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Spectroelectrochemical responses of thin-film conducting copolymers prepared electrochemically from mixtures of 3,4-ethylenedioxythiophene and 2,2'-bithiophene†

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Here we have studied the electrocopolymerisation of binary mixtures of functionalised thiophenes in varying compositions and determined independently for each copolymer the

spectroelectrochemical responses and the composition of the material using x-ray photoelectron spectroscopy. We have observed strong correlations between the composition of the copolymer material and the composition of the binary solution from which the polymer was grown. In addition, we have shown that the spectroelectrochemical properties of the copolymers indicate the presence of random copolymer material where the λ_{Max} values of the neutral, undoped, polymer scales with composition but also suggest that there may be small amounts of block copolymer or phase-separated mixtures of the homopolymer components.

Introduction

Poly(3,4-ethylenedioxythiophene), (PEDOT), along with other derivatised thiophene systems, has been the subject of a sustained and intensive research effort over the past ten years or so.^{1, 2, 3, 4} Such materials are relatively easy to work with and provide a generic framework in which to study the electrochemical, physical and spectroscopic properties of conducting polymer systems. The PEDOT system in particular is especially interesting for several reasons: it is very stable to the environment because of its β -substituents; similarly cross linking during polymerisation is minimised; the oxidation potential of the parent monomer (EDOT) is very low, making electrochemical polymerisation facile; and the resultant *p*-doped polymer is highly conducting. Also the spectroscopic properties are unusual in that the neutral PEDOT material is blue in colour whilst the *p*-doped conducting material is almost colourless, seeming transparent to the eye. This is in contrast to most other polythiophenes where the neutral material is usually red in colour changing to blue in the *p*-doped state. For this reason PEDOT has potential application in electrochromic devices^{5, 6, 7, 8, 9} as well as many other areas including electroluminescent displays^{10, 11, 12, 13, 14} and antistatic coatings.^{15, 16}

Composite properties for electronic polymers are often sought by combinatorial methods, for example through co-electropolymerisation of two (or more) monomers, and there have been many examples of copolymerised materials as well as layered structures.^{17, 18, 19, 20, 21} However, in such studies it is often assumed that if the oxidation potential of the two monomers are similar then the composition of the copolymer

will be related to the composition of the solution (in mole-fraction terms) from which the polymer was prepared by a simple (monotonic linear) function. Consequently there are few studies in which the composition of the polymer is independently measured. We have shown in previous studies of conducting-polymer systems that the redox potentials of the monomers are not the only determinants of polymer composition. For example the solubility of oligomers and the reactivity of the radical cations are also critical factors^{22, 23} especially when polymerisation is performed under a diffusion-controlled regime. Often it is the case that even though the oxidation potentials of monomers are similar, electrocopolymerisation from a 1:1 binary mixture yields a polymer material that significantly favours one component or the other.²²

Here we have studied the electrocopolymerisation of a range of thiophene species including 3,4-ethylenedioxythiophene (EDOT) and 2,2'-bithiophene (BT), 3-octylthiophene (OT) and 2,2'-terthiophene (TT). In particular the EDOT-BT system has been treated as an important model,^{24, 25} being helpful in the elucidation of the mechanism of *p*-doping and in understanding the relationship between conductivity and doping state.²⁶

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In addition the incorporation of PEDOT into copolymers, blends or layers is an attractive proposition because of the unusual electrochromic properties, suggesting that the spectroelectrochemical response of a polymer system can be modulated or tuned by incorporation of additional electrochemical chromophores. In this study we have prepared copolymer materials by electrocopolymerisation from binary mixtures of monomers in varying compositions. We have determined independently for each copolymer the composition using X-ray photoelectron spectroscopy (XPS) and the spectroelectrochemical response. We have observed strong correlations between the measured composition of the copolymer material and the composition of the binary solution from which the polymer was grown. In addition from the observed compositional correlation we are also able to show unambiguously that the spectroscopic properties of the copolymer materials show a stoichiometric (statistical) dependence on the measured composition.

Experimental

Electrochemical measurements

Electropolymerisations were performed under controlled potential conditions using a silver wire pseudo reference electrode. Under the conditions employed for these experiments, the pseudo-reference electrode had a potential of -450 mV with respect to the ferricinium/ferrocene couple. All electrochemical experiments were performed using a PAR EG&G model 263A potentiostat in a three-compartment cell under an atmosphere of N_2 . The solvent for electropolymerisation was dry acetonitrile (HPLC grade) containing 0.1 M $LiClO_4$ as supporting electrolyte. Copolymer materials were prepared using Au-coated glass electrodes (*ca.* 1 cm^2); the Au was evaporated onto glass microscope slides to a thickness of either 100 nm, for use in XPS quantification, or 50 nm for transparent electrodes used in spectroelectrochemical experiments. The thickness of Au coatings was monitored during evaporation using a resonant quartz crystal. Occasionally this calibration was checked by removal of the Au from the substrate (using adhesive tape) and then by subsequent measurement of the step edge using high resolution AFM (see supplementary data†). Polymer film thickness was measured using AFM in the same way. In a typical example the polymer was grown potentiodynamically (cyclic voltammetry, CV) by repetitive cycling from -0.2 to +1.2V (*versus* Ag-wire reference) and back to -0.2V, at a scan rate of 50 mV s^{-1} . The thickness of the polymer was varied according to the number of cycles.

EDOT-BT copolymers: EDOT homopolymers were grown from a 0.05 M EDOT-0.1 M $LiClO_4$ -MeCN solution. Sequential additions of BT were then made increasing the mole fraction of BT (X_{BT}) in the mixture to $X_{BT} = 0.1, 0.3, 0.5, 0.7, 0.9$. Homopolymers of BT were separately prepared from a 0.05 M BT-0.1M $LiClO_4$ -MeCN solution.

EDOT-TT and EDOT-OT copolymers: TT (or OT) homopolymers were grown from a 0.1 M TT-0.1 M $LiClO_4$ -MeCN (or 0.1M OT-0.1M $LiClO_4$ -MeCN) feed solution. Sequential additions of EDOT were then made increasing the mole fraction of EDOT (X_{EDOT}) in the mixture to $X_{EDOT} = 0.1, 0.3, 0.5, 0.7, 0.9$. Homopolymers of EDOT were separately prepared from a 0.1M EDOT-0.1 M $LiClO_4$ -MeCN solution.

The anodic limit for all electropolymerisation (either CV or potential-step) was always kept at least 200 mV more positive than the most anodic monomer potential.

EDOT, TT, OT and BT monomers were purchased from Aldrich and used without further purification.

XPS measurement and quantification

XPS spectra were recorded on a Scienta ESCA 300 instrument (NCESS Daresbury Laboratory, UK) using monochromated Al $K\alpha$ (1486.7 eV) radiation, a slit width of 0.8 mm, a take off angle of 90° and a flood gun energy of either 1.0 or 3.0 eV. The energy scale of the spectra presented is corrected to the C-H (1s) peak at 285 eV using the S(2p) peak at 164 eV from the thiophene species to assure consistent corrections were made when the C (1s) spectra contained a number of broad peaks close to 285 eV.

The C(1s) XPS spectra of copolymers were quantified using best-fit linear combination methods. Reference spectra, S_1 and S_2 , were recorded for the homopolymers of each material (*e.g.* poly(bithiophene) and PEDOT) and in each case the measured copolymer data, S_{Exp} , were then numerically compared to a linear sum, S , of the two reference spectra in varying proportion using either eqn (1) or eqn (2). The residual difference, r , between the experimental data and the linear sum of the reference spectra was then calculated according to eqn (3). The best fit was obtained by iterative minimisation of the residual difference and the error was expressed according to eqn (4). Microsoft Excel was used for iterative fitting either with custom written macros (Visual Basic for Applications, VBA) or using the built-in *Solver* function.

$$S = XS_1 + (1 - X)S_2 \quad (1)$$

$$S = nS_1 + mS_2 \quad (2)$$

such that for example $X_1 = \frac{n}{(n+m)}$

$$r = |S - S_{Exp}| \quad (3)$$

$$Error = \frac{\sum_a^b r}{\sum_a^b S_{Exp}} \times 100\% \quad (4)$$

The summation method shown in eqn (1) uses a single parameter (mole fraction), whereas that in eqn (2) uses two independent parameters, n and m , which are subsequently used to calculate mole fraction. Although the latter of these two approaches is less constrained, both fitting methods yielded very similar results with comparable errors. Consequently, the simplest of the two methods was generally adopted.

Spectroelectrochemistry

Spectroelectrochemical (UV-Vis) measurements were acquired using a Hewlett Packard 8452A Diode Array Spectrophotometer under computer control in conjunction with the PAR EG&G 263A potentiostat. Working electrodes consisted of either transparent Au (50 nm) or ITO on glass (Delta Technologies). In a typical experiment the potential of the copolymer film was scanned between -500 mV and +1000 mV at a scan rate of 5 mV s⁻¹ and spectra were acquired between 300 nm – 800 nm every 15 seconds, this corresponds to a potential resolution of 75 mV.

Results and Discussion

Electrochemical deposition

Insoluble polymer films (0.1–0.5 µm thickness) were prepared by anodic oxidation of monomers in a binary mixture at a Au-coated glass (approx. 1 cm²) electrode in degassed acetonitrile (MeCN), containing electrolyte. In a typical experiment the electrode potential was cycled repetitively between -0.2 V and +1.2 V at a scan rate of 50 mV s⁻¹ until sufficient polymer was deposited on the electrode surface. The polymer-coated electrode was then removed from the cell and rinsed in fresh MeCN prior to characterisation. The polymer coatings thus grown were even and homogeneous to visual inspection over the area of the electrode surface. A series of samples were prepared in sequence starting with a homopolymer, *e.g.* PEDOT. The composition of the solution was then increased incrementally by successive additions of the second component monomer, *e.g.* BT, as described in the experimental section and shown in Table 1. In addition, for purposes of comparison, polymers were prepared from solutions of the same composition (mole fraction) by potential-step methods. For example, in a typical experiment the working electrode was stepped from -0.2 V to +1.2 V and held for 20 s.

Table 1

X_{EDOT} in Solution	X_{EDOT} in EDOT–BT	X_{EDOT} in EDOT–TT	X_{EDOT} in EDOT–OT
1.0	1.00	1.00	1.00
0.9	0.86	0.34	0.95
0.7	0.75	0.10	0.97
0.5	0.55	0.08	0.99
0.3	0.46	0.01	0.98
0.1	0.28	0.07	0.97
0.0	0.00	0.00	0.00

Subsequent quantification analysis and fitting of XPS data showed no significant compositional differences between samples prepared consecutively from the same solutions (composition) but by different polymerisation methods (*i.e.* potential-cycling or potential-step methods). In addition the effect of total monomer concentration was probed: in one experiment a sample was prepared by electrochemical polymerisation from a binary solution mixture having a total monomer concentration of 0.2 M. Half the volume of the solution was then removed and replaced with fresh (monomer free) MeCN electrolyte. A second polymer sample was prepared from this solution in the same way. This procedure was repeated for a further dilution of 50%. Again no significant compositional differences were observed in quantification of the XPS data from the three samples. This demonstrates that the composition of the copolymer, whilst a function of the mole ratio composition (described below), was not sensitive to the total monomer concentration (within the limits tested here).

The polymers prepared (above) were examined by cyclic voltammetry in fresh electrolyte solution (0.1 M LiClO₄–MeCN). The data presented in Fig. 1 show the CV responses of two homopolymers, EDOT and BT together with that for a copolymer prepared from a solution containing a binary mixture of the two homopolymers with a composition of $X_{BT} = 0.5$. The CV responses of the homopolymers are consistent with previous reports^{27,28,29,30} with the PEDOT showing doping/dedoping behaviour at a potential that is 750 mV less positive than that for the homopolymer of BT. The polymer grown from the mixture ($X_{BT} = 0.5$) however, shows an intermediate response with a less well-defined doping /dedoping process spread over a wider potential range. This is as expected for the electrochemical response of a blended mixture or a copolymer system because there exists a range of polymer strands with different sizes and compositions.

Fig. 1 Cyclic voltammograms of pure PEDOT (blue), pure poly(BT) (black) and a copolymer grown from solution composition $X_{BT} = 0.5$ (red) in MeCN–0.1 M LiClO₄ at a scan rate of $\nu = 5$ mV s⁻¹, using a working electrode fabricated from Au-coated glass (*ca.* 1 cm²) and a Ag-wire pseudo-reference electrode. [NB: Here the voltammograms have been

independently scaled and normalised to enable overlay and to compensate for differences in electrode area and film thickness.]

Compositional analysis using XPS

XPS data were recorded for each copolymer sample in the C(1s) and S(2p) regions of the spectrum. The S(2p) peak of the thiophene sulfur atom showed very little sensitivity to structural differences or polymer composition, presumably because this atom is, in each case, remote from the site of β -substitution. Consequently the S(2p) peak was used to calibrate binding energies and compensate for flood-gun shifts. A typical data set of C(1s) spectra for the range of copolymers prepared from EDOT:BT mixtures is shown in Fig. 2(a).† Here the spectra of the two homopolymers are quite distinct with the PEDOT polymer showing a much higher intensity at lower binding energies. This is consistent with the presence of saturated carbon (CH₂) groups absent in poly(BT).³¹ The intermediate copolymers show a qualitative progression between the two extremes.

Quantification of the copolymers in terms of the relative mole fraction of each monomer unit is complicated here by the fact that all the monomer systems treated are both carbon-rich and none have any unique spectral label (*e.g.* a halogen or other atom) with which to carry out comparison. In principle, comparative integration of the S(2p), C(1s) or O(1s) spectral regions for PEDOT can yield the required information, but in practice the errors are large because these integral ratios are often distorted by small amounts of surface air-borne (adsorbed) contamination. Here we have taken an alternative approach: quantification has been achieved by iterative, numerical, fitting of the measured spectral data in the C(1s) region with numerically-generated combinations of reference spectra for the individual homopolymers. This procedure has been used previously for determination of enzyme concentrations in conducting polymer films for biosensors³² and is illustrated in Fig. 2(b). Here the two reference spectra, PEDOT and poly(BT), are shown alongside the measured copolymer data (for a solution where $X_{BT} = 0.5$) together with the best-fit linear combination of reference spectra. The best fit is defined by the minimum in the plot of residual difference versus mole fraction which is shown here as an insert.

Fig. 2 (a) XPS data, C(1s), for the series of copolymers containing EDOT and BT. The legend shows the corresponding value of mole fraction, X_{EDOT} , in the solution binary mixture from which the copolymer was prepared. (b) XPS data, C(1s), for a typical fitting procedure: pure PEDOT (black), pure poly(BT) (red), measured copolymer data (blue) and linear combination best fit (grey). Linear combination of reference (pure) spectra shows minimum residual error at $X_{BT} = 0.52$ (insert).

This procedure is described in detail in the experimental section. In this example the minimum residual difference is obtained at a mole fraction $X_{BT} = 0.52$. All the copolymer data were quantified in this way and the results are summarised in Table 1 and presented graphically in Fig. 3.

Here it is evident that attempts to copolymerise OT or TT with EDOT were unsuccessful and Fig. 3 (as well as Table 1) shows that the compositions of polymers grown in these experiments are almost invariant with the increased mole fraction of EDOT. Where OT is the co-monomer then the resultant polymer consists essentially only of EDOT whilst if TT is the co-monomer the inverse is true and the polymer contains mainly TT (except at very high loadings with $X_{EDOT} > 0.9$). Close examination of the list of monomer redox potentials (relative to EDOT monomer) presented in Table 2 (here the redox potentials correspond to the foot of the anodic wave that denotes the onset of polymerisation) shows evidence of a correlation between copolymer composition and relative potential. The oxidation of the OT monomer is 370 mV more anodic where as that of the TT monomer is 140 mV cathodic. In contrast to this, the composition of the polymer prepared from the EDOT–BT solution mixture varies progressively with increasing EDOT mole fraction in a quasi-linear fashion. Duplicate data sets are shown in Fig. 3 that exhibit good consistency and maximum error around $0.3 < X_{EDOT} < 0.5$ (mean values are presented in Table 1). Here the difference in redox potential between the two monomers is only 60 mV (Table 2).

Fig. 3 Mole fraction compositional data from XPS best fit calculations for copolymers derived from EDOT in combination with terthiophene ($\square$), octylthiophene (∇) and bithiophene, BT ($\bullet$, $\blacktriangle$), where two independent (duplicate) data sets are presented. Error bars were evaluated using the residual difference from the best-fit calculations as indicated in eqn. 1.

In an electrochemical process the rate of heterogeneous reaction is, in the absence of surface kinetic effects, most simply expressed as a function of the electrode potential and the mass transport. For any given process it can easily be shown that when the applied electrode overpotential is greater than 100–200 mV then the reaction is no longer controlled by electrode potential but by the rate of mass transport of reacting species to the electrode surface.³³ Consequently increasing the overpotential beyond this point has no effect upon reaction rate.

Table 2

Monomer	Monomer oxidation potential E_p^{ox} / mV (versus EDOT)
OT	+370
BT	+60
EDOT	0
TT	-140

Here we have prepared polymer films by potential-step methods (as well as by potential cycling) with an overpotential of at least +200 mV. (For example if monomer OT has $E_p^{ox} = +350$ mV and monomer EDOT has $E_p^{ox} = 0$ mV then an overpotential of +200 mV is equivalent to an electrode potential of +570 mV) Consequently, the rates of electrochemical oxidation for both monomers are diffusion controlled and not determined by the magnitude of difference between monomer redox potentials, E_p^{ox} , or by the difference between either of these and the applied electrode potential. In addition, we observe only minor experimental deviation between composition of polymers prepared from the same solutions by either potential-cycling or potential-step methods. We conclude that the observed compositional dependencies of the copolymers are not, in fact, a function of

thermodynamics, *i.e.* monomer redox potential, but rather a manifestation of differential reactivities of the “monomer” species towards polymer formation. Such reactivity is a combination of various kinetic factors that include the intrinsic reactivity of the monomer and oligomer radical cations but also the solubility and surface-nucleation properties. Hence whilst it is true that the longer oligomers will be intrinsically less reactive, the polymer is nevertheless precipitated because the oligomers are less soluble. This phenomenon is well known in other areas of polymer chemistry, for example tables of reactivity ratios for various monomers are published with respect to copolymerisations of bulk commodity polymers and plastics.³⁴

Spectroelectrochemical responses

The UV-Vis spectra ($300 < \lambda < 800$ nm) of the polymer films were recorded during voltammetric scans as a function of time (and potential) and three typical data sets are presented in Fig. 4. The spectra were recorded at intervals of 15 seconds during a voltammetric scan at a potential scan rate, $\nu = 5 \text{ mVs}^{-1}$; consequently the potential resolution is 75 mV. The full sets of spectra for each complete voltammogram are shown as surface plots, Fig. 4a, c and e, whilst selected sample spectra are also presented with corresponding potential labels Fig. 4b, d and f. For experimental consistency, the spectroelectrochemical measurements were performed on the same sample films as those subjected to compositional measurements (XPS). Here the polymer films were deposited to a thickness of 100–500 nm such that the coatings were homogeneous over the whole of the sample area (*ca.* 1 cm^2). As a consequence of the film thickness the absorbance values observed in the spectra, (Fig. 4), are rather high. However, here we discuss only the trends in wavelength at peak absorbance (*i.e.* λ_{Max}) and make no attempt at quantitative analysis, or correlation, of the peak absorbance values.

The data set shown in Fig. 4a and b corresponds to the spectroelectrochemical response of pure PEDOT. At potentials of -0.5 V the polymer is strongly absorbing at 582 nm and consequently appears dark blue in colour. The onset of electrochemical doping occurs at relatively low anodic potentials (see Fig. 1) and as the potential has reached +0.35 V the absorbance at 582 nm is almost totally bleached being replaced by a broad absorbance in the near IR ($\lambda > 800$ nm) corresponding to the conduction band. In this state the polymer film appears very pale blue, almost transparent. This spectroelectrochemical response is consistent with previous reports.^{28,35} The data set shown in Fig. 4c and d corresponds to the spectroelectrochemical response of pure poly(BT). Here the peak absorbance of the undoped (neutral) polymer is centred at 464 nm resulting in the red colour. In this case the spectroelectrochemical response does not occur until much more anodic potentials consistent with the voltammogram shown in Fig. 1. At potentials $E > +0.7$ V the absorbance at 464 nm is very weak whilst a new absorbance peak has emerged at $\lambda = 690$ nm and consequently the *p*-doped pure poly(BT) is blue in colour. Both homopolymer responses were stable, such that the value of peak absorbance at the cathodic end of each cycle remained essentially constant over

many voltammetric scans.

The spectroelectrochemical response of a copolymer prepared from a solution mixture, $X_{EDOT} = 0.5$, having a composition of $X_{EDOT} = 0.55$ (from fitting of XPS data) is presented in Fig. 4e and f. Here the λ_{Max} for the undoped (neutral) polymer occurs at an intermediate value of 504 nm. This is somewhat lower than the (blue shifted) the value of 528 nm that might be predicted from a statistical admixture of both homopolymers calculated using the measured composition. This absorbance is gradually bleached during

anodic oxidation and a new absorbance is visible at potentials, $E > +0.25$ V, having $\lambda_{Max} = 750$ nm. At more anodic potentials, $E > +0.55$ V, this becomes dominated by a much stronger absorbance at $\lambda_{Max} > 800$ nm. These values of λ_{Max} together with those for the intermediate copolymer compositions are summarised in Table 3 and presented graphically in Fig. 5.

Fig. 4 Spectroelectrochemical, UV-Vis, data for pure PEDOT, (a, b), pure BT, (c, d) and a copolymer grown from a solution composition $X_{EDOT} = 0.5$ with a measured (XPS) copolymer composition of $X_{EDOT} = 0.55$ (e, f). Surface projections (a, c, e) show the complete data sets acquired over a single

voltammetric scan (in each case) according to the potential limits shown ($\nu = 5 \text{ mV s}^{-1}$). Plots (b, d, f) show selected spectra from the same scans with the corresponding values of potential.

Fig. 5 Spectroelectrochemical data for copolymers of BT and EDOT grown electrochemically from a solution containing the binary mixture at the composition shown.

Given that the absorbance band of the undoped copolymers ($X_{EDOT} = 0.55$ shown) is not significantly broader than those of either homopolymer these spectra show evidence of two types of polymer. The λ_{Max} trend exhibited in Table 3 and Fig. 5 indicate that a random copolymer is formed such that the electronic structure of the conjugated-polymer backbone is determined by the weighted average contribution from each of the two types of monomer unit. On the other hand, for the copolymer EDOT–BT ($X_{EDOT} = 0.55$) the spectrum that emerges at $E = +0.4 \text{ V}$ (Fig. 4f), after bleaching of the absorbance at 504 nm is strikingly similar to that of the native BT.

Table 3

X_{BT} in Solution	Polymer λ_{Max} / nm (Undoped)
0.0	582
0.1	564
0.3	518
0.5	504
0.7	488
0.9	466
1.0	464

Although electrochemical copolymerisations are generally assumed to result in random copolymers, there is little experimental evidence to support these assumptions; our observations (above) can be interpreted as evidence of either phase separation (during polymerisation) or block copolymerisation. In addition the presence of two isosbestic points has, in the case of PEDOT, been interpreted as showing first a transition between undoped (non-conducting) and p-doped (conducting) phases followed by a second transition to an over-doped non-conducting phase at high anodic potentials.²⁶ Here, however, it may be that the multiple isosbestic points observed in the spectra of the copolymer,

$X_{EDOT} = 0.55$ (Fig. 4e and f), indicate the presence of phase separated segments of homopolymers rather than a homogeneous random copolymer.

Fig. 6 Cyclic voltammetry data, red, (where current represents charge flux $I = dQ(E)/dt$) and corresponding differential absorbance $dA(E)/dt$, black, data acquired during the same scans (with scan rate $\nu = 5 \text{ mV s}^{-1}$, see Fig 4.) for (a) pure PEDOT, (b) pure BT and (c) a copolymer grown from a solution composition $X_{EDOT} = 0.5$ and a measured (XPS) copolymer composition of $X_{EDOT} = 0.55$. Arrows indicate the direction of change with the potential scan. All data are normalised to facilitate overlay presentation.

Finally in order to observe the synchronisation between potential-driven charge flux (*i.e.* current, where, $I = dQ(E)/dt$), during the cyclic voltammogram and changes in the absorbance spectra of the polymer during potential cycling

we have presented in Fig. 6 the normalised CV curves (*i.e.* charge flux) overlaid with the normalised differential absorbance traces, $dA(E)/dt$, at the peak absorbance for the undoped polymers for each of the examples shown in Fig. 4. Fig. 6a and b represent the normalised flux curves for the two homopolymers PEDOT and poly(BT) respectively. In each case the anodic current corresponding to p-doping of the polymer is accompanied by a synchronous drop in the differential absorbance (*i.e.* bleaching). Similarly on the cathodic scan the situation is closely mirrored. In both cases it is evident that charge injection and colour change occur on similar time scales and that there is very little hysteresis. It is noteworthy, however, that for PEDOT the differential absorbance, Fig. 6a, drops to zero at potentials $E > +500$ mV therefore charge injection at potentials more anodic than this value does not contribute to colour change. Such determinations are useful if polymers and polymer blends are to find application in practical devices. The differential absorbance curve for the copolymer, Fig. 6c, shows that the potential region where the absorbance is most sensitive to potential occurs in the range $-200 < E < 300$ mV. This again shows a composite response being the result of a combination of the two monomer units. However, the potential at this point is much closer to the parent PEDOT polymer than to poly(BT). In this case the differential absorbance trace provides more insight than the CV (charge flux) as this latter is essentially featureless. The cross-over in the differential absorbance-flux trace close to the cathodic vertex point is evidence of activity at this potential and again tends to indicate the presence of BT segments.

Conclusions

Here we have studied the co-electropolymerisation of 3-octylthiophene (OT), 2,2'-terthiophene (TT) and 2,2-bithiophene (BT) with 3,4-ethylenedioxythiophene (EDOT) focussing primarily on the latter system. We have prepared copolymer materials by electrocopolymerisation from binary mixtures of monomers in varying compositions and determined independently for each copolymer the spectroelectrochemical responses and the composition of the material using component fitting of X-ray photoelectron spectroscopy data. We have observed strong correlations between the composition of the copolymer material and the composition of the binary solution from which the polymer was grown. Using both potentiodynamic and potentiostatic techniques we have concluded that the redox potentials of the monomers were not the most important determinant of polymer composition. In addition, we have shown that the spectroelectrochemical properties of the copolymers indicate the presence of random copolymer material where the λ_{Max} values of the neutral, *undoped*, polymer scales with composition but also suggest that there may be small amounts of block copolymer or phase separated mixtures of the homopolymer components.

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