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Frequency/temperature response of conductivity in poly(*p*-styrene sulphonate) salts of polypyrrole

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Electrical conductivities of a series of polypyrrole (PPY) films with poly(*p*-styrene sulphonate) (PSS) counterions, prepared electrochemically from various water/1,4-dioxane solutions, were investigated at several frequencies ranging from 0 Hz to 10.3 GHz within the temperature range 10–300 K. The frequency response of conductivity was found to increase systematically with increasing amounts of 1,4-dioxane in the polymerization solutions. At 10.3 GHz, the temperature dependencies of conductivity for samples from solutions ranging from 0 to 40% 1,4-dioxane became similar. This behaviour is related to changes in the spatial distribution of counterion sites induced by addition of 1,4-dioxane to the polymerization solutions. Calculations from the a.c. conductivity results, according to the hopping model of Mott, require decay lengths of localized states less than 10 Å to provide reasonable densities of localized states. We conclude on this basis that the entities responsible for charge transport in these systems are likely to be unpaired.

(Keywords: conducting polymers; polypyrrole salts; poly(*p*-styrene sulphonate); polycounterion conformation; a.c. conductivity; hopping charge transport)

INTRODUCTION

In an earlier publication[1] the idea was introduced that morphological control of conductivity behaviour in polypyrrole (PPY) could be qualitatively demonstrated using PPY salts of polymeric counterions (poly(*p*-styrene sulphonate) (PSS)). D.c. conductivities of PPY films with PSS counterions, prepared electrochemically from water/1,4-dioxane solutions, were investigated in the temperature range 10–450 K. Although the chemical compositions of the films from polymerization solutions with different concentrations of 1,4-dioxane were essentially the same, it was found that their electrical properties varied systematically; increasing the proportion of 1,4-dioxane in the solutions resulted in a continuous decrease in room temperature conductivity from *ca.* $5\,\mathrm{S\,cm^{-1}}$ (0 vol% dioxane) to *ca.* $3\times10^{-2}\,\mathrm{S\,cm^{-1}}$ (40%). There was also a strong concurrent increase in the temperature dependence of the conductivity. That these effects were not due to any direct (e.g. chemical) influence of having 1,4-dioxane present during polymerization was shown by the fact that for a non-polymeric counterion (ClO_4^-), films grown from both 0 and 20% 1,4-dioxane solutions exhibited essentially the same conductivity behaviour as well as chemical analyses. It was also noted that for such PPY (PSS) systems, there is a pronounced deviation from $\log\sigma\propto T^{-1/4}$ behaviour predicted by the 3-dimensional variable range hopping model of Mott[2] which has been often used to describe d.c. conductivity behaviour in polypyrrole salts of small anions. These changes in conductivity behaviour for such PPY (PSS) systems were explained by assuming that collapsing of the polycounterions in the polymerization solutions by addition of 1,4-dioxane leads to changes in the spatial distribution of anion sites in the solid films, resulting in relatively highly conducting microregions of varying size, shape and connectivity. The problem of bulk d.c. conductivity was then qualitatively treated as a percolation problem according to the model of hopping conductivity in granular disordered systems proposed by Sheng and Klafter[3]. Fits of the experimental data to curves predicted by this model were not attempted because differences in the morphology of these films could not be quantitatively defined due to a broad distribution of counterion molecular weights. Furthermore, the possibility that homogeneous changes in the effective degree of oxidation of these PPY salts could affect the density of localized states and thus modify their electronic properties, could not be rigorously excluded. However, homogeneous densities of states did not appear consistent with the strong deviations of the temperature dependence of conductivity observed for these PPY salts from $T^{-1/4}$ behaviour.

A.c. conductivity measurements at high enough frequencies should afford an insight into the local electronic properties of well conducting microregions, even when separated by barriers. PPY salts of small counterions have shown little or no substantial frequency dependence of conductivity[4], likely reflecting a lack of morphological barriers. If the differences in conductivity behaviour between different PPY (PSS) samples are solely morphological in origin, an increase in the frequency response of conductivity should be observed with increasing morphological barriers. At sufficiently high frequencies, the temperature dependencies of

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conductivity for the different samples should become similar. If the changes in conductivity behaviour were due to homogeneous changes in the density of states, it would be expected that some differences in the temperature dependencies of the conductivity would be preserved at high frequencies. In this paper we present the results of variable temperature a.c. conductivity studies for PPY (PSS) salts in the frequency range 0–10.3 GHz, which are in qualitative agreement with our hypothesis that d.c. conductivity behaviour in such systems is strongly influenced by their molecular superstructure. The implications of these investigations concerning the nature of charge carriers and the mechanism of charge transport in these systems are discussed.

EXPERIMENTAL

Polypyrrole salt films used in this study were prepared under nitrogen as previously described[1], by potentiostatic (+0.80 V *versus* a standard calomel electrode) electropolymerization at 20°C on a platinum electrode, from aqueous solutions of pyrrole (0.10 M) and poly(sodium *p*-styrene sulphonate) (10 g/L, Aldrich Chemical Co., molecular weight *ca.* 30 000 by viscometry[1]) containing various proportions of 1,4-dioxane. Films of *ca.* 20 micron thickness were used.

D.c. conductivity measurements in the temperature range 10–300 K were performed using a linear four probe technique and apparatus as described in ref. 1.

Hall and magnetoresistance effects were not observed in these materials at room or liquid nitrogen temperatures in a magnetic field of *ca.* 1 Tesla. According to the arguments of Mott and Davis[5], a weak Hall effect is to be expected in disordered materials where hopping-type conductivity is observed: non-homogenities in the material can further diminish the effect.

Measurements of a.c. conductivity were carried out at 1 KHz and 1 MHz on samples with 2 and 4 probe geometries using a Hewlett Packard 4192A Impedence Analyzer. Both probe geometries gave consistent conductivity values within experimental error. Sample temperature in the range 80–300 K was controlled using a standard gas (N_2) flow cryostat with temperature regulating unit.

Microwave measurements of the complex dielectric constant $\varepsilon = \varepsilon' - \varepsilon''$, were performed using a cavity perturbation technique[6]. Rectangular (*ca.* 2.0 × 0.5 × 0.02 mm) sample strips were placed at the centre of a rectangular reflection TE_{111} cavity at 10.3 GHz. For measurements at 4.6 GHz a coaxial line cavity was used.

Temperature was controlled in the case of 4.6 GHz measurements using a nitrogen exchange gas cryostat and at 10.3 GHz using a helium evaporation cryostat.

RESULTS AND DISCUSSION

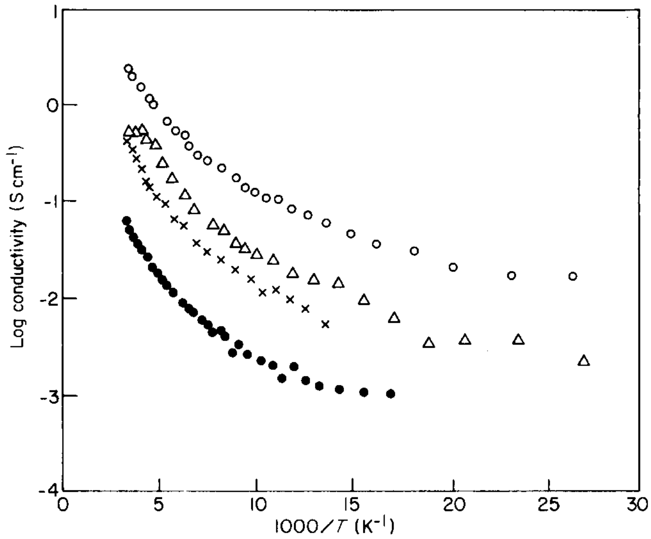

Figure 1 Temperature dependencies of conductivity at 10.3 GHz for PPY (PSS) samples obtained from aqueous electropolymerization solutions containing (○) 0%, (△) 20%, (+) 30% and (●) 40% 1,4-dioxane under otherwise identical polymerization conditions

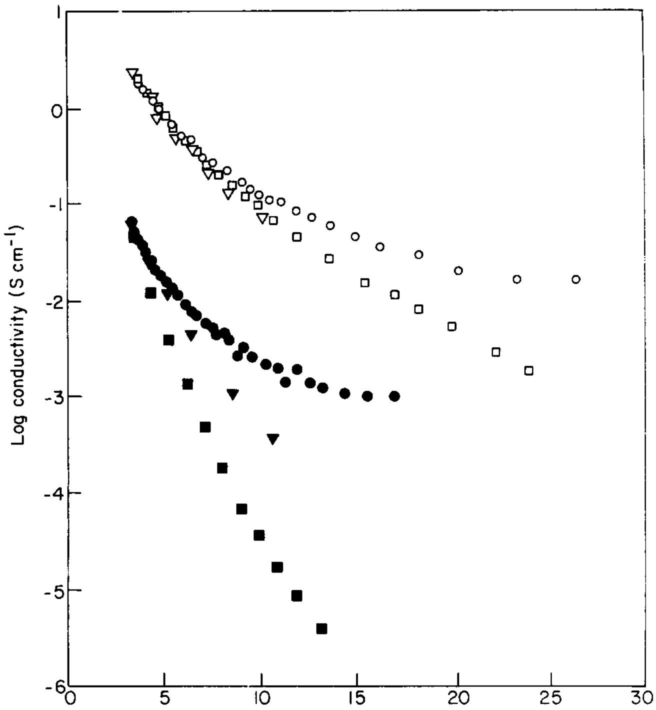

Figure 2 Temperature dependencies of conductivity: d.c. (squares), at 1 MHz (triangles) and 10.3 GHz (circles) for PPY (PSS) samples obtained from aqueous electropolymerization solutions containing 0% (open symbols) and 40% (filled symbols) 1,4-dioxane under otherwise identical polymerization conditions

Figure 1 shows the temperature dependencies of microwave conductivity at 10.3 GHz for the PPY (PSS) samples investigated. The most striking feature of these results is that, although the absolute values of conductivity differ considerably for the different materials, the temperature dependencies at these frequencies are quite similar. This is in strong contrast to the d.c. conductivity behaviour of these samples, where the materials with lower conductivity exhibit increasingly stronger temperature dependencies of conductivity. This contrast is clearly illustrated in *Figure 2* which compares the temperature dependencies of d.c. conductivity and a.c. conductivity at 1 MHz and 10.3 GHz, for the samples made with minimal (0%) and maximal (40%) amounts of 1,4-dioxane in the polymerization solutions. For the sample obtained from solutions without 1,4-dioxane (extended polycounterion conformation), the differences in temperature dependence between d.c. and microwave conductivity appear only in the low temperature range. For the sample obtained from 40% 1,4-dioxane in the polymerization solution (collapsed polycounterion structure), the temperature dependence of d.c. conductivity is much stronger over the entire temperature range and there is a pronounced difference between d.c. and a.c. conductivity already at 1 MHz. The same measurements for the PPY (PSS) samples made from solutions of 1,4-dioxane content between 0 and 40%, not shown in *Figure 2* for clarity, follow the illustrated trends continuously.

The total conductivity $\sigma(\omega,T)$ measured for a sample can be considered to be the sum of the frequency independent d.c. conductivity ($\sigma_{\text{d.c.}}$) and the frequency dependent a.c. conductivity ($\sigma_{\text{a.c.}}$) as follows:

$$\sigma(\omega,T)=\sigma_{\text{d.c.}}(T)+\sigma_{\text{a.c.}}(\omega,T) \qquad (1)$$

For charge transport among disorder induced localized states, $\sigma_{\text{a.c.}}$ should vary approximately as a function of ω^s for $\omega \ll \nu_{\text{ph}}$ (the phonon frequency) with $s<1$.[7]

The low temperature regions of the data presented in *Figure 1* were used for analysis so that it can be assumed that the frequency dependent a.c. conductivity overcomes the contribution of the d.c. conductivity. Equation (1) can then be written as $\sigma(\omega,T)\simeq\sigma_{\text{a.c.}}(\omega,T)$.

The possibility that charge transport in the investigated materials occurs via localized states at the edges of the valence band would appear to be precluded because in such a case, the a.c. as well as the d.c. conductivities would exhibit simply activated character, which is not observed, especially at low temperatures. The other possibility, hopping transport by charge carriers with energies close to the Fermi level, can be considered using the analysis of Austin and Mott[7] where:

$$\sigma_{\text{a.c.}}(\omega,T)=\tfrac{1}{3}\pi e^2kT\{N(E_{\text{f}})\}^2\alpha^{-5}\omega\left(\ln\frac{\nu_{\text{ph}}}{\omega}\right)^4 \qquad (2)$$

In this expression $N(E_{\text{f}})$ is the density of states at the Fermi level, α^{-1} is the decay length of the localized states, ν_{ph} is the phonon frequency in the studied material, k is the Boltzman constant and e is the elemental charge. This analysis predicts the frequency dependence of conductivity for such materials to have the form $\sigma_{\text{a.c.}}(\omega)\propto\omega^s$ where s is given by

$$s=1-\frac{4}{\ln\left(\dfrac{\nu_{\text{ph}}}{\omega}\right)} \qquad (3)$$

Assuming that $\nu_{\text{ph}}=10^{13}\,\text{s}^{-1}$ and is the same for all samples[8], then at $\omega=10.3$ GHz we obtain from equation (3) $s=0.21$.

Incomplete data for our samples did not allow for determination of the frequency dependencies of conductivity at high frequencies. However, measurements carried out at 4.6 GHz, for the PPY (PSS) sample obtained from 20% 1,4-dioxane solution, confirms such a low value of s. A similarly low value of s (0.35) was reported for poly(dimethylpyrrole) salts[9].

Linear $\sigma\propto T$ dependencies according to (2) were obtained in the following temperature regimes for various PPY (PSS) samples: 35 K–70 K, 40–90 K and 50–110 K for samples from solutions containing 0.20 and 40% 1,4-dioxane, respectively. The observed shift of the upper temperature to which the data can be fitted to (2) is consistent with the observed effect that for the PPY (PSS) sample from 40% 1,4-dioxane solution, the d.c. conductivity decreases very strongly with temperature and can be neglected in equation (1) at relatively high temperatures.

The values of $N(E_{\text{f}})$ for different samples were calculated assuming different decay lengths of localized states and are shown in *Table 1*. Decay lengths were chosen to give a range which covers values expected for localization of an unpaired charge carrier on a single pyrrole unit to those expected for a bipolaron extended over a few pyrrole units[10]. The average density of states per eV and per monomer unit $N_{\text{m}}(E_{\text{f}})$ were calculated taking into account the density and chemical composition of our materials[1].

From *Table 1* it can be seen that only decay lengths of localized states smaller than 10 Å result in acceptable values of the density of states. In fact, the density of states obtained from e.s.r. measurements on PPY salts have been reported to be of the order of 0.03 eV^{-1} monomer^{-1}.[10] It should be emphasized that the calculated $N_{\text{m}}(E_{\text{f}})$ values are average values, both from our measurements and e.s.r. measurements. If our model of non-homogeneous distributions of counterions is valid for these materials, the local concentration of localized states in the highly conducting microregions should be higher.

By comparing values of $N_{\text{m}}(E_{\text{f}})$ for different samples at fixed values of the decay length of localized states, some increase in the average density of states can be seen with decreasing concentration of 1,4-dioxane in the polymerization solutions, corresponding to increasing magnitudes of both d.c. and a.c. conductivity. For example, at a 5 Å decay length, the density of states for the samples from 0 and 40% 1,4-dioxane solutions are *ca.* 0.036 and 0.011 eV^{-1} monomer^{-1}, respectively.

From the above and previously reported results[1], the following picture of the investigated PPY (PSS) systems would appear reasonable. Due to non-homogeneous distributions of counterion sites, regions of relatively high conductivity are formed which are separated by poorly oxidized, poorly conducting regions. With increasing 1,4-dioxane content in the polymerization solutions, the polycounterions collapse somewhat, leading to more

Table 1 Densities of localized states near the Fermi level for the series of PPY/PSS salts obtained from electropolymerization solutions with varying 1,4-dioxane content; calculated using equation (5) assuming $\nu_{\text{ph}}=10^{13}\,\text{s}^{-1}$ for various decay lengths of the localized states

Sample (% 1,4-dioxane in electropolymerization solution)	α^{-1} (Å)	$N(E_{\text{f}})$ ($\text{eV}^{-1}\,\text{cm}^{-1}$)	$N_{\text{m}}(E_{\text{f}})$ (eV^{-1} monomer^{-1})
0	3	4.1×10^{21}	0.47
20	3	2.9×10^{21}	0.32
40	3	1.2×10^{21}	0.14
0	5	3.2×10^{20}	0.036
20	5	2.2×10^{20}	0.025
40	5	9.5×10^{19}	0.011
0	10	1.0×10^{19}	1.1×10^{-3}
20	10	6.9×10^{18}	7.8×10^{-4}
40	10	3.0×10^{18}	3.3×10^{-4}
0	20	3.1×10^{17}	3.5×10^{-5}
20	20	2.2×10^{17}	2.5×10^{-5}
40	20	9.2×10^{16}	1.0×10^{-5}

effective separation of conducting 'islands' by poorly conducting barriers.

Additionally, this collapsing of polycounterions is accompanied by some decrease in the local density of localized states in the highly conducting microregions, most likely due to poorer accessibility of the PPY to counterion sites and perhaps stemming from increased binding of polyelectrolyte counterions (Na^+) due to addition of 1,4-dioxane. The d.c. conductivity is determined mainly by the width of the morphological barriers (percolation problem) between conducting regions and gives rise to the very large differences in the temperature dependencies of d.c. conductivity observed for PPY (PSS) salts grown from polymerization solutions with different concentrations of 1,4-dioxane. These morphological factors also cause the deviations from $\log \sigma_{\mathrm{d.c.}} \propto T^{-1/4}$ behaviour expected for hopping conductivity among localized states. Such morphological barriers are overcome in a.c. conductivity measurements at sufficiently high frequency and the temperature dependencies of a.c. conductivity are similar for all the investigated samples. The differences in the temperature dependencies and magnitudes of a.c. conductivity are due to small differences in the local densities of states.

Although the investigations reported here were related only to the mechanism of charge transport and not to the origin and nature of charge carriers, the results would appear to preclude bipolarons as being the mobile charge carriers in the systems investigated. The small decay lengths of localized states needed to accommodate our results suggest that the charge carriers are unpaired (or forced to pair at small distances). Correlated jump or tunneling of paired charge carriers through the relatively large morphological barriers that appear to be present in these materials would also seem unlikely.

CONCLUSIONS

We have demonstrated that the conductivity behaviour of PPY salts can be controlled by morphology as well as oxidation level. From a.c. conductivity measurements on PPY (PSS) systems, we conclude that charge transport occurs by hopping of unpaired charge carriers among localized states near the Fermi level; at low frequencies or in d.c. conductivity, the charge carriers must overcome considerable morphological barriers. This morphological factor can in fact, determine the temperature dependence of d.c. conductivity in such systems, making analyses of such data in terms of the intrinsic electronic properties and nature of charge carriers, very difficult and even misleading. Although the non-homogeneous distribution of counterion sites in the investigated PPY (PSS) systems are artificially introduced (polymer counterion effect), it is likely that with certain non-polymeric counterions, similar effects due to aggregation or other distribution phenomena can occur.

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