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The influence of the monomer and the ionic liquid on the electrochemical preparation of polythiophene

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Abstract

Thiophene, bithiophene and terthiophene have been electropolymerised using ionic liquids as the growth medium and the supporting electrolyte. Both imidazolium and pyrrolidinium-based ionic liquids were used to assess the influence of the nature of the ionic liquid on the morphology and electrochemical activity of the conducting polymers. The pyrrolidinium-based ionic liquid produced slightly smoother films for all the thiophene species studied. A number of the polymers displayed multiple redox peaks, the possible origins of which are discussed. Both the ionic liquid and the choice of monomer had a significant influence on the polymer produced.

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1. Introduction

There is a steadily expanding range of electrochemical devices being developed that utilise conducting polymers, such as polyaniline, polythiophene and polypyrrole, including chemical sensors, batteries, supercapacitors, conducting textiles and electromechanical actuators [1–3]. One of the most intensely researched of these areas of application is the use of conducting polymers in photovoltaic devices [4,5], driven by the need for sustainable, cheap and efficient energy sources as fossil fuel supply diminishes and greenhouse gas production increases. Polythiophene derivatives are of particular interest in photovoltaic applications as a result of their stability and ease of derivatisation, and devices under development range from simple solar cells and electroluminescent devices to light harvesting paints and fabrics [5–8]. This and the variety of other potential applications has precipitated extensive research into the development of polythiophenes, focusing both on the synthesis of new materials as well as improving their electrochemical and physical properties [3,9]. These properties are strongly influence by the nature of the dopant and electrolyte used in the preparation and cycling of the polymer [10–12]. Recent research has shown that use of an ionic liquid as the electrolyte, which then becomes the source/sink of dopants when the polymer is oxidized/reduced, in place of the traditional molecular solvent/salt system, can be extremely beneficial to the electromechanical efficiency and lifetime of conducting polymers [13–15].

Research into ionic liquids has increased exponentially in the last decade, particularly with regard to their use in synthesis [16–19]. These materials are composed entirely of cations and anions, the nature of which dictates their physical and chemical properties—thus, these properties are, to some extent, tunable. Use of ionic liquids is often initiated by safety and environmental considerations, where the negligible volatility and non-flammability of ionic liquids make them ideal replacements for more toxic molecular solvents and, importantly, overcomes the problem of solvent evaporation that exists with the long-term

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use of volatile solvents in electrochemical applications. Additionally, ionic liquids are recyclable, have a wide liquid range, good thermal stability and, of particular importance, exceptional electrical stability, with electrochemical windows typically over 4 V wide.

The electrochemical synthesis of conducting polymers in tetrachloroaluminate ionic liquids was first demonstrated in the 1980s for polypyrrole [20,21], polythiophene and polybithiophene [22], and polyfluorene [23], but the air and water instability of this type of ionic liquid, which hydrolyses to release HCl, is extremely problematic and the corrosive hydrolysis product can decompose the polymer.

Upon the discovery of air and water stable ionic liquids, studies concentrated on their use as supporting electrolytes in applications such as actuators [13,24,25], electrochromic devices [15,26], light-emitting electrochemical cells [27], and supercapacitors [28], and significant enhancements in the electrochemical stabilities of the polymers have been reported [29]. Recent work has suggested that when a conducting polymer is oxidized and reduced in an ionic liquid, the intercalation/de-intercalation of a cation rather than the anion can occur [13,25]. Thus, the nature of both ions may influence the growth of polymer, and the very high ion concentration of the ionic liquid may also be significant. It is interesting to note that many of the anions presently utilised in ionic liquids have been proven to be beneficial dopants for conducting polymer films, such as trifluoromethanesulfonate [30,31], hexafluorophosphate [32–35], and, particularly, bis(trifluoromethanesulfonyl)amide (TFSA) [36–41].

It is only recently that attention has turned to the potential benefits of using ionic liquids as the growth solvents for the electrochemical synthesis of conducting polymers. Shi et al. [42] presented a growth CV of polythiophene in 1-butyl-3-methylimidazolium hexafluorophosphate, and similarly Sekiguchi et al. reported the successful polymerisation of pyrrole, thiophene and aniline [43,44] in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate. The synthesis of poly(3-(4-fluorophenyl)thiophene) has been reported [45], and there have been a number of reports on the growth of poly(3,4-ethylenedioxythiophene) in ionic liquids [46–49]. Finally, Boxall et al. [50] examined the switching potentials of polypyrrole films grown from 1-butyl-3-methylimidazolium hexafluorophosphate, Zein El Abedin and co-workers [51] have electropolymerised benzene in an ionic liquid, and we have recently observed significantly altered film morphologies and improved electrochemical activities of polypyrrole grown in ionic liquids [52].

As polythiophenes are of particular interest for incorporation into photoelectrochemical (PEC) cells [4,5,8], and ionic liquids are typically incorporated into PEC cell electrolytes, we were interested in utilizing ionic liquids for the synthesis of polythiophene starting from a range of different thiophene monomers, and assessing the influence of monomer and ionic liquid on the chemical activity and morphology of the films produced. We were particularly interested in ascertaining how important the nature of the ionic liquid is in determining the properties of the polymer films; the range of ionic liquids available, both commercially and through simple laboratory synthesis, is constantly expanding, but the range that has been studied in relation to conducting polymers is presently extremely limited.

Here we report, for the first time, the electropolymerisation of bithiophene and terthiophene in air and water stable room temperature ionic liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (emiTFSA) and *N*,*N*-butylmethylpyrrolidinium bis(trifluoromethanesulfonyl) amide ($P_{1,4}$TFSA), and compare these to the electrochemical polymerisation of thiophene. Polymerisation of the thiophene monomers in a pyrrolidinium-based ionic liquid is reported for the first time and the morphological differences between the films grown from the two different ionic liquids are investigated.

2. Experimental

The ionic liquids were prepared using published procedures and were thoroughly dried before use [53,54]. Purity was confirmed using mass spectroscopy, NMR and electrochemical analysis. This is essential, as we have previously observed that the presence of even small amounts of impurities in the ionic liquids can result in differences in monomer oxidation potential, polymer growth rate and electrochemical response of the films. All CVs were recorded in air using a three electrode glass cell with a platinum disc working electrode with a surface area of 0.021 cm^2 (Bioanalytical Systems), a platinum mesh counter electrode and silver pseudo-reference electrode. The working electrode was polished before each experiment using BAS polishing alumina and rinsed with hexane. The platinum counter electrode was cleaned by heating to red heat in a hydrogen flame followed by rinsing in ethanol, and the silver reference electrode was cleaned with ethanol. The scan rate used was 50 mV s^{-1}, starting at the most negative potential. The films were grown over 30 potentiodynamic cycles and 15 cycles obtained for post-polymerisation CVs at room temperature using an Autolab Potentiostat Galvanostat running Autolab GPES software system.

SEM analysis was performed on films grown at constant potential onto ITO glass. The polythiophene films were grown from 0.2 M solutions over 200 s at 1.9 V. The poly(bithiophene) films were grown from 0.1 M solutions over 100 s at 1.4 V. Poly(terthiophene) films were grown from 0.01 M solutions over 600 s at 0.9 V from emiTFSA and 0.95 V in $P_{1,4}$TFSA. SEM analysis was performed using a Cambridge 250Mk3 Scanning Electron Microscope in the secondary electron mode.

Capacitance measurements were made on polythiophene films grown onto ITO glass from 0.2 M solutions of either emiTFSA or $P_{1,4}$TFSA during 500 s at 1.9 V with

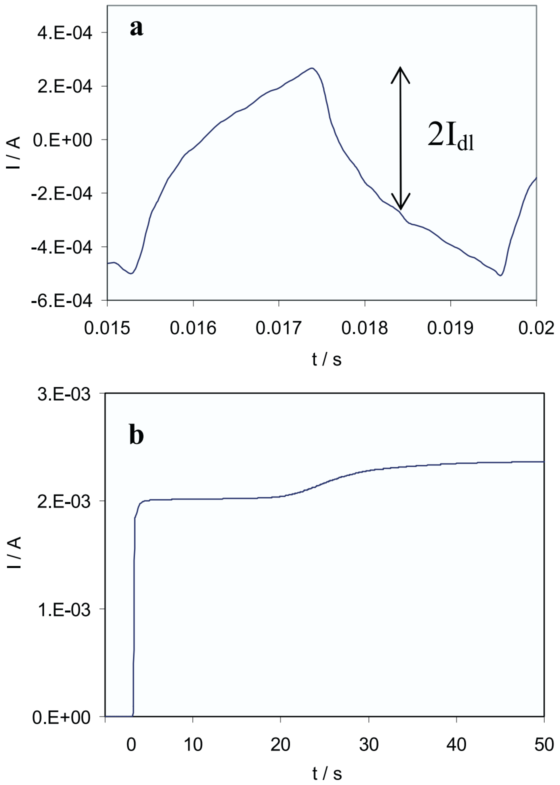

Fig. 1. Poly(thiophene) from $P_{1,4}$TFSA (a) Typical current-time curve for triangular potential sweep used for double-layer capacitance calculations, $E=0.1$ V versus Ag, potential sweep rate 5.8 V s^{-1}. (b) Current-time transient for the potentiostatic (1.9 V) electropolymerisation of thiophene (0.2 M) in $P_{1,4}$TFSA for $t \leq 50$ s for the film shown in Fig. 4.

chronocoulometric monitoring. After polymerization, the films were rinsed in acetonitrile (ACN). Capacitance measurements were performed at room temperature in 0.1 M tetrabutylammonium perchlorate in ACN with a platinum mesh counter electrode and silver pseudo reference electrode by superimposing a rapid triangular waveform (GoldStar FG-2002C generator) onto a base potential (0.1 V for both films) (EG&G Instruments, Princeton, Model 362 potentiostat) using the method of Tilak et al. [55]. The current response is a distorted 'square wave', which may be related to an equivalent circuit consisting of a resistance and capacitance in parallel; the resistance being faradaic and the capacitance due to the charging of the double layer. Thus, the current consists of two components, I_{dl} and I_f, the capacitance and resistance current, respectively. I_{dl} is related to the double-layer capacitance C_{dl} by

$$C_{dl} = \frac{I_{dl}}{vA}$$

where v is the potential sweep rate [V s^{-1}], A is the geometrical surface area [cm^2], C_{dl} is the double-layer capacitance [F cm^{-2}] and I_{dl} is the double-layer charging current [C s^{-1} cm^{-2}].

A typical current response used for double-layer capacitance calculations is shown in Fig. 1(a).

3. Results and discussion

The ionic liquids used in this investigation are 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide (emiTFSA) and *N*,*N*-butylmethylpyrrolidinium bis(trifluoromethanesulfonyl) amide ($P_{1,4}$TFSA) (Fig. 2). The TFSA anion is well known to impart good electrochemical stability and relatively low viscosity to the ionic liquids and thus is ideal for electrochemical applications [54]. Utilisation of pyrrolidinium-based ionic liquids for the synthesis of polythiophenes has not been reported previously. Whereas the imidazolium cation is planar and aromatic, this cation is larger, non-planar and aliphatic, and it was predicted that these differences would result in significant changes to the growth and physical properties of the polythiophene. For consistency and ease of comparison, the TFSA anion was used throughout. The solubility of the monomers in both ionic liquids was found to decrease with increasing monomer length. This suggested that the resulting polymers would not be soluble in either ionic liquid and this was indeed found to be the case.

3.1. The effect of the ionic liquid on thiophene monomer oxidation potentials

Comparison of the oxidation potentials (monomer V_{ox}) of the three monomers investigated, thiophene, bithiophene and terthiophene, in the two different ionic liquids, are given in Table 1. The oxidation potential of each of the substrates decreases as the monomer chain length increases, consistent with conventional electrolyte/solvent systems [56].

The oxidation potentials for all monomers are higher in $P_{1,4}$TFSA by approximately 0.1 V. This phenomena is

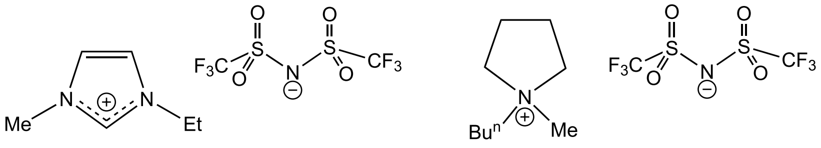

Fig. 2. The chemical structures of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide (emiTFSA) and *N*,*N*-butylmethylpyrrolidinium bis(trifluoromethanesulfonyl) amide ($P_{1,4}$TFSA).

Table 1
Electrochemical data for polythiophene, poly(bithiophene) and poly(terthiophene) in emiTFSA and $P_{1,4}$TFSA

	Thiophene		Bithiophene		Terthiophene	
	emiTFSA	$P_{1,4}$TFSA	emiTFSA	$P_{1,4}$TFSA	emiTFSA	$P_{1,4}$TFSA
Monomer V_{ox} [V]	1.95	2.01	1.22	1.36	0.89	0.96
Growth $I_{ox}\times10^4$ [A]	1.1	0.9	6.1	1.0	0.8	0.3
Polymer V_{ox} [V]	0.65	1.2	0.9	0.9	0.4, 0.8, 1.3	0.67, 0.93, 1.15
Polymer $I_{ox}\times10^4$ [A]	1.1	0.8	6.5	1.3	0.5	0.3
Polymer V_{red} [V]	0.35	0.35	0.4	0.5, 0.2	0.32, 0.75, 1.3	0.7
Polymer $I_{red}\times10^4$ [A]	−1.1	−0.8	−8.5	−2.2	−0.4	−0.3
Q_{red}/C cm^{-2}	0.062	0.068	0.683	0.159	0.044	0.027
Q_{ox}:Q_{red}	1.10: 1	1.04: 1	1.01: 1	1.03: 1	1.06: 1	1.10: 1

Onset of polymerization, monomer V_{ox}, was taken from the maximum of the oxidation peak of the first growth CV. The peak polymer growth current (Growth I_{ox}) was taken after 30 growth cycles and is used as an indication of the amount of polymer formed. Polymer oxidation and reduction potentials, currents and the corresponding ratio of charges were taken from the final post-polymerisation CVs. The oxidation and reduction potentials were taken from the top of the peak rather than the onset.

primarily attributed to the higher viscosity and lower conductivity of $P_{1,4}$TFSA compared to emiTFSA; 85 cP and 2.2 mS cm^{-1}, respectively, at 25 °C for $P_{1,4}$TFSA [53] compared to 34 cP and 8.8 mS cm^{-1} at 20 °C for emiTFSA [54], which is likely to relate to slower ion/molecule transport kinetics. It has also been reported that the nature of the electrolyte cation can influence the rate of conducting polymer film growth [57].

3.2. Electropolymerisation of thiophene

The electropolymerisation of thiophene monomers

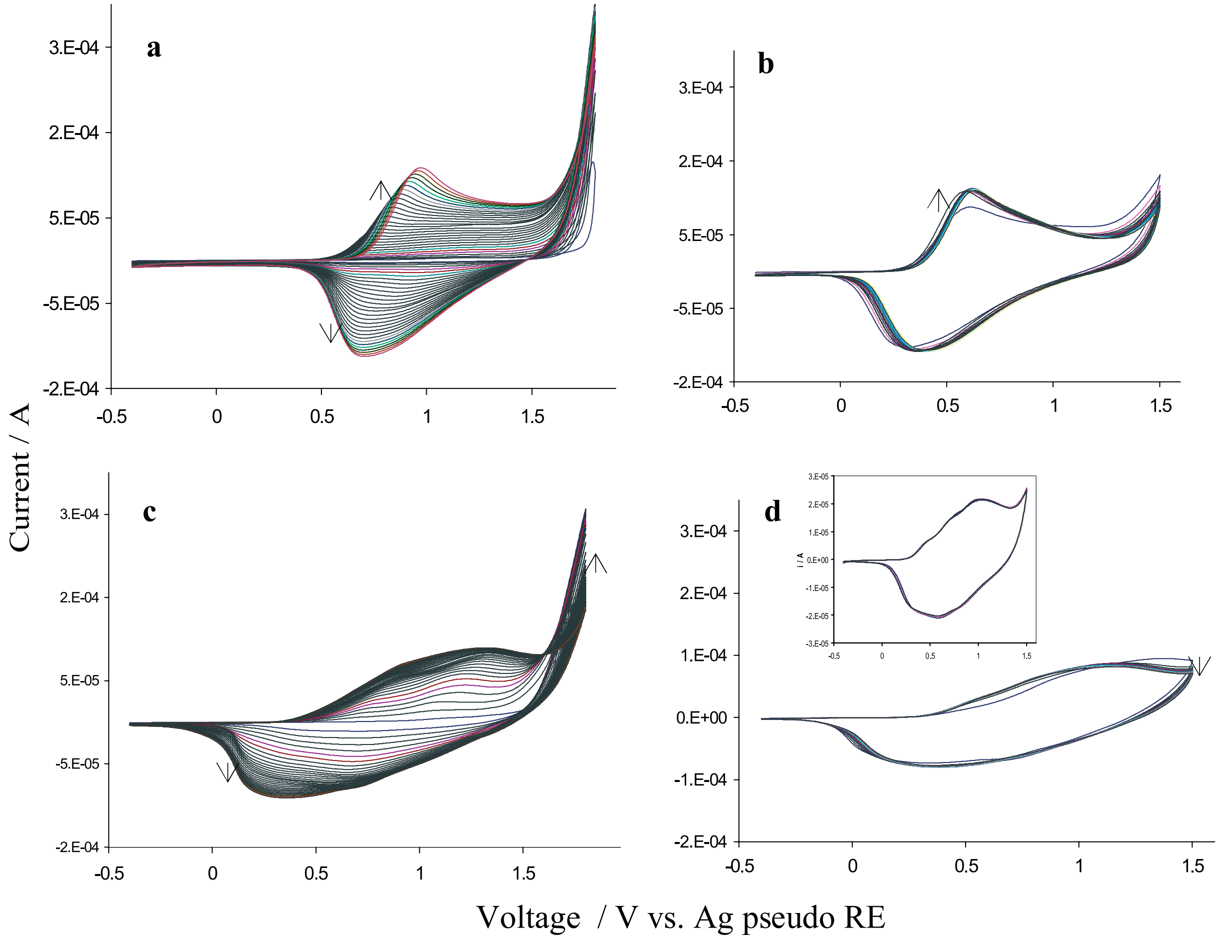

Fig. 3. Cyclic voltammograms of thiophene polymerisation (0.2 M, 50 mV s^{-1}). (a) Growth in emiTFSA, (b) post-growth in emiTFSA, (c) growth in $P_{1,4}$TFSA (0.2 M), (d) post-growth in $P_{1,4}$TFSA (inset 10 mV s^{-1}). Arrows indicate the peak development with successive scans.

can be performed potentiostatically, galvanostatically or potentiodynamically. Growth of the polymer film potentiodynamically (i.e. by cyclic voltammetry) is the most time-consuming technique and not generally employed for the synthesis of significant quantities of film, but it is an advantageous technique for detailed electrochemical analysis as the redox characteristics of the polymer can be monitored during film growth. Thus, a potentiodynamic technique was employed in this study to allow a more detailed comparison of the electropolymerization processes in the different ionic liquids. Comparison of the electrochemical data recorded for the different thiophene monomers in the two ionic liquids is given in Table 1. We have reported the peak polymer oxidation current (growth I_{ox}) from the final growth cycle to enable comparison of polymer film growth. We have also reported the total cathodic charge passed during the reduction of the polymer in the final post-polymerisation CV (Q_{red}). This latter value is often used as an indication of the amount of polymer grown, but this assumes that the electrochemical activities of the films are identical. The value of Q_{red} has been determined from the final post-polymerisation cycle, after the film has been repeatedly oxidized and reduced, so that any differences are not attributable to differences in the initial doping levels of the films. Thus, here we use a comparison of the growth I_{ox} and Q_{red} values as a means of assessing the relative electrochemical activities of the films while taking into account the relative amounts of polymer produced.

The CVs recorded during the electrochemical polymerization and cycling of thiophene in emiTFSA and $P_{1,4}$TFSA are shown in Fig. 3. Following electropolymerisation, the working electrode with the film attached was removed from the growth solution, washed with a little ionic liquid and placed in a monomer-free solution of the ionic liquid for post-polymerisation CV analysis. All CVs indicate a significant dependence on the nature of the ionic liquid.

Both growth CVs show the increase in current with successive cycles indicative of successful electroactive film growth. As the film thickens during polymerization, the voltametric wave associated with the oxidation of the polymer becomes slightly more anodic and reduction becomes more cathodic with successive scans, which is due to heterogeneous electron-transfer kinetics and a decrease in conductivity, counter-ion mobility and possibly conjugation length [58]. This is particularly marked for the film growth in $P_{1,4}$TFSA. The colours of the films produced were consistent with previous reports [1,3], blue when doped and red when undoped.

The peak oxidation currents during the final growth cycle (growth I_{ox}) in the different ionic liquids (Table 1) suggest the formation of slightly more polymer in the emiTFSA ionic liquid than in the $P_{1,4}$TFSA. The onset of polymer oxidation is a little higher in the $P_{1,4}$TFSA, which contributes to the somewhat lower growth rate—the same potential range and scan rate was used for both ionic liquids and thus in the $P_{1,4}$TFSA the time during which the potential is sufficient to effect polymerization is less than in the emiTFSA. Thus, the simplest explanation for the small difference in polythiophene growth rate is that the less viscous, more conductive emiTFSA allows faster diffusion of the monomer through the solution to the electrode surface.

The $P_{1,4}$TFSA film shows a larger total reduction charge, Q_{red}, than the film grown and cycled in emiTFSA. This may indicate better electrochemical activity of the $P_{1,4}$TFSA film, possibly as a result of slower, more ordered film growth.

The oxidation and reduction peaks of the film in the $P_{1,4}$TFSA are extremely broad. This may be due to the reorganization of the polymer chain that occurs with ion movement into/out of the film or result from a range of oxidation potentials due to defects in the polymer chain [59]. It is a common feature of the post-polymerisation CVs that the first CV is slightly different from the subsequent cycles. The origin of this is not well understood but it is evident that it takes the first electrochemical cycle for the film to fully re-establish its normal electrochemical activity following transfer from the growth solution into the fresh, monomer-free ionic liquid.

Post-polymerisation CVs subsequently run at a slower scan rate of 10 mV s^{-1} show the decrease in peak current and peak separation that is expected for a reversible electron transfer process [60]. Similarly, the ratio of oxidation to reduction charges passed during the post-polymerisation CVs is close to unity in both ionic liquids, again indicating good reversibility of the redox processes. At the slower scan rate in $P_{1,4}$TFSA, three oxidation peaks are visible (inset Fig. 3(d)). There is extensive and inconclusive discussion in the literature regarding the possible origin of the multiple redox peaks sometimes observed for polythiophene species. It has been proposed that these peaks are due to the transitions between the neutral, polaron, bipolaron and metallic states of the polymer [60], which may also be influenced by the rate of counterion transport [61], the reduction of different areas of the polymer film or of polymer chains of significantly different lengths [62,63], the effect of 'charge-trapping' [64], conformational changes accompanying radical cation formation [65], or consideration of the mechanical strain on the polymer that results from the forced intrusion of anions into the film [66]. We have not undertaken any detailed investigation into the origin of these peaks but it is interesting to note that the ionic liquid used for the electropolymerisation of the different thiophene monomers does appear to have a significant influence on the number of redox peaks observed.

The influence that the ionic liquid has on the morphology of the conducting polymer films was investigated using scanning electron microscopy (SEM) (Fig. 4). The polythiophene film grown in emiTFSA (Fig. 4(a) and (b))

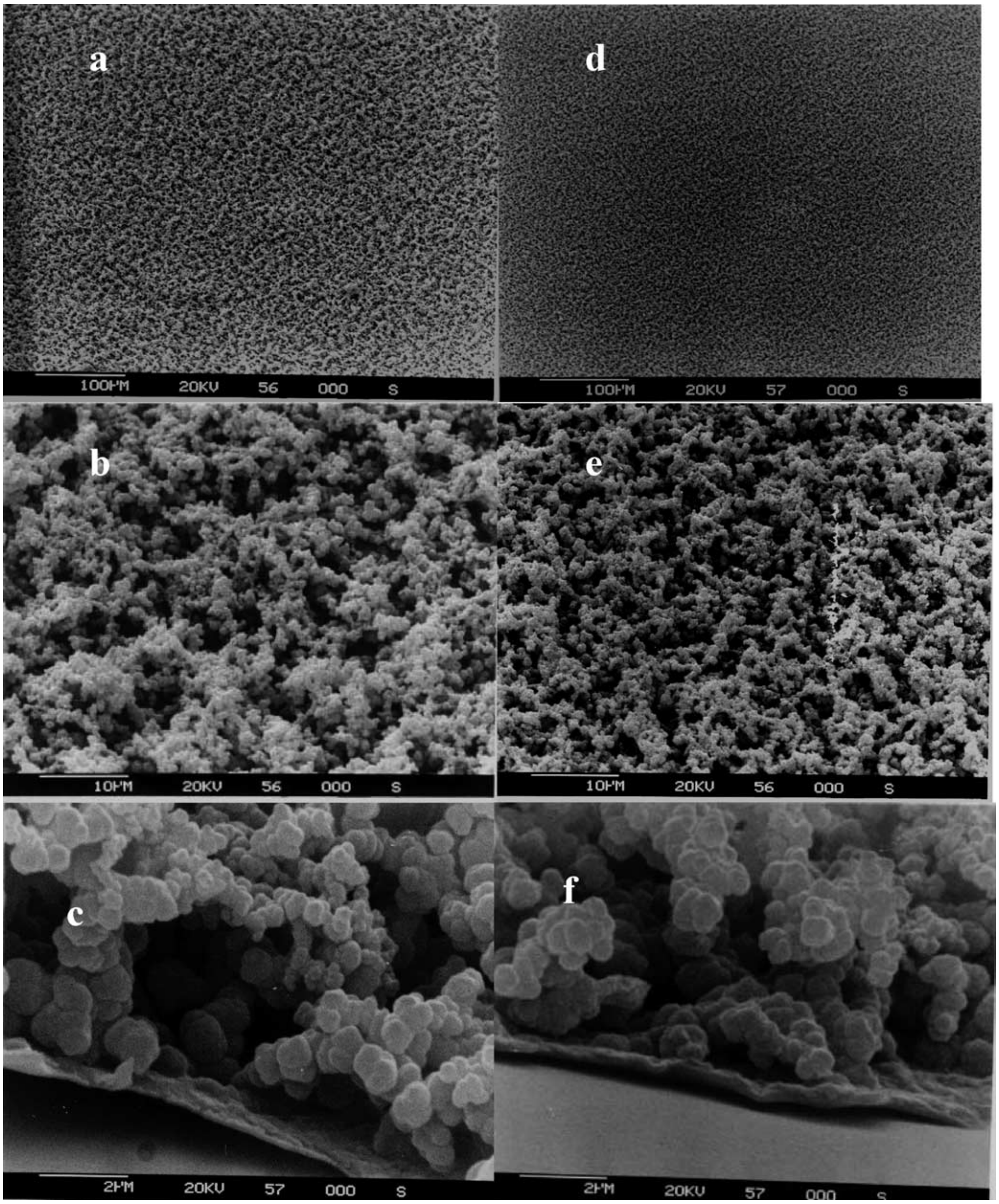

Fig. 4. SEMs of polythiophene films grown from emiTFSA (100 µm (a), 10 µm (b), and 2 µm edge-view (c)) and $P_{1,4}$TFSA (100 µm (d), 10 µm (e), and 2 µm edge-view (f)).

displays a 'packed grain' structure commonly observed in polythiophene films, and is very similar to that reported by Sekiguchi et al. [43], who noted that the grain size was smaller than that obtained when acetonitrile was used as the solvent. This grain morphology is typical of 3D nucleation and growth [67]. The film grown from $P_{1,4}$TFSA (Fig. 3(d) and (e)) also has this morphology but is slightly smoother, suggesting a more ordered film, which is consistent with slightly slower film growth [68].

The edge-on views (Fig. 4(c) and (f)) provide a striking exposition of the full growth characteristics of the films. It is clear from the dense film on the ITO electrode that a different nucleation and growth mechanism operates at the onset of film growth, as has been proposed by Schrebler et al. [69]. Therefore, initial film growth is consistent with an instantaneous 2D mechanism as a result of soluble oligomer growth at the ITO electrode and subsequent oligomer deposition onto the electrode at some critical chain length to form a compact film. This is then followed by progressive 3D nucleation and growth, which presumably results from the formation of a more branched polythiophene affording the grain morphology. This is not unique to growth of polythiophene in ionic liquids as similar behaviour is reported in other solvents and electrolytes [69–71]. An analysis of the early stages of the current-time transient for the polythiophene film grown in $P_{1,4}$TFSA (Fig. 1(b)) supports this mechanistic proposal, which is consistent with that reported by del Valle and co-workers for polythiophene

Table 2
Data used in the calculation of true surface areas for the polymer films grown in ionic liquids from thiophene

Polythiophene film	A (cm^2)	ν (V s^{-1})	I_{dl} (μA)[a]	C_{dl} (μF cm^{-2})
$P_{1,4}$TFSA	0.9	5.8 ± 0.5	267.5 ± 20.4	50.9 ± 5.5
emiTFSA	0.81	5.9 ± 0.5	328.5 ± 20.6	68.6 ± 7.5

ν is the potential sweep rate, A is the geometrical surface area, I_{dl} is the double-layer charging current and C_{dl} is the double-layer capacitance.

[a] I_{dl} values are reported as an average of twelve current response measurements (Fig. 1(a)).

grown in acetonitrile, who demonstrate that sequential instantaneous 2D and progressive 3D nucleation and growth processes take place [70].

However, although the SEMs show that films grown in the two different ionic liquids have similar growth behaviour, morphologies and thicknesses (~6 μm), the emiTFSA grown film appears to be somewhat less dense than the $P_{1,4}$TFSA film. In order to probe this further, we undertook capacitance measurements on the two films in order to determine the difference in electroactive surface area.

Double-layer capacitances were measured and the data presented in Table 2. The C_{dl} values are of the same order of magnitude as those found by Refaey et al. for up to 2 μm polythiophene films prepared from bithiophene in acetonitrile using lithium trifluoromethanesulphonate as electrolyte [72]. Comparison of $C_{dl\ (emiTFSA)}$ and $C_{dl\ (P1,4TFSA)}$ gave a 31% difference in the surface area of the two films, supporting the observation of the higher film density of the $P_{1,4}$TFSA-grown film. This may be attributed to the slower polymer growth in the more viscous $P_{1,4}$TFSA and likely increased polymer chain packing density.

3.3. Electropolymerisation of bithiophene

Despite the relative ease of polymerisation of thiophene in the ionic liquids, there are a number of disadvantages to using this monomer that prompted us to investigate the possible use of bithiophene and terthiophene in the ionic liquids. The potential required to oxidise thiophene is high

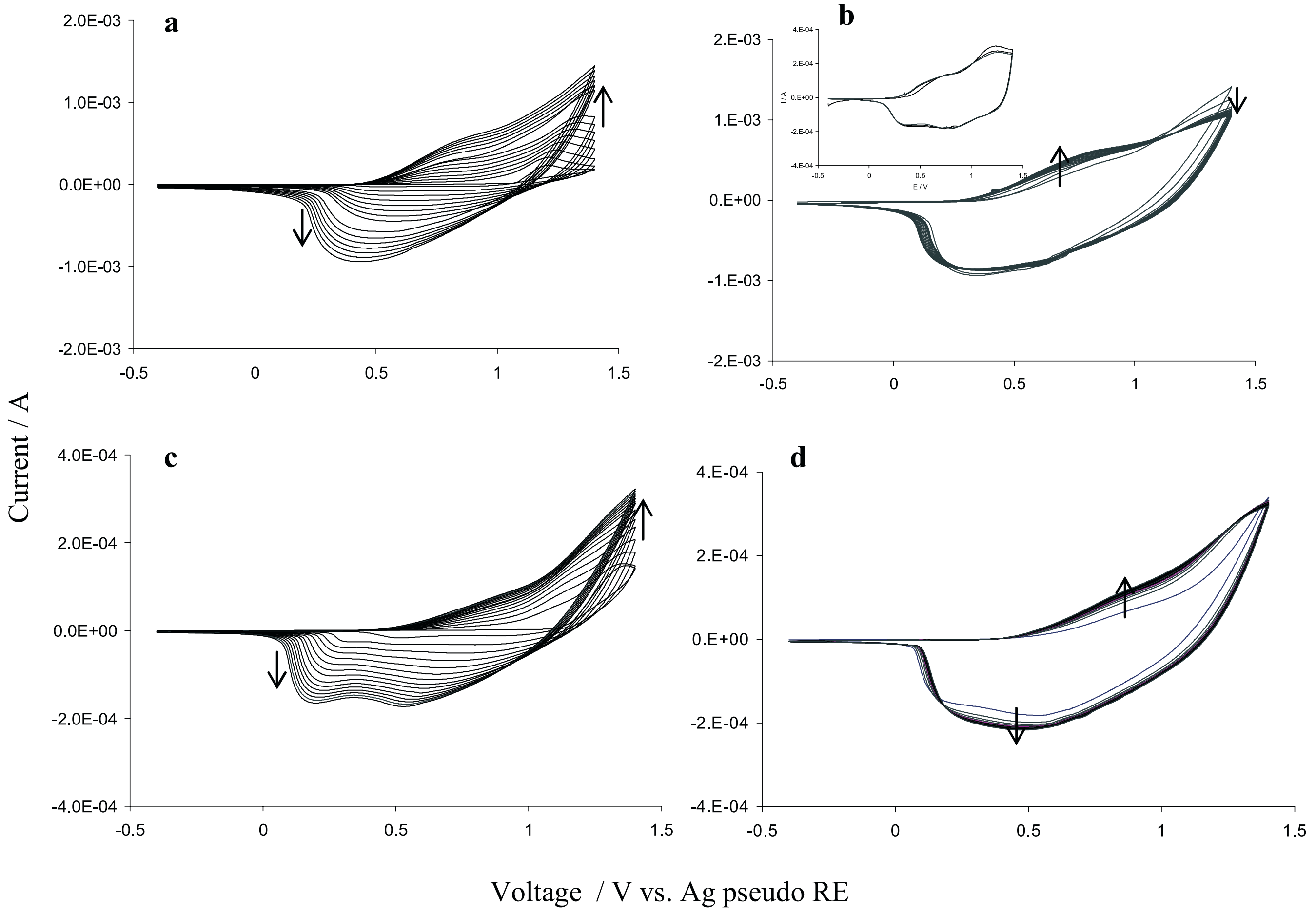

Fig. 5. Cyclic voltammograms of bithiophene polymerisation (0.1 M, 50 mV s^{-1}). (a) Growth in emiTFSA, (b) post-growth in emiTFSA (10 mV s^{-1} inset), (c) growth in $P_{1,4}$TFSA (0.1 M), (d) post-growth in $P_{1,4}$TFSA. Arrows indicate the peak development with successive scans.

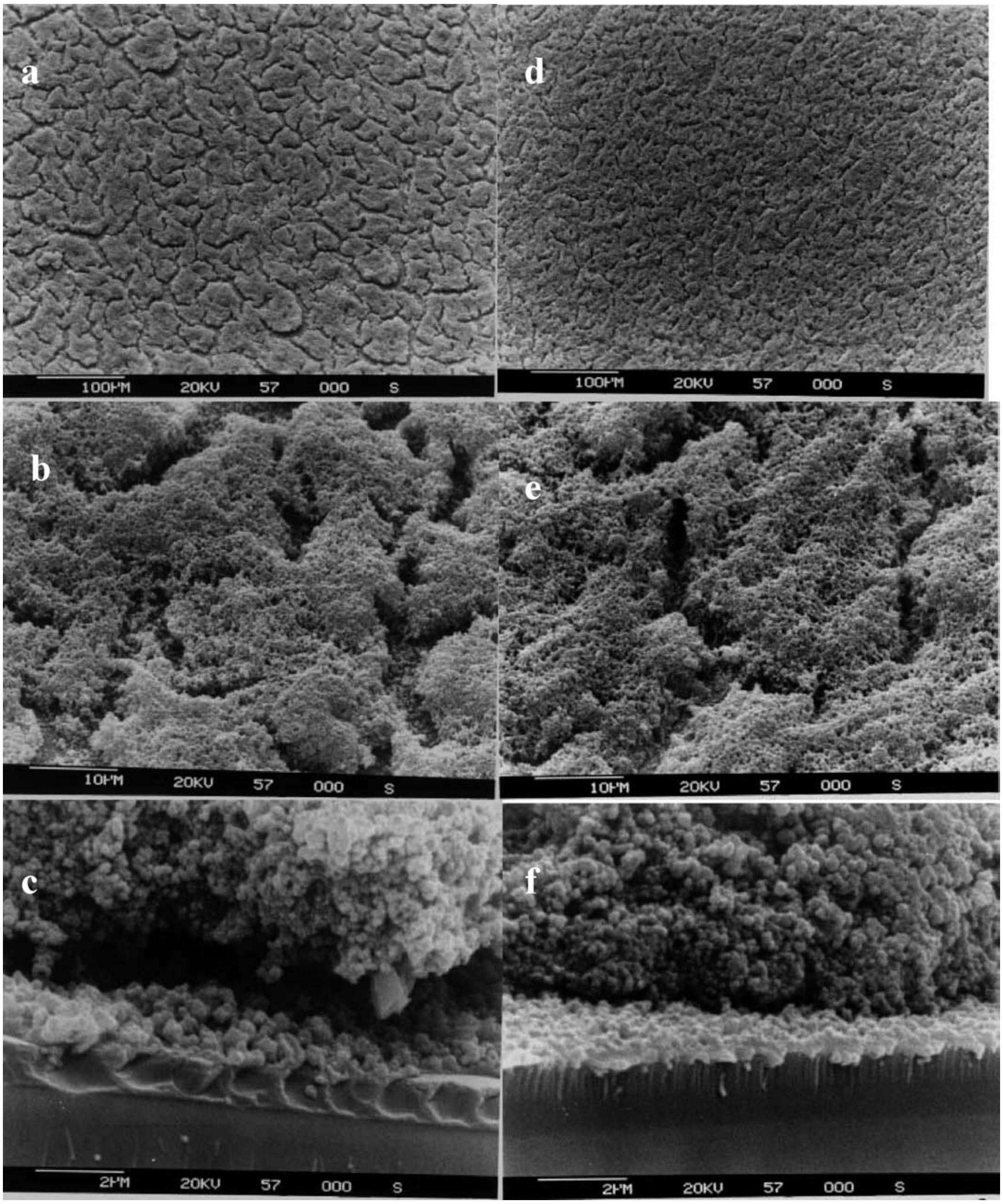

Fig. 6. SEMs of poly(bithiophene) films grown from emiTFSA (100 μm (a), 10 μm (b), and 2 μm edge-view (c)) and $P_{1,4}$TFSA (100 μm (d), 10 μm (e), and 2 μm edge-view (f)).

and can result in side-reactions and overoxidation of the polythiophene polymer film; i.e. polythiophene is not stable at the potentials required for its synthesis [9,73]. Use of dimers or oligomers of thiophene is one way of overcoming this ‘polythiophene paradox’ [74], and increasing the stereoregularity of the polymer by reducing the number of β,β or α,β mis-linkages. Ideally the conjugation length of the polymer would also be increased, although in reality the opposite may occur [9,56]. As previously observed (Section 3.1), the oxidation potentials of thiophene, bithiophene and terthiophene in the two ionic liquids decreases with increasing monomer chain length.

While the lower solubility of dimers and oligomers can limit their use in molecular solvents, bithiophene was found to be adequately soluble in both the emiTFSA and $P_{1,4}$TFSA ionic liquids. The CVs recorded during film growth in emiTFSA and $P_{1,4}$TFSA are shown in Fig. 5(a) and (c), respectively, and the post-polymerisation CVs in Fig. 5(b) and (d).

The growth CVs indicate both the successful polymerisation of bithiophene as well as a marked dependence of growth on the nature of the ionic liquid. Film growth appears to be more than four times faster in emiTFSA than in $P_{1,4}$TFSA, and the Q_{red} of the resultant poly(bithiophene) film grown from emiTFSA is proportionally larger (Table 1), reflecting the larger amount of film deposited. The

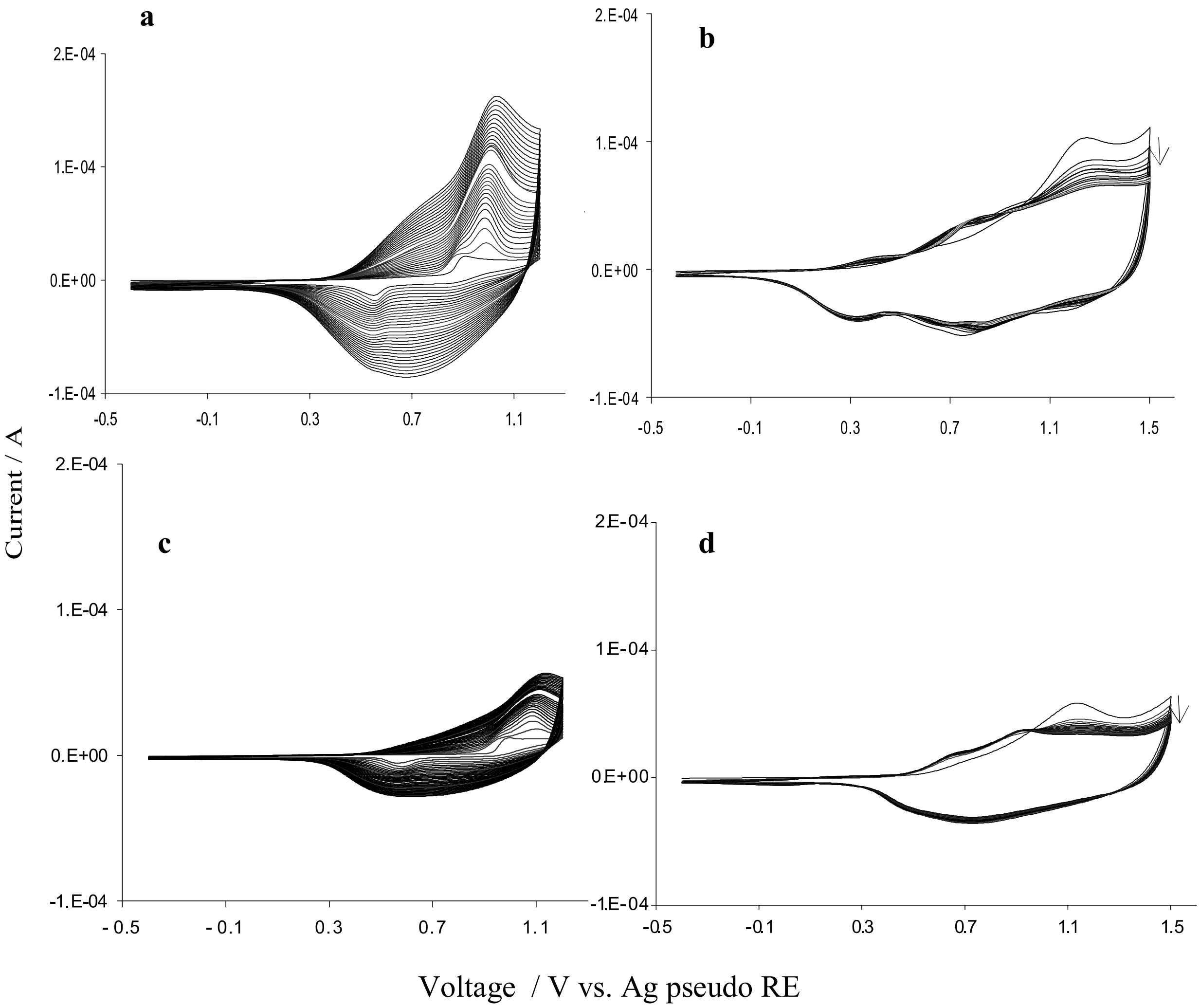

Fig. 7. Cyclic voltammograms of terthiophene polymerisation (0.01 M, 50 mV s^{-1}). (a) Growth in emiTFSA, (b) post-growth in emiTFSA, (c) growth in $P_{1,4}$TFSA, (d) post-growth in $P_{1,4}$TFSA.

second notable difference is that there are two distinct reduction peaks evident during growth and cycling of the film in $P_{1,4}$TFSA. Only one broad peak is visible during growth in emiTFSA, but in the post-polymerisation cycles this is broader, and at a slower scan rate (10 mV s^{-1}, inset Fig. 5(b)) multiple reduction peaks are apparent. As mentioned previously, there are many possible explanations for the multiple redox peaks sometimes observed for polythiophene species. However, there is also the possibility of cation incorporation rather than anion expulsion to achieve charge balance during the reduction of the film in ionic liquids [13,25], similar to that observed in molecular solvent/electrolyte systems when the anion is sufficiently large to make expulsion from the polymer difficult [59,75]. This event may be strongly influenced by the type of cation used, which may explain the differences in the CVs in the two ionic liquids, and these two alternative mechanisms of charge balance may, in this case, account for the two reduction peaks observed. We are currently investigating the intercalation of cations from different ionic liquids into conducting polymers using solid-state NMR techniques. Use of a slower scan rate for the post-polymerisation CVs also decreases the peak separation and currents produced, indicative of reversible redox processes [60,74]. The ratio of Q_{ox}:Q_{red} is close to unity for both films, again indicating good reversibility. The reduction of poly(bithiophene) occurs at a more positive potential than for polythiophene, which may reflect a decrease in the mean conjugation length of the polymer [56].

The morphology of the poly(bithiophene) films were analysed by SEM and are shown in Fig. 6. The morphology of the bithiophene films appears to be similar to that described by Roncali et al. [56] who reported a thin film on the surface of the electrode, covered by a thick brittle powdery deposit, from the galvanostatic polymerization of bithiophene in acetonitrile. The SEM images taken at 100 μm resolution suggest that the film grown in $P_{1,4}$TFSA is slightly smoother, but the difference is not as marked as for the polythiophene films. The nodular structures are smaller in the poly(bithiophene) films than in the

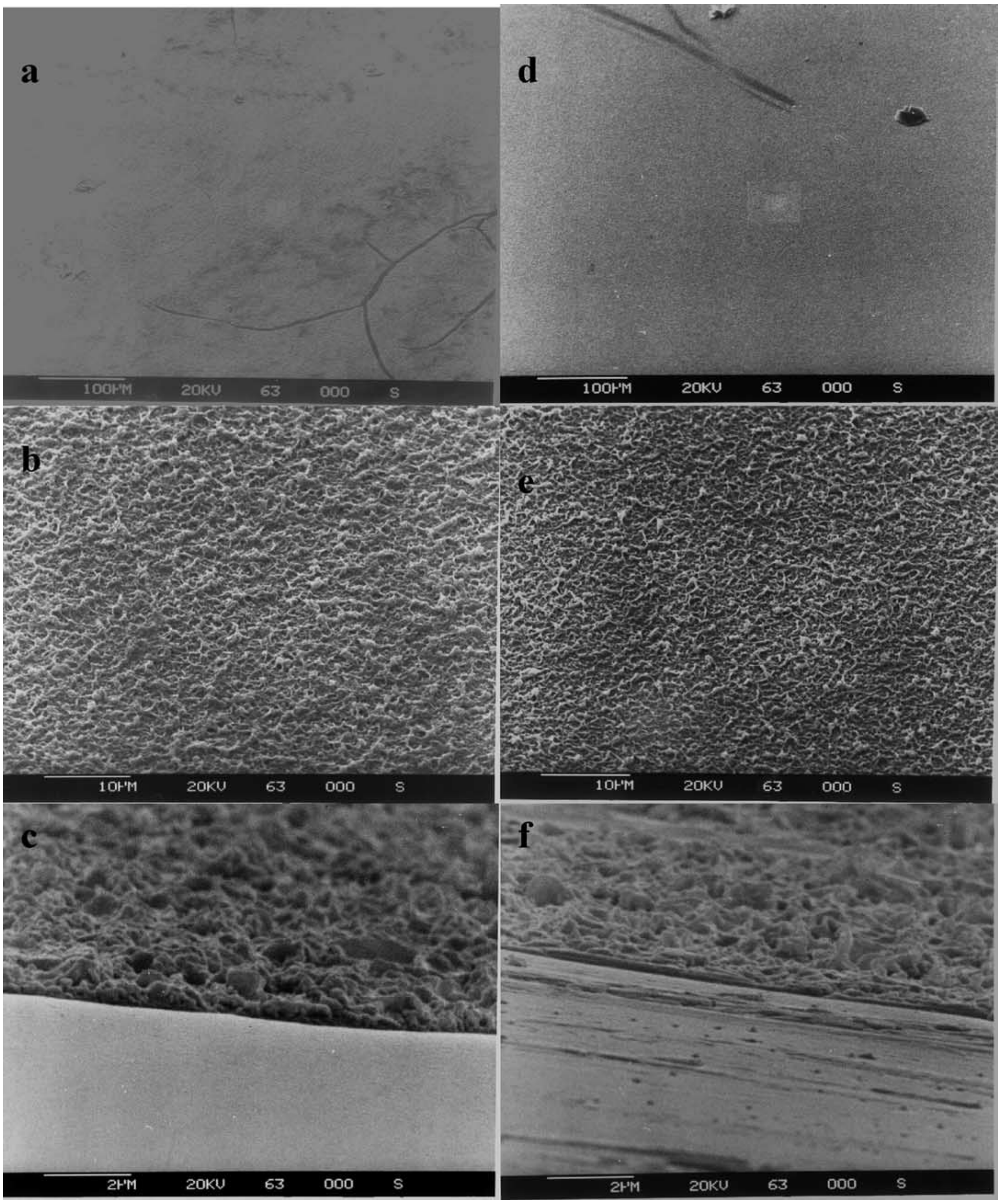

Fig. 8. SEMs of poly(terthiophene) films grown from emiTFSA (100 μm (a), 10 μm (b), and 2 μm edge-view (c)) and $P_{1,4}$TFSA (100 μm (d), 10 μm (e), and 2 μm edge-view (f)).

polythiophene (Fig. 4), which is consistent with the formation of shorter chain polymers [9], but this does not appear to result in inferior electrochemical activity. However, while the redox behaviour of the poly(bithiophene) films from the two different ionic liquids is markedly different, the films appear morphologically similar. This suggests that the dominant differences in the films produced from the two ionic liquids are on an atomic or sub-micron rather than macroscopic level.

The edge-on views (Fig. 6(c) and (f)) again shed some light on the polymer growth mechanism. In contrast to the polythiophene films, the initial growth layer of both poly(bithiophene) films is granular, suggestive of a 3D nucleation and growth mechanism, and this appears to be followed by a second granular 3D nucleation and growth phase [70], reflecting the influence of the starting monomer.

3.4. Electropolymerisation of terthiophene

Terthiophene was less soluble in the ionic liquids than thiophene or bithiophene, but concentrations of 0.01 M were attainable in both emiTFSA and $P_{1,4}$TFSA. The CVs recorded during film growth are shown in Fig. 7(a) and (c).

The influence of the nature of the ionic liquid on the growth rate of the polymer films is again evident, with significantly faster growth in the emiTFSA. The reduction charge, Q_{red}, of the film from emiTFSA is proportionally larger than for the film from $P_{1,4}$TFSA (Table 1).

Post-polymerisation CVs run in the potential range of −0.4 to 1.2 V at 50 mV s^{-1} (not shown) display only one oxidation peak and two reduction peaks but extending the potential range out to 1.5 V (Fig. 7) reveals three oxidation peaks and three reduction peaks, more clearly defined in the emiTFSA film (Fig. 7(b)) than the $P_{1,4}$TFSA film (Fig. 7(d)). Apart from the anomalous first cycle mentioned previously, there is only a small decrease in the currents produced upon repeated cycling in the ionic liquid and the ratio of charge passed during the oxidation and reduction events (Q_{ox}:Q_{red}) is again close to unity for both films. This indicates good reversibility.

Analysis of the films by SEM revealed an exceptionally smooth surface morphology (Fig. 8). They display a spongy morphology at the micron level similar to that described by Sezai Sarac and co-workers [76] for poly(terthiophene) grown in acetonitrile, but without the large amount of powdery deposit that was observed in the poly(bithiophene) films (Fig. 6). Again, the film from $P_{1,4}$TFSA appears to be slightly more compact. The edge views of the films reveal at 2 μm the conical morphology that del Valle et al. [70] report at 20 μm for polythiophene grown in acetonitrile, indicative of a predominant progressive 3D charge transfer nucleation and growth process. Thus, it is likely that polymer growth is charge transfer rather than diffusion controlled as a result of oxidised monomers precipitating onto the electrode before a significant oligomeric region can develop close to the electrode [70]. The smaller features in these films may reflect a decrease in the polymer chain length as is typically obtained in terthiophene polymerisations [9]. This may also contribute to the much thinner films than those obtained from thiophene or bithiophene, which is also consistent with the lower monomer concentration used and the much smaller polymer oxidation and reduction currents displayed (Table 1).

4. Conclusions

Thiophene, bithiophene and terthiophene have been successfully electropolymerised in imidazolium and pyrrolidinium-based TFSA ionic liquids. All of the films produced show good electrochemical activity and reversible redox chemistry. The films grown from the different thiophene monomers display significantly different morphologies, redox potentials and growth mechanisms, indicating the importance of monomer choice. The reduction potentials of the films increase as the monomer size increases, suggesting a decreased average conjugation length in the polymer. The choice of ionic liquid has proven to have a strong influence on redox chemistry of the polymers, affecting both oxidation and reduction potentials and also the total number of redox peaks displayed. This influence, however, is more significant for thiophene, decreasing for bithiophene and terthiophene. Use of the pyrrolidinium species consistently produces slightly smoother films, which, at least in the case of the polythiophene film, are denser and have a lower electroactive surface area than those from the imidazolium analogue.

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