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Electrochemical Polymerization of Pyrrole and Electrochemistry of Polypyrrole Films in Ambient Temperature Molten Salts

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Abstract: Oxidative electrochemical polymerization of pyrrole has been shown to occur in the 1:1 mol ratio $AlCl_3$:*N-1*-butylpyridinium chloride (BuPyCl) molten salt at 40 °C. Polypyrrole cannot be prepared in analogous 0.8:1 (basic) or 1.2:1 (acidic) mol ratio melts. The polypyrrole prepared in the molten salt is electrochemically similar to polypyrrole prepared in acetonitrile; both materials are conductors when oxidized, can be used as electrode materials for the electrochemistry of solution species (eg., ferrocene), and are oxidized and reduced at ca. -200 mV vs. SSCE in CH_3CN. The cyclic voltammetry of materials prepared in both CH_3CN and in the neutral melt has been investigated in the $AlCl_3$/BuPyCl molten salt system and in CH_3CN. The most significant differences appear in the kinetics of the redox chemistry. The most facile behavior was observed in a 0.8:1 melt with polypyrrole prepared in the 1:1 melt.

Electrodes coated with polymer films have been the subject of considerable interest in recent years.[1] An especially important class of polymers in this respect are electronically conducting polymers such as polypyrrole (PP).[2-16] PP coatings have been used as an organic electrode material,[7] to protect semiconductor electrodes from photocorrosion,[17] as an "ion gate" membrane,[18-20] and in electrocatalysis.[21] An important potential application of PP is as a charge-storing material in rechargeable batteries. However, in CH_3CN, in which PP is normally prepared and studied, long-term stability and charging rates are problems.

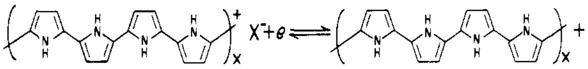
We have recently shown[22] that a number of redox polymers as films on electrodes can be rapidly electrochemically oxidized and reduced in the ambient temperature molten salt system $AlCl_3$/*N*-1-butylpyridinium chloride (BuPyCl). Since this solvent system is viewed as a promising material for batteries, we were interested in using it as a medium for PP electrochemistry.

Mixtures of $AlCl_3$ and BuPyCl in the mol ratios 0.75:1 through 2:1 are ionic liquids at temperatures above 27 °C.[23,24] The dominant equilibrium is[25]

$$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^- \qquad \log K = -16.9 \pm 2^{26}$$

and the 1:1 melt is almost pure $BuPyAlCl_4$ with a considerable amount of ion pairing.[27,28] Any $AlCl_3$ (a Lewis acid) added to the 1:1 melt complexes with $AlCl_4^-$ to form $AlCl_7^-$ and the melt is then acidic. When the $AlCl_3$/BuPyCl mole ratio is 2:1, the melt is almost pure $BuPyAl_2Cl_7$. Addition of BuPyCl to the 1:1 melt results in a corresponding increase in free chloride ion (a Lewis base) concentration and the melt becomes basic. Thus the Lewis basicity (pCl) of the melt can be varied between 0 and 19. In this work we use the neutral melt (mol ratio = 1:1), two basic melts (0.8:1 and 0.95:1) and an acidic melt (1.2:1).

The electrochemical oxidation of pyrrole in acetonitrile produces a polypyrrole film on the electrode.[2] When the electrode is transferred to a CH_3CN/electrolyte solution the polypyrrole film can be electrochemically driven between the black, highly conducting (100 Ω^{-1} cm^{-1}) oxidized form and the yellow, nonconducting neutral form. This redox reaction has been characterized as[8]



(1)

We have found, and report here, that pyrrole can be electrochemically polymerized in neutral melt (but not in 0.8:1 or 1.2:1 melts) to form conducting films on electrodes. We also describe the electrochemistry of PP films in pure melts and melts containing electroactive species.

Experimental Section

The preparation and use of the melts used here have been described elsewhere.[24] All experiments in melts were performed at 40 °C in a Vacuum Atmospheres Co. drybox under purified argon. Experiments in

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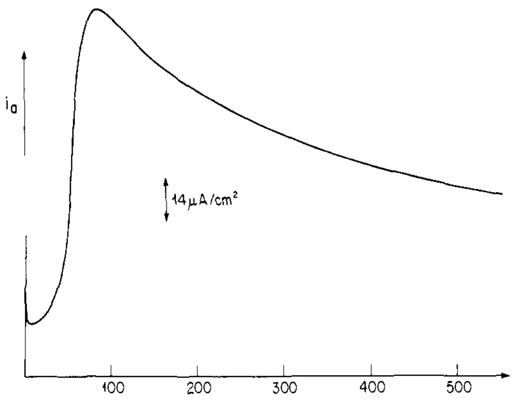

Figure 1. Current vs. time profile for pyrrole polymerization at +0.7 V (vs. Al/Al(III) in 2:1 $AlCl_3$:BuPyCl melt) onto a glassy carbon electrode from 0.17 M pyrrole in neutral $AlCl_3$/BuPyCl melt.

CH_3CN were performed at 25 ± 5 °C.

Electrochemical experiments were performed by using an IBM EC/225 Voltammetric analyzer and a Hewlett-Packard 7046A *X-Y* recorder. A NaCl saturated SCE (SSCE) was used for experiments in CH_3CN, and an Al wire immersed in 2:1 melt was used as the reference electrode in the melt. Using ferrocene as an internal reference the Al wire was found to be +110 mV relative to SSCE in CH_3CN (The formal potential of ferrocene is +270 mV vs. Al in the melt system and +380 mV vs. SSCE in CH_3CN). Working electrodes were either glassy carbon of geometric area 0.071 cm² sealed in Pyrex glass, Pt wire (area = 0.0079 cm²) shrouded in Teflon, or Pt foil.

Pyrrole was purified on a dry alumina column: acetonitrile (Burdick and Jackson, UV grade) and Et_4NClO_4 (Baker) were used as received.

Results and Discussion

Film Growth. In neutral melt pyrrole (0.17 M) oxidation begins at ca. +0.5 V and the peak current occurs at ca. +1.2 V at both glassy carbon and Pt electrodes. Polymer films were grown by setting the potential between +0.7 and +0.9 V (depending on the required growth rate), switching on the cell, allowing a measured quantity of charge to flow, and then switching off the cell. A typical current vs. time profile is shown in Figure 1. After the initial charging current the current falls and then rises to a peak as the film begins to grow. The current then gradually falls as the film gets thicker. The peak time varies from one experiment to the next and the rate of current decrease after the peak is variable but the overall shape of the *i* vs. *t* plot is the same for C and Pt electrodes and for different potentials between +0.7 and +0.9 V. On Pt, film growth can be verified by inspection: very thin films (<50 nm) are brown and transparent; thicker films are black. On C, film growth is verified by cyclic voltammetry in pure melt.

In 0.8:1 melt (basic) containing pyrrole (0.17 M), an oxidation wave begins at +0.5 V, but attempts to grow PP films from this melt failed. The oxidation current at +0.7 V decreased continually with time showing no peak. Failure to grow polymer from this melt is not surprising considering the high Cl^- concentration (ca. 0.9 M). In the 0.8:1 melt pyrrole oxidation and Cl^- oxidation occur at about the same potential. Bard and co-workers[13] have shown that oxidation of Cl^- at PP-coated electrodes destroys the polymer. Diaz et al.[2] reported that nucleophilic species inhibit PP formation, and we have found that LiCl prevents pyrrole polymerization in 99% aqueous CH_3CN.

In 1.2:1 melt (acidic) only a very small pyrrole (0.17 M) wave was observed at ca. +1.2 V. The peak current at C was only 1/40th of that observed in the neutral melt, and at Pt the current was down by a factor of over 250. In fact, at Pt the pyrrole oxidation was hardly discernable. No PP films could be grown from the 1.2:1 melt. Presumably pyrrole forms some adduct with $AlCl_3$ in the acid melt that cannot be oxidized.

In veiw of the above results, all films (except those grown in CH_3CN) were prepared in neutral melt (the criterion for a neutral $AlCl_3$/ByPyCl melt is that the electrochemical window at C is at least −1 to +2 V).[29] PP can be prepared in slightly basic melt (eg., 0.99:1), but such films were not used in this work.

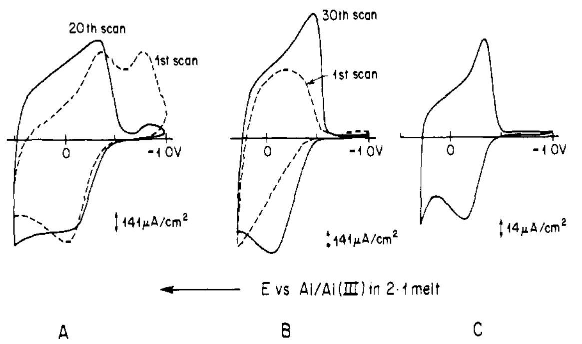

Figure 2. Cyclic voltammetry of a C/polypyrrole (0.2 μm) electrode in neutral (A) and basic (0.8:1; B and C) $AlCl_3$/BuPyCl melts. Scan speeds = 100 mV/s for A and B, 5 mV/s for C.

Cyclic Voltammetry of Polypyrrole in Pure Melts. Polypyrrole-coated electrodes, prepared in a neutral melt, were washed with neutral melt, and their cyclic voltammetry in a neutral melt and then in a 0.8:1 melt, neither containing dissolved pyrrole, was investigated. Figure 2A shows the first scan (at 100 mV/s) for a ca. 0.2 μm thick (see below) PP film on C in neutral melt. On subsequent scans the cathodic peak at −0.77 V quickly disappeared (after four scans) and was replaced by a small cathodic peak at −0.94 V, which shifted to −0.80 V during the next 20 scans. The cathodic peak at −0.36 V increased during the first eight scans and then decreased. The anodic peak at 0 V increasd during the first four scans and then it too decreased. After ca. 20 scans the voltammograms showed little change on subsequent scans, and the 20th scan is also shown in Figure 2A.

By comparison with the cyclic voltammetry of PP in CH_3CN[8] we interpret the cathodic wave at −0.36 V and the anodic wave at 0 V as reduction and oxidation, respectively, of the polymer. The large charging current anodic of this redox couple has been interpreted as indicating that the oxidized form of the polymer is a conductor.[13] We have not assigned the cathodic waves in the region −0.7 to −1 V, but we believe that they could be associated with the known proton-containing species impurity in the melt or with trace oxygen.[30]

When the above electrode was transfered to 0.8:1 melt and its potential scanned between −1 and +0.3 V at 100 mV/s, cathodic and anodic peaks developed at −0.44 and −0.05 V, respectively (Figure 2B). A small cathodic wave at −0.85 V was seen only on the first scan. After all changes in the voltammogram were complete the voltammogram at 5 mV/s shown in Figure 2C was obtained.

We interpret the above behavior and the gradual decrease in the polymer redox waves in neutral melt in terms of the solvent content of the polymer. Oxidation and reduction of the polymer require that anions enter and leave the film or that cations leave and enter the film, respectively. These ion movements and hence oxidation and reduction of the film are presumably facilitated by incorporation of the melt into the polymer (solvent swelling).[31,32] Since the polymer was prepared in a melt, we can assume that initially it contained some melt. The gradual loss of redox activity in the neutral melt could be due to loss of melt from the film (deswelling) producing a more compact polymer with restricted ion mobility. The return of activity in basic melt would then be due to chloride ions, which, being the smallest ion in the melts, would be expected to have the highest mobility within the polymer[33] (contrary to bulk melt[34]). This explains the great improvement in the oxidation wave in basic melt. Oxidation requires

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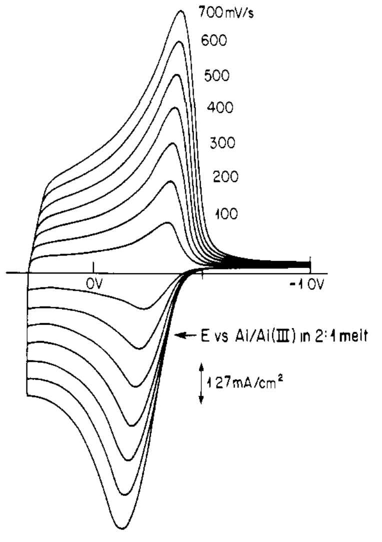

Figure 3. Cyclic voltammetry as a function of scan speed for a Pt/polypyrrole (0.2 μm) electrode in 0.8:1 $AlCl_3$:BuPyCl melt.

movement of anions into a neutral polymer (or cations out of the polymer) and thus is expected to exhibit the greatest kinetic limitations.[31] The break-in period observed in the basic melt suggests that more melt is being incorporated into the polymer.[22,31,32]

The cyclic voltammetry of PP on Pt electrodes is very similar to that on C electrodes but appears to be more facile. Figure 3 shows voltammograms of a ca. 0.2-μm film of PP on Pt in 0.8:1 melt after potential cycling in the neutral melt and then break-in in the basic melt. The linear dependence of i_{pa} on scan speed and the average i_{pa}/i_{pc} of 0.95 indicate that the redox reaction is facile and almost electrochemically reversible under these conditions. The small constant cathodic current between -0.5 and -1 V is presumably due to a proton-containing species that diffuses through the PP film[33] to the Pt electrode where it is reduced.[30]

Film Thickness and Analysis of the Cyclic Voltammetry of PP. Estimation of the amount of pyrrole in the PP films and the thickness of the films is not straightforward. For films prepared in CH_3CN, a number of approaches have been taken. Diaz et al.[5,8] measured an *n* value of 2.25 for the polymerization reaction and estimated the film thickness from the charge passed during film preparation and the measured density (1.5 g cm^{-3}) of the film. Their results were supported by measured thicknesses of thick films (ca. 20 μm) and by the observation that the area under the voltammogram of a PP-coated electrode corresponds to 9% (theoretically 11% if $n = 2.25$) of the charge used to prepare the film. Thus it appears that in CH_3CN the polymerization involves 2 electrons per pyrrole molecule and 0.25 electrons per pyrrole unit in the polymer to oxidize the film (as in eq 1).

However, the literature contains other thickness/charge relationships. To produce a 1 μm thick film on a 1-cm^2 electrode the following charges (mC) are suggested: 0.38,[7] 30,[9] 80–400,[10] 240,[4,13] and 400.[8] Presumably the yield of polymer depends upon factors that are not controlled (such as cell design), and so it does not seem advisable to estimate film thicknesses from the charge used to prepare the film.

Perhaps the best way to estimate the quantity of PP in a film is from the area under a slow-scan cyclic voltammogram of the film. However, there are two problems. First, the shape of the PP voltammogram (Figure 3), with a small charging current on one side and a large one on the other, makes it difficult to decide what area to measure. Second, the charge per pyrrole unit in the polymer is not certain. These two problems are intimately related since the voltammogram merely reflects charging of the polymer film (plus a small constant charging current for the underlying electrode). There seems to be the misconception in the literature that the anodic and cathodic waves at ca. -0.2 V correspond to the redox reaction of the polymer, and the large currents anodic of these waves are "background" and should be ignored. Any current in the voltammogram that cannot be attributed to the underlying electrode nor to dissolved redox species must be due to charging and hence formal oxidation or reduction of the polymer film.

One would not expect PP to exhibit a typical redox polymer surface wave[35-39] since presumably it consists of chains or conjugated segments of chains with a range of lengths and hence with different formal potentials.[6,16] (A conjugated segment is a section of a chain that is electronically isolated from the rest of the chain by a bend, twist, or defect.) It is not reasonable to assume that PP consists of noninteracting or only weakly interacting redox sites with one formal potential. The inverse relationship between chain length and anodic peak potential found for pyrrole oligomers ($E_{pa,N} = (1.35/N) - 0.15$)[6,16] gives some indication of the distribution of $E^{\circ\prime}$ values for the segments of polymer. There is some evidence[6] that these segments are predominantly short, possibly only 5–10 pyrrole units long.

The problem of multiple oxidations and reductions of these segments makes theoretical simulations of this model difficult, but intuitively it is compatible with the observed cyclic voltammetry. The peaks in the voltammogram correspond to oxidation and reduction of the longer segments whose formal potentials are bunched together by the $1/N$ relationship; the large "charging current" anodic of the peaks corresponds to primary redox reactions of the shorter segments and secondary and higher order redox reactions of the longer segments. Thus the average charge per pyrrole unit must be potential dependent at all potentials anodic of -0.5 V.

The alternate and previously assumed explanation for the "charging currents" anodic of the main redox waves is that the oxidized form of PP is similar to a porous metal and that these currents are double-layer charging currents of the PP. This model has been investigated by Bard and co-workers[13] and theoretically formulated by Feldberg.[15]

The relative valitity of these two models depends upon the microscopic structure of the PP when immersed in and swollen by the solvent If the swollen PP consists of chains of PP that are each in contact with solvent, then the former model is the more appropriate. However, if the PP chains are arranged in fibers of diameter large relative to the size of a pyrrole molecule, which are impervious to the solvent, then the porous metal model is more reasonable.[15]

At this stage we cannot say which model best describes PP in the molten salts used in this work. However, the break-in behavior observed in the basic melt, the sensitivity of the PP electrochemistry to chloride ion concentration, and the differences between PP prepared in a melt and PP prepared in CH_3CN (see below) suggest that in the melts PP is nonrigid and contains pores of molecular dimensions.[31-33] We feel that this behavior is more compatible with the solvated redox polymer model than with the porous metal model.

The average charge per pyrrole unit in oxidized PP has been estimated a number of times.[5,8,10-12] The films were removed from the preparation solution while at the preparation potential (ca. +0.8 V vs. SSCE), washed, dried, and analyzed. The analyses correspond to one anion per three or four pyrrole units depending upon the anion. To estimate the number of pyrrole units in a PP film, one should thus measure the charge under the voltammogram and divide by 3 or 4. However, the measured charge should include the "background" or "charging current" (except that due to the underlying electrode) up to the preparation potential (ca. +0.8 V) since this additional charge also must lead to incorporation of anions into the film. This last conclusion is *independent of the model* used to describe the charging of the polymer film.

Diaz et al.[8] indicate that they measured only the charge under the anodic peak and could not "account properly for the change

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Table I. Apparent Formal Potentials for PP in Neutral and Basic Melts

substrate	approx film thickness, nm	$E^{\circ\prime}{}_{\text{app}}$, mV[a] in 1:1 melt	in 0.80:1 melt
C	20	no anodic peak	−150
C	200	−160	−240
Pt	30	−240	−250
Pt	170	−200	−280
		av −200	−230

[a] Versus Al/Al(III) in 2:1 melt.

in background current". Accordingly the measured charge (9% of preparation charge) corresponds to less than the expected 11% of the charge used to prepare the film. However, it is clear from the published voltammogram that if the anodic current is extrapolated to the preparation potential (+0.81 V) the measured charge (ca. 16% of preparation charge) corresponds to significantly more than expected. Analysis of our results for PP in melts yields ca. 16% for $Q_{\text{cv}}/Q_{\text{prep}}$ (where Q_{cv} is the average of anodic and cathodic charges under the cyclic voltammogram). This indicates that either more than one pyrrole unit in four is oxidized at E_{prep} or that less than 2 electrons per molecule are required for the polymerization. The latter is certainly likely since there must be end units, which only need one electron. However, if this were the sole explanation, the average chain length would have to be three, which is unreasonable. Thus this analysis suggests that at +0.81 V in CH_3CN and at +0.70 V in the melt more than one pyrrole unit in four is oxidized.

The above discussion indicates that no reliable way of quantifying PP films has been found. For films prepared in molten $BuPyAlCl_4$ the problem is even greater because the films cannot be washed and dried with any confidence that the final product will be representative of the initially prepared film. From inspection of the voltammograms of Figures 2 and 3, it is clear that the charge under the voltammogram cannot accurately be measured as described above. It seems therefore that the best approach is to use the charge used to prepare the film as a relative measure of the quantity of film produced. As a rough conversion to film thickness, we assume that 240 mC/cm² yields a film 1 μm thick.[4,13] We do this merely to allow some comparison with the literature on PP in CH_3CN.

Formal Potential. The discussion in the preceeding section implies that PP does not have a unique $E^{\circ\prime}$. It is made up of many segments with different and multiple formal potentials.

In CH_3CN the "$E^{\circ\prime}$" of PP has been measured as the midpoint between E_{pa} and E_{pc} and found to be −220 mV vs. SSCE,[8] which translates to −330 mV vs. the melt refrence system (assuming ferrocene/ferrcenium has the same formal potential in both sovent systems). Using this mehtod for PP in melts, we obtain the apparent formal potentials ($E^{\circ\prime}{}_{\text{app}}$) shown in Table I. These show that in the melt the PP is oxidized and reduced at a potential slightly more positive than in CH_3CN and that there appears to be a slight dependence on melt basicity. The nature of the PP electrochemistry and the variable kinetics which influence the peak positions make $E^{\circ\prime}{}_{\text{app}}$ a poor parameter from which to draw more complete conclusions.

Cyclic Voltammetry in Basic Melt of PP Films Prepared in CH_3CN. PP films on C and Pt electrodes were prepared at +0.75 V vs. SSCE from 99% aqueous CH_3CN containing Et_4NClO_4 (0.1 M) and pyrrole (0.1 M). Figure 4A shows voltammograms in 0.8:1 melt and 0.1 M Et_4NClO_4/CH_3CN of a Pt electrode coated with PP using 14 mC/cm² of charge. The potential axes have been aligned so that ferrocene would have the same $E^{\circ\prime}$ in both solvents. The voltammogram in the melt was recorded first; then after washing the electrode well with CH_3CN the voltammogram in CH_3CN was recorded. The charge used to prepare this film is a third of that (42 mC/cm²) used to prepare the film of Figure 3. It can be seen that the PP film made in CH_3CN does not function well in the melt, even after cycling (over 30 scans between −1 and +0.3 V). Even in CH_3CN the voltammogram is not as sharp and symmetrical as that of the thicker film prepared and used in the melt (Figure 3). Thus PP films prepared and used in the melt exhibit more facile electrochemistry than those made in CH_3CN. This is especially noticeable and important for reduction of the film, which is a problem in CH_3CN.[8] The same conclusions result from experiments with PP on C electrodes.

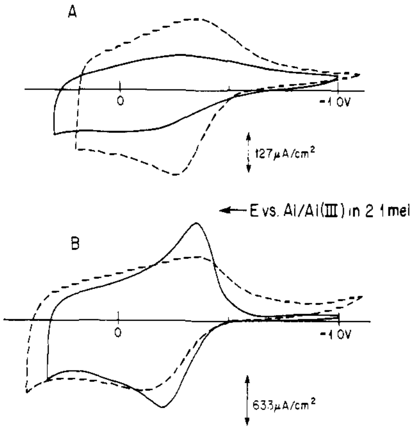

Figure 4. Cyclic voltammetry of Pt/polypyrrole electrodes in 0.8:1 $AlCl_3$:BuPyCl melt (—) and in 0.1 M Et_4NClO_4/CH_3CN (---). (A) 0.06-μm PP film prepared in CH_3CN, (B) 0.20-μm film prepared in neutral melt. Scan speed = 100 mV/s.

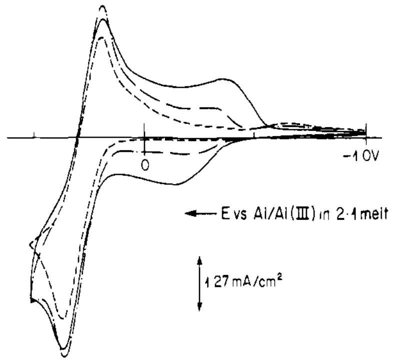

Figure 5. Cyclic voltammetry of 130 mM ferrocene in 0.8:1 $AlCl_3$:BuPyCl melt at naked Pt (---) and at Pt/polypyrrole (0.25 (-·-) and 1.0 μm (—)) electrodes. Scan speed = 100 mV/s.

Cyclic Voltammetry in CH_3CN of PP Films Prepared in Neutral Melt. Figure 4B shows cyclic voltammograms in 0.8:1 melt and in CH_3CN/Et_4NClO_4 (0.1 M) of a Pt/PP (0.2 μm) electrode which was prepared in a neutral melt. The potential axes have been aligned so that ferrocene would have the same $E^{\circ\prime}$ in both solvents. The film was washed with toluene between prepration and use in 0.8:1 melt; it was then washed with toluene, acetonitrile, and water and dried in air before use in CH_3CN.

The voltammogram of the PP film in the melt has more pronounced peaks than the voltammogram of the same film in CH_3CN. We take this as indicating that the redox chemistry of the film is more facile in the melt than in CH_3CN although the difference could possibly be due to thermodynamic factors. The differences in peak positions in Figure 4B is not regarded as significant given the variability of $E^{\circ\prime}{}_{\text{app}}$ (see Tables I and II).

Ferrocene Electrochemistry at PP-Coated Electrodes. PP in its oxidized form represents a new class of electrode materials.[7,8] Conducting organic materials are potentially useful electrode materials for organic electrochemistry. Another potential application of PP coatings is the modification of the electrochemical properties of inexpensive electrode materials such as nickel[40] so that such electrodes are useful for both analytical and synthetic electrochemistry. We have therefore investigated the electrochemistry of ferrocene at PP-coated electrodes in basic and acidic melts.

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Table II. Cyclic Voltammetric Data For Polypyrrole Films[a] (all potentials vs. Al/Al(III) in 2:1 melt)

substrate	Q_{prep}, mC/cm^2	approx film thickness, nm	melt or solvent	scan rate, mV/s	E_{pa}, mV	E_{pc}, mV	$E^{\circ\prime}_{app}$, mV	ΔE_p, mV	$\Delta i_p/Q_{prep}\nu$
Pt	25	100	0.95:1	40	−220	−350	−280	130	0.51
				80	−220	−330	−290	140	0.48
				200	−200	−330	−260	130	0.48
				400	−200	−350	−270	150	0.47
Pt	42	170	0.80:1	20	−240	−320	−280	80	0.66
				60	−220	−340	−280	120	0.61
				100	−230	−340	−290	110	0.60
				300	−190	−360	−280	170	0.56
				500	−170	−380	−280	210	0.53
				700	−130	−400	−270	270	0.51
C	48	200	0.80:1	5	−150	−330	−240	180	0.52
				20	−130	−380	−260	250	0.47
				60	−80	−420	−250	340	0.40
				100	−40	−450	−250	410	0.35
				300	+180	−590	−200	770	0.30
				500	+350	−690	−170	1040	0.27
Pt	239	1000	0.80:1	10	−90	−340	−220	250	0.44
C	7	31	0.80:1	100	−170	−330	−250	160	0.41
			CH_3CN[c]	100	−250	−350	−300	100	0.29
Pt	47	200	0.80:1	100	−230	−350	−290	120	0.45
			CH_3CN[c]	100	−140	−360	−250	220	0.32
Pt[b]	14	58	0.80:1	100	−10	−310	−160	300	0.15
			CH_3CN[c]	100	−260	−360	−310	100	0.31
Pt[b]	50	206	0.80:1	100	−90	−340	−210	250	0.06
			CH_3CN[c]	100	−260	−390	−330	130	0.10

[a] All potentials vs. Al/Al(III) in 2:1 melt. [b] PP prepared in CH_3CN. [c] Potentials adjusted to melt reference system by comparison with ferrocene.

Figure 5 shows the cyclic voltammetry of 130 mM ferrocene in 0.8:1 melt at naked Pt and at Pt/PP (0.25 and 1.0 μm) electrodes. There is a large "charging current" in the region of the $Fe^{III/II}$ couple at the PP-coated electrodes, but the ferrocene wave is virtually unaffected. To decide whether the results of Figure 5 clearly show that the ferrocene reactions occur predominantly at the film–solution interface requires a comparison between the film thickness (d), the thickness of the diffusion layer (δ), the diffusion coefficient of ferrocene in the bulk solution (D_s) and in the polymer film (D_p), and the partition coefficient of ferrocene from the solution to the film (P).[8] Were the film nonconducting, the ferrocene electrochemistry would only be insensitive to the presence of the polymer if[41]

$$D_pP/d >> D_s/\delta \qquad (2)$$

In the present case $D_s = 4.8 \times 10^{-7}$ cm^2 s^{-1},[42] $\delta \sim 10^{-3}$ cm (estimated from $(2D_st)^{1/2}$ with $t = 1$ s), and $d = 2.5 \times 10^{-5}$ cm for the thinner film of Figure 5. Therefore, D_pP would have to be greater than 1.2×10^{-8} cm^2 s^{-1} for the film to have no effect. This seems unreasonably high since there is no reason to expect that P is much greater than 1, and we have presented evidence that the mobility of the melt ions and hence presumably ferrocene is low in the polymer. Thus, we take the lack of a significant difference in the ferrocene wave at the three electrodes as indicating first that the PP films are conducting and have negligible resistance compared to the solution resistance and second that ferrocene electrochemistry takes place rapidly and reversibly at the PP/solvent interface. These results are consistent with the results obtianed by other workers using CH_3CN.[8,13]

In an acidic melt (1.2:1) the PP redox wave ($E^{\circ\prime} = -0.2$ V) cannot be seen because the cathodic limit of the melt is ca. −0.3 V. However, ferrocene ($E^{\circ\prime} = 0.27$ V) electrochemistry in a 1.2:1 melt at a Pt/PP (0.17 μm) electrode is almost identical with that at naked Pt for the first few scans between 0 and +1 V. On subsequent scans the wave broadens and the peak currents decrease.

These results show that PP may be useful electrode material in ambient temperature molten salts. When oxidized it has excellent conductivity and its charge transfer rate to ferrocene in solution is fast in both acidic and basic melts. The origin of the stability problem in the acidic melt has not been determined.

Conductivity. The cyclic voltammetry of PP prepared in the neutral melt suggests that the polymer is conducting when oxidized and nonconducting when reduced. These conclusions are supported by the fact that ferrocene electrochemistry ($E^{\circ\prime} = 0.27$ V) can be observed at the PP/melt interface but HCl electrochemistry ($E^{\circ\prime} \sim -0.5$ V in 0.8:1 melt) cannot. HCl (from H_2O) is an impurity in all the melts used in this work and exhibits a quasi-reversible redox wave at Pt electrodes. At thin film Pt/PP electrodes some reduction of HCl at Pt is observed as a membrane diffusion wave, but there is no evidence for reduction at the PP/melt interface. There are two possible explanations for the inability of the PP film to reduce HCl. Either the reduced form of the polymer is nonconducting or the kinetics of HCl reduction on PP are very slow.

In order to estimate the conductivity of the PP prepared in the neutral melt, a thick film of PP (ca. 20 μm) was grown on a Pt flag. The film was removed from the melt while still potentiostated at 0.85 V, washed with CH_3CN and water, and dried in air. During this process the film noticeably shrank and peeled from the electrode. The resistance of the film was measured between two clips separated by ca. 2 cm. A rough estimate of the conductivity was 1 Ω^{-1} cm^{-1}.

Summary of Cyclic Voltammetry of PP and Conclusions. Table II lists cyclic voltammetric data for a number of Pt/PP and C/PP electrodes in various melts and in CH_3CN. The term $\Delta i_p/Q_{prep}\nu$ (where Δi_p is the difference between the peak anodic and cathodic currents and Q_{prep} is the charge used to prepare the film) should be constant and any variation should reflect kinetic limitations.

A number of important conclusions can be drawn from Table II.

(a) For films thicker than 100 nm, the kinetics of oxidation and reduction influence the voltammetry at scan speeds as low as 20 mV/s. This appears as an increasing ΔE_p and a decreasing $\Delta i_p/Q_{prep}\nu$ with increasing scan speed or increasing film thickness.

(b) The 100-nm film on Pt appears to show no kinetic limitations up to 200 mV/s since ΔE_p is effectively constant. However, there is a residual ΔE_p, which is presumably thermodynamic in origin.[6] This thermodynamic ΔE_p must be lower in a 0.8:1 melt than in a 0.95:1 melt.

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(c) PP electrochemistry is much more facile on Pt than on glassy carbon. This conclusion is also supported by other data not included in Table II.

(d) The anodic wave is more susceptibile to kinetic limitations than is the cathodic wave. Thus, as the scan speed or the film thickness is increased and ΔE_p increases, E_{pa} changes more than E_{pc}, and so $E^{\circ\prime}_{app}$ moves to more anodic potentials.

(e) Films prepared in a neutral melt exhibit more facile electrochemistry in a 0.8:1 melt than in CH_3CN.

(f) Films prepared in CH_3CN show very poor electrochemistry in a 0.8:1 melt when compared to similar films prepared in the neutral melt. In CH_3CN they are similar to films prepared in the neutral melt.

(g) Peak positions are poorly reproducible. This is probably due to different degrees of swelling and hence variable kinetics and thermodynamics.

It should be noted that the differences between CH_3CN and the melt may be in part due to the different temperatures employed for experiments in the two solvents.

Conclusions

Polypyrrole films can be prepared in molten $BuPyAlCl_4$ and the electrochemistry of such films in 0.8:1 mol ratio $AlCl_3$:BuPyCl melt appears to be more facile than that of PP films prepared in CH_3CN. The films prepared in the melt are conducting when oxidized and are potentially useful electrode materials. Their charge storing properties are superior to those of previously described PP films.

Further work concerning the nature of the electrochemical reaction of PP and the conductivity of films prepared in molten salts is in progress.

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Registry No. $AlCl_3$, 7446-70-0; Pt, 7440-06-4; C, 7440-44-0; BuPyCl, 1124-64-7; ferrocene, 102-54-5; pyrrole, 109-97-7; polypyrrole, 30604-81-0.

Calculation of NMR Spin–Spin Coupling Constants Using the Extended Hückel Molecular Orbital Method

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Abstract: NMR spin–spin coupling constants are calculated by means of the extended Hückel molecular orbital theory (EHMO). The contributions to the coupling constant from orbital, spin–dipolar, and Fermi-contact interactions are included. By use of the Ruedenberg expansion the evaluation of multicenter integrals in the orbital and spin–dipolar contributions is circumvented. For the Fermi-contact contribution all one- and two-center integrals are retained. It is shown that a reparametrization of the EHMO parameters results in quantitative agreement between experimental and calculated coupling constants. An optimization of the EHMO parameters upon a data set containing $^1J_{CH}$ and $^3J_{HH}$ couplings shows systematic deviations of the idealized regression line both for the $^1J_{CH}$ and for the $^3J_{HH}$ subset. The best results are obtained with a separate optimization of EHMO parameters for the subsets $^1J_{CH}$ and $^3J_{HH}$. With the use of these parameter sets, a host of experimental trends due to substituent effects or to stereochemical effects are reproduced. The use of the optimized parameters for $^1J_{CH}$ may be extended to the calculation of $^1J_{CC}$. The $^3J_{HH}$ parameter set allows the prediction of the dependence of gauche and trans couplings upon the electronegativity and orientation of substituents in 1,2-disubstituted ethane-like fragments.

One of the prime reasons for the success of NMR spectroscopy as a structural tool has been the application of spin–spin coupling constants to stereochemistry. As the magnitude of the coupling constants depends upon variety of molecular parameters, such as torsion angles, bond angles, bond lengths, substitution, etc., much attention has been given to their theoretical calculation[1] in order to derive useful relationships between coupling constants and molecular structure.

Theoretical investigation of coupling constants in small molecules is frequently carried out by means of ab initio methods. However, in conformational analysis one is usually interested in large-size molecules containing many heavy atoms. Then ab initio methods are too expensive, forcing the use of semiempirical methods. A comparison of the ability to reproduce experimental couplings by the most common semiempirical approaches (CNDO, INDO, and extended Hückel theory) can be found in ref 2–5.

In the present paper we investigate the calculation of coupling constants $^3J_{HH}$ and $^1J_{CH}$ with two objectives in mind: (i) the calculated coupling constants must be reliable, as demonstrated by a quantitative agreement with experimental data; (ii) the method used should be as economical as possible.

The first objective is necessary for a detailed theoretical investigation of the dependence of coupling constants upon stereochemical and/or substituent effects. The second objective makes it possible to study these effects in relatively large molecules. Moreover, with a fast and "simple" computational method, calculations can be performed on small-size computers.[6]

Attention is focused solely on the calculation of $^3J_{HH}$ and $^1J_{CH}$ because these types of couplings are important from the view of stereochemistry and conformational analysis. Geminal couplings of the type $^2J_{HH}$ and $^2J_{CH}$ were not included in the data set. Pilot calculations showed that, e.g., $^2J_{HH}$ depends markedly upon the H–C–H bond angle and upon the C–H bond distances, and in general these parameters are not known experimentally to a high degree of precision.

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