3-Alkylthiopyrroles: Synthesis and Oxidative Polymerization to Conductive Materials

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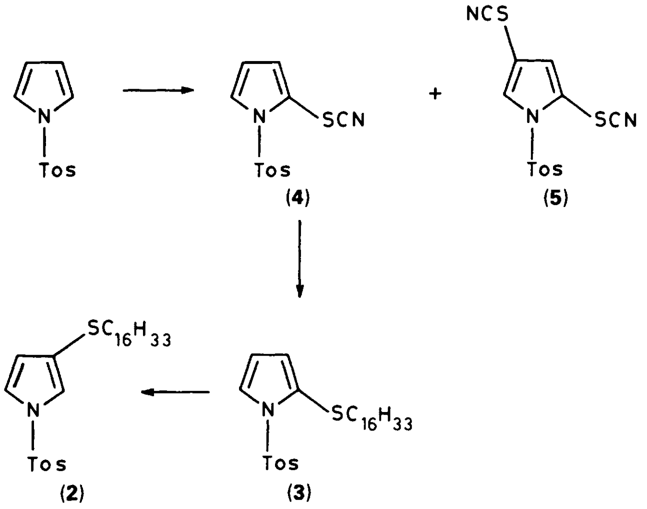
3-Alkylthiopyrroles are obtained by decarboxylation of 4-alkylthiopyrrole-2-carboxylic acids, in turn prepared by alkaline hydrolysis of the corresponding methyl ester. These compounds were accessible by thiocyanation of 2-methoxycarbonylpyrrole, followed by alkylation in basic media. Anodic coupling of 3-thioalkylpyrroles in 0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP) + acetonitrile produces polypyrrole films which are reversibly oxidized around 0.0 V *vs.* Ag/Ag^{+} with 0.3 electrons per monomeric unit. Polymers were characterized by IR reflectance spectroscopy and elemental analysis. Conductivities are in the range (1–30) × 10^{-3} S cm^{-1}.

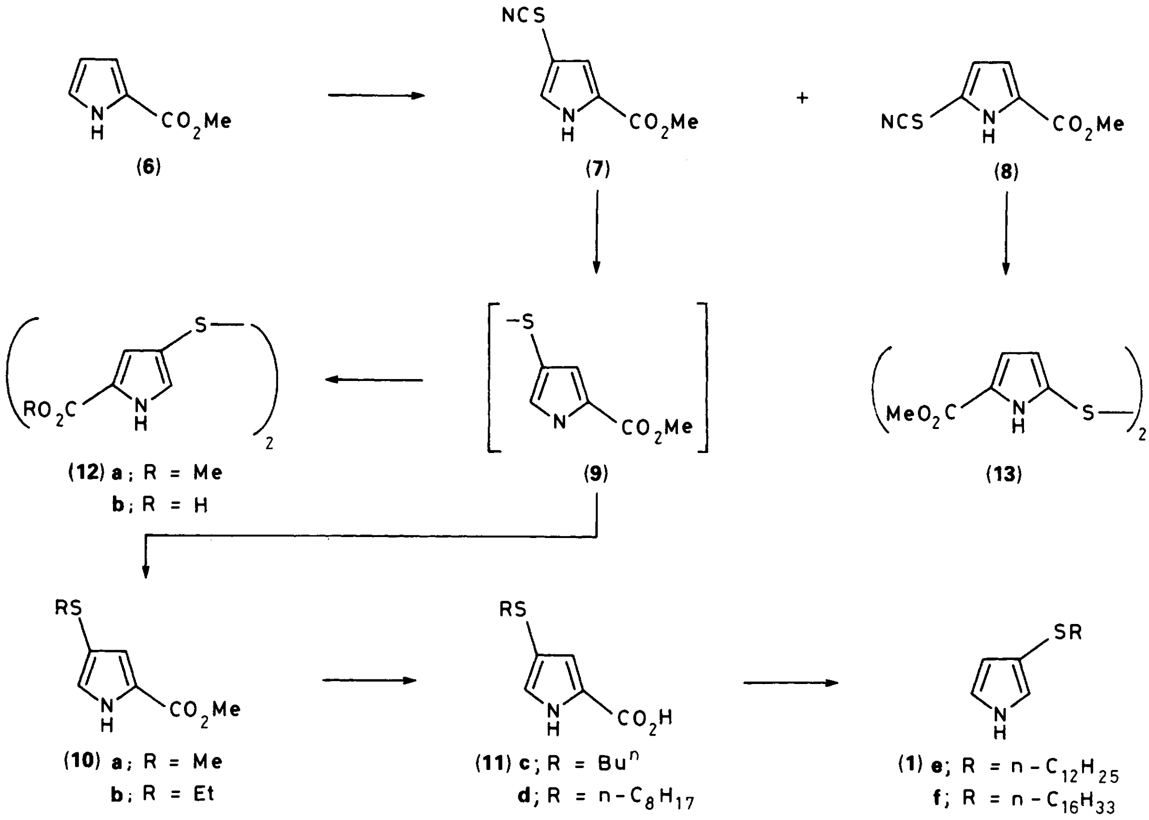
In connection with the electroactivity of 'doped' (oxidized) polypyrrole and polythiophene,[1] considerable interest has been attached to the functionalization of these polymers with a view to improving some of their physical properties. Thus the oxidative polymerization of substituted pyrroles and thiophenes such as 3-alkylpyrroles,[2] 3-alkylthiophenes,[3] 3,4-cycloalkylpyrroles,[4] and 3-methylthio- and 3-methoxy-thiophenes[5] has been extensively studied. No reports appear to deal with the polymerization of 3-alkylthiopyrroles, presumably because of the limited accessibility of such monomers. Yet such systems should be interesting because of the expectedly rather long (*ca.* 1.72 Å) bond between S and the sp^2 carbon of the ring. Indeed, in contrast with thiophene derivatives in which it was found[3] that 3-alkyl substitution brings about an increase of conductivity in respect to the unsubstituted monomer, polymers containing pyrrolic units variously modified show conductivities lower than or at least similar to that of the unmodified parent monomer pyrrole. The C(sp^2)–C(sp^3) bond length (*ca.* 1.48 Å) between C-3 of the ring and the alkyl chain may hinder coplanarity between adjacent rings, and hence would not favour conductivity. The expected longer C(sp^2)–S bond would help to relieve such steric congestion. 3-Alkylthiopyrroles are, however, a rather rare class of compounds:[6,7] a recently described synthesis involves the acid-catalysed isomerization of *N*-tosylpyrrol-2-yl alkyl sulphides, followed by alkaline cleavage of the protecting group.[7] Prompted by this last report, we planned the synthesis of a number of 3-alkylthiopyrroles with a variable length of the alkyl chain in the hope that such side residues would favourably improve the solubility properties of the corresponding oxidized polymers. In this paper we report on the synthesis of some 3-alkylthiopyrroles with a linear alkyl chain ranging from 1 to 16 carbon atoms, their electrochemical polymerizations, and the characterization of the resulting polymers, with particular regard to conductive properties.

Results and Discussion

Synthesis of 3-Alkylthiopyrroles.—(*a*) via *Isomerization of 2-alkylthiopyrroles.* Preparation of 3-hexadecylthiopyrrole (**1f**) was first attempted according to the method of Kakushima and Frenette[7] by acid (CF$_3$CO$_2$H) catalysed isomerization of hexadecyl *N*-tosylpyrrol-2-yl sulphide (**3**) to the 3-isomer (**2**), followed by detosylation. Compound (**3**) was prepared in 44% yield starting from *N*-tosyl-2-thiocyanopyrrole (**4**)[7] with hexadecyl bromide in the presence of sodium hydroxide. The reported[4] thiocyanation of *N*-tosylpyrrole with thiocyanogen chloride prepared *in situ* gave, in our hands, after chromatography, compound (**4**) in 55% yield, together with 2,4-dithiocyano-*N*-tosylpyrrole (**5**) (22% yields) and some unchanged starting material (9%). The acid-catalysed isomerization of (**3**) gave (**2**) in 21% yield only. The expected yields of 3-alkylthiopyrroles would therefore be about 5% starting from *N*-tosylpyrrole: in view of this, the above synthetic route was abandoned and a new one sought that could possibly provide better total yields.



(*b*) via *2-Methoxycarbonyl-4-thiocyanopyrrole.* 2-Methoxycarbonylpyrrole (**6**) was subjected to thiocyanation with thiocyanogen to give a mixture of 4- and 5-thiocyano-2-methoxycarbonylpyrroles (**7**) and (**8**), respectively, in the ratio 3:2 and with a total yield of 70%. Separation of the isomers was performed by flash chromatography. The alkyl 2-methoxycarbonylpyrrol-4-yl sulphides (**10b–f**) were obtained by treatment of the thiocyano derivative (**7**) with alkali hydroxide in t-butyl alcohol and with the appropriate alkyl halide. If methanol is used as the solvent instead of t-butyl alcohol, varying quantities of the methyl sulphide (**10a**) are formed together with the desired alkyl sulphide, whatever the alkyl



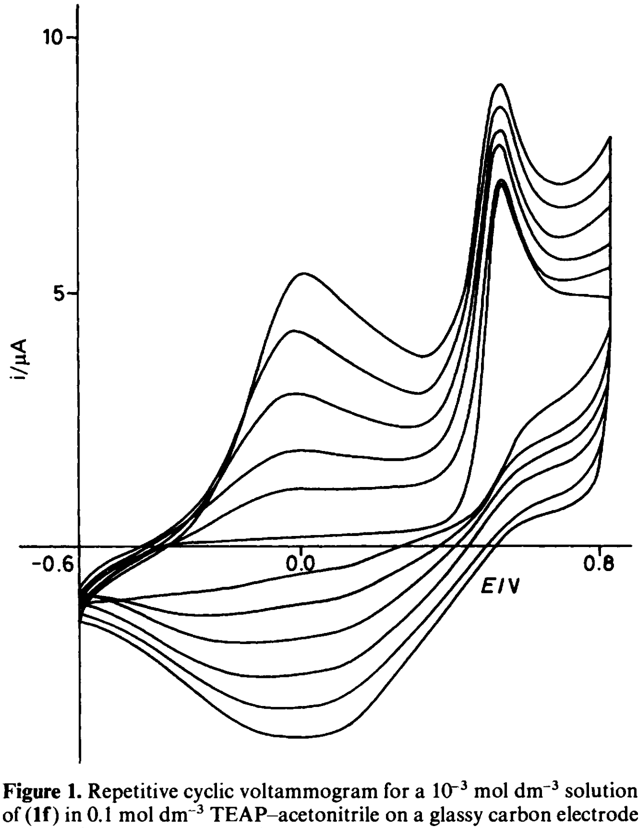


Figure 1. Repetitive cyclic voltammogram for a 10^{-3} mol dm^{-3} solution of (**1f**) in 0.1 mol dm^{-3} TEAP–acetonitrile on a glassy carbon electrode (0.02 cm^2): scan rate 0.1 V s^{-1}.

halide used. The origin of the methyl sulphide (**10a**) under these conditions is ascribed to the methylation of the intermediate pyrrolethiolate (**9**) by the methyl cyanate, in turn formed by the attack of methoxide ion on the nitrile carbon of the thiocyanate group. Evidence for this is provided by the fact that substantial quantities of 2-methoxycarbonylpyrrol-4-yl methyl sulphide are formed on treatment of the 2-methoxycarbonyl-4-thiocyanopyrrole (**7**) with methoxide ion in the *absence* of methyl iodide. This side reaction was expected to be eliminated by preventing the

$$\mathrm{MeOH} + \mathrm{OH}^- \rightleftharpoons \mathrm{MeO}^- + \mathrm{H_2O}$$

$$\begin{tikzcd} \mathrm{Pyrr{-}SCN} + \mathrm{MeO}^- \arrow[r] & \mathrm{Pyrr{-}S}^- + \mathrm{MeOCN} \arrow[d, dash] \\ \mathrm{Pyrr{-}SMe} + \mathrm{NCO}^- & \arrow[l] \end{tikzcd}$$

formation of the alkyl cyanate: this could possibly be performed by using alkaline hydro-alcoholic solutions with negligible alkoxide concentration at the equilibrium, *i.e.* with an alcohol much less acidic than methanol. On treatment of (**7**) in t-butyl alcohol with alkyl bromides in the presence of alkali hydroxide, alkyl pyrrol-4-yl sulphides (**10**) are the only products formed in good yields. Conversely, under the same conditions but in the absence of the alkylating agent and with air bubbling into the solution, the intermediate thiolate (**9**) originating from (**7**) can be oxidized smoothly to the disulphide diester (**12a**), which is easily hydrolysed to the diacid disulphide (**12b**). Analogously, the 2-methoxycarbonyl-5-thiocyanopyrrole (**8**) can be converted into the disulphide (**13**). The alkyl 2-methoxycarbonylpyrrol-4-yl sulphides (**10**) are converted into the corresponding acids (**11**) by alkaline treatment and subsequently decarboxylated in high yields to the alkyl pyrrol-3-yl sulphides (**1**).

Cyclic Voltammetry of the Monomers.—Cyclic voltammetry of all the 3-alkylthiopyrroles in 0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP) in acetonitrile (Figure 1) shows a single oxidation peak with the character of a diffusion-

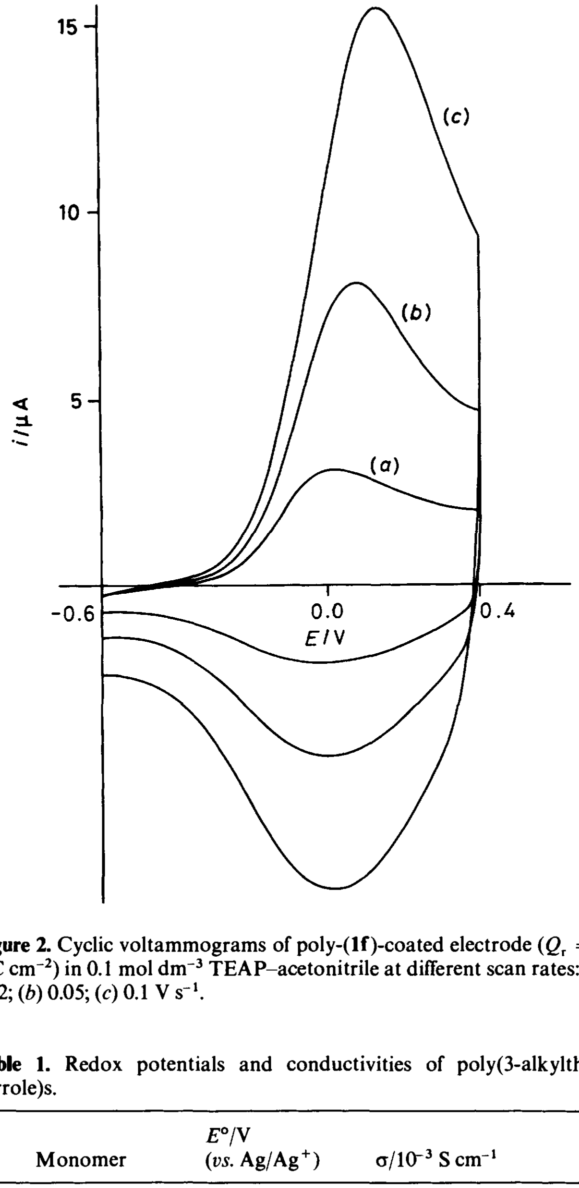


Figure 2. Cyclic voltammograms of poly-(**1f**)-coated electrode (Q_r = 3 mC cm^{-2}) in 0.1 mol dm^{-3} TEAP–acetonitrile at different scan rates: (*a*) 0.02; (*b*) 0.05; (*c*) 0.1 V s^{-1}.

Table 1. Redox potentials and conductivities of poly(3-alkylthiopyrrole)s.

Monomer	$E°$/V ($vs.$ Ag/Ag$^+$)	σ/10^{-3} S cm^{-1}
(**1a**)	−0.16	5
(**1b**)	−0.10	10
(**1c**)	0.05	1
(**1d**)	−0.07	30
(**1e**)	0.02	3
(**1f**)	0.04	2

controlled process: the ratio of peak current i_p over the square root of scan rate v is constant for scan rates in the range 0.2–100 V s^{-1}. Peak potential is the same for all monomers (0.52 V at 0.1 V s^{-1}) with the exception of (**1a**), which is oxidized at a slightly more positive value (0.56 V). The $E_p - E_{p,\frac{1}{2}}$ value of 50 mV, the positive shift of peak potential E_p with scan rate v [dE_p/d(log v) = 30 mV], and the absence of a reduction peak in correspondence with the oxidation peak on the reverse scan up to 500 V s^{-1} are indicative of a fast chemical reaction (in this case coupling of produced cation radicals to polymer) following a fast one-electron exchange (EC mechanism). The value of $i_p/v^{\frac{1}{2}}$, after correction of the peak current function for an EC process,[8] corresponds to that of a one-electron process when comparison is made with one-electron model compounds such as tetrathiafulvalene and tetracyanoquinodimethane. In any case,

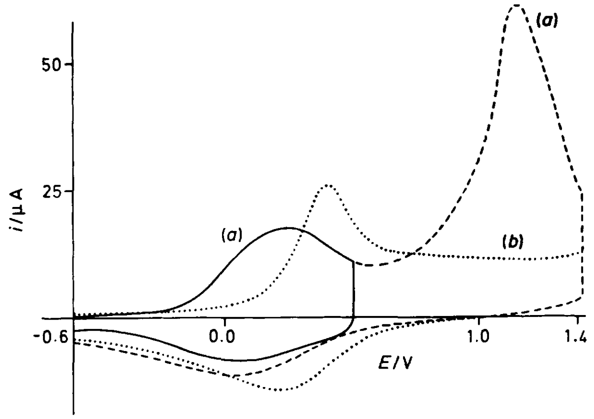


Figure 3. Over-oxidation (*a*) and resulting redox cycle (*b*) of poly-(**1f**)-coated electrode (Q_r = 3 mC cm^{-2}) in 0.1 mol dm^{-3} TEAP–acetonitrile: scan rate 0.1 V s^{-1}.

when cyclic voltammetry is performed with 1% added water, the $i_p/v^{\frac{1}{2}}$ ratio for the oxidation peak, while maintaining its one-electron value at high scan rates ($v \geqslant$ 10–20 V s^{-1}), increases up to values of *ca.* 1.5 electrons per molecule when the scan rate is decreased down to 0.02 V s^{-1} and attains a value of *ca.* 2.3 at the higher time scale of electrolysis (see below). As previously reported,[9] protons released in anodic coupling protonate the monomer itself, making its oxidation more difficult and therefore reducing the oxidation peak current to a one-electron value. If a proton scavenger such as water is present, oxidation occurs at the expected level of (2 + x) electrons per molecule, *i.e.*, 2 electrons for coupling and x electrons (0.3 in the present case) for polymer charging. Repetitive cycling with a starting potential of −0.6 V and a switching potential typically 0.1 V beyond the peak produces for the higher homologues (**1e**) and (**1f**), immediately and progressively, the build-up of a reversible process around 0.0 V (Figure 1), while for the lower homologues the development is more difficult. The electrode is covered with a dark deposit, but appreciable dissolution is observed, as deduced from blue colouration of the solution near the electrode surface. This is reflected in the yield of polymer, measured *in situ* by comparing the reversible charge Q_r with that used for deposition, Q_d. The ratio Q_r/Q_d was found to be 0.10–0.11 for (**1f**), decreasing to 0.06–0.07 for (**1e**) and to 0.01–0.02 for the others. The same trend is provided by the polymer yields in preparative electrolyses as reported below. Thus it appears that the solubility of the oligomers in acetonitrile decreases with increasing chain length. The monomers are polymerizable in water as well. In 0.1 mol dm^{-3} $HClO_4$ the peak potential is at 0.66 V and the redox cycle at 0.25 V *vs.* SCE. In this medium the Q_r/Q_d ratio is the same for all the monomers (10–11%). Thus no dissolution takes place in water, in accord with the fact that polymer formation is easy and no colouration of the solution is observed.

Cyclic Voltammetry of the Polymers.—The cyclic voltammogram of a polymer-coated electrode transferred in acetonitrile containing the electrolyte (Figure 2) shows the reversible redox cycle observed in the filming solution. Redox potentials are given in Table 1. The cycle displays the characteristics of a surface-confined process since i_p/v is constant in the range 20–200 mV s^{-1}.[10,11] The redox process is unaltered by cycling if the switching potential is kept below *ca.* 0.7 V. As for the generality of polyconjugated polymers, however, at higher potentials the polymeric films are oxidized in a broad process around 1.2 V (Figure 3) involving a charge *ca.* 2–3 times the reversible charge. Over-oxidation does not destroy the electroactivity of the deposit but displaces the redox process to potentials *ca.* 0.2–0.3

V higher and makes it slower; the amount of reversible charge is unchanged. It is suggested that over-oxidation may involve the free 3-positions of the alkylthio monomeric units, in analogy with the over-oxidation of polypyrrole with a charge 4–6 times the reversible charge,[12] a fact that can be explained by the availability of all the 3-positions in the pyrrolic units, *i.e.*, twice those available in the polymers considered here.

Spectral Characterization, Elemental Composition, and Conductivity of the Polymers.—The electronic spectrum of polymers deposited on ITO electrodes shows a shoulder at *ca.* 350 nm in the neutral yellow form and a broad absorption, with a maximum at 600–700 nm, in the oxidized form, strictly resembling that of polypyrrole.[13] IR reflectance spectra of polymeric films in the oxidized form show signals due to the perchlorate anion at 1 100 and 620 cm^{-1} and to the alkyl group at 2 920, 2 840, and 1 430 cm^{-1}, and the broad structureless absorption in the high frequency region commonly observed in the conductive state of polyconjugated polymers. Further bands are displayed at 1 520, 1 250, 950, and 870 cm^{-1}, *i.e.*, a picture quite similar to that of polypyrrole in its oxidized state.[14] Electrolysis, which in anhydrous conditions tend to require 1 electron per molecule, in the presence of 1% water require 2.3 electrons per monomer, confirming the cyclic voltammetric result, and produce the deposition of the polymer as dark granular and plastic material and a blue colouration of the solution, which is particularly deep for the short-chain monomers (**1a–d**). Accordingly, yields decrease progressively from (**1f**) to (**1a**) in the range 90 to 50%, respectively. Elemental analyses of the polymers (Table 2) give the same C/N/S ratios as for the monomers and indicate the presence of about 0.35 anions per monomeric unit, in substantial agreement with the electrochemical data. Conductivities (Table 1) fall in the range 10^{-3}–10^{-2} S cm^{-1}, without any apparent trend with the aliphatic chain length. Instead, with the exception of the first member of the series, conductivity increases as $E°$ decreases. This trend, which is also observed in an homologous series of substituted pyrroles,[15] is due to the increased conductivity upon increasing conjugation, the latter being reflected in the redox potential. The oxidized polymers with shorter alkyl chains are slightly soluble in dimethylformamide and in dimethyl sulphoxide while those with longer alkyl chains are slightly soluble in chloroform. In every case the solubility appears to decrease with ageing in solution and in the solid state, suggesting that soluble oligomers undergo further polymerization.

Conclusions

Functionalization of the pyrrole ring with thioalkyl residues does not appear to improve the conductivity of the polymers relative to polypyrrole itself. Since an analogous result was obtained with poly(3-methylthiothiophene), it may be concluded that the presence of thioalkyl chains on five-membered heterocycles is detrimental to the conductivity of the derived polymers. Also, it does not appear that the advantage of the increased solubility of the polymers is sufficient to counterbalance their decreased conductivity: the reasons for this behaviour deserve further investigation.

Experimental

^{1}H NMR spectra were recorded on a Varian 90 MHz instrument; melting points are uncorrected.

Materials.—*N*-Tosylpyrrole[16] and 2-methoxycarbonylpyrrole[17] were prepared according to known procedures. Acetonitrile was distilled twice from phosphorus pentaoxide and subsequently from calcium hydride and stored under dry nitrogen. Tetraethylammonium perchlorate (TEAP, from Carlo Erba) was dried under vacuum at 70 °C. All other products were of reagent grade quality and used without further purification.

Thiocyanation of N-*Tosylpyrrole: Formation of* N-*Tosyl-2-thiocyanopyrrole* (**4**) *and* N-*Tosyl-2,4-dithiocyanopyrrole* (**5**).—Potassium thiocyanate (4.93 g, 50.7 mmol) was added to a stirred solution of chlorine (3.57 g, 50.35 mmol) in acetic acid (150 cm^3); stirring was maintained for 1 h. The resulting solution was rapidly added, under nitrogen, to a stirred solution of *N*-tosylpyrrole[16] (3.74 g, 16.9 mmol) in the same solvent (80 cm^3); the reaction mixture was stirred at room temperature for 15 min and was then poured into cold water (2 dm^3). The suspension was extracted with diethyl ether (3 × 300 cm^3), the organic phase was washed with a saturate solution of sodium hydrogen carbonate, dried (Na_2SO_4), and evaporated at reduced pressure to give an oily dark residue (4.38 g). Chromatography on silica gel (200 g) with hexane–AcOEt (5:1, v/v) gave, in the following order: *N*-tosylpyrrole (0.35 g), 2,4-dithiocyano-*N*-tosylpyrrole (**5**) (1.2 g), m.p. 61–63 °C (Found: C, 46.2; H, 2.8; N, 12.5. $C_{13}H_9N_3O_2S_3$ requires C, 46.55; H, 2.7; N, 12.5%); $\delta_H(CDCl_3)$ 2.52 (3 H, s, Me), 6.52 (1 H, d, H-3), 6.63 (1 H, d, H-5), and 7.40–7.96 (4 H, AA′BB′ system, phenyl ring protons), and 2-thiocyano-*N*-tosylpyrrole (**4**) (2.55 g), m.p. 92 °C (lit.,[7] m.p. 93–95 °C).

*2-Hexadecylthio-*N-*tosylpyrrole* (**3**).—To a mixture of 2-thiocyano-*N*-tosylpyrrole (1.3 g, 4.7 mmol) and hexadecyl bromide (4.3 g, 14.1 mmol) in t-butyl alcohol (60 cm^3) kept under nitrogen, was added 1 mol dm^{-3} sodium hydroxide (14.1 cm^3) with stirring. After 2.5 h the solution was diluted with water (50 cm^3), acidified with 1 mol dm^{-3} HCl, and extracted with methylene chloride (2 × 50 cm^3). Removal of the solvent under reduced pressure and chromatography of the residue on silica gel (130 g) with hexane–AcOEt (10:1, v/v) afforded the desired *product* (**3**) (1 g), m.p. 51–53 °C (Found: C, 67.55; H, 9.0; N, 2.8. $C_{27}H_{43}NO_2S_2$ requires C, 67.8; H, 9.1; N, 2.9%); $\delta_H(CDCl_3)$ 0.9 (3 H, m, Me), 1.3 [28 H, m, $(CH_2)_{14}$], 2.4 (3 H, s, Me), 2.7 (2 H, t, SCH_2, J 7.5 Hz), 6.2 [1 H, t, $J(3,4) = J(4,5) = 3$ Hz, H-4], 6.3 [1 H, dd, $J(3,5)$ 1.5 Hz, H-3], 7.5 (1 H, dd, H-5), and 7.25–7.80 (4 H, AA′BB′ system, phenyl ring protons).

*Isomerization of 2- to 3-Hexadecylthio-*N-*tosylpyrrole* (**2**) *catalysed by Trifluoroacetic Acid.*—A mixture of (**3**) (0.57 g, 1.2 mmol), 1,2-dichloroethane (2.5 cm^3), and trifluoroacetic acid (2.5 cm^3) was refluxed for 2 h. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with hexane–AcOEt (5:1, v/v) afforded the isomer (**2**) (0.12 g, 21%), m.p. 52–53 °C (Found: C, 67.9; H, 9.1; N, 2.9. $C_{27}H_{43}NO_2S_2$ requires C, 67.8; H, 9.1; N, 2.9%); $\delta_H(CDCl_3)$ 0.9 (3 H, m, Me), 1.3 [28 H, m, $(CH_2)_{14}$], 2.4 (3 H, s, Me), 2.7 (2 H, t, SCH_2), 6.2 (1 H, m, H-4), 7.1 (2 H, m, H-2 and H-5), and 7.25–7.75 (4 H, AA′BB′ system, phenyl ring protons).

Thiocyanation of 2-Methoxycarbonylpyrrole: 2-Methoxycarbonyl-4-thiocyanopyrrole (**7**) *and 2-Methoxycarbonyl-5-thiocyanopyrrole* (**8**).—A solution of bromine (27.2 g, 170.3 mmol) in methanol (80 cm^3) was added to a suspension of potassium thiocyanate (33.1 g, 341 mmol) in methanol (100 cm^3) with vigorous stirring, keeping the temperature at −70 °C. The temperature was allowed to rise to −30 °C and a solution of (**6**)[17] (21.3 g, 170 mmol) in methanol (120 cm^3) was added dropwise. The temperature was allowed to rise to 20 °C and the reaction mixture was poured into cold water (2.5 dm^3); the resulting cloudy solution was kept at −5 °C for 1 h and the precipitate filtered off, washed with water, and air dried. ^{1}H NMR analysis showed that the crude product consisted of a mixture of isomers (**7**) and (**8**) in the ratio 2:1. Flash

Table 2. Analytical data for poly(3-alkylthiopyrrole)s.

	Found (%)					
Monomer	C	H	Cl	N	S	Minimal experimental formula[a]
(1a)	38.6	3.3	10.0	9.2	19.7	$C_{4.9}H_5NS_{0.93}(ClO_4)_{0.42}O_{0.13}$
(1b)	43.9	4.2	7.6	8.5	18.7	$C_6H_{8.3}NS_{0.96}(ClO_4)_{0.35}O_{0.36}$
(1c)	50.7	5.8	6.9	7.5	16.3	$C_{7.9}H_{10.9}NS_{0.95}(ClO_4)_{0.36}O_{0.04}$
(1d)	58.1	7.9	5.2	5.6	12.9	$C_{12.1}H_{19.7}NS_1(ClO_4)_{0.36}O_{0.19}$
(1e)	62.9	9.1	3.9	4.5	11.2	$C_{16.4}H_{28.6}NS_{1.1}(ClO_4)_{0.34}O_{0.26}$
(1f)	66.1	10.1	3.6	3.9	9.0	$C_{19.8}H_{36}NS_1(ClO_4)_{0.36}O_{0.2}$

[a] Oxygen by difference; nitrogen taken as the reference.

Table 3. Analytical data for compounds (**10**), (**11**), and (**1**).

Compound (formula)	Yield (%)	M.p. or b.p./°C (mmHg)	Found (required)		
			C	H	N
(10b)	54	44	52.0	6.1	7.5
($C_8H_{11}NO_2S$)			(51.9)	(6.0)	(7.6)
(10c)	47	34–35	56.1	6.95	6.4
($C_{10}H_{15}NO_2S$)			(56.3)	(7.1)	(6.6)
(10d)	55	44–45	62.6	8.5	5.1
($C_{14}H_{23}NO_2S$)			(62.4)	(8.6)	(5.2)
(10e)	52	63–64	66.6	9.8	4.2
($C_{18}H_{31}NO_2S$)			(66.4)	(9.6)	(4.3)
(10f)	50	73–74	69.0	10.2	3.5
($C_{22}H_{39}NO_2S$)			(69.2)	(10.3)	(3.7)
(11a)		164	46.0	4.6	9.05
($C_6H_7NO_2S$)			(45.85)	(4.5)	(8.9)
(11b)		152–153	49.3	5.4	8.5
($C_7H_9NO_2S$)			(49.1)	(5.3)	(8.2)
(11c)		145	54.45	6.5	7.2
($C_9H_{13}NO_2S$)			(54.25)	(6.6)	(7.0)
(11d)		143	61.3	8.2	5.4
($C_{13}H_{21}NO_2S$)			(61.1)	(8.3)	(5.5)
(11e)		142–143	65.35	9.3	4.4
($C_{17}H_{29}NO_2S$)			(65.55)	(9.4)	(4.5)
(11f)		140	68.4	9.95	3.75
($C_{21}H_{37}NO_2S$)			(68.6)	(10.1)	(3.8)
(1a)	70	65	52.8	6.3	12.5
(C_5H_7NS)		(0.04)	(53.05)	(6.2)	(12.4)
(1b)	78	70	56.6	7.0	11.0
(C_6H_9NS)		(0.07)	(56.65)	(7.1)	(11.0)
(1c)	90	100	62.0	8.55	9.15
($C_8H_{13}NS$)		(0.05)	(61.9)	(8.45)	(9.0)
(1d)	71	160	68.0	10.0	6.7
($C_{12}H_{21}NS$)		(0.06)	(68.2)	(10.0)	(6.6)
(1e)	61	180	71.6	11.0	5.3
($C_{16}H_{29}NS$)		(0.06)	(71.85)	(11.0)	(5.2)
(1f)	56	42	74.1	11.4	4.4
($C_{20}H_{37}NS$)			(74.2)	(11.5)	(4.3)

chromatography on silica gel with hexane–AcOEt (7:3, v/v) afforded (**8**) as the first eluate (8 g, 26%), m.p. 153–154 °C (Found: C, 46.3; H, 3.2; N, 15.5. $C_7H_6N_2O_2S$ requires C, 46.15; H, 3.3; N, 15.4%); $\delta_H(CDCl_3)$ 4.05 (3 H, s, Me), 6.62 (1 H, d, H-3), 6.9 (1 H, d, H-4), and 10.6 (1 H, br s, NH). *Compound* (**7**) was obtained as the second eluate (13.8 g, 44%), m.p. 126–127 °C (Found: C, 46.3; H, 3.2; N, 15.6. $C_7H_6N_2O_2S$ requires C, 46.15; H, 3.3; N, 15.4%); $\delta_H(CDCl_3)$ 3.97 (3 H, s, Me), 7.1 (1 H, m, H-3), 7.28 (1 H, m, H-5), and 10.5 (1 H, br s, NH).

2-*Methoxycarbonyl*-4-*methylthiopyrrole* (**10a**).—An aqueous methanolic (1:1, v/v, 6 cm^3) solution of potassium hydroxide (0.7 g, 12.5 mmol) was added under nitrogen to a stirred solution of (**7**) (2 g, 11 mmol) and methyl iodide (1.7 g, 12 mmol) in methanol (50 cm^3), maintaining the temperature at 0 °C. Stirring was continued at room temperature for 6 h. Most of the methanol was then removed under reduced pressure, water (50 cm^3) was added, and the mixture was extracted with methylene chloride (3 × 50 cm^3). The combined extracts were dried (Na_2SO_4) and the solvent was removed under reduced pressure to give *compound* (**10a**) (1.86 g, 90%), m.p. 63–64 °C [from benzene–light petroleum (b.p. 90–120 °C)] (Found: C, 48.85; H, 5.4; N, 8.3. $C_7H_9O_2S$ requires C, 49.1; H, 5.3; N, 8.2%); $\delta_H(CDCl_3)$ 2.4 (3 H, s, SMe), 3.9 (3 H, s, OMe), 6.9 (2 H, m, H-3 and H-5), and 9.7 (1 H, br s, NH).

2-*Methoxycarbonyl*-4-*alkylthiopyrroles* (**10**): *General Procedure*.—The reactions were run under nitrogen with solvents previously purged with nitrogen. A solution of sodium hydroxide (3.3 g, 58.6 mmol) in water (12 cm^3) was added with stirring to a mixture of (**7**) (5.3 g, 29.3 mmol) and the appropriate alkyl bromide (with the exception of ethyl iodide) (32.2 mmol) in t-butyl alcohol (50 cm^3). The resulting solution was stirred at 60 °C for 4 h, most of the solvent was then evaporated, and the residue was treated with water (50 cm^3) and extracted with methylene chloride (2 × 60 cm^3). The dried (Na_2SO_4) extracts were evaporated and the residue was chromatographed on silica gel with hexane–AcOEt (9:1, v/v) to give *compounds* (**10b–f**). Analytical and ^{1}H NMR data are presented in Tables 3 and 4, respectively.

4-*Alkylthiopyrrole*-2-*carboxylic Acids* (**11**): *General Procedure*. An aqueous methanolic (1:2, v/v) solution of the esters (**10**) (1 mmol) and potassium hydroxide (5 mmol) was refluxed for 1 h, cooled at 0 °C, made acidic with concentrated hydrochloric acid, and diluted with water. The solid precipitate was filtered off, washed with water, and air-dried. The crude products can be used for the following decarboxylation step without further purification. Analytical and ^{1}H NMR data are in Tables 3 and 4, respectively.

4-*Alkylthiopyrroles* (**1**): *General Procedure*.—A solution of the carboxylic acids (**11**) (7.8 mmol) in ethanolamine (25 cm^3) was refluxed for 2 h, cooled to room temperature, diluted with water, and extracted with diethyl ether (3 × 70 cm^3). The combined organic phases were dried (Na_2SO_4) and the solvent was removed under reduced pressure: the residue was purified by distillation under reduced pressure, with the exception of the product (**1f**) which was purified by chromatography on Florisil with hexane–AcOEt (9:1, v/v). Analytical and ^{1}H NMR data are in Tables 3 and 4, respectively.

2,2′-*Dimethoxycarbonyldipyrrole*-4,4′-*diyl Disulphide* (**12**).—Air was bubbled at room temperature for 7 h into a solution of (**7**) (2.84 g, 15.6 mmol) and sodium hydroxide (0.67 g, 16.75 mmol) in t-butyl alcohol–water (10:1, v/v; 77 cm^3). The white precipitated solid was filtered off, washed with water to neutrality, and dried to give the product (**12**) (1.57 g, 68%), m.p. 215 °C (from AcOH) (Found: C, 46.1; H, 3.95; N, 8.8.

Table 4. ^{1}H NMR data for compounds (**10**), (**11**), and (**1**).

Compound	Solvent[a]	CH_3	$(CH_2)_n$	SCH_2	OCH_3	Pyrrole protons 2	3	5	4	NH
(**10b**)	A	1.24 t		2.71 q	3.89 s		6.95 m			9.75
(**10c**)	A	0.90 t	1.50 m	2.70 t	3.80 s		6.90 m			9.32
(**10d–f**)	A	0.90 t	1.35 m	2.70 t	3.92 s		6.90 m			9.35
(**11a**)	B	2.32 s					6.86 m			10.84
(**11b**)	B	1.24 t		2.66 q			6.86 m			8.31
(**11c**)	B	0.89 t	1.46 m	2.66 t			6.83 m	6.92 m		
(**11d–f**)	B	0.87 t	1.34 m	2.64 t			6.83 m	6.92 m		
(**1a**)	A	2.45 s				6.81 m		6.81 m	6.30 m	8.20
(**1b**)	A	1.35 t		2.80 q		6.81 m		6.81 m	6.30 m	8.42
(**1c**)	A	0.90 t	2.55 m	2.75 t		6.81 m		6.81 m	6.30 m	8.30
(**1d–f**)	A	0.90 t	1.30 m	2.65 t		6.81 m		6.81 m	6.25 m	8.25

[a] A = $CDCl_3$; B = $CDCl_3$–DMSO-d_6.

$C_{12}H_{12}N_2O_4S_2$ requires C, 46.1; H, 3.9; N, 8.9%); δ_H[$(CD_3)_2SO$] 3.8 (6 H, s, Me), 6.75 (2 H, m, H-3), and 7.1 (2 H, m, H-5).

5,5′-Dimethoxycarbonyldipyrrole-2,2′-diyl Disulphide (**13**).—A procedure analogous to that followed for the synthesis of the disulphide (**12**) was used to prepare (**13**) in 58% yields, m.p. 197 °C (from ethanol–methylene chloride 6:1, v/v) (Found: C, 45.9; H, 4.0; N, 9.0. $C_{12}H_{12}N_2O_4S_2$ requires C, 46.1; H, 3.9; N, 8.9%); δ_H[$(CD_3)_2SO$] 3.79 (6 H, s, Me), 6.3 (2 H, m, H-3), 6.73 (2 H, m, H-4), 12.53 (2 H, br s, NH); *m/z* 312 (M^+).

Electrochemical Apparatus and Procedures.—Electrochemical experiments were performed at room temperature in three-electrode cells in nitrogen-degassed acetonitrile solutions containing 0.1 mol dm^{-3} TEAP. Monomer concentrations were typically in the range 1×10^{-3} mol dm^{-3} for cyclic voltammetry and 1×10^{-2} mol dm^{-3} for preparative electrolysis. Filmed electrodes were usually tested in acetonitrile–0.1 mol dm^{-3} $HClO_4$. Reference electrodes were either silver/0.1 mol dm^{-3} silver perchlorate electrode in acetonitrile (*ca.* 0.3 V *vs.* SCE) or SCE, depending on whether acetonitrile or aqueous solutions were investigated. Working electrodes were glassy carbon disks (0.02 cm^2) in voltammetric experiments and platinum sheets (15 cm^2) in IR reflectance measurements and preparative electrolyses. Spectroelectrochemical measurements were performed with indium–tin oxide (ITO) electrodes (*ca.* 80% transmittance, *ca.* 300 ohm/square resistance from Balzers, Liechtenstein).

Polymers were produced potentiostatically, with an applied voltage 0.1 V beyond the oxidation peak of the monomer.

The voltammetric apparatus consisted of an AMEL 553 potentiostat modulated by a 568 programmable function generator and coupled with a 731 digital integrator. The recording device was a Hewlett-Packard 7090A measurement plotting system.

IR reflectance spectra were taken on Perkin-Elmer 682 spectrometer with a Specac reflection unit (Analytical Accessories Ltd., England); spectroelectrochemical experiments were performed *in situ* with a Perkin-Elmer Lambda 15 spectrometer.

Conductivity measurements were performed at room temperature with the four-probe technique using a Keithley 220 programmable current source and a Keithley 195A digital multimeter.

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