# Electrochemical and optical properties of thiophene – alkylheteroaromatic copolymers

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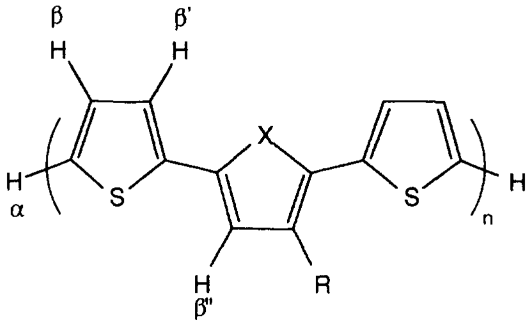
α-Terthienyl and 2,5-di(2-thienyl)pyrrole, *n*-alkylated at the β-position of the central ring, have been oxidized electrochemically or chemically to afford electroactive polymers which were characterized by cyclic voltammetry, spectroelectrochemistry and *FT*i.r. These systems, which can be viewed as α-linked alternating copolymers of bithiophene with a 3-alkylthiophene or 3-alkylpyrrole, display superior effective degrees of conjugation compared with homopolymers of similarly substituted 3-alkylheteroaromatics. Chemically generated materials are soluble in a variety of organic solvents, but fail to produce coherent films when cast from these due to lower degrees of polymerization than similarly produced 3-alkylthiophene homopolymers. Electrogenerated polymers are insoluble despite apparently comparable degrees of polymerization as determined by *FT*i.r. end-group analysis. Oxidation potentials of the monomers are reduced in proportion to the number of alkyl substituents.

**(Keywords: thiophene-3-alkylthiophene copolymers; thiophene-3-alkylpyrrole copolymers; electropolymerization; cyclic voltammetry; *FT*i.r.; spectroelectrochemistry)**

## INTRODUCTION

Among the more significant recent achievements in the field of electroactive polymers were the discoveries of melt and solution processible materials[1]. One approach relies on substituents (alkyl, alkyl sulphonate, ethylene glycol oligomers, etc.) placed at the 3-position of heteroaromatics like thiophene, pyrrole and furan, which disrupt the otherwise inflexible aromatic backbone. Although this is a recognized technique for enhancing processibility in rigid rod polymers, the steric ramifications of such substitutions would appear at first to be antithetical to achieving high electrical conductivity, which depends on extended conjugation, facile achievement of interring coplanarity, high crystallinity, etc. This is certainly the case for N-substituted pyrrole homopolymers whose electrical properties are vastly inferior to the parent system[2–4]. In these, adjacent rings are sterically prevented from achieving coplanarity[5] thus impeding both the formation and mobility of the bipolaron charge carriers. Similar substitutions at the 3-position evidently pose less severe constraints since these polymers can achieve conductivities comparable to the parents, polythiophene and polypyrrole[1]. Substitution on both β-positions, however, does impart steric interactions which reduce the effective degree of conjugation[6].

We have been concerned with controlling the electrical, optical and electrochemical properties of poly(heteroaromatics) via compositional and steric manipulation of the monomers shown in *Figure 1* ($n = 1$) (**1**–**8**)[7–10]. The steric demands of substituents on N in **3**–**8** are manifested in the redox and optical properties of the monomers and corresponding polymers as well as the electrical properties of the latter, but are not as striking as in the similarly N-substituted pyrrole homopolymers due to their 'dilution' by the intervening thiophenes[7–10]. We wished to ascertain if a similar relaxation of steric effects could be exhibited in the 3-substituted polymers **9**–**11**, where the substituent is present on every third ring, and if processibility could be maintained.



| X | R | Acronym where n=1 | |
|---|---|---|---|
| S | H | SSS | 1 |
| O | H | SOS | 2 |
| NH | H | SNS | 3 |
| NCH$_3$ | H | SN1S | 4 |
| NC$_2$H$_5$ | H | SN2S | 5 |
| NC$_7$H$_{15}$ | H | SN7S | 6 |
| NC$_{18}$H$_{37}$ | H | SN18S | 7 |
| NCH(CH$_3$)$_2$ | H | SNIPS | 8 |
| S | C$_7$H$_{15}$ | 3-C7SSS | 9 |
| S | C$_{18}$H$_{37}$ | 3-C18SSS | 10 |
| NH | C$_{18}$H$_{37}$ | 3-C18SNS | 11 |

**Figure 1** Monomer/polymer molecular structures

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## EXPERIMENTAL

### *General*

All reagents were ACS reagent grade and used without further purification unless otherwise noted. Solvents were dried and distilled prior to use. $^1H$ and $^{13}C$ n.m.r. were recorded on a Jeol JNM-FX200 *FT*n.m.r. spectrometer on solutions in $CDCl_3$ with chemical shifts referenced to tetramethylsilane internal standard. *FT*i.r. spectra were obtained on a Nicolet 5DX *FT*i.r. spectrometer. Electronic spectra of monomers were recorded on a Hewlett Packard HP-8450A u.v./vis. spectrometer. Elemental analyses were performed by Galbraith Laboratories and Oneida Research Services. Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected.

### *Monomer syntheses*

*1,4-di(2-thienyl)-2-(*n*-octadecyl)-1,4-butane dione (C18-dione).* A 500 ml three-necked round bottomed flask equipped with mechanical stirring, dry ice/isopropanol (IPA) condenser and $N_2$ gas inlet was cooled in a dry ice/IPA bath. Anhydrous liquid $NH_3$ (200 ml) was transferred under $N_2$ and $NaNH_2$ (1.70 g, 44 mmol) was added all at once. The mixture was stirred at −78°C for 30 min after which 10.0 g (40 mmol) of 1,4-di-(2-thienyl)-1,4-butane dione[11] dissolved in 175 ml of dry tetrahydrofuran (THF) were added dropwise over 2 h while maintaining the reaction temperature between −45 and −50°C. The reaction mixture changed colour from mustard brown to burgundy as the reaction was warmed to −33°C. Stirring was continued for 1 h at that temperature. Octadecyl bromide (13.3 g, 40 mmol), dissolved in 35 ml THF was added dropwise. The reaction was then allowed to warm to room temperature overnight to evaporate the $NH_3$, leaving a THF solution. This mixture was heated to reflux for 48 h with stirring and quenched with water. The products were extracted with diethyl ether which was washed with water, dried over $MgSO_4$ and removed *in vacuo* to afford a dark red oil. Chromatography over alumina with 5% ethyl acetate–95% hexane, followed by recrystallization from hexane yielded 10.0 g of the C18-dione (50%) as a white solid melting at 46–48°C.

$^1H$ n.m.r. ($CDCl_3$): 7.70 (m, 4H), 7.18 (m, 2H), 3.93 m, 1H), 3.56 (m, 1H), 3.15 (m, 1H), 1.80 (m, 2H), 1.60 (m, 1H), 1.24 (s, 30H), 0.88 $\delta$ (t, 3H).

*1,4-di(2-thienyl)-2-(*n*-heptyl)-1,4-butane dione (C7-dione).* A three-necked 250 ml round bottomed flask equipped with reflux condenser, $N_2$ inlet, rubber septum and magnetic stirring was flushed with dry $N_2$ and charged with 80% NaH (1.2 g, 50 mmol) and 50 ml of dry dimethylsulphoxide (DMSO). 1,4-di-(2-thienyl)-1,4-butane dione (10 g, 40 mmol) dissolved in dry DMSO was added dropwise at room temperature at an appropriate rate to control $H_2$ evolution. The mixture was stirred for an additional hour to ensure anion formation, after which *n*-heptyl bromide (7.16 g, 40 mmol) dissolved in dry DMSO was added dropwise ($\approx$30 drops $min^{-1}$). A reddish colour ensued, the reaction temperature was increased to 60°C by external heating and was stirred at this temperature under $N_2$ for 48 h, then cooled and poured into water. Extraction with ether, followed by water washing, drying over $MgSO_4$ and removal of the solvent *in vacuo* afforded a yellow oil. Chromatography over silica gel with hexane elution yielded 10.4 g (75%) of the C7-dione as a low melting solid.

$^1H$ n.m.r. ($CDCl_3$): 7.70 (m, 4H), 7.18 (m, 2H), 3.92 (m, 1H), 3.56 (m, 1H), 3.15 (m, 1H), 1.23 (s, 8H), 0.85 $\delta$ (t, 3H). $^{13}C$ n.m.r. ($CDCl_3$): 195.61, 191.06, 143.99, 133.49, 131.97, 127.99, 43.03, 41.13, 32.84, 31.52, 29.37, 28.86, 27.15, 22.41, 13.87 $\delta$.

*2,2′:3-(*n*-heptyl):5′,2″-terthienyl (**9**).* A 250 ml round bottomed flask equipped with $N_2$ purge was charged with 1.9 g $NaHCO_3$, 7.6 g $P_4S_{10}$ and 100 ml of ethyl ether. C7-dione (2.65 g, 7.6 mmol) was added and the resulting mixture refluxed under $N_2$ for 24 h. Insolubles were removed by filtration and rinsed with ether. The filtrate and rinsings were combined, washed with water and dried over $MgSO_4$. The solvent was removed *in vacuo* and the resultant yellow oil chromatographed twice over silica gel with hexane elution to afford 1.5 g **9** (57%).

*FT*i.r. (neat): 2953, 2853, 1460, 839, 820, 692 $cm^{-1}$. $^1H$ n.m.r. ($CDCl_3$): 7.13 (m, 7H), 2.70 (t, 2H), 1.64 (m, 2H), 1.26 (s, 8H), 0.88 $\delta$ (t, 3H). $^{13}C$ n.m.r. ($CDCl_3$): 140.19, 137.19, 135.88, 135.07, 129.52, 127.77, 127.33, 126.45, 125.79, 125.21, 124.19, 123.46, 31.78, 30.54, 29.52, 29.30, 29.15, 22.64, 14.11 $\delta$. U.v./vis. ($\lambda_{max}$/log $\varepsilon$): 350 nm/4.42. Analysis: calculated for $C_{19}H_{22}S_3$, C: 65.85, H: 6.40; found, C: 66.09, H: 6.51.

*2,2′:3-(*n*-octadecyl):5′,2″-terthienyl (**10**).* A 500 ml round bottomed flask equipped with $N_2$ purge was charged with 2 g $NaHCO_3$, 8 g $P_4S_{10}$ and 150 ml ethyl ether. To the stirred suspension were added 4 g (8 mmol) of the C18-dione and the resultant mixture was refluxed under $N_2$ for 24 h. Insoluble materials were removed by filtration and rinsed with $Et_2O$. These rinses were combined with the filtrate and washed with water then dried over $MgSO_4$. The solvent was removed *in vacuo* and the resulting solid chromatographed over silica gel with hexane elution. Recrystallization from pentane afforded 2.5 g (62%) **10** melting at 58.0–58.5°C.

*FT*i.r. (KBr): 2953, 2850, 1457, 838, 834, 719, 695 $cm^{-1}$. $^1H$ n.m.r. ($CDCl_3$): 7.15 (m, 7H), 2.72 (t, 2H), 1.56 (m, 2H), 1.25 (s, 30H), 0.88 $\delta$ (t, 3H). Uv/vis. ($\lambda_{max}$/log $\varepsilon$): 342 nm/4.21. Analysis: calculated for $C_{30}H_{44}S_3$, C: 71.94, H: 8.85; found, C: 72.06, H: 8.92.

*2,5-di-(2-dithienyl)-3-*n*-hexadecyl-pyrrole (**11**).* A three-necked 250 ml round bottomed flask equipped with reflux condenser, $N_2$ inlet and mechanical stirrer was charged with 4 g (8 mmol) of the C18-dione, 6 g ammonium acetate and 7.2 ml glacial acetic acid. Slowly, 2.0 ml of acetic anhydride was added dropwise into the stirred solution at room temperature. After refluxing for 12 h, 5 ml of toluene were added and the mixture was held at 60°C for 12 h then cooled and poured into water. The products were extracted with ether, washed and dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude solid chromatographed twice over alumina with 5% ethyl acetate–95% hexane followed by recrystallization from pentane to yield 2.2 g **11** as a white solid (55%), m.p. 58.5–59.0°C.

*FT*i.r. (KBr): 3412, 2951, 2917, 1263, 846, 818, 797, 713, 687, 654 $cm^{-1}$. $^1H$ n.m.r. ($CDCl_3$): 8.11 (s, 1H), 7.24 (m, 2H), 7.04 (m, 4H), 6.36 (s, 1H), 2.63 (t, 2H), 1.57 (m, 2H), 1.25 (s, 30H), 0.88 $\delta$ (t, 3H). Uv/vis. ($\lambda_{max}$/log $\varepsilon$): 315 nm/4.71. Analysis: calculated for $C_{30}H_{45}NS_2$, C:

74.53, H: 9.32, N: 2.90%; found: C: 74.67, H: 9.34, N: 2.93%.

### *Electrochemical polymerizations into films*

Growth conditions (solvent, monomer/electrolyte concentrations, current densities) were optimized in open atmosphere but films used in this study were grown in a helium-filled glove box (Vacuum Atmospheres, Inc.). Films were grown from 3 ml solutions of 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) in nitrobenzene in which monomer was dissolved to achieve concentrations of 5 mM (**9**, **10**) or 10 mM (**11**). The nitrobenzene was carefully dried over $CaH_2$ and fractionally distilled under vacuum through a 90 cm column packed with stainless steel wool. Its water content was <5 ppm by Karl Fisher titration (Aquatest Photovolt IV). The electrolytic cell consisted of a 1 cm × 9 cm indium-tin oxide (ITO) coated glass anode held parallel to a polished 1.2 cm × 9 cm aluminium cathode placed 3 mm away by a glass spacer.

The polymerizations were performed galvanostatically using a PARC Model 173 potentiostat/galvanostat equipped with a PARC Model 178 electrometer and PARC Model 376 logarithmic current converter using a silver wire pseudo-reference electrode. Current densities of 500 $\mu A\ cm^{-2}$ (for **9** and **10**) or 100 $\mu A\ cm^{-2}$ (for **11**) were applied. Thick, free-standing films used for *FT*i.r. were obtained after 5–8 min growth while thinner films grown for 0.5–2 min were used for electronic absorption spectroscopy (EAS).

### *Chemical polymerizations*

The monomers were chemically polymerized[12,13] with anhydrous $FeCl_3$ in $CHCl_3$. After stirring at room temperature for 24 h, the reaction mixture was washed with water, aqueous ammonia and then water again. The red organic phase was dried over $MgSO_4$ and the solvent removed *in vacuo* to afford the red polymer which was freed from lower molecular weight fractions by extraction with hot methanol. Alternatively, after the reaction had proceeded for 24 h, the solvent was removed *in vacuo* and the residual Soxhlet extracted with methanol (1 week), then acetone (1 week) to remove oligomers. The remaining solids were completely soluble in xylene.

### In situ *doping/EAS studies*

Film oxidations and reductions were studied by *in situ* vis/near i.r. EAS. Evolving spectra were captured on a Perkin Elmer/Coleman EPS-3T spectrometer interfaced to an Apple IIe microcomputer via a 12 bit A/D converter (Applied Engineering, Inc.). Doping experiments were performed with a PARC Model 173 potentiostat/galvanostat equipped with a PARC Model 179 digital coulometer and a PARC Model 178 electrometer which was connected to a piece of lithium metal that served as a pseudo-reference and counter-electrode. This was sealed under helium in an air-tight one compartment glass cell containing an ITO-coated glass slide working electrode onto which a ≈1 μm thick film had been grown. The electrolytic solution consisted of 7 ml of 0.25 M $LiBF_4$ in dry propylene carbonate. An initial potential of $\leqslant 3.2$ V *versus* Li was applied and maintained until the current ceased. Only one optical transition was observed at this potential. The potential was raised in ≈100 mV steps and a spectrum was recorded after the current had decreased to $\leqslant 50$ nA and no changes in the spectrum were observed from the previous recording at that potential. This typically took ≈30 min between voltage settings. The coulombs passed were also monitored.

### *Voltammetry*

Voltammetry experiments were performed in a $N_2$ purged cell consisting of two compartments separated by a fine glass frit. One compartment contained a carbon counter-electrode while the other housed a 100 μm diameter Pt working electrode separated by 5 mm from a reference electrode. For monomer voltammetry the reference electrode consisted of a silver wire immersed in 0.1 M $TBABF_4$/nitrobenzene saturated with $AgNO_3$ separated from the electrolysis solution by 3 mm of unfused Vycor™ glass. For polymer voltammetry, a similar silver wire reference electrode immersed in 0.25 M $LiBF_4$ in propylene carbonate saturated with $AgNO_3$ was used. The measured potentials were referenced to SCE by comparing the ferrocene/ferrocenium couple (0.31 V *versus* SCE) under these electrolytic conditions. Cyclic and repetitive cyclic voltammetry experiments were performed with a PARC 173 potentiostat/galvanostat equipped with a PARC model 376 logarithmic current converter and a PARC Model 175 universal programmer. Data were acquired on a Nicolet 2090-IIIA digital oscilloscope interfaced to a Zenith 159 microcomputer equipped with an IEEE 488 bus. Data were manipulated using the commercially available software, PC Waveform Basic™ (Blue Feather Software, Inc.). A constant scan rate of 50 $mV\ s^{-1}$ was used for repetitive cyclic voltammetry on the monomers. The scan rate was varied between 50 and 500 $mV\ s^{-1}$ in 50 $mV\ s^{-1}$ steps for cyclic voltammetry of the polymers. Monomer concentrations were typically 2.5–10.0 mM.

### FT*i.r. spectroscopy*

Free-standing polymer films between 2 and 9 μm thick were electrochemically grown, neutralized with ammonia gas and/or electrochemical reduction, transferred via anhydrous methanol to NaCl plates and dried *in vacuo*. Films which were not transferable by this technique were scraped from the slide after drying and mulled with KBr. Chemically polymerized materials were neutralized in aqueous ammonia, washed with water, methanol and then dried. The resulting solids were studied as KBr pellets.

## RESULTS AND DISCUSSION

### *Monomer voltammetry*

The repetitive cyclic voltammograms of **9**–**11** are displayed in *Figures 2–4*, respectively. Peak anodic potentials ($E_{pa}$) which were extracted from the first scan of a fresh solution of monomer are listed in *Table 1*.

3-Alkyl substituted thiophenes have $E_{pa}$ values about 150–180 mV lower than thiophene[14]. In our systems, the monoalkyl substituted tri-ring monomers display $E_{pa}$ reductions approximately one third this value (60–80 mV), consistent with the number of alkyl substituents on the monomers[14]. In a detailed study of steric effects in a series of poly(3-alkylthiophenes), Roncali *et al.*[14] were able to optimize the mean degree of conjugation by varying the length of the alkyl chain and the electrochemical growth conditions. *n*-Alkyl chain lengths of 7–9 carbons gave enhanced conjugation lengths for poly(3-alkylthiophenes) which were reflected by the long wavelength absorption maximum in the range

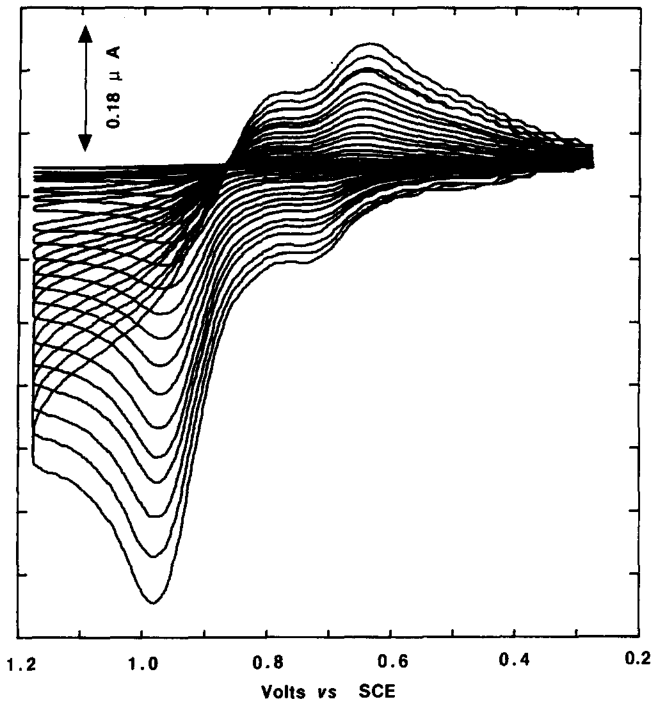


**Figure 2** Repetitive cyclic voltammogram for 3-C7SSS monomer

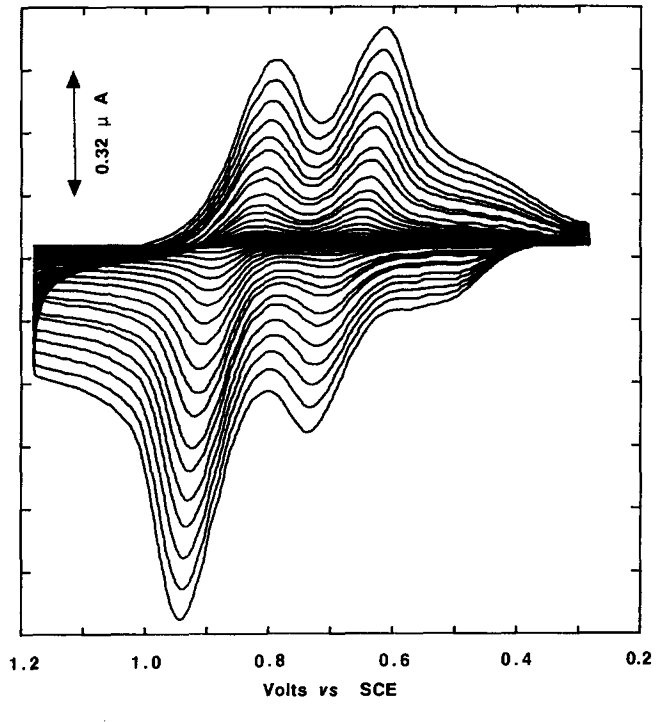
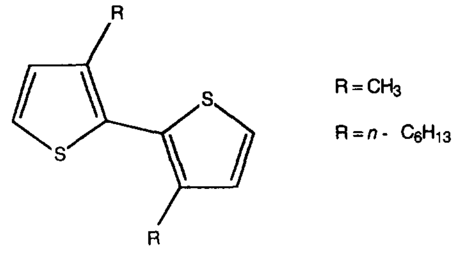


**Figure 3** Repetitive cyclic voltammogram for 3-C18SSS monomer

495–542 nm. For *n*-alkyl chain lengths >14, the $\lambda_{max}$ values were ≈460 nm. In our SSS derivatives, where the alkyl substituent is present on only one third of the rings, we achieve similar enhancements for both poly-**9** and poly-**10** ($\lambda_{max} = 540$ nm), suggesting that the mean conjugation length of the polymer may be a property of the number (and position) of alkyl substituents rather than the latter's length. These polymers were grown at current densities of ≈0.5 mA cm$^{-2}$ which provided films of best optical clarity. A study by Maior *et al.*[15], in which unfavourable steric interactions were deliberately introduced at the $\beta$-positions of bithiophene-based monomers **12** to model head-to-head polymerization, revealed that $\beta$-substituents (even as small as methyl) impart considerable steric hindrance to the achievement of coplanarity in adjacent rings, reducing the long wavelength absorption maxima by 90–110 nm compared with the corresponding, similarly prepared, head-to-tail polymers.



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The monomer peak oxidation (reduction) potential shifts anodically (cathodically) with increasing scan number, suggesting either an increased electrical resistance in the growing polymer film and/or a greater diffusional barrier to counter-ions. The peak-to-peak separations for **10** and **11**, displayed in *Figure 5*, depend linearly on scan rate, with an essentially identical extrapolated intercept of ≈30 mV.

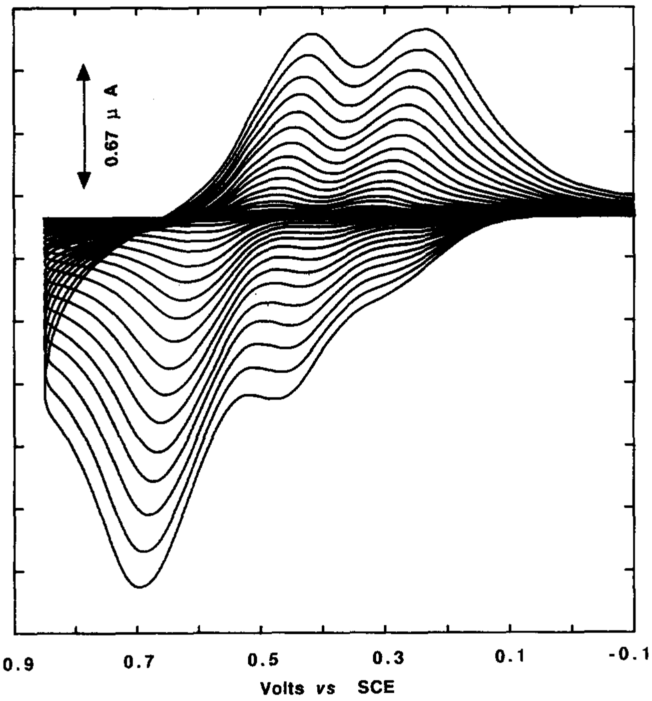

**Figure 4** Repetitive cyclic voltammogram for 3-C18SNS monomer

**Table 1** Peak anodic potentials for monomers

| System | $E_{pa}^{mono}$(V v. SCE) | $E_{pa}^{poly}$(V v. SCE) |
|---|---|---|
| **1** | 0.96 | 0.88 |
| **9** | 0.90 | 0.58 |
| **10** | 0.91 | 0.63 |
| **3** | 0.69 | 0.61 |
| **11** | 0.51 | 0.36 |

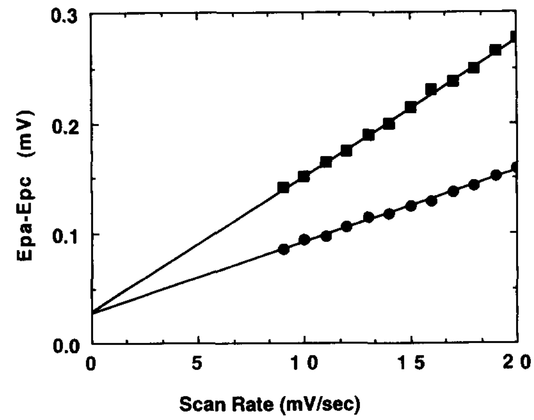

**Figure 5** Peak-to-peak separation for anodic and cathodic waves for the polymers derived in the repetitive cyclic voltammograms of 3-C7SSS (●) and 3-C18SSS (■) as a function of scan number

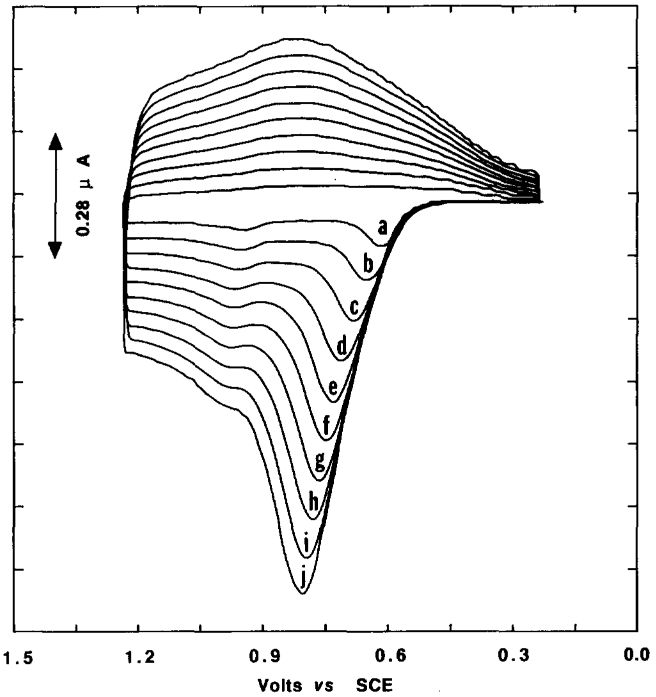

**Figure 6** Cyclic voltammograms of poly-**9** as a function of scan rate. (a) 50 mV $s^{-1}$; (b) 100 mV $s^{-1}$; (c) 150 mV $s^{-1}$; (d) 200 mV $s^{-1}$; (e) 250 mV $s^{-1}$; (f) 300 mV $s^{-1}$; (g) 350 mV $s^{-1}$; (h) 400 mV $s^{-1}$; (i) 450 mV $s^{-1}$; (j) 500 mV $s^{-1}$

*Polymer voltammetry*

Cyclic voltammograms of poly-**9** and poly-**10** are shown in *Figures 6* and *7*, respectively. Current peaks in the oxidation cycle are much 'sharper' than the corresponding reduction waves, but since we have not attempted to correct for capacitive effects in these measurements, we cannot comment on the reversibility of the process. *Figure 8* displays the normalized peak currents for poly-**9**, **10**, and **11** for the oxidation and reduction cycles. The currents were linear with scan rate between 50 and 500 mV $s^{-1}$. The peak oxidation potentials, extrapolated to zero scan rate, are listed in *Table 1*. In all cases, the increased conjugation of the polymer results in a lower oxidation potential compared with the corresponding monomer but the relative decrease for the alkyl-substituted systems (**9**, **10**, **11**) is significantly greater than for their parents (**1** and **3**).

*Spectroelectrochemistry*

The electronic absorption spectra as a function of applied potential for poly-**9** and poly-**10** films electrodeposited onto ITO-coated glass slides are displayed in *Figures 9* and *10*, respectively. The clear signature of transitions to bipolaron states is evident as the degree of oxidation (i.e. applied potential in V *versus* Li) increases. An estimate of the band gap for the polymers is obtained from the x-axis crossing in difference spectra[16] generated by referencing each trace to its corresponding neutral (here $V_{\mathrm{appl}} = 3.2$ V *versus* Li) spectrum. Such treatment yields a gap of ≈1.8 eV, somewhat smaller than for the parent poly-**1** (2.0–2.2 eV)[7–10,16]. The charge passed for each potential step was monitored and is plotted in *Figure 11*. No discontinuities are observed at this level of potential resolution, and when normalized (to remove differences in sample thicknesses), the charging behaviour for the poly-**9** and poly-**10** films is the same.

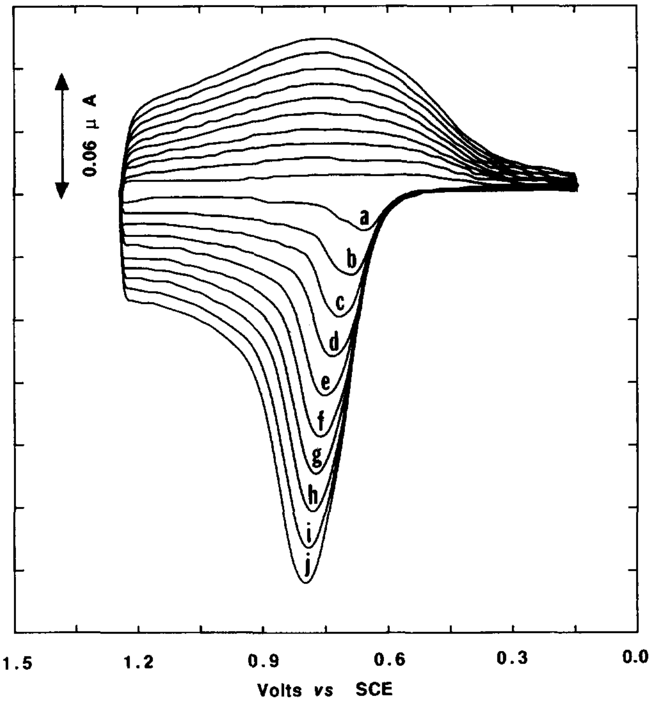

**Figure 7** Cyclic voltammograms of poly-**10** as a function of scan rate. (a) 50 mV $s^{-1}$; (b) 100 mV $s^{-1}$; (c) 150 mV $s^{-1}$; (d) 200 mV $s^{-1}$; (e) 250 mV $s^{-1}$; (f) 300 mV $s^{-1}$; (g) 350 mV $s^{-1}$; (h) 400 mV $s^{-1}$; (i) 450 mV $s^{-1}$; (j) 500 mV $s^{-1}$

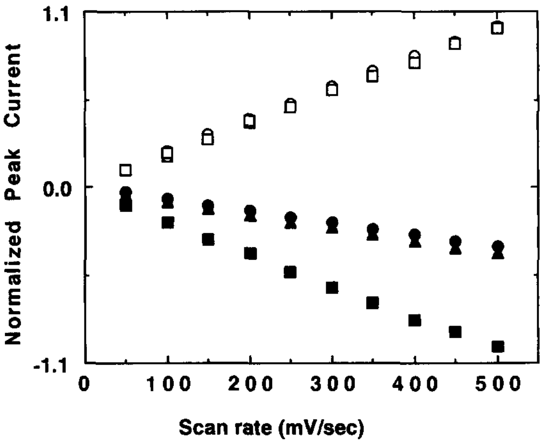

**Figure 8** Normalized peak currents for anodic (open symbols) and cathodic (closed symbols) for poly-**9** (▲), poly-**10** (●) and poly-**11** (■) as a function of scan rate

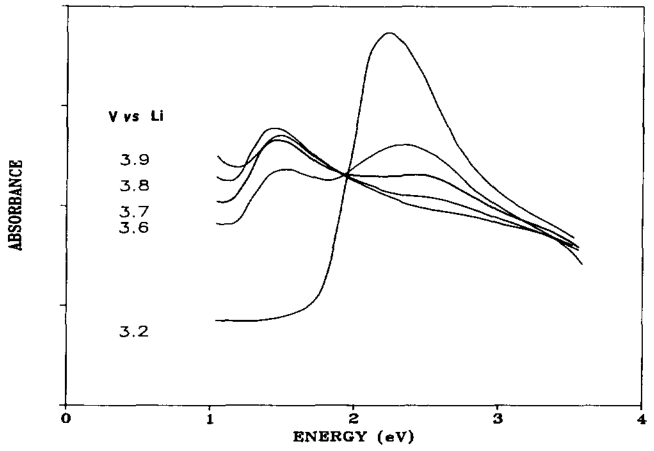

**Figure 9** Electronic absorption spectra of poly-**9** deposited on ITO-coated glass electrodes as a function of applied potential *versus* Li

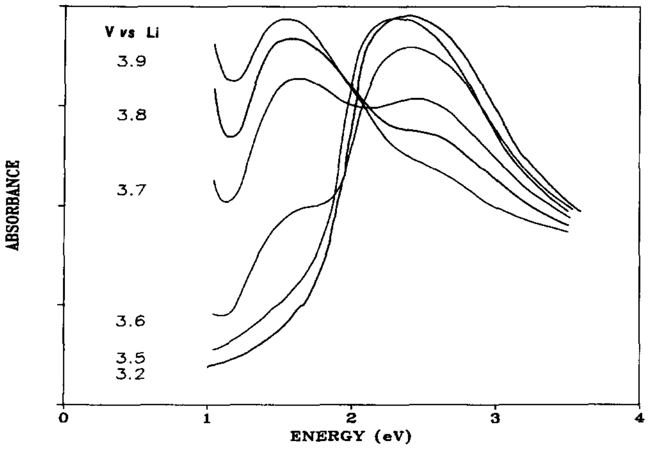

**Figure 10** Electronic absorption spectra of poly-**10** deposited on ITO-coated glass electrodes as a function of applied potential *versus* Li

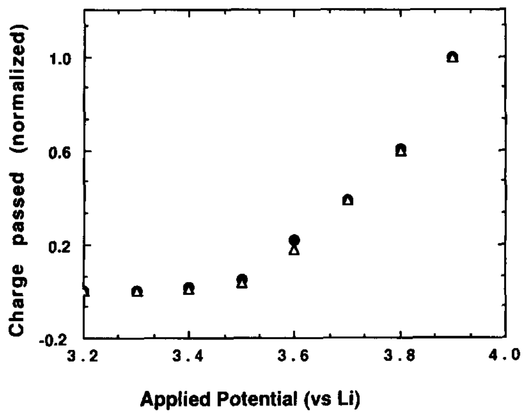

**Figure 11** Normalized accumulated charge passed as a function of applied potential for poly-**9** (●) and poly-**10** (△)

FT*i.r. spectroscopy*

*FT*i.r. spectroscopy can be used to assess the mode of coupling (α *versus* β) and estimate the degree of polymerization for polyheteroaromatics. The C–H out of plane bending modes for the monomers appear in the range 900–600 $cm^{-1}$ and fall in three distinct regions. The α-protons absorb between 680 and 710 $cm^{-1}$, the β and β′ protons between 850 and 830 $cm^{-1}$, and the methylene 'rock' from alkyl substituents (longer than *n*-butyl) appears around 720 $cm^{-1}$. *Figure 12* displays the *FT*i.r. spectra of **10** and its electrochemically and chemically prepared polymers (A, B and C, respectively). Several features can be noted. First, upon polymerization, a new dominant absorption appears around 790–800 $cm^{-1}$, which is due to the β-hydrogens of all internal thiophene rings[7–10]; second, the absorptions from the α-, β- and β′-protons from the two terminal rings are considerably reduced relative to the monomer; and third, the methylene rock absorption is sufficiently resolved in the polymers to serve as an internal standard against which we can normalize the end groups. The small relative intensity of the 830 $cm^{-1}$ peak compared with the one at 800 $cm^{-1}$ indicates that significant amounts of α, β′ coupling have not occurred. Assuming that the α-absorptions can be ascribed solely to the polymer termini, we estimate degrees of polymerization of $\geqslant 5$ ($\geqslant 15$ rings) for our systems, which are in the same range as reported for similar polymers[17].

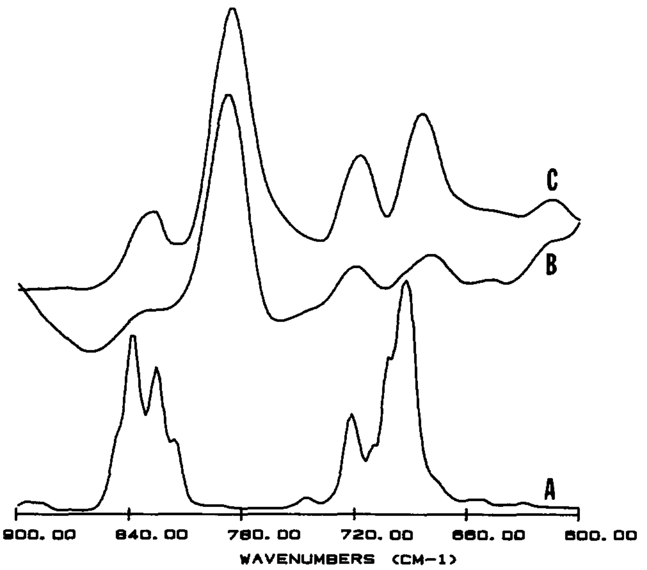

**Figure 12** *FT*i.r. spectra for monomer **10** (A) and its electrochemically (B) and chemically (C) produced polymers

*Processibility*

The electrochemically generated polymer films of **9** and **10** were insoluble in organic solvents including nitrobenzene, propylene carbonate, acetone, methanol and in aqueous ammonia. The analogous chemically polymerized materials were soluble in $CHCl_3$, $CH_2Cl_2$, THF and xylene but did not form self-supporting films when cast from these solvents. This difference in solubilities is inconsistent with the similar degrees of polymerization assigned from *FT*i.r., but could be due to a small amount of crosslinking in the electro-polymerized polymers which we were unable to detect.

## CONCLUSIONS

α-Terthienyl and 2,5-di (2-thienyl)pyrrole *n*-alkylated at the β-position of the central ring readily polymerize via electrochemical or chemical inducement to afford electroactive polymers. These materials were characterized by cyclic voltammetry, spectroelectrochemistry and *FT*i.r. These systems, which can be viewed as α-linked alternating copolymers of bithiophene with a 3-alkyl thiophene or 3-alkyl pyrrole, display superior effective degrees of conjugation compared with homopolymers of similarly substituted 3-alkylheteroaromatics. Chemically generated materials are soluble in a variety of organic solvents, but fail to produce coherent films when cast from these due to lower degrees of polymerization than similarly prepared 3-alkylthiophene homopolymers[11]. Electrogenerated polymers are insoluble despite apparently comparable degrees of polymerization as determined by *FT*i.r. end-group analysis. Oxidation potentials of the monomers are reduced in proportion to the number of alkyl substituents.

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