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Controlled conductivity behaviour in poly(*p*-styrenesulphonate) salts of polypyrrole

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A series of polypyrrole (PPY) films with poly(*p*-styrenesulphonate) (PSS) counterions was prepared electrochemically from water/1,4-dioxane solutions. D.c. conductivities of these films were investigated in the temperature range 10–450 K. It was found that the electrical properties could be varied systematically by increasing the proportion of 1,4-dioxane in the polymerization solution, resulting in a decrease of room temperature conductivity from *ca.* $5\,\mathrm{S\,cm^{-1}}$ with 0% dioxane to *ca.* $3\times10^{-2}\,\mathrm{S\,cm^{-1}}$ with 40% dioxane. There is also a strong concurrent increase in the temperature dependence of conductivity. We conclude that the observed modification of the electrical properties of these PPY/PSS systems can be related, by a percolation model, to changes in the polycounterion conformation induced by addition of non-solvent (1,4-dioxane) to the polymerization solutions.

(Keywords: polypyrrole salts; poly(*p*-styrenesulphonate); electrochemical synthesis; electrical conductivity; polyanion conformation; percolation)

INTRODUCTION

Of the two major aspects of conductivity mechanisms in polymeric systems, charge carrier generation and transport, the latter is especially difficult in investigation and interpretation. Although there are several models describing the origin and nature of charge carriers on polymer chains which take into account the specific electronic structure of a given polymer[1,2], the lack of long range order in most polymer systems does not allow extension of such treatments to completely describe their actual macroscopic electronic properties. Rather, the observed bulk conductivity of a polymer system is a complex function of the number of charge carriers and their transport: along polymer chains (also influenced by various defect states), between polymer chains and across morphological barriers.

Polypyrrole (PPY) is a good example of this situation. The concept of bipolarons (dications) appears to account for the optical and electron spin resonance behaviour of PPY salts[3]. (We note here only that there is not yet complete agreement on such results in the literature.) However, because the structure of PPY (i.e. conjugation length, crosslinking, morphology) is not well defined[4], the choice of one of several models of charge transport is difficult to justify. The observed temperature dependencies for various PPY salts have most often been described using the 3-dimensional variable range hopping model of Mott[5]. One example of a recent alternative treatment of conductivity behaviour in polypyrrole salts has been presented by Buhks and Hodge[6].

Of the structural factors determining the electronic properties of PPY salts, the size, shape and distribution of counterions would appear to be especially important as these ions must spatially separate PPY chains to some extent and because the level of PPY oxidation, as connected with the number of counterions, plays a critical if not yet well defined role in determining conductivity[7]. It is also generally assumed that in the electrochemical synthesis of PPY salts, the distribution of counterions throughout the films is homogenous. How the formation of segregated clusters or domains of counterions might affect their local interactions with charges on the polymer chains and the conductivity behaviour of PPY salts is not known. In particular, if such counterion segregation would result in domains of higher and lower conductivity, the problem of bulk charge transport might be regarded as being dominated by a percolation process determined mainly by barriers separating the conducting phase.

The properties of PPY salts with conventional small counterions such as perchlorate or tetrafluoroborate can vary widely depending on synthesis conditions but it is difficult to determine if any changes in conductivity behaviour arise from anion distribution effects and if so, how to study such effects systematically. The use of poly(*p*-styrenesulphonate) (PSS) as counterions however, should ensure that the anion sites cannot be truly homogeneously dispersed in the PPY matrix because each anion site is chemically bound to the PSS chains. Furthermore, it is well established that lowering the dielectric constant of the solvent in a polyelectrolyte solution leads to some collapse of the extended polymer chains[8]. Thus by addition of a water-miscible non-solvent for PSS (e.g. 1,4-dioxane) to an aqueous solution of pyrrole and poly(sodium-*p*-styrenesulphonate), it is possible to change the conformation and size (radius of gyration) of the PSS polyion in solution. If some differences in polyion conformation are retained in the PPY films after polymerization from these solutions, it should be possible to observe changes in conductivity

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behaviour caused by variable spatial distributions of anion sites and to study these effects systematically. We report here the synthesis and characterization of a series of PPY films with PSS counterions, prepared electrochemically from aqueous solutions containing various amounts of 1,4-dioxane, which supports these hypotheses.

EXPERIMENTAL

Materials

Pyrrole was freshly distilled from KOH under reduced pressure before each polymerization. Water was deionized and distilled once before use. 1,4-dioxane was distilled from sodium before use. Sodium *p*-toluenesulphonate was recrystallized from ethanol and dried *in vacuo* over silica gel. Lithium perchlorate and poly(sodium *p*-styrenesulphonate) (Aldrich Chemical Co.) were used without further purification but were dried under reduced pressure at 80°C to constant weight before use. Viscosity measurements in 0.5 M NaCl provided an estimate of the PSS molecular weight (30 000) according to ref. 9. All viscosity measurements were performed at 20°C using a Schott AVS 300 Ubbelohde-type viscometry system. A low molecular weight (3000) PSS fraction was obtained by adding ethanol (450 ml) to a solution of poly(sodium *p*-styrenesulphonate) (50 g) in water (340 ml), then evaporating the supernatent solution to dryness.

Electropolymerization

Pyrrole (0.10 M) was potentiostatically (Bank LT-78 Wenking Potentiostat) polymerized on a vertical, single face (Teflon mount) platinum electrode (4.5 × 5.5 cm working area) at +0.80 V *versus* a standard calomel reference electrode (SCE) in a thermostatically controlled (20°C) single compartment cell (500 ml solution) equipped with a nitrogen inlet and bubbler, from various water/1,4-dioxane/electrolyte solutions. The counter-electrode was an 8 × 7 cm stainless steel plate mounted parallel to the working electrode at a distance of 5 cm by Teflon spacers. The reference electrode was separated from the polymerization solutions by a small, fine glass frit to prevent contamination of the solutions with chloride ions. The working electrode was cleaned after every polymerization with a 1:1 mixture of 30% H_2O_2 and concentrated NH_4OH. The solutions were not stirred during polymerization in order to avoid disturbing any evolving morphological features by turbulent flow. We have observed that even slow stirring of the solutions during polymerization produced films which were strongly nonuniform with respect to their electrical properties. After thorough purging, a slow, thin stream of nitrogen was bubbled through the solution from behind the counterelectrode during polymerization. Approximately two hundred coulombs of charge were allowed to pass through the cell (Bank EVI 80 Wenking Voltage Integrator) during each polymerization to give continuous films of *ca.* 20–40 micron thickness. Background currents were not significant. The films were carefully removed from the electrode with a razor blade, washed with water and slowly (to prevent cracking) dried between two glass plates under gradually reduced pressure over silica gel. The samples were kept under reduced pressure over silica gel between measurements.

Characterization

Elemental analyses were carried out by the Analytische Laboratorien, Engelskirchen, West Germany. Densities were estimated using a chloroform/ethanol density gradient. Room temperature conductivity measurements were carried out on *ca.* 2 × 0.5 cm sample strips using four wires laid across the strips perpendicular to their long axis at regular intervals and contacted to the films using GC Electronics silver paint. Standard linear four-probe measurements were then carried out using a Knick Precision Current Source No. J300 and Data Precision Voltmeter Model 3600.

Conductivity measurements in the temperature range 10–300 K were performed under reduced pressure (10^{-5} mbar) using a Cryosystems LTS-21 Closed Cycle Refrigerator System. A linear four-probe technique was again used but electrical contact was made using four thin conducting graphite foil strips which were pressed to the sample between two copper plates which were insulated from the sample by thin Teflon films. Good thermal contact between the cryostat cold finger and the sample holder was obtained through indium foil. A dual heat shield system was used to prevent heat flow by radiation. Maximum heat power released due to current flow during measurements never exceeded three microwatts and in the electric field range used, conductivity was ohmic at each temperature. Measurements and calculations were performed through an interface with an Apple IIe computer. No hysteresis effects were observed on thermal cycling. The reproducibility of these materials and measurements was confirmed by independent measurements on several samples using free mounted probes in a gas exchange cryostat[10].

Conductivity measurements in the temperature range 300–450 K were carried out in a glass cell under argon using the same probe configuration described above but with the sample set-up sandwiched between two ceramic resistance heaters. Temperature was monitored using a copper-constantan thermocouple. Both temperature control and current/voltage measurements were performed manually.

RESULTS

The conditions and results of the electrochemical synthesis of PPY films used in this study are summarized in *Table 1*. The films obtained using PSS as electrolyte are smooth and continuous when observed by optical microscopy. They are brittle compared with films made using *p*-toluenesulphonate as counterions; the brittleness increasing with increasing 1,4-dioxane content in the polymerization solutions. The densities of the films are between 1.38 (40% 1,4-dioxane) and 1.40 (0% 1,4-dioxane) g cm^{-3} as determined by flotation in ethanol/chloroform. The reduced viscosities of the polyelectrolyte solutions show that increasing the concentration of 1,4-dioxane leads to a gradual reduction of viscosity, indicating a continuous collapse of the polyelectrolyte molecules.

The room temperature conductivities of the PPY/PSS films decrease continuously as a function of increasing 1,4-dioxane content in the polymerization solution. However, the ratio of sulphur to nitrogen in the PPY/PSS samples does not vary either significantly or systematically with the addition of 1,4-dioxane to the

Table 1 Conditions and results for the electrochemical polymerization of pyrrole in water/1,4-dioxane solutions; 0.10 M pyrrole, +0.80 V vs. SCE, *ca.* 200 Coulombs, 20°C, Pt anode working area of 24.75 cm^2, no stirring

Electrolyte[a] (concentration)	Volume % 1,4-dioxane	Reduced[b] viscosity (dL/g)	Average current density (mA cm^{-2})	Room temperature conductivity (S cm^{-2})	Sulphur to nitrogen ratio	Film thickness (microns)
NaPSS (10.0 g/L)	0	3.24	0.300	5	0.171	20
NaPSS (10.0 g/L)	10	3.13	0.217	2	0.154	20
NaPSS (10.0 g/L)	20	2.86	0.155	0.7	0.150	18
NaPSS (10.0 g/L)	30	2.37	0.098	0.5	0.156	25
NaPSS (10.0 g/L)	40	2.26	0.062	0.03	0.165	20
NaPSS[c] (10.0 g/L)	0	–	0.448	9	0.212	26
NaOTS (9.42 g/L)	0	–	0.322	40	0.308	36
LiClO4 (0.20 M)	0	–	1.192	7	0.280[d]	28
LiClO4 (0.20 M)	20	–	0.635	8	0.265[d]	25

[a] NaPPS, NaOTS and LiClO4 stand for poly(sodium *p*-styrenesulphonate), sodium *p*-toluenesulphonate and lithium perchlorate, respectively

[b] Viscosity measured without pyrrole in the solutions

[c] Low molecular weight fraction

[d] Chlorine to nitrogen ratio

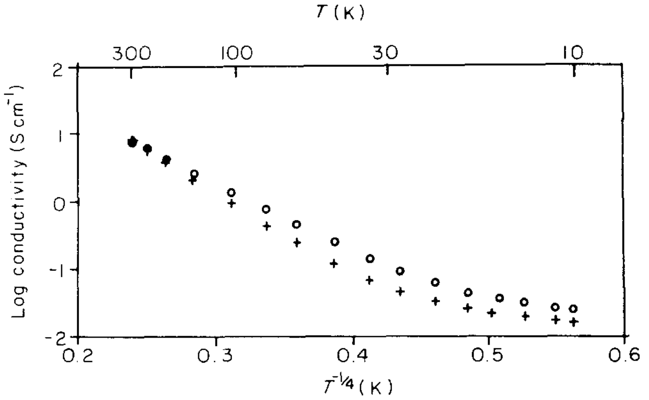

Figure 1 Temperature dependencies of conductivity for polypyrrole salt films grown from 0.2 M lithium perchlorate solutions in (○) water and (+) 20 vol% 1,4-dioxane; 0.1 M pyrrole, +0.80 V vs. SCE, 20°C

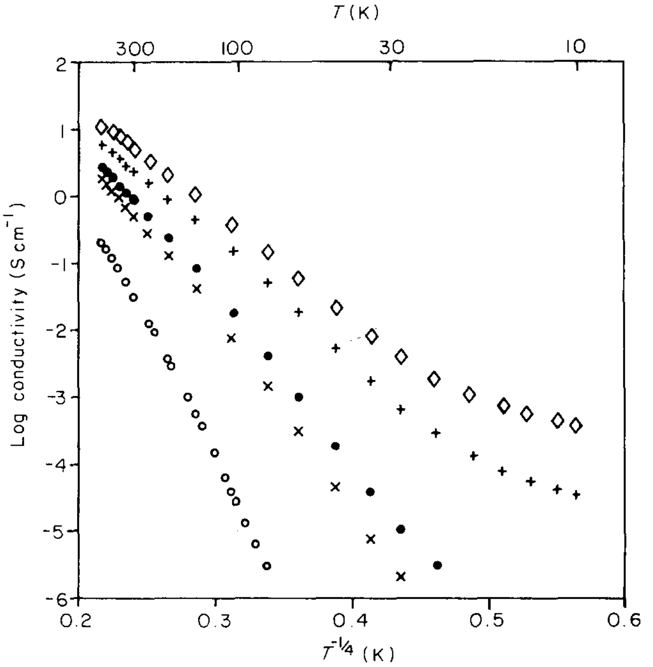

Figure 2 Temperature dependencies of conductivity for polypyrrole salt films grown from 10.0 g/litre aqueous poly(sodium *p*-styrenesulphonate) solutions containing (◇) 0 vol%, (+) 10%, (●) 20%, (×) 30% and (○) 40% 1,4-dioxane; 0.1 M pyrrole, +0.80 V vs. SCE, 20°C

polymerization solutions. This suggests that the sample composition with respect to PPY and PSS remains relatively constant at about six pyrrole units per anion site. With low molecular weight PSS and *p*-toluenesulphonate as counterions, the conductivities of the resulting PPY films are somewhat higher and the sulphur to nitrogen ratio increases systematically, presumably as a function of decreasing molecular size increasing anion site availability. Both the conductivities and chlorine to nitrogen ratios for PPY films made using more conventional perchlorate salts as electrolyte with and without added 1,4-dioxane do not vary significantly, indicating that any chemical effects of having 1,4-dioxane present during polymerization are negligible.

Figure 1 shows the temperature dependencies of conductivity ($T^{-1/4}$ coordinate, see following paragraph) in the range 10–300 K for samples made with perchlorate counterions from water and from 20% 1,4-dioxane solution. In both cases the temperature dependence of conductivity is weak and very nearly the same, confirming the elemental analyses results and showing that there is a little direct effect on the electronic properties of PPY salts from having 1,4-dioxane present during polymerization.

The temperature dependencies of conductivity for the PPY/PSS films in the temperature range 10–450 K are shown in *Figure 2* and are plotted in log conductivity *versus* $T^{-1/4}$ coordinates as suggested by the variable range hopping model (VRH)[5]. This model has often been used in interpretation of temperature dependencies of conductivity observed in PPY salts and we use these coordinates to facilitate comparison with other work in the literature. However, one cannot expect applicability of the VRH model over the entire range, especially at higher temperatures. Our results clearly do not fit this model, the curves exhibiting a somewhat sigmoidal shape. From these curves it can be seen that, in contrast to the perchlorate salts of PPY, increasing the amount of 1,4-dioxane in the polymerization solutions leads not only to a continuous decrease in conductivity but results in a dramatic increase in the temperature dependence of conductivity. The effect of this increase in temperature dependence of conductivity is so strong that at low temperatures the resistance of the samples made from 20, 30 and 40% 1,4-dioxane solutions became greater than the measurement limits of our apparatus. However, even by simple extrapolation from the results at low temperatures on samples from 0 and 10% 1,4-dioxane solutions, it can be estimated that the conductivity of the sample made from 40% 1,4-dioxane solution may vary by more than nine orders of magnitude in the temperature range 10–450 K.

The effect of repeat unit connectivity (polymer effect) on the distribution of counterions and the resulting properties of PPY salts can be seen in *Figure 3* which shows the temperature dependencies of conductivity for PPY films made under identical conditions but with different molecular weight counterion analogues. The low molecular weight PSS film has a somewhat higher conductivity than the higher molecular weight PSS sample but the temperature dependencies of conductivity are quite similar, indicating that barriers caused by segregation of counterions exist for both. For samples containing *p*-toluenesulphonate counterions the conductivity is both higher and its temperature dependence much weaker than those of the PPY/PSS films, consistent with a higher average concentration and more homogeneous distribution of the counterions resulting in better connectivity between conducting regions. Together *Figures 2* and *3* demonstrate that by varying only the structural features of the counterions in the synthesis of PPY salts, materials with a very broad spectrum of conductivity behaviour can be produced.

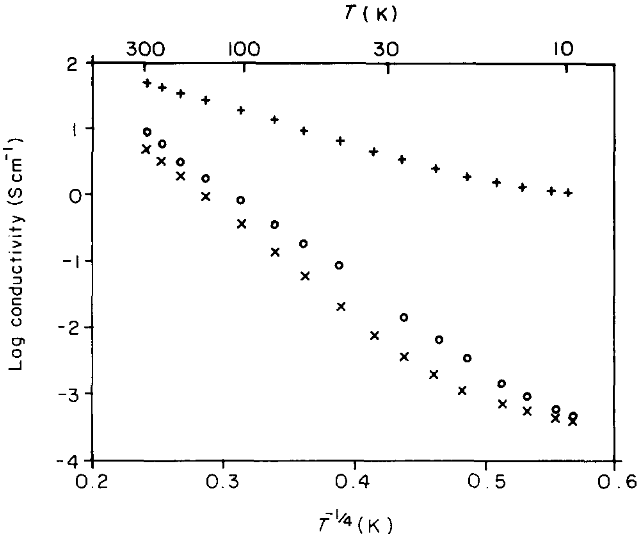

Figure 3 Temperature dependencies of conductivity for polypyrrole salt films grown from aqueous solutions of (×) 10.0 g/litre poly(sodium *p*-styrenesulphonate), molecular weight *ca.* 30 000; (○) 10.0 g/litre low molecular weight poly(sodium *p*-styrenesulphonate) fraction, *ca.* 3000 and (+) 9.4 g/litre sodium *p*-toluenesulphonate; 0.1 M pyrrole, +0.80 V vs. SCE, 20°C

DISCUSSION

Although the effect of added 1,4-dioxane to aqueous solutions of PSS can be interpreted in a straightforward manner and its effect on the resulting properties of PPY films grown from such solutions is dramatic, it is difficult to say what is actually occuring in terms of modification of the PPY salts in the solid state. Little is known about the behaviour of polyelectrolytes near electrode surfaces and what occurs during PPY growth is still mainly speculation. Attempts to characterize morphological differences in these PPY/PSS films using small-angle X-ray scattering techniques have met with little success so far.

We have therefore attempted to qualitatively explain the observed changes in conductivity behaviour in PPY/PSS films using the assumption that some differences in PSS conformation are retained on going from solution to being incorporated into the PPY films. Such spatial counterion segregation should result in various domains of higher and lower conductivity with different 3-dimensional connectivities. Bulk conductivity can then be regarded as a percolation process in analogy to charge carrier transport in non-homogeneous systems. A relatively universal approach to hopping conductivity in granular disordered systems, based on the critical path method[11], was proposed by Sheng and Klafter[12]. In this model two factors, intergrain tunneling distance and grain energy (related to grain size), determine the conductance and its temperature dependence between any two grains. The system is then analysed as a bond-percolation problem; at a given temperature, the macroscopic conductivity is determined by a critical value of intergrain conductance such that intergrain bonds with this or higher conductance can form an infinite cluster.

This model predicts a $T^{-1/4}$ temperature dependence of log conductivity at low temperatures, the range of which extends to higher temperatures with decreasing grain size, approaching behaviour expected for hopping among localized states. In our systems this behaviour is most closely approximated by the *p*-toluenesulphonate salts of PPY (*Figure 3*). At higher temperatures the model predicts a stronger temperature dependence of conductivity (σ) with $\sigma \propto T^{-a}$ ($1/2 < a < 1$), which extends toward lower temperatures with increasing grain size.

This model could then qualitatively account for the observed change in shape of the $\sigma(T)$ curves with increasing temperature (*Figure 2*) and for the increase in the temperature dependence of conductivity with increasing degree of polymerization (size) of the counterions (*Figure 3*). The decrease of conductivity accompanied by a strong increase of temperature dependence of conductivity shown in *Figure 2* should be related to an increase in the width of barriers separating regions of higher conductivity and a decrease in the effective volume of the higher conductivity phase caused by collapsing of the PSS chains in the presence of 1,4-dioxane. The PSS chains form additional barriers to charge carrier transport and when collapsed can more effectively interrupt conducting paths in the PPY salt.

The discussed model is dependent on parameters such as the volume fraction of the conducting phase and the distribution of grain sizes; parameters which we cannot yet reasonably estimate in the investigated systems. It is also clear that such a model is too simple for complete description of the PPY systems; the differences in conductivity between different regions are not so great as in the case of conductor/insulator granular systems and the boundaries between these regions are not so distinct. For these reasons we have not attempted to fit curves predicted by the above model to our experimental results. By tuning different parameters such fits could probably be achieved but would not afford any additional meaningful information.

An alternative mechanism which could account for the observed conductivity behaviour of the investigated systems or even amplify the mechanism discussed above, is that although the composition of PPY and PSS in the sample series from 1,4-dioxane appears to be constant, the actual oxidation level of the PPY decreases (either homogeneously or non-homogeneously) systematically as more 1,4-dioxane is added to the polymerization solutions. Tighter binding of sodium to the polyelectrolyte molecules as a result of decreasing the dielectric constant of the polymerization solution might result in the incorporation of increasing numbers of sodium/anion site pairs on the PSS chains into the PPY matrix, thus acting both as a barrier to conductivity and reducing the effective oxidation level. This explanation does not seem likely because elemental analyses of selected samples have not shown substantial sodium contents and even when the oxidation level is clearly higher from the sulphur to nitrogen ratio (e.g. low molecular weight PSS versus high molecular weight PSS, *Table 1*), the electronic properties (*Figure 3*) do not change so drastically as is observed for addition of 1,4-dioxane to the polymerization solutions (*Figure 2*). Both ultraviolet–visible and infra-red spectroscopic investigations of the 0 and 40% 1,4-dioxane systems did not show any effects clearly interpretable as being due to different oxidation levels. However, such an explanation has not been rigorously excluded, especially if the oxidation levels of our samples are in a region where small changes can have pronounced effects, e.g. in a region close to a percolation threshold.

CONCLUSION

We have used the qualitative model described above to illustrate that the macroscopic electronic properties of PSS salts of PPY are clearly dominated by morphological factors. That is to say that although the bulk electronic properties of these materials is a function of charge carrier transport along and between PPY chains, the actual electronic properties of these chains and the nature of the charge carriers generated on them are in fact masked by effects from the polymer superstructure. It would seem likely then, that in other conducting polymeric systems, especially those in which 'doping' processes are non-homogeneous, not only morphological effects on the macroscopic scale (e.g. fibrillar or granular structure) but also on the microscopic scale must be reckoned with in describing the electronic properties of these materials.

In order to elucidate the nature of charge carrier transport in PPY/PSS systems in more detail, we are currently undertaking studies on their frequency/temperature response of conductivity; to be reported in a forthcoming paper.

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