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Covalent binding of redox active centres to preformed regioregular polythiophenes

Ahmed Iraqi,[†] Joe A. Crayston and John C. Walton

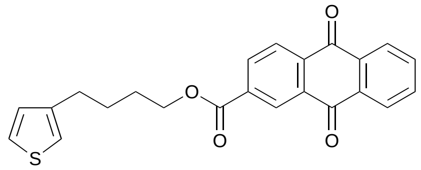
School of Chemistry, University of St. Andrews, St. Andrews, Fife, UK KY16 9ST

The synthesis of regioregular head-to-tail poly[3-(6-bromohexyl)thiophene] is reported, together with its reaction with 2-carboxyanthraquinone (Anth) to give an example of a regioregular polythiophene containing pendant functional groups (87% loading). NMR data on the two soluble polymers are reported together with preliminary studies of some of their physical properties. Cyclic voltammetric studies of anthraquinone polymer coated electrodes show that the observed response is coverage dependent: thin films display four redox couples due to the Anth$^{0/-/2-}$ processes and the p- and n-doping of the conjugated thiophene backbone. Thick films are rectifying in the sense that reduction of the Anth groups is inhibited on the negative sweep. Spectroelectrochemical studies confirm the nature of the anodic p-doping process (the film turns red to nearly colourless) and show characteristic changes on reduction (red to black).

There is considerable interest in the binding of redox active and mesogenic groups to organic conjugated polymers for their potential electrocatalytic, photochemical and electronic applications.[1–3] Polythiophene is emerging as a popular choice for the conjugated polymer backbone compared to, say, polypyrrole, not only due to the relative ease of synthesis of thiophene derivatives but also the relative stability of the polymer towards over-oxidation.[4] Recent examples of redox active groups attached to polythiophene include ferrocenes,[5,6] viologens,[6] fullerene,[7] quinones,[8] nitroxide[9] and nitro groups[10] and tetrathiafulvalene (TTF).[11] Other types of functional group have included metal complexes[12] or complexing agents such as crown ethers[13] or calixarenes.[14] Cyano groups have a marked influence on the redox properties of thiophene,[15] while photochromic,[16] polymerisable,[17] or molecular recognition[18] sites confer additional properties or reactivity to the final polymer.

Most of the reported redox functionalised conjugated polymers were formed by direct chemical or electrochemical polymerisation of the corresponding functionalised monomers. The first major problem with the monomer functionalization approach used in most of the examples cited above is that it often led to insoluble materials that were difficult to characterise fully by NMR spectroscopy and GPC. Secondly, one of the main factors affecting the physical properties of conjugated polymers was shown to be the regioregularity and homogeneity of their backbone structures. This was clearly demonstrated in the case of alkyl and alkoxy substituted polythiophenes[19] where structurally homogeneous materials displayed lower band gaps and higher intrinsic conductivities than the corresponding materials with random structures.

We decided to investigate a new route to soluble and easily processible functionalised polymers relying on the post-functionalisation in solution of soluble regioregular preformed polymer precursors. Recently, we discovered that the Grignard coupling reaction leading to regioregular poly(3-alkylthiophenes) could be extended to a number of substituted polythiophenes.[20,21] As a result of this work poly(3-bromoalkylthiophenes) were chosen as attractive precursors for functionalised polymers. The 3-(ω-bromoalkyl)thiophene monomers were already known to be useful intermediates for the synthesis of 3-functionalised thiophene monomers.[22] In this contribution we report the regioregular synthesis of poly[3-(6-bromohexyl)thiophene] (precursor polymer), together with its further reaction with 2-carboxyanthraquinone and preliminary studies on the physical properties of the two polymers. We shall show that this functionalisation process is remarkably efficient. We shall also compare our results with our previously reported *regio-random* polymer [poly(**4**)][8b] based on the electrochemical random polymerisation of monomer **4**. Since we completed this work we became aware of work by Bauerle *et al.* which describes the post-functionalisation of an ester substituted polymer; in this case it is important to note that the reactions were carried out with the polymer remaining on the electrode surface.[23]



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Results and Discussion

Poly[3-(6-bromohexyl)thiophene] was the novel key precursor polymer to be made using the regioselective synthetic strategy. The synthesis begins with selective bromination of 3-(6-bromohexyl)thiophene **1** at the 2-position using *N*-bromosuccinimide in DMF. The brominated monomer **2** was then selectively lithiated at the 5-position, followed by reaction with magnesium dibromide–diethyl ether. Addition of the nickel catalyst afforded poly(**1**) in 60% yield (see Scheme 1).

Poly(**1**) was isolated as a deep red powder readily soluble in methylene chloride and chloroform. Gel permeation chromatography (GPC) in chloroform revealed an average molecular mass of 12 300 with a polydispersity of 1.5. These data are comparable with those reported for regioregular poly(3-alkylthiophenes) prepared by a similar route. NMR studies of poly(**1**) in chloroform revealed a single chemical environment for the aromatic protons of the thiophene rings on the backbone of the polymer (δ_H 6.98) and essentially a single chemical environment for the methylene groups attached directly to the thiophene rings (δ_H 2.80), with a small trace (6%) of another triplet in a different environment at δ_H 2.60. The ^{13}C NMR spectrum revealed only four carbon environments for the thiophene rings suggesting a homogeneous structure of the polymer and *ca.* 94% selective head-to-tail coupling along the

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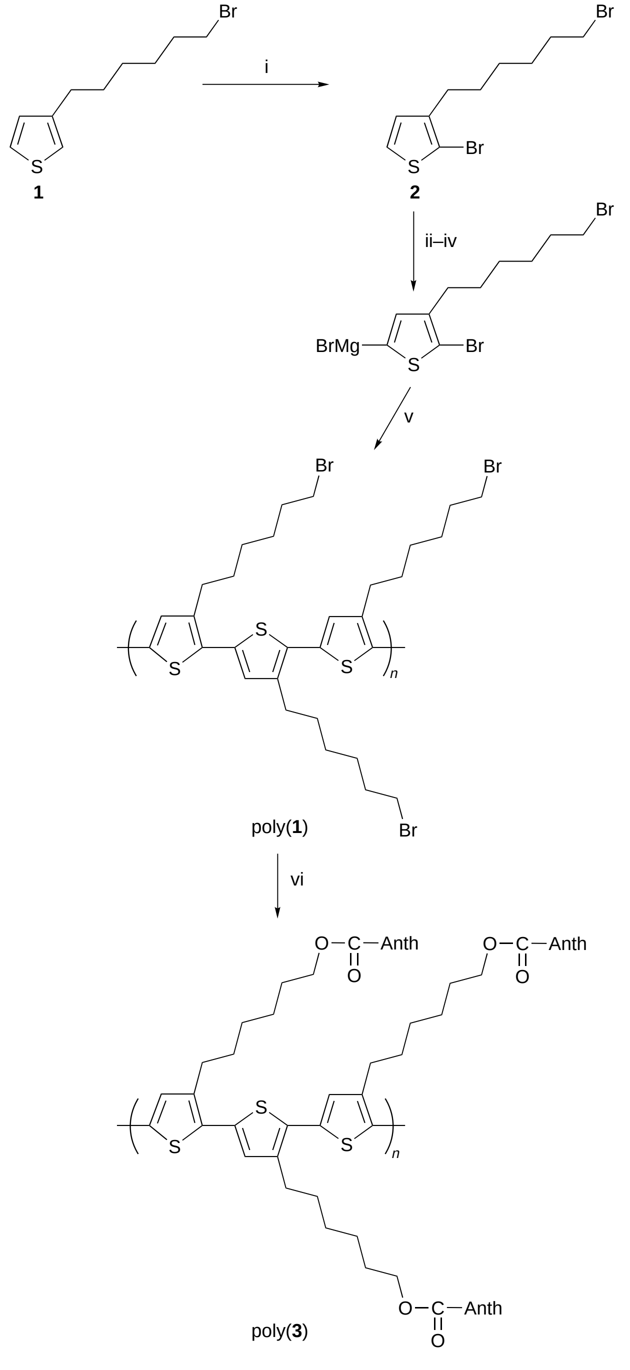
[†] Present address: School of Physics and Chemistry, University of Lancaster, Lancaster, UK LA1 4YA.



Scheme 1 *Reagents and conditions*: i, NBS, DMF; ii, LDA, THF, −60 °C, 90 min; iii, $MgBr_2 \cdot OEt_2$, −60 °C, 20 min; iv, −60→−5 °C; v, 0.5 mol% $[NiCl_2(dppp)]$, −80→20 °C, 15 h; vi, 2-carboxyanthraquinone, DBU, THF, 80 °C, 15 h

backbone. UV–VIS spectral analysis on the regioregular polymer in solution in $CHCl_3$ showed an absorption band (λ_{max} 445 nm) with a band edge (onset of absorption) at 560 nm. For films cast from CH_2Cl_2 an absorption band was observed at λ_{max} 511 nm with a band edge at 670 nm (band gap 1.8 eV). This band gap is comparable with those reported for alkyl-substituted polythiophenes made by the same method.[19]

Poly(**1**) was further reacted with 2-carboxyanthraquinone in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to yield the anthraquinone functionalised polymer **3** as a deep red powder isolated in 56% yield. Polymer **3** was also readily soluble in methylene chloride and chloroform. NMR studies on polymer **3** in chloroform confirmed that 87±2% of the total number of thiophene chains were grafted to an anthraquinone group. The extent of anthraquinone incorporation was determined by comparing integral heights of the hydrogens directly attached to the backbone of the polymer (δ_H 2.80 signal, 3H, CH_2-thienyl) to one on the anthraquinone (δ_H 8.84, 1H, aromatic proton adjacent to ester linkage).

UV–VIS spectral analysis on polymer **3** in solution in $CHCl_3$ showed an absorption peak at λ_{max} 445 nm with a band edge (onset of absorption) at 576 nm. For films cast from CH_2Cl_2 an absorption at λ_{max} 530 nm with a band edge at 700 nm (band gap 1.77 eV) was observed. This energy is comparable to that of poly(dodecylthiophene) in the solid state and suggests a lamellar structure in the film.[19a] There were, however, no long wavelength shoulders on this band ('fine structure'), which, if present, are thought to be indicative of long range order in the sample.

Electrochemical properties of polymer 3

Polymer-coated electrodes were prepared by droplet evaporation of a CH_2Cl_2 or $CHCl_3$ solution of polymer **3**. We first describe the cyclic voltammetric behaviour of thin polymer films with $\Gamma \leqslant 10^{-8}$ mol cm^{-2} corresponding to an estimated thickness of 50 nm, assuming unit density of the film. These films showed not only the expected thiophene-like response at positive potentials (Fig. 1), but also the two cathodic reductions associated with the pendant anthraquinone groups. The thiophene oxidation wave was somewhat more symmetrical (E_{pa} +0.716 *vs.* SCE, E_{pc} +0.656 V), and the peak separation (ΔE_p 60 mV) somewhat smaller than usual for thiophene films (the ideal surface wave should have zero peak separation). As expected, the oxidation of the polythiophene backbone occurs at lower potentials than non-regioregular polymers.[4] But there was no evidence for two clearly separated oxidation processes as observed in previous work on regioregular polythiophenes.[4,19b] The first reduction was signalled by an unsymmetrical set of peaks with a broad cathodic wave (E_{pc} −1.028 V *vs.* SCE) and a much sharper anodic wave (E_{pa} −0.82 V). This

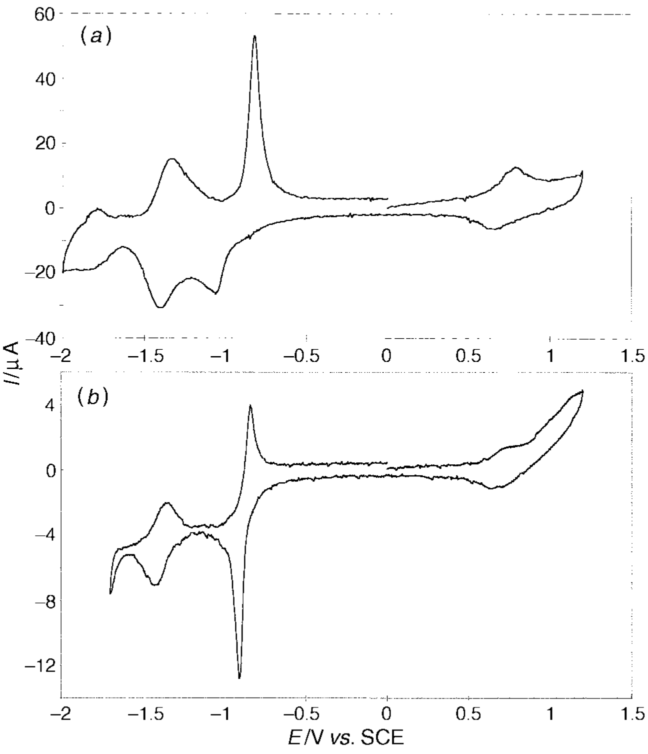


Fig. 1 Cyclic voltammetry of a poly(**3**) coated glassy carbon electrode (area 0.071 cm^2) in 0.1 mol dm^{-3} Bu_4NPF_6–acetonitrile. The coverage is approximately 6.9 × 10^{-9} mol cm^{-2} of Anth sites. Scan rates: (*a*) 100 and (*b*) 10 mV s^{-1}.

peak was assigned to the formation of the semiquinone radical anion ($Anth^{\bullet -}$) from the anthraquinone (Anth): eqn. (1).

$$Anth + e^{-} \rightarrow Anth^{\bullet -} \qquad (1)$$

This wave considerably sharpened at slower scan rates [Fig. 1(*b*), 10 mV s^{-1}], behaviour typical of sudden changes in the solvation of redox polymers such as polyvinylferrocences. At slow scan rates the film will have had time to reach its compact, non-solvated, neutral state at potentials between −0.8 and +0.4 V. Reduction of the quinone sites (*via* the electronic conducting backbone as there is always considerable residual electronic conductivity in polythiophene even in its neutral state) demands rapid ingress of cations and associated solvent in order to achieve neutrality.

The second reduction wave will not be subject to these effects, and indeed was more symmetrical (E_{pc} −1.408, E_{pa} −1.344 V) with a peak area similar to the first cathodic peak area, consistent with formation of the dianion: eqn. (2).

$$Anth^{\bullet -} + e^{-} \rightarrow Anth^{2-} \qquad (2)$$

We should point out that the regioregular polymer was found to be much more stable to redox cycling than the random polymer.[8b] Thus after 10 min of cycling at 20 mV s^{-1} over both the thiophene backbone and the quinone waves, poly(**4**) had lost over 50% of the faradaic charge associated with these redox processes. Under the same conditions polymer **3** had lost less than 2% of its charge. Moreover, polymer **3** seemed to be more stable after the deliberate addition of oxygen or water (as indicated by the unchanged CV response). In the case of water addition to the solvent, the quinone waves began to merge (at 50% v/v water–acetonitrile) into a single wave centred at about −0.80 V (Fig. 2).

We also noted in Fig. 1 a further reversible reduction at (E_{pc} −1.824, E_{pa} −1.792 V). This peak has a similar height to that of the thiophene oxidation and has a comparable position to that of similar polythiophenes such as regioregular **5** which has E_{pc} −1.95 V for n-doping.[20] We therefore attribute this reduction to the reversible n-type doping of the polymer.

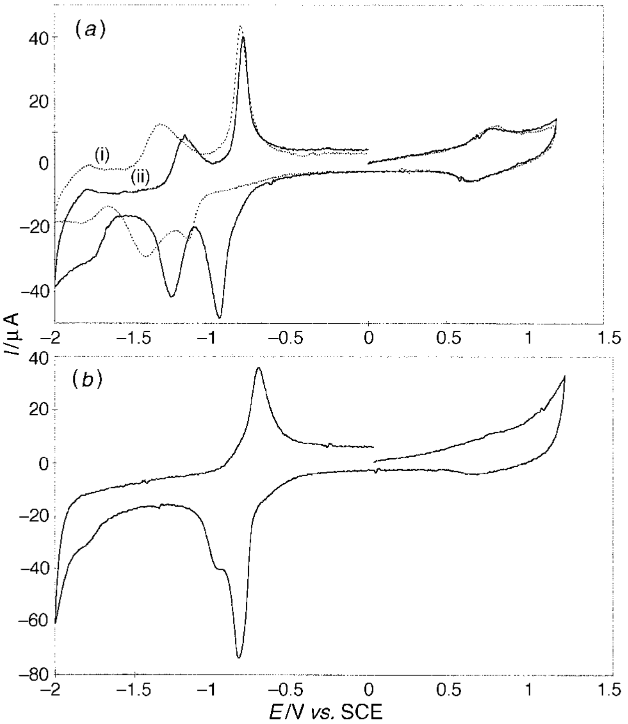
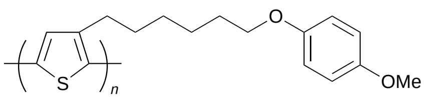


Fig. 2 (*a*) Cyclic voltammetry (100 mV s^{-1}) of a poly(**3**) coated glassy carbon electrode (area 0.071 cm^2; coverage *ca.* 6.9×10^{-9} mol cm^{-2} of Anth sites) in 0.1 mol dm^{-3} Bu_4NPF_6–acetonitrile (i) before and (ii) after 1% v/v water addition. (*b*) After 50% v/v water addition.



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As we mentioned earlier, the grafting of the anthraquinone onto the polymer occurs on 87% of possible sites. For these thin films the electroactivity approached 100% based on the amount of polymer applied to the electrode during droplet evaporation. We may then use the ratio of the observed peak areas for quinone and thiophene redox processes to calculate the number of electrons removed per thiophene ring (equivalent to the 'doping level'). This calculation yields a redox level of 0.20 to 0.25 electrons per ring (1 electron per 4–5 thiophene rings). This result is entirely consistent with accepted doping levels for polythiophenes.[4]

Electrochemistry of thick polymer films

When polymer film coverages greater than about 50 nmol cm^{-2} are used (*ca.* 50 nm thickness) a vastly different redox response is observed (Fig. 3). In this case all cathodic current is postponed until the onset of n-type doping near −1.8 V. This means that before the first scan the film is not sufficiently solvent swollen (and therefore permeable to ions) to allow charge transfer to the quinones. Subsequent scans and lower scan rates [Fig. 3(*b*)] have the effect of allowing the polymer to equilibrate with the solution. Similar unusual effects have been reported for other polymers (often described as the first scan or 'break-in' effect). The break-in effect is particularly noticeable during the n-doping process; this is thought to be due to the difficulty of cation injection, particularly when the cation is a tetraalkylammonium ion. Less significant break-in effects were for previously described polythiophenes or polypyrroles containing quinone groups.[8] The reason for this may be that the regioregular polymer begins the cycle in its neutral,

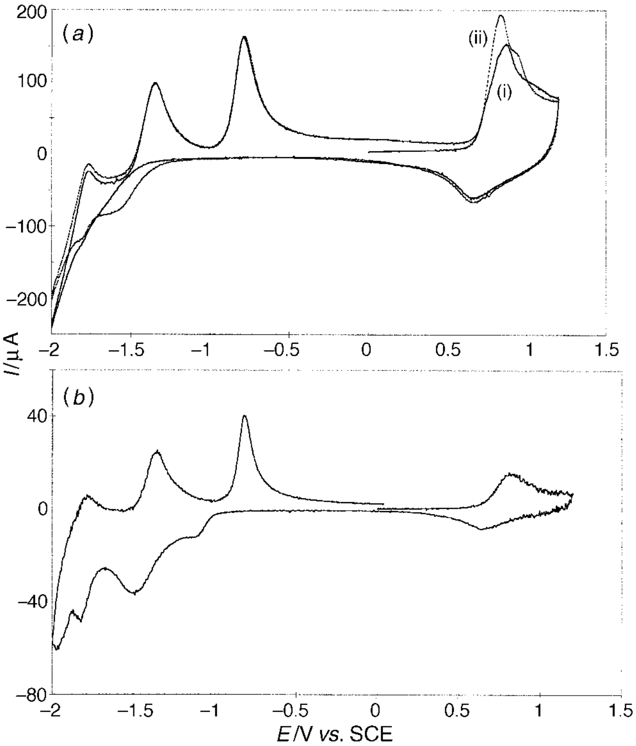

Fig. 3 Cyclic voltammetry of a thick film of poly(**3**) deposited on a glassy carbon electrode (area 0.071 cm^2) in 0.1 mol dm^{-3} Bu_4NPF_6–acetonitrile. The coverage is approximately 3.5×10^{-8} mol cm^{-2} of Anth sites. (*a*) 100 mVs^{-1}; (i) 1st scan, (ii) 2nd scan. (*b*) 10 mV s^{-1}.

insulating state whereas the electropolymerised polymers still retain some residual conductivity as they are prepared in the fully conducting (p-doped) state. Our own studies of the electropolymerisation of **4** to give regiorandom polythiophene with pendant anthraquinone groups[8b] showed both redox couples clearly, although the wave due to reaction (2) was diminished. However, the polymerisation was not very efficient and only rather low polymer film coverages were achievable.

In summary, for the thick films the polymer backbone must undergo redox processes in order to cause the film to swell with ions and solvents sufficiently to allow electron transfer to the quinone groups. The behaviour for thick films mirrors the fast scan behaviour for thin films. The insertion of ions and solvent into the film during the quionone redox processes is a much slower process than for the polymer processes because the structure of the thiophene polymer film is more compact in its neutral state.

Spectroelectrochemistry

The spectroelectrochemistry and electrochromic properties of polymer **3** were investigated after it was cast onto an indium–tin oxide (ITO) coated glass electrode from a solution of the polymer in methylene chloride. It was possible to measure the change in absorption as a function of the potential applied at the electrode (Fig. 4). At 0 V *vs.* Ag/Ag$^+$ reference electrode the polymer π–π* absorption dominates at λ_{max} 530 nm.

On increasing the potential to +0.6 V no colour change was observed, but at +0.8 V a sudden bleaching of colour occurred with a significant decrease in absorbance at this wavelength. At the same time a new absorption peak at λ_{max} 810 nm started to develop. The sudden approach to this state probably reflects the 'break-in' effect mentioned earlier. Visually, the electrode colour faded from deep red at 0 V, to colourless at +0.8 V, finally reaching a light yellow shade at +1.0 to +1.3 V. These transformations are associated with the introduction of bipolaron sub-gap states into the polymer backbone on oxidation.[24] The transition to a transparent conducting material appears to be characteristic of these regioregular polymers as we ourselves have noted elsewhere.[20] Other authors have noticed that further oxidation increases the amount of absorption at longer wavelengths[24] and there is evidence for such absorption at >1000 nm in our spectra.

The radical anion, Anth$^{\bullet -}$, is expected to be green and the doubly charged anion, Anth^{2-}, is blue. On reduction, provided that the cell was thoroughly degassed, it was possible to see a reversible darkening of the red neutral polymer film into a black film at potentials more negative than where the first quinone wave appears (*ca.* −1.0 V). The *in situ* spectroelectrochemistry revealed that the initial reduction (*ca.* −1.1 V) led to increases in the bands at 375 and 1090 nm (Fig. 5). Further reduction at −1.5 V causes the appearance of a shoulder at *ca.* 650 nm on the main polymer band and a simultaneous increase in absorption between 700 and 1000 nm due to broad

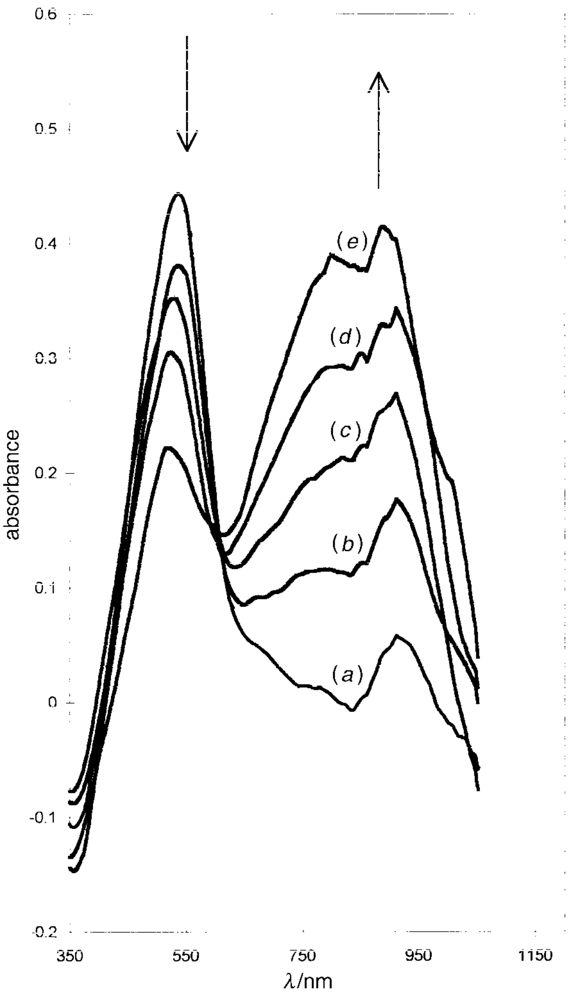

Fig. 4 UV–VIS spectroelectrochemistry of the oxidation of anthraquinone thiophene poly(**3**) coated onto an ITO electrode (3.8 nmol cm^{-2}) in degassed 0.1 M Bu$_4$NBF$_4$–acetonitrile at the following potentials: (*a*) +0.6, (*b*) +0.8, (*c*) +1.0, (*d*) +1.1 and (*e*) +1.3 V *vs.* Ag/Ag$^+$

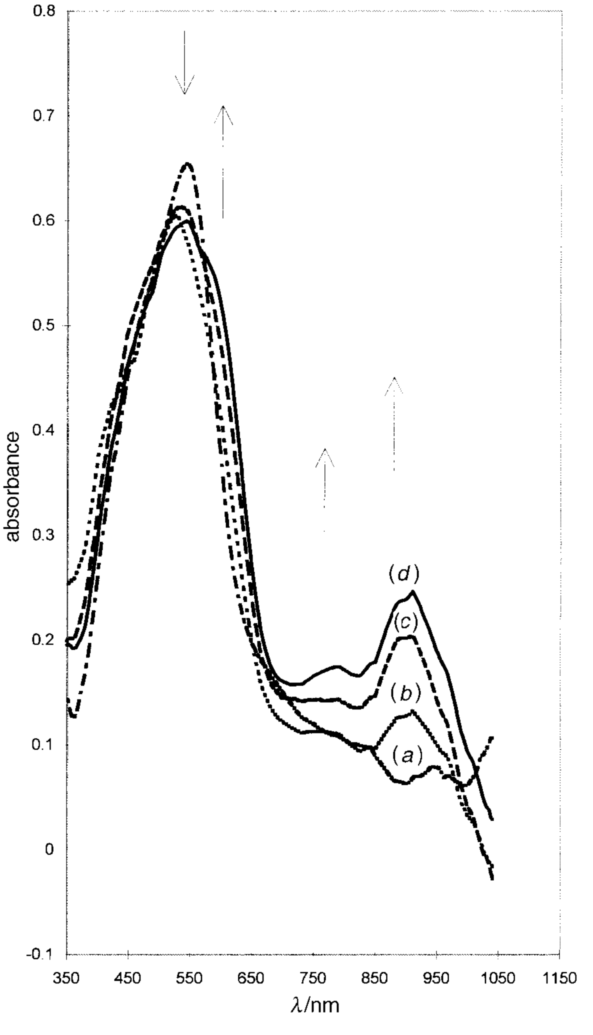

Fig. 5 UV–VIS spectroelectrochemistry of the reduction of anthraquinone thiophene polymer **3** coated onto an ITO electrode (3.8 nmol cm^2) in 0.1 M Bu$_4$NPF$_6$ in degassed acetonitrile. Successive spectra were recorded at (*a*) −1.1, (*b*) −1.3, (*c*) −1.4 and (*d*) −1.5 V *vs.* Ag/AgCl.

bands centred at *ca.* 800 and 920 nm. These changes appear to occur near the potentials expected for $Anth^{\bullet -}$ and $Anth^{2-}$ formation and indeed we would expect the spectra to indicate the build up of $Anth^{\bullet -}$. The spectral changes do not seem to correspond precisely to previous studies such as the polypyrrole–anthraquinone case described by Audebert *et al.* (using tetraethylammonium tetrafluoroborate as the electrolyte),[25] or the aqueous work on the spectroelectrochemistry of anthraquinones.[26] However, our results are comparable with those on a fully conjugated polyanthraquinone which is reduced first to the semiquinone (bands at 380 and 546 nm), and then to the dianion (412, 658, 743 and 885 nm).[27] The bands at longer wavelength are not expected for monomeric quinones and in line with these authors we assign them to polaronic or bipolaronic species in the polymer. Spectroelectrochemical studies of polythiophene and polybithiophene have shown that n-doping leads to similar changes in the UV–VIS spectrum to those occurring on p-doping, with the loss of the main visible band and the appearance of broad absorption bands at longer wavelengths.[28] If the polymer-coated ITO was held at potentials $\leqslant -1.5$ V for extended periods then the polymer became partially detached from the electrode. Our spectra also display considerable amounts of 'noise'. The reason for this is unclear, but may reflect the fact that we need thick films for the optical measurements and we noticed that the difficulty of cation insertion into these films on reduction (noted above) caused patchy changes in the film transmission.

Thermochromism

The polymer poly(**3**) changed colour when heated either in solution or in the solid state, although the changes were more prominent in solution. In $CHCl_2CHCl_2$ solution a stepwise increase in the temperature was accompanied by a shift of λ_{max} to higher energies, *i.e.* from 445 nm at 10 °C to 426 nm at 90 °C. The changes were reversible and are thought to arise from the twisting of the backbone of the polymer due to thermal agitation with increased movement of the substituents affecting the planarity of the backbone and hence the extent of conjugation.[29] These changes can be described as a continuous modification of the polymer chain with a progressive increase of conformational defects with increased temperature leading to a monotonic blue shift of the absorption maximum. A less prominent blue shift was observed when the measurements were done on polymer **3** in the solid state (film) over the temperature range (10–90 °C), although a pronounced colour change from deep red to orange was observed on heating to 200 °C.

Conclusions

The functionalised regioregular polymers described here display some, but not all, of the typical physical, spectroscopic and electrochemical properties familiar from the parent polyalkylthiophenes. The overriding advantage that they offer is their solubility and processing possibilities. However, from the optical and electrochemical evidence these materials do not appear to have structures as ordered as their relatives, and their unusual electrochemical behaviour shows that the solvent content of the neutral film is low. In a future publication we shall address the properties of poly(**3**) coated electrodes for the electrocatalysis of O_2 reduction. We are also interested in the rates of charge transport within conducting polymers which may be very large due to the proximity of redox groups and increased number of charge hopping pathways.

Experimental

NMR spectra were recorded using a Bruker AM300 spectrometer (300 MHz, ^{1}H and 75.5 MHz, ^{13}C) and a Varian Gemini-200 spectrometer (200 MHz, ^{1}H and 50 MHz, ^{13}C). *J* Values are in Hz. UV–VIS spectra were recorded using a Perkin-Elmer Lambda 5 or Lambda 14 spectrophotometer. A digital temperature controller was included in the spectrophotometer, allowing the temperature to be increased stepwise. Before each absorption spectrum was recorded, the sample was kept at the desired temperature for 5 min. Electrochromic measurements were performed on polymer films coated from a CH_2Cl_2 solution (6.3 mg polymer cm^{-3}; or 15 mmol dm^{-3} with respect to each monomeric unit) onto an indium–tin oxide (ITO) glass electrode ($9 \times 50 \times 2$ mm, resistance 20 $\Omega/\square$). A known volume of solution (microlitre syringe) was placed onto the ITO electrode, covering an area of 2 cm^2. The solvent was allowed to evaporate in a solvent-saturated atmosphere at room temp., and then the film was removed and dried in an oven at 70 °C for 30 min. The film coated electrode was then immersed in 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBAT, Fluka, puriss.) or hexafluorophosphate ($TBAPF_6$, Fluka, puriss.)–acetonitrile solution in a quartz UV cell equipped with a platinum wire as a counter electrode and a silver wire as reference electrode. The cell was degassed with a fine stream of argon supplied from a balloon; it was particularly important to degas the cell thoroughly on the reductive cycle. Controlled potentials across the electrochemical UV cell were generated using a Pine Instruments RDE4 potentiostat or an EG & G PAR 273A potentiostat (both from EG & G, Wokingham, UK). Cyclic voltammetry was performed on films cast onto 3 mm diameter glass carbon electrodes (BAS, Stockport, UK). GPC measurements were kindly performed by Rapra Technology Ltd., Shrewsbury. The GPC results were calibrated against polystyrene standards and the reported molecular masses are therefore expressed as polystyrene equivalent molecular masses.

Tetrahydrofuran and diethyl ether were distilled over sodium benzophenone; chloroform was dried and distilled over $CaCl_2$. Dimethylformamide (DMF) was dried and distilled over CaH_2. Diisopropylamine was dried and distilled over sodium hydroxide. 3-(6-Bromohexyl)thiophene[22] **1** and $[NiCl_2(dppp)]$[30] [dppp = 1,3-bis(diphenylphosphino)propane] were made according to literature procedures. Light petroleum (bp 40–60 °C), *N*-bromosuccinimide and magnesium dibromide–diethyl ether were obtained commercially and used without further purification.

2-Bromo-3-(6-bromohexyl)thiophene (2)

A solution of *N*-bromosuccinimide (6.48 g; 36.41 mmol) in DMF (45 cm^3) was added dropwise under nitrogen, in the dark and at −20 °C, to a solution of **1** (9.0 g; 36.41 mmol) in DMF (70 cm^3) over a period of 4 h. The solution was left stirring at room temp. overnight and then poured over ice (300 g) and extracted with methylene chloride (3×200 cm^3). The organic extracts were washed with water (2×150 cm^3), dried over magnesium sulfate and the solvent evaporated to dryness *in vacuo* to yield a yellow oil. Remaining traces of DMF were eliminated by heating the oil (50 °C for 1 h) in high vacuum (yield 11.5 g; 97%). δ_H ($CDCl_3$, $SiMe_4$) 1.43 (m, 4H), 1.60 (m, 2H), 1.85 (m, 2H), 2.62 (t, *J* 7, 2H), 3.44 (t, *J* 7, 2H), 6.79 (d, *J* 6, 1H), 7.20 (d, *J* 6, 1H). δ_C ($CDCl_3$, $SiMe_4$) 28.50 (1C), 28.83 (1C), 29.78 (1C), 30.10 (1C), 33.27 (1C), 34.59 (1C), 109.47 (1C), 125.86 (1C), 128.72 (1C), 142.13 (1C).

Preparation of head to tail poly (1)

To a solution of diisopropylamine (2.74 g; 27.11 mmol) in THF (85 cm^3) was added *n*-butyllithium (16.33 cm^3 of 1.6 M solution in hexanes, 26.11 mmol) at room temp. After 15 min stirring at room temp., the resulting LDA solution was cooled to −80 °C. A solution of **2** (8.52 g; 26.13 mmol) in THF (100 cm^3) was added at −80 °C and the temperature allowed to rise slowly to −40 °C where it was stirred for 40 min. The solution was then cooled to $-60\,°C$ and $MgBr_2{\cdot}Et_2O$ (6.75 g; 26.14 mmol) added. The mixture was stirred at $-60\,°C$ for 20 min then at $-40\,°C$ for 20 min and allowed to rise to $-5\,°C$ slowly whereupon all the $MgBr_2{\cdot}Et_2O$ had reacted. The resulting solution was cooled down to $-80\,°C$ and $[NiCl_2(dppp)]$ (100 mg; 0.18 mmol) was added. The mixture was allowed to warm to room temp. overnight. The solution was then evaporated under reduced pressure to half the volume and was poured over methanol (800 cm^3). The resulting red precipitate was filtered, washed with methanol, water and methanol again, and dried under high vacuum to afford the polymer as a deep red powder (yield 4.0 g; 62%).

The polymer was readily soluble in methylene chloride, chloroform and tetrahydrofuran. NMR spectra of the polymer in chloroform were recorded and showed 94% head-to-tail coupling. δ_H ($CDCl_3$, $SiMe_4$) 1.48 (m, 4H), 1.70 (m, 2H), 1.90 (m, 2H), 2.60 (br t, 0.12H), 2.80 (br t, 2H), 3.40 (t, J 7, 2H), 6.98 (s, 1H). δ_C ($CDCl_3$, $SiMe_4$) 28.01 (1C), 28.66 (3C), 29.31 (1C), 30.35 (1C), 32.76 (1C), 33.96 (1C), 128.81 (1C), 130.78 (1C), 133.87 (1C), 139.80 (1C). UV–VIS ($CHCl_3$) λ_{max} 445 nm, band edge 560 nm. (Film cast from CH_2Cl_2, λ_{max} 511 nm, band edge 670 nm (1.8 eV). Gel permeation chromatography (GPC) in chloroform revealed an average molecular mass of 12 300 with a polydispersity of 1.5.

Preparation of polymer 3

1,8-Diazabicyclo[5.4.0]undec-7-ene (0.24 g; 1.57 mmol) was added to a solution of 2-carboxyanthraquinone (0.78 g; 3.09 mmol) in THF (50 cm^3). The solution was stirred for 1 h after which a precipitate was formed and poly(**1**) (0.38 g; 1.55 mmol) was then added and the mixture placed in a sealed tube and heated at 100 °C for 18 h. The solution was evaporated to dryness in high vacuum. The residue obtained was dissolved in methylene chloride (20 cm^3), and the precipitate (ammonium bromide) formed was filtered off. Upon reducing the solution to 10 cm^3 and addition of light petroleum (bp 40–60 °C) (250 cm^3), a red precipitate formed and was filtered and isolated. It was then mixed with water (250 cm^3) and stirred for 30 min, filtered and washed with MeOH (250 cm^3) then diethyl ether (200 cm^3) and dried under high vacuum to afford the polymer as a deep red powder. (Yield 0.47 g; 73%). The polymer was readily soluble in methylene chloride and chloroform. NMR spectra of the polymer in chloroform were recorded and showed that 87% grafting of anthraquinone had occurred. The ratio of anthraquinone incorporation was determined by comparing integral heights of the hydrogens directly attached to the backbone of the polymer to the ones from the anthraquinone substituents. δ_H ($CDCl_3$, $SiMe_4$) 1.51 (m, 4H), 1.61 (m, 2H), 1.77 (m, 2H), 2.76 (br t, 2H), 4.37 (m, 2H), 6.90 (s, 1H), 7.75 (m, 2H), 8.28 (m, 4H), 8.84 (m, 1H). UV–VIS spectral analysis on polymer **3** showed an absorption peak at λ_{max} 445 nm in solution in $CHCl_2CHCl_2$ with a band edge (onset of absorption) at 576 nm. For films cast from CH_2Cl_2 an absorption at λ_{max} 530 nm with a band edge at 700 nm (band gap 1.77 eV) was observed.

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