The Effect of 'Water and Transition Metal Ion Doping' on the Conductivity of Poly(3-substituted Thiophene-2,5-diyls)

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Poly(3-substituted thiophene-2,5-diyls) incorporating co-ordinated transition metals have been shown to exhibit a dramatic increase in conductivity on 'doping' with water from 10^{-8} to greater than 10^{-1} S cm^{-1}; however, only the polymer containing Cu^{II} exhibits electronic conduction and internal electrochemical redox waves.

Poly(thiophene-2,5-diyl), after doping with iodine, has been shown to exhibit significant conductivity.[1] The polymeric material was obtained by transition metal induced polymerization of the bis(Grignard compound) derived from 2,5-dibromothiophene. It was of interest to note that Yamamoto et al. mentioned that part of the metal remained incorporated in the polymer and could not be removed or exchanged.[1] As we are interested in studying conducting polymeric materials containing attached redox centres as potential electrocatalytic surfaces, we have synthesized a series of poly(3-substituted thiophene-2,5-diyls) (1) containing various incorporated transition metal ions,[2] in a similar manner, but using 3-substituted 2,5-dilithiothiophenes instead of the bis(Grignard compounds).

The conductivities of dry pressed pellets[2a,b] of all the insoluble fraction polymers obtained were found to be in the 10^{-7} to 10^{-8} S cm^{-1} range. The iodine-doped[1] polymers showed increased conductivities in the 10^{-3} S cm^{-1} region. Cyclic voltammetric studies using these polymers as electrodes were carried out in aqueous media (pH varied from 1 to 13; Li$^+$, Na$^+$, and K$^+$ as the cation in the supporting electrolyte, and Cl$^-$, Br$^-$, ClO$_4^-$, and NO$_3^-$ as the anion in the supporting electrolyte). A BAS model three-electrode potentiostat was employed in standard configuration. The undoped polymer disks were mounted as previously described.[3] All solutions were deaerated with purified N$_2$ and the reference electrode used was a normal calomel electrode (n.c.e.).

Most of the above mentioned undoped M^{n+}-polymers showed no redox waves for the internal M^{n+} and no electrode activity for the ferro/ferricyanide couple in the electrolyte phase. Some of them, namely the Pt^{II} and Fe^{III} polymers, seemed to exhibit poorly defined and small internal redox waves initially, but were quite unstable and the occurrence of a redox wave in the presence of ferri/ferrocyanide couple was questionable. All the Cu^{II} poly(3-substituted thiophene-2,5-diyls) showed very well defined redox waves for the internal Cu^{II} and the electrolyte phase ferri/ferrocyanide. Typical example cyclic voltammograms for the poly(3-SnMe$_3$-thiophene-2,5-diyl) containing Cu^{II} are shown in Figure 1. Note that on the initial scan, no significant redox waves are observed. However, on repeated cycling, a well defined redox
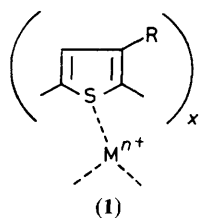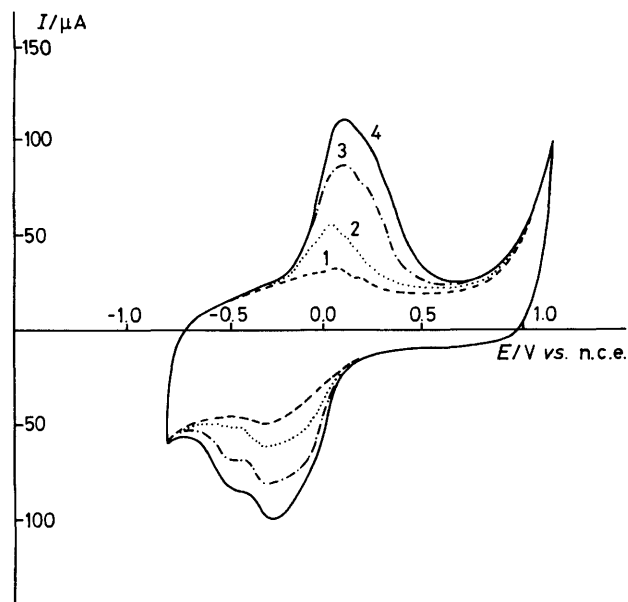
couple grows in and eventually reaches a steady state. The rate at which the steady state is attained is dependent on the substituent in the 3-position of the thiophene moiety but the $(Ep_c - Ep_a)/2$ value does not vary significantly with the 3-substituent. We interpret this behaviour to mean that Cu^{II}, incorporated in the polymer, is responsible for the redox waves.† The redox wave for the ferro/ferricyanide couple in the electrolyte phase at a 'steady state' Cu^{II} polymer electrode is very similar to that obtained at carbon and platinum electrodes. All of the Cu^{II} polymer electrodes of this type exhibit a remarkable stability. Electrodes have been continuously cycled in aqueous media for weeks without any observable change in the cyclic voltammogram. Also the presence of oxygen in the electrolyte solution has no measurable effect and the electrodes can be dried (in air) and then used again by immersing into water (in this case the same 'induction' period before reaching steady state cyclic voltammograms is observed). Furthermore, virtually none of the copper is leached out of the polymer.‡§ There is only minor variation of the cyclic voltammograms with respect to the nature of the supporting electrolyte. It is clear that the Cu^{II}-containing polymer conducts electrons.

The electrochemical behaviour of all these poly(3-substituted thiophene-2,5-diyls) suggests that water plays an important role in the *electronic conductivity* of the Cu^{II} polymer. Previously, Diaz et al.[4] observed that water did have an effect on the conductivity and other properties of polypyrroles in nonaqueous media, but the effect on the conductivity was only one order of magnitude. We have carried out standard 4-point probe conductivity studies on all the described poly(3-substituted thiophene-2,5-diyls) which were either exposed to water-saturated air under ambient conditions, sprayed with water, or immersed in water. As mentioned above, the dry material has a conductivity in the range of 10^{-7} to 10^{-8} cm^{-1}. Surprisingly, all of the disks exposed to

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† The ratio of M^{n+} : thiophene unit during synthesis is less than unity and varies from about 1 : 4 to 1 : 10 in the studies reported here. There seemed to be no differences in the electrochemical behaviour and the conductivity for ratios in this range.

‡ During the long term cycling experiments, the solution was periodically tested for Cu^{II} by the i.c.p. (inductively coupled plasma) method. Only part per million traces of copper were found in the solution phase even after weeks of continuous cycling.

§ The long term stability and, hence, chemical reversibility on continuous cycling suggests that the redox process does not involve the organic chain and the redox potentials are very close to those observed for 10^{-3} M CuCl$_2$ in the electrolyte phase at these electrodes. An indication that the redox couple is internal in the redox matrix is the fact that the peak heights of the redox waves are inversely proportional to the sweep rate and that the peak heights and potentials are independent of stirring of the electrolyte phase. Also, there is no change in colour of the material, as is observed for electrodeposited poly(thiophenediyls) on potential scan: R. J. Waltman, J. Bargen, and A. F. Diaz, *J. Phys. Chem.*, 1983, **87**, 1459.

(1)

R = H, Me, SiMe$_3$, SnMe$_3$, GeMe$_3$ for Cu^{II} polymers and M^{n+} = Cu^{II}, Cu^I, Mo^{VI}, W^{VI}, Ru^{III}, Fe^{III}, Co^{II}, Ni^{II}, Pt^{II} for poly(3-methyl-thiophene-2,5-diyl)

Figure 1. The cyclic voltammograms of Cu^{II}-containing poly(3-trimethylstannylthiophene-2,5-diyl) electrode in 0.1 M $NaClO_4$: (1) initial scan, (2) fourth scan, (3) ninth scan, and (4) steady state voltammogram after 11 scans. Sweep rate was 100 mV s^{-1}. Electrode surface area was approximately 0.4 cm^2.

to increase the *ionic conductivity* of all the polymers and the electronic conductivity of the Cu^{II}-containing polymer. Qualitatively, the extent of M^{n+} and water incorporation is proportional to the ionic conductivity and the electronic conductivity in the Cu^{II} case. Quantitative relations are not yet known. Furthermore, it does not seem that the water is involved with co-ordination at the M^{n+} site.¶ The fact that the Cu^{II}-containing material (and perhaps the Pt^{II} and Fe^{III}) appears to be unique in this study cannot be explained at this time. However, it appears that the incorporated M^{n+} plays an important role in the *electronic conductivity* of these polymers. The effect of M^{n+} suggests that either co-ordination geometry alone or a combination of the co-ordination geometry plus the high stability constants of the Cu^{II}-containing materials are important factors in the electronic conductivity of this organic polymer.

water show a conductivity of about 10^{-1} S cm^{-1}. Only the time required to reach this conductivity value is dependent on the nature of R, M^{n+}, and the method of moisture contact. Soaking in water is the fastest approach to reach the high conductivity values. The conductivity values of our 'water doped' polymer are in the range of ionic conductivity for other good solid ionic conductors.[5]

The remarkable effect of water on the conductivity (increase of 10^6 to 10^7 S cm^{-1}) of all the M^{n+} containing poly(3-substituted thiophene-2,5-diyls) is not understood at this time. It is clear that each polymer, regardless of the nature of the incorporated M^{n+}, has essentially the same conductivity and only the Cu^{II}, and perhaps, the Pt^{II} and Fe^{III} exhibit electron transfer for both the internal M^{n+} and the electrolyte phase ferro/ferricyanide couple. The effect of water doping is

References

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¶ The fact that the ionic conductivities of all these materials are independent of the chemical nature of the M^{n+} site and that some of the M^{n+} catalysts are fully co-ordinated as inert complexes, suggests that the ionic conductivity doping effect of water does not involve water co-ordination to the M^{n+}.