodeposited galvanostatically from OP (0.1 M)/TBAP (0.1 M)/TBApTS (0.025 M)/CH ₃ CN (75%)/CH ₂ Cl ₂ (25%)	141 \pm 6	4.6 $\times 10^{-3}$ \pm 2 $\times 10^{-4}$

Table 7 Conductivity data for copolymer of ODP with pyrrole

Copolymer	Method of preparation	Thickness (μm)	Conductivity (Scm^{-1})
PODP/PPy-pTS	Electrolysed potentiostatically at 3 V from ODP (0.1 M)/Py (0.1 M)/pTS.H (0.1 M)/pTS.H (0.1 M)/CH ₃ CN (30%) and cast by solvent evaporation from xylene at 70°C	159 \pm 1	31.4 \pm 5.1
PODP/PPy-pTS	Electrodeposited potentiostatically at 5 V from ODP (0.1 M)/Py (0.1 M)/pTS.H (0.1 M)/CH ₂ Cl ₂ (70%)/CH ₃ CN (30%) and peeled off as stand-alone film	10.0 \pm 1.8	0.6 \pm 0.1

Table 8 Elemental analysis of PODP and POP polymer and copolymers with pyrrole

Element (%)	PODP-ClO ₄ deposit	PODP/PPy-pTS deposit grown at 3 V	PODP/PPy-pTS deposit grown at 5 V
C	60.57	65.78	64.91
H	9.85	7.63	6.95
N	3.08	6.18	7.46
O	12.12	11.84	12.92
Cl	5.07	—	—
S	—	5.81	6.72

Element (%)	PODP-ClO ₄ /pTS deposit	PODP-ClO ₄ /pTS from liquor	PODP-pTS deposit	PODP-pTS from liquor
C	77.87	76.53	65.53	62.70
H	12.36	12.59	10.71	10.06
N	3.63	3.52	3.48	2.31
O	5.09	4.40	12.39	7.09
Cl	1.76	2.63	—	—
S	1.36	0.84	5.28	3.05

Element (%)	POP-pTS deposit	POP-pTS from liquor	POP-ClO ₄ /pTS deposit	POP-ClO ₄ /pTS from liquor
C	66.44	69.62	65.45	69.06
H	9.61	11.04	11.10	10.43
N	4.71	3.93	6.40	4.27
O	10.93	8.89	5.67	5.48
Cl	—	—	10.26	7.77
S	4.23	4.39	1.78	0.86

electroactive. For example, POP-pTS was electroactive (Figure 5) in TBAP (0.1 M)/CH₃CN with peak potentials $E_{p(a)}$ of +0.33 V and $E_{p(c)}$ of +0.15 V.

When the polymers were cast from solution, however, electroactivity also depended upon the polymer and the casting solvent. Thus PODP-ClO₄ cast from dichloromethane was electroactive (Figure 6), but it was not electroactive when cast from xylene. In this case $E_{p(a)}$ was +0.32 V and $E_{p(c)}$ was +0.11 V.

Solubility of polymer

Three solvents were tested, namely CH₂Cl₂ (dielectric constant 9.08), CCl₄ (dielectric constant 2.24) and xylene (dielectric constant 2.27 to 2.57). During electropolymerization it was found that some polymer was electrodeposited but some of the polymer produced dissolved in the electrolyte solution. Consequently, the polymers recovered from the liquor are much more soluble than those that have been electrodeposited (Tables 3, 4 and 5). For PODP, solubility depended upon the solvent used in the electrosynthesis of the polymers (Table 3). Higher solubilities for the PODP polymers (fraction recovered from the liquor) were obtained when PODP polymers were electrosynthesized in THF (90%)/CH₃CN (10%) medium. This is not surprising given that the fractionation of the polymers during electrosynthesis is dependent upon the solvent system used. Shorter chain fractions will be recovered from the liquor if the polymer is less soluble in it. The highest solubility (681 g dm⁻³ in CH₂Cl₂) was obtained for PODP-ClO₄ electrosynthesized in THF (90%)/CH₃CN (10%). It is also apparent that the more soluble shorter-chain fractions are less doped. These polymer solutions have been cast to form stand-alone films and also as coatings on electrodes and conventional porous substrates.

Conductivity

Tables 6 and 7 summarize the conductivity data for the polymers and copolymers. The PODP-ClO₄/pTS cast from xylene are conductive (Table 6), but the conductivities are greatly affected by the electrosynthesis conditions (solvent system and electrolyte) of the polymer. Similarly, it can be seen from the POP polymers that the type of counterion(s) used as electrolytes during electrosynthesis affects the conductivity. Thus POP-pTS is very much (20 times) less conductive than POP-ClO₄/pTS. Elemental analysis reveals that the latter is more doped than the former (Table 8). Tables 6 and 7 also show that the conductivities of the copolymers are not significantly different from those of the homopolymers. The best conductivity for the polymers was obtained from PODP-ClO₄/pTS (30.3 S cm⁻¹) that was electrodeposited galvanostatically from ODP (0.1 M)/TBAP (0.1 M)/TBAPTS (0.025 M)/CCl₄ (80%)/CH₂Cl₂ (20%), and then cast from xylene at 70°C. In contrast, the best conductivity for the copolymer PODP/PPy-pTS (31.4 S cm⁻¹) was obtained from the fraction recovered from the liquor that was electrolysed at 3 V from ODP (0.1 M)/Py (0.1 M)/pTS.H (0.1 M)/CH₂Cl₂ (70%)/CH₃CN (30%), and then cast from xylene at 70°C.

Elemental analysis

The results of the elemental analyses for PODP and POP polymer, and copolymers with pyrrole are given in Table 8. The probable structures deduced from the

elemental analysis are given in Figure 7. Electrodeposited PODP polymers tend to be more highly doped than those recovered from the liquor. The doping levels of POP polymers, however, depend upon the counterion(s). Therefore, electrodeposited POP-pTS is less doped than the fraction recovered from the liquor, whereas electrodeposited POP-ClO₄/pTS is more highly doped than POP-ClO₄/pTS recovered from the liquor. In cases where there are very high levels of doping, such as one monomer unit to one counterion deduced from elemental analysis, there might be some entrapped free salts in these samples despite having carefully washed the samples by grinding with acetonitrile using a mortar and pestle.

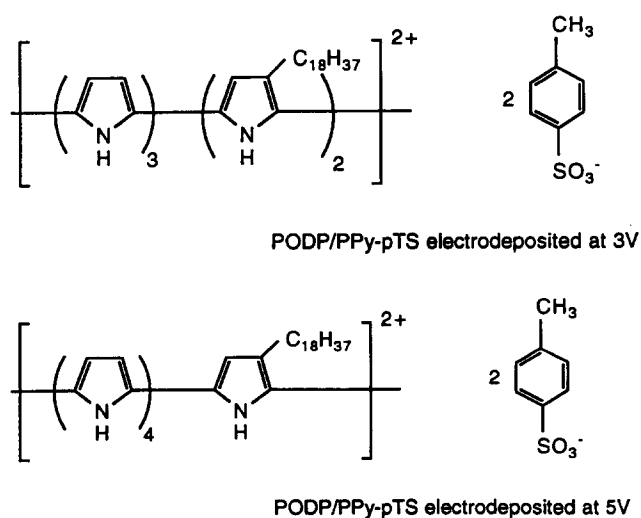
Electrocopolymerization

The formation of copolymers of pyrrole and 3-octadecylpyrrole using electrochemical methods was then considered. Only potentiodynamic or potentiostatic methods could be employed since galvanostatic polymerization would result in preferential deposition of the easier-to-oxidize (PODP) polymer.

Electropolymerization was considered in dichloromethane/acetonitrile mixed solvent. The c.v. of the potentiodynamic method for the copolymer synthesis shows that the currents increased with subsequent scans even when scanned to +3.0 V, which is a similar behaviour to that of polypyrrole synthesis under the same conditions. This indicates that the copolymer, like PPy, is more conductive than PODP-pTS, where cyclic voltammetric responses decreased on subsequent scans.

The copolymer produced potentiostatically at 3.0 V could not be cleanly stripped off the Pt substrate, whereas that produced at 5.0 V could be peeled off as a stand-alone film. On the other hand, the copolymer produced at the lower of the two potentials is slightly soluble in organic solvent (6 g dm⁻³ in xylene) whereas that produced at 5.0 V is insoluble.

The copolymer electrodeposited at 3 V has a lower pyrrole content than that electrodeposited at 5 V (see elemental analysis in Table 8). This is because ODP is easier to oxidize than pyrrole; thus at 3 V, the rate of ODP oxidation is 1.4 times the rate of pyrrole oxidation as calculated from chronoamperometric experiments. Therefore, at the higher potential of 5 V, more pyrrole will be oxidized than at 3 V. Elemental analysis suggests the following structures:



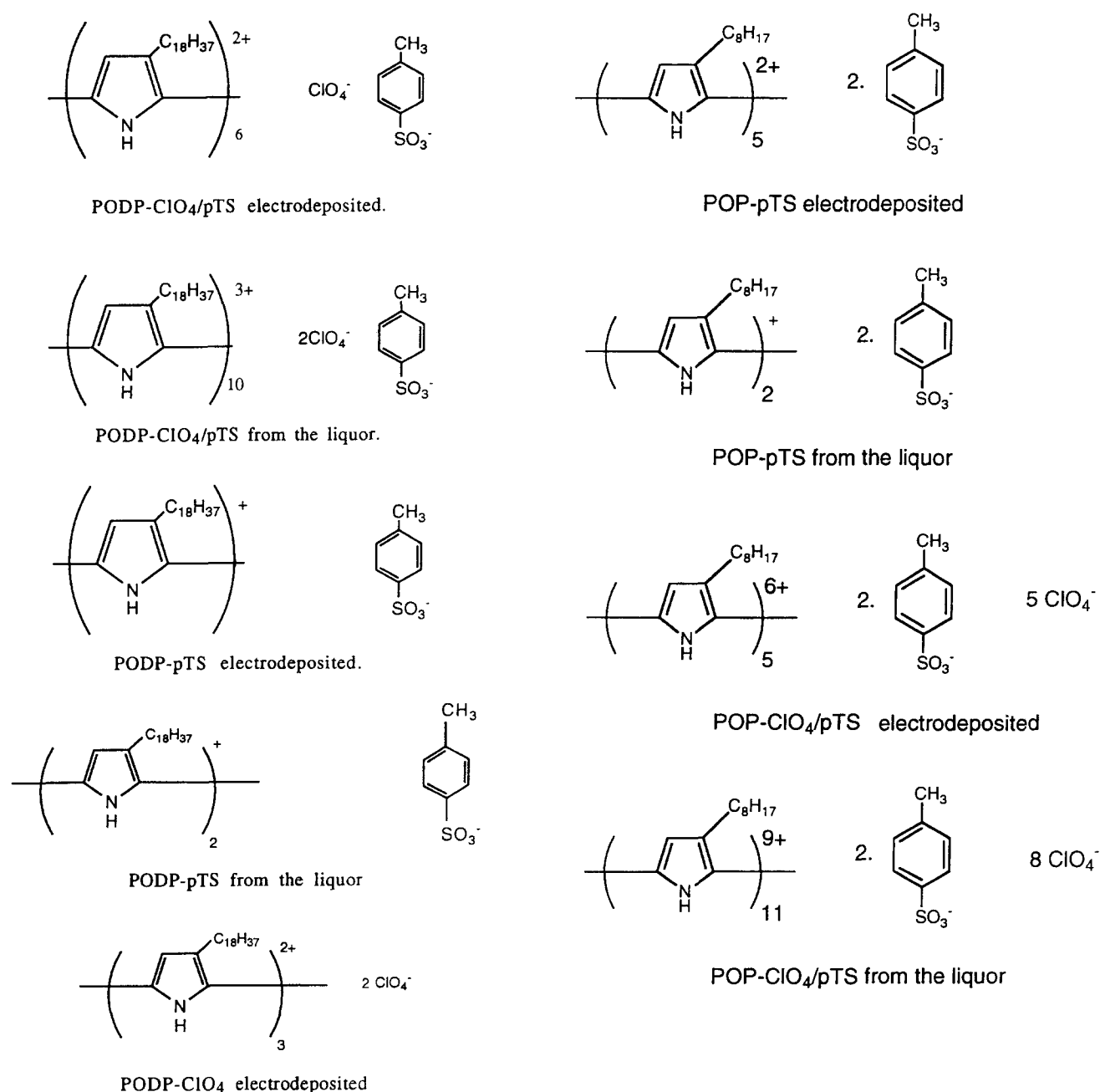


Figure 7 Structures of conducting polymers deduced from elemental analysis (Table 8)

CONCLUSIONS

Poly(3-octadecylpyrrole) and poly(3-octylpyrrole) can be electrochemically synthesized in bulk quantities and are found to be soluble in common organic solvents such as CH_2Cl_2 , CCl_4 and xylene. The techniques we have developed combine electrosynthesis and fractionation in a single step. The yield and fractionation are influenced by the solvent system as well as by the electrolyte used for electrosynthesis. The solubility of polymers recovered from the liquor after electrolysis is much higher than that produced by electrodeposition. This is probably due to the greater degree of crosslinking and longer chains in the electrodeposited polymers. The solvent used in electrosynthesis also affected the solubility of these polymers because it affected the fractionation and therefore the chain lengths of the fractions.

The copolymer of ODP with pyrrole can also be produced electrochemically. It was found that PODP/

PPy produced at 3 V could not be cleanly peeled off the Pt substrate but it was soluble in xylene. In contrast, PODP produced at 5 V could be peeled off as a stand-alone film but it was insoluble in xylene. Elemental analysis confirmed, as expected from this disparity in solubility, that the copolymer produced at 5 V had a lower ODP content than that produced at 3 V.

The polymer and copolymer films produced were conductive, but conductivity depended upon the solvent and electrolyte used for electrosynthesis. These polymers and copolymers were electroactive, but this depended upon the electrolyte/solvent system used as test solutions. Furthermore, the electroactivity of cast polymers depended not only upon the polymer but also upon the casting solvent. In terms of electrosynthesis and processing, the electrolysed products were obtained with higher yields and the polymers are much more soluble in the solvents used for casting.

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