Conducting polymers prepared by template polymerization: polypyrrole

A. Mohammadi, I. Lundström, O. Inganäs and W. R. Salaneck

Department of Physics and Measurement Technology, Linköping Institute of Technology, S-581 83 Linköping, Sweden

Electrically conducting polymer composite films have been synthesized from the exposure of poly(4-vinylpyridine) (P-4VP) complexed with an oxidizing agent such as cupric chloride or ferric chloride to pyrrole and water vapour. Polypyrrole was formed in the matrix polymer of P-4VP complexed with iron ions when the mole ratio of polymer to oxidant was less than 2, whereas the growth of polypyrrole occurred at all P-4VP/Cu^{2+} ratios. Polymer composite films with electrical conductivities up to 100 $(\Omega cm)^{-1}$ have been obtained by this method. Transparent thin films with a high electrical conductivity were also produced. The electrically conducting polymer composite films have been characterized by X-ray photoelectron, ultraviolet/visible and infra-red spectroscopy and by scanning electron microscopy.

INTRODUCTION

In the last decade, there has been an increasing interest in the preparation and characterization of organic conducting polymers such as polyacetylene (PA), polypyrrole (PPY), polythiophene, polyaniline (PAN) and their derivatives. Organic conducting polymers both as homopolymers as well as in composite form have also been studied extensively for possible use in batteries[1,2], electrochromic displays[3-9], solar energy conversion[10,11], chemical sensing devices[12-15], etc.

One serious technological disadvantage of the conducting polymers is that they have very poor mechanical properties. Polypyrrole (PPY), motivated by its stability, has been studied intensively since 1979[16-20]. In the last few years, electrochemical polymerization of pyrrole in thick electroinactive polymer networks such as poly(vinyl chloride)[21], poly(vinyl alcohol)[22] and Nafion[23] and chemical polymerization of pyrrole in paper[24] have been reported. This approach may give a polymer composite with improved mechanical properties.

The increase of order and orientation is essential to realize the ultimate properties of conductive polymers, and also in order to understand their fundamental limitations. The use of polymer matrices could be one route towards enabling the synthesis of more ordered forms of conductive polymers. We have attempted to grow conductive polymers inside polymer matrices using a form of template polymerization. This is a process in which some pre-existing structure is used as a template, along which polymerization occurs. Polymers may of course also be the templates, as they already have structures of the right dimension. The possibility to orient and elongate polymer templates is of course also attractive for further advances in ordering.

Polypyrrole can be synthesized by chemical oxidation, and many oxidants have been used to form the polymer[25,26]. Our route is based on the immobilization of the oxidant inside a polymer matrix, based on a molecular level definition of the structure. A good approximation to this is found in the complexation of metal ions with poly(4-vinylpyridine) (P-4VP)[27].

Poly(4-vinylpyridine) like pyridine has the ability to form complexes with several metal ions including Cu^{2+} or Fe^{3+}. It is known that the complexation is based on the pyridine nitrogen in interaction with metal ions. Such metal ions may act as crosslinks between linear P-4VP chains. Stretching the complex at elevated temperature should enable alignment of the oxidant ions. By aligning the oxidant in the matrix polymer, it may be possible to grow conducting polypyrrole in an ordered structure which may result in a high electrical conductivity.

Poly(vinylpyridine) can be made to adhere to glass, ceramic material, most metals and different plastics. It is thermally stable up to 300-350°C (nitrogen atmosphere)[28]. Conducting polymers grown into a P-4VP/oxidant complex film may introduce a new type of material, suitable for future technological applications.

In this paper, we report on the results of the preparation and characterization of electrically conducting polypyrrole/P-4VP (PPY/P-4VP) composite films using a template-polymerization process. We used $FeCl_3$ as the oxidant because of our previous experience[25] and due to the solubility of the P-4VP in the aqueous solution of the $FeCl_3$. Furthermore, we also used $CuCl_2$ because of the fact that Cu^{2+} is a stronger oxidant than Fe^{3+} (refs 26 and 29).

We have carried out a variety of measurements in order to help define the chemical and electronic nature of these composite films. The materials have been characterized by their electrical conductivity, and studied further by X-ray photoelectron spectroscopy (X.p.s.), ultraviolet/visible optical absorption (u.v./vis) spectroscopy, infra-red (i.r.) absorption spectroscopy, and scanning electron microscopy (SEM).

EXPERIMENTAL

A 150 mm diameter beaker with a flat flange on top, together with a lid, which had three inlets, was chosen
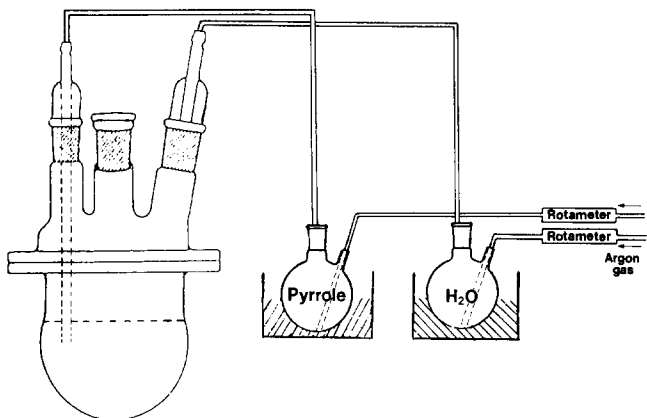
Figure 1 Schematic diagram of the reaction vessel

as a reaction vessel (*Figure 1*). The substrates were mounted around the walls inside the reaction vessel. Pyrrole and water vapour were introduced into the reaction vessel by a carrier gas (argon). The flows of the pyrrole vapour and water vapour to the vessel were measured with rotameters. Distilled pyrrole was stored at $-15°C$ in sealed ampules in the dark until time of use. It was loaded into a small flask, and argon was bubbled through the pyrrole. Water was loaded into another flask which was immersed in warm water and was used in the same way as the pyrrole described above.

Linear P-4VP ($M_w = 50\,000$) was used as received. Reagent grade ferric chloride ($FeCl_3.6H_2O$) and cupric chloride ($CuCl_2.2H_2O$) were used as oxidizing agents for the polymerization of pyrrole without further purification. After dissolving P-4VP and $FeCl_3$ in water or P-4VP and $CuCl_2$ in water and some drops of concentrated HCl (pH ≈ 1) the solutions were cast on glass slides. The glass slides were dried in laboratory atmosphere for 24 h. The preparation of PPY/P-4VP composite films was carried out in the reaction vessel by exposing the P-4VP films containing $FeCl_3$ or $CuCl_2$ to pyrrole and water vapour. X.p.s. (or electron spectroscopy for chemical analysis (e.s.c.a.)) was carried out using an ultra high vacuum system of our own construction. The system is equipped with a turbo-pumped vacuum interlock for quick sample insertion into a base pressure vacuum of $P < 1 \times 10^{-10}$ mbar. Unfiltered MgKα radiation was used under analysing conditions so that the full width at half maximum of the Au 4f$_{7/2}$ line was about 1 eV. Fourier transform infra-red (*FT* i.r.) measurements were performed at $2\,cm^{-1}$ resolution on a Bruker FTS 113V Fourier transform spectrometer. Optical absorption measurements were performed using a Perkin-Elmer Lambda 9 u.v./vis/n.i.r. dual beam optical spectrometer. The conductivity was measured with standard two- and four-point probes. The thickness of the films was determined with a Sloan Dektak 3030 surface profile measuring system. The morphology of the film was investigated using a 'Cambridge Instruments' scanning electron microscope.

RESULTS AND DISCUSSION

For the growth of the PPY films into the substrate of P-4VP complexed with Fe ions, the ratio of the base polymer to the oxidant P-4VP/Fe^{3+} seemed to have a significant effect on the pyrrole polymerization. PPY film

was only formed into the matrix polymer when the mole ratio of P-4VP/Fe^{3+} is less than 2. This probably indicates that each Fe ion reacts with two pyridine rings to produce a P-4VP–Fe complex. Consequently, these complexed Fe ions can no longer polymerize pyrrole monomers. The optical absorption spectrum of the matrix polymer with a mole ratio less than 2 showed a weak absorption at 4.3 eV which is associated with the absorption of $FeCl_3$. A strong absorption at 5 eV due to the Fe^{3+} complexed with P-4VP was, however, observed. Probably, uncomplexed Fe^{3+} in the form of unreacted $FeCl_3$ which fills the interfibrillar spaces existing in the P-4VP[30] are responsible for the PPY film formation. Composite films produced by the above method had electrical conductivities that varied from 10^{-3} to about 10^{-1} $(\Omega cm)^{-1}$, depending on the concentration of $FeCl_3$. Further investigations indicate that the electrical conductivity of these films increases with the decrease of the mole ratio between P-4VP/Fe^{3+}, but the relation was not linear.

The optical absorption spectrum of the PPY/P-4VP composite films exhibits a broad absorption maximum at 1.1 eV. This intense low-energy absorption due to bipolarons is associated with the conducting PPY[31,32]. A limiting step in the present experiments concerning the growth of ordered PPY was the disability of P-4VP complexed with Fe^{3+} to polymerize pyrrole monomers. Due to this incapacity, we investigated the possibility of using P-4VP complexed with Cu^{2+} for further developments of the composite material.

In the process of PPY film growth, the ratio of P-4VP/Cu^{2+} seemed to have no significant effect on the pyrrole polymerization, indicating that even Cu^{2+} bonded to vinylpyridine rings has the ability of polymerizing pyrrole monomers. PPY grown into the P-4VP complexed with Cu^{2+} (mole ratio P-4VP/Cu^{2+} was varied between 1 and 11) showed electrical conductivities from 5 to 150 $(\Omega cm)^{-1}$. The highest conductivities were obtained for the smallest ratios.

Some of these composite films were only slightly coloured, and almost transparent thin films with high electrical conductivity were obtained. The high electrical conductivity of PPY grown into the P-4VP complexed with Cu^{2+} can be understood as due to a very efficient dispersion of conducting segment. This was also revealed by SEM micrographs, in which no separate phases can be identified (*Figure 2a*), at a resolution of $\times 1500$.

For matrix polymer with a high ratio of P-4VP/Cu^{2+}, we found evidence for segregation of P-4VP/Cu^{2+} complexes in the matrix of P-4VP[33] (*Figure 2b*). This segregation was also revealed from metal microscope investigation of the complex films etched with methanol, where methanol will dissolve the uncomplexed polymer but not the complexed polymer. The lower electrical conductivity of PPY films grown into the matrix polymer with a high ratio of P-4VP/Cu^{2+} was a consequence of an uneven growth of the conducting polymer within this inhomogeneous film.

Experiments were made to investigate the effect of the time of exposure to pyrrole vapour on the electrical conductivity of the composite film. It was observed that at a low P-4VP/Cu^{2+} ratio, the electrical conductivity of the composite film is proportional to the time of exposure. Further investigations by SEM of these films revealed that a 150 min exposure time had not been enough for a complete diffusion of pyrrole vapour
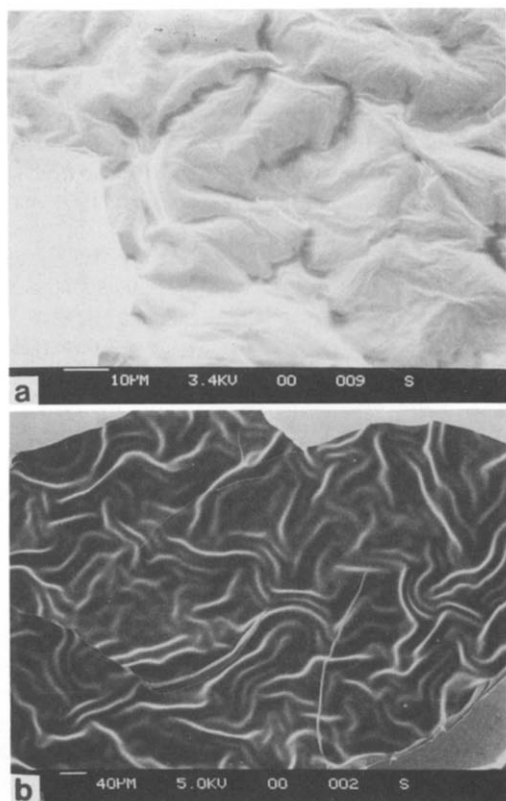
Figure 2 SEM micrograph of conducting composite film (a) with a mole ratio of $P-4VP/Cu^{2+} = 1.6$ and (b) with a mole ratio of 4
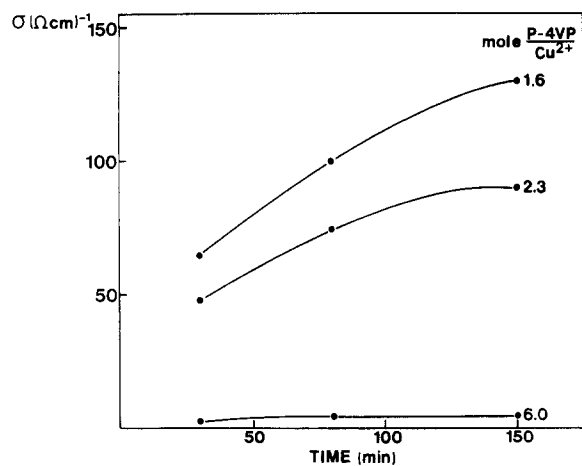

Figure 3 Electrical conductivity *versus* exposure time

The optical absorption spectra of electrically conducting composite film together with the optical absorption spectrum of P-4VP complexed with Cu ions are shown in *Figure 6*. Our PPY/P-4VP composite film exhibits a broad absorption maximum at 1.1 eV, which is similar to the long wavelength part of the optical absorption spectrum of electrochemically prepared PPY[34]. The optical absorption maximum centred at 3 eV is due to the absorption spectrum of the P-4VP complexed with Cu ions, as seen from the lower curve in *Figure 6*.

Infra-red studies were carried out both on P-4VP and P-4VP complexed with Cu ions in order to obtain some information about the structure of the complex. There was only a small frequency shift (less than 5%) in bands at 1600, 1557, 1495, 1452, 1221, 1069, 1001, 824, and 566 cm^{-1} between the polymer and polymer–copper complex which is expected due to the lone pair electrons of the nitrogen atom. On the other hand, there are other regions of the spectrum which show considerable changes. For example, bands at 1637, 1357, 1100, and 647 cm^{-1} are new vibrations appearing in the polymer–copper complex (*Table 1*). Absorption at 1637 cm^{-1} is evidence for a quaternized pyridine group[35] and the intensity of this peak is directly related to the concentration of Cu ions in the matrix polymer[36]. The *FT* i.r. spectrum of the conducting composite film showed a featureless increase in absorption from 4000 to
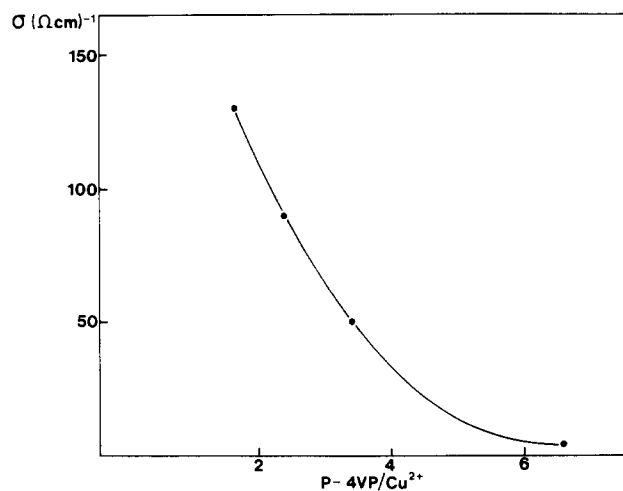

Figure 4 Electrical conductivity *versus* the $P-4VP/Cu^{2+}$ ratio

through the matrix polymer. Consequently, a long enough exposure time to pyrrole monomer is necessary to produce a homogeneous electrically conducting composite film at low $P-4VP/Cu^{2+}$ ratios. However, at a high ratio, the electrical conductivity of the film is almost independent of exposure time (*Figure 3*).

Further investigations were carried out to examine the relation between the electrical conductivity and the $P-4VP/Cu^{2+}$ ratio. As expected, the results showed an increase in the electrical conductivity upon a decrease in this ratio (*Figure 4*).

The long term stability of the conductivity of the composite films was also investigated. It was found that the electrical conductivity decreased by about 50% during a few weeks and later remained almost constant for more than 20 weeks (*Figure 5*).
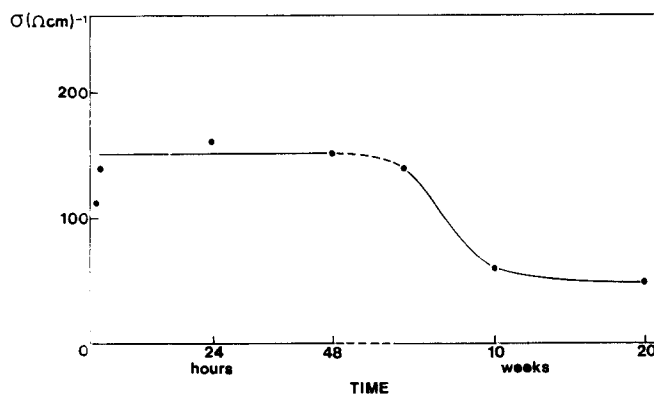

Figure 5 Electrical conductivity *versus* time for a composite film with mole ratio of $P-4VP/Cu^{2+} = 0.9$

1800 cm^{-1} which is due to the tail of the absorption peak located at 1.1 eV belonging to PPY in its oxidized conducting state[34]. The spectrum exhibits bands near 1555, 1308, 1171, 1036, 910 and 782 cm^{-1} which are characteristics of PPY. The high i.r. absorption at 910 and 4000 cm^{-1} is consistent with the high electrical conductivity of these composite films. The remaining bands such as 1601, 1555, 1495, 1454, 1420, and 559 cm^{-1} belong to pyridine ring vibrations (*Table 1*). Characteristically, we find that the bands due to the P-4VP/Cu complex at 1637, 1357, 1246, 1100, and 647 cm^{-1} appear very poorly in the *FT* i.r. spectrum of the P-4VP/PPY composite. This supports our basic concept of template polymerization that P-4VP complexed with Cu ions are active in the polymerization of pyrrole, and converted from their complex form during polymerization.

X.p.s. (or e.s.c.a.) measurements were carried out to further characterize the conducting composite films. The conducting composite film became detached from the gold-coated glass substrate under the vacuum conditions of the X.p.s. measurements. This caused a charging of the thin film and, therefore, the peak energies were corrected through comparison with the relative position of the O(1s) peak of our sample compared with the sample which adhered to the substrate.

The Cl(2p) binding energy of 197.7 eV which is less than the binding energy of Cl(2p) in both $CuCl_2$ (199 eV, refs 37 and 38) and CuCl (198.6 eV, ref. 38), was found to be the same in polymeric complexes prepared from materials with both low and high P-4VP/Cu^{2+} ratios. The low Cl(2p) binding energy probably indicates that
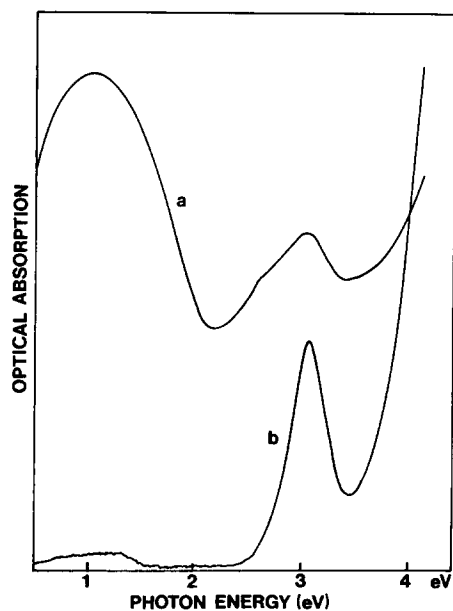
partial charge transfer from the nitrogen lone pair to copper and consequently to chlorine has occurred[37] (*Figure 7*).

The N(1s) spectra of the PPY grown into the matrix polymer with low and high P-4VP/Cu^{2+} ratio, shown in *Figure 8*, provide additional information. The N(1s) binding energies in these two samples were 399.3 eV and 399 eV, respectively. The N(1s) spectrum of the conducting composite film grown into a matrix polymer with a low P-4VP/Cu^{2+} ratio had a symmetric N(1s) peak (399.3 eV) (*Figure 8a*). On the other hand, the N(1s) spectrum of the sample grown into a matrix polymer with a high P-4VP/Cu^{2+} ratio exhibits an asymmetric N(1s) peak (*Figure 8b*). The peak occurs at 399 eV, and is due mainly to the nitrogen atoms in P-4VP[39]. The slight contribution from the nitrogen atoms in P-4VP complexed with copper (399.3 eV), and the small contribution of the nitrogen atoms in PPY (400 eV, ref. 40), is the cause of the asymmetric line shape.
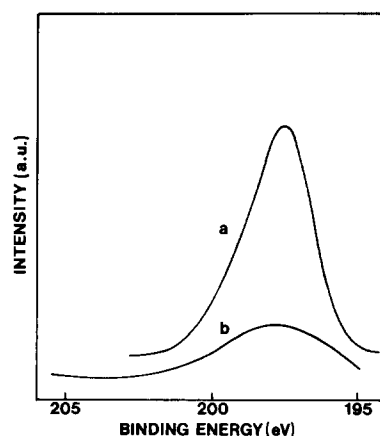

Figure 7 Chlorine (2p) X.p.s. spectrum of conducting composite film with (a) mole ratio of $\text{P-4VP/Cu}^{2+} = 1.6$ and (b) mole ratio $= 6$
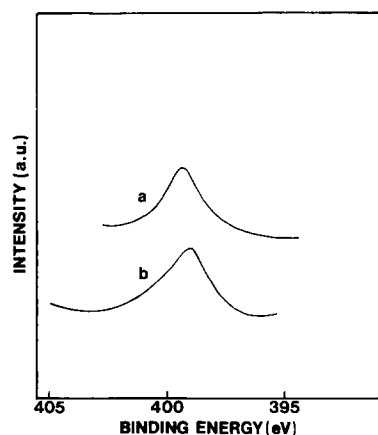

Figure 6 Optical absorption spectra of (a) conducting composite film and (b) P-4VP complexed with Cu ions

Figure 8 Nitrogen (1s) X.p.s. spectrum of conducting composite film (a) mole ratio of $\text{P-4VP/Cu}^{2+} = 1.6$ and (b) mole ratio $= 6$

Table 1 Infra-red spectra of different samples

Sample	Infra-red absorption (cm^{-1})															
P(4-VP)		1600	1557	1495	1452	1418		1221		1069	1001		824	744		566
P(4-VP) complexed with $CuCl_2$	1637	1602	1503	1454	1435	1357	1246	1204	1100	1059	1000	900	799	735	647	550
P(4-VP)/PPY composite		1601	1555	1495	1454	1420	1308	1171		1036		910	782			559
Polypyrrole			1555				1308	1771		1036		910	782			

CONCLUSIONS

We have prepared electrically conducting polymer composite films in a template polymerization process. The films which were produced by the polymerization of pyrrole monomer into a matrix polymer of P-4VP complexed with Cu ions exhibit a high electrical conductivity and a good mechanical and environmental stability. Furthermore, high conductivity was obtained also for transparent films. Proof of the template polymerization was obtained by i.r. spectroscopy, showing immobilization of the oxidant/catalyst on the molecular scale in P-4VP with subsequent conversion on polymerization of pyrrole. The results are encouraging, and we will develop the technique further to optimize the properties of the PPY/P-4VP composites.

ACKNOWLEDGEMENTS

REFERENCES

1 Mohammadi, A., Inganäs, O. and Lundström, I. *J. Electrochem. Soc.* 1986, **133**, 947
2 Kaneto, K., Maxfield, M., Nairms, D. P., MacDiamid, A. G. and Heeger, A. J. *J. Chem. Soc., Faraday Trans. 1* 1982, **78**, 3417; Kaner, R. B. and MacDiarmid, A. G. *J. Chem. Soc., Faraday Trans 1* 1984, **80**, 2109
3 Bookbinder, P. C. and Wrighton, M. S. *J. Electrochem. Soc.* 1982, **130**, 1080
4 Diaz, A. F., Castillo, J. I., Logan, J. A. and Lee, E.-Y. *J. Electroanal. Chem. Interfacial Electrochem.* 1983, **129**, 389
5 La Caze, P. C., Dubois, J. E., Desebene-Monvernay, A., Desebene, P. L. and Bassetier, J. J. *J. Electroanal. Chem. Interfacial Electrochem.* 1983, **148**, 107
6 Collins, G. C. S. and Schiffrin, D. J. *J. Electroanal. Chem. Interfacial Electrochem.* 1982, **139**, 335
7 Itaya, K., Akaboshi, H. and Toshima, S. *J. Electrochem. Soc.* 1982, **129**, 762
8 Haufman, F. B., Schraeder, A. H., Edward, M. and Patel, V. V. *Appl. Phys. Lett.* 1980, **36**, 422
9 Akaboshi, H., Toshima, S. and Itaya, K. *J. Phys. Chem.*, 1981, **85**, 818
10 Fan, F.-R. F., Wheeler, B. L., Bard, A. J. and Noufi, R. N. *J. Electrochem. Soc.* 1981, **129**, 2042; Noufi, R. N., Frank, A. J. and Nozik, A. J. *J. Am. Chem. Soc.* 1981, **103**, 1849; Noufi, R. N., White, J. and Warren, L. F. *J. Electrochem. Soc.* 1982, **129**, 2261
11 Skotheim, T., Lundström, I. and Prejza, J. *J. Electrochem. Soc.* 1981, **128**, 1625; Simon, R. R., Ricco, A. J. and Wrighton, M. S.

J. Am. Chem. Soc. 1982, **104**, 2031; Noufi, R. N., Tench, D. and Warren, L. J. *J. Electrochem. Soc.* 1981, **128**, 2596
12 Josowicz, M. and Janata, J. *Proc. 2nd Int. Meeting on Chemical Sensors*, Bordeaux, France, 1986, p. 457
13 Josowicz, M. and Janata, J. *Anal. Chem.* 1986, **58**, 514
14 Chague, B., Germain, J. P., Maleysson, C. and Robert, H. *Sensors and Actuators* 1985, **7**, 199
15 Nylander, C., Armgarth, M. and Lundström, I. *Proc. Int. Meeting on Chemical Sensors*, Fukuoka, Japan, 1983, p. 203
16 Diaz, A. F., Kanazawa, K. K. and Gardini, G. P. *J. Chem. Soc., Chem. Commun.* 1979, 635
17 Kanazawa, K. K., Diaz, A. F., Geiss, R. H., Gill, W. D., Kwak, J. F., Logan, J. A. and Street, G. B. *J. Chem. Soc., Chem. Commun.* 1979, 845
18 Diaz, A. F., Castillo, J. I., Logan, J. A. and Lee, W.-Y. *J. Electroanal. Chem. Interfacial Electrochem.* 1981, **129**, 115
19 Kanazawa, K. K., Diaz, A. F., Gill, W. D., Grant, P. M., Street, G. P., Gardini, G. P. and Kwak, J. F. *Synth. Met.* 1979/80, **1**, 329
20 Prejza, J., Lundström, I. and Skotheim, T. *J. Electrochem. Soc.* 1982, **129**, 1687
21 Niwa, O. and Tamamura, T. *J. Chem. Soc., Chem. Commun.* 1984, 817; Wang, T. T., Tasaka, S., Hutton, R. S. and Lu, P. Y. *J. Chem. Soc., Chem. Commun.* 1985, 1343; De Paoli, M.-A., Waltman, R. J., Diaz, A. F. and Bargon, J. *J. Polym. Sci., Polym. Chem. Edn.* 1985, **23**, 1687; Niwa, O., Hikita, M. and Tamamura, T. *Appl. Phys. Lett.* 1985, **46**, 444
22 Lindsey, S. E. and Street, G. B. *Synth. Met.* 1984/1985, **10**, 67
23 Fan, F.-R. F. and Bard, A. J. *J. Electrochem. Soc.* 1986, **133**, 301; Nagasubramanian, G., DiStefano, S. and Moacanin, J. *J. Phys. Chem.* 1986, **90**, 4447
24 Bjorklund, R. B. and Lundström, I. *J. Electr. Mater.* 1984, **13**, 211
25 Mohammadi, A., Hasan, M. A., Liedberg, B., Lundström, I. and Salaneck, W. R. *Synth. Met.* 1986, **14**, 189
26 Yosimira, R., Hirata, M., Haga, Y., An, H. and Seki, M. *Makromol. Chem., Rapid Commun.* 1986, **7**, 697
27 Agnew, N. H. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 2819
28 Brandrup, J. and Inmergut, E. H. (Eds) 'Polymer Handbook', John Wiley and Sons, New York, 1975, pp. 111–155
29 Yosomiya, R. and Fujisawa, T. *Polym. Bull. (Berlin)* 1985, **13**, 7
30 Castineira, M., Conesa, J. C., Palacios, J. M. and Castaneda, E. *Synth. Met.* 1987, **21**, 361
31 Bredas, J. L., Chance, R. R. and Sibley, R. *Phys. Rev. B* 1982, **26**, 5843
32 Kaufman, J. H., Colaneri, N., Scott, J. C. and Street, G. B. *Phys. Rev. Lett.* 1984, **53**, 1005
33 Golina, L. V., Kasaikin, V. A., Lukovkin, G. M. and Kabanov, V. A. *Vysokomol. Soedin. A* 1984, **26** (11), 2344
34 Street, G. B., Clark, T. C., Krounbi, M., Kanazawa, K. K., Lee, V., Pfluger, P., Scott, J. C. and Weiser, G. *Mol. Cryst. Liq. Cryst.* 1982, **83**, 253
35 Nishide, H., Deguchi, J. and Tsuchida, E. *Chem. Lett.* 1976, 169
36 Chanda, M., O'Driscoll, K. F. and Rempel, G. L. *J. Mol. Catal.* 1981, **12**, 197
37 Briggs, D. (Ed.) 'Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy', Heyden, London, 1977; Wagner, C. D., Riggs, W. M., Davis, L. E., Moulder, J. E. and Mullenberg, G. E. (Eds) 'Handbook of X-ray Photoelectron Spectroscopy', Perkin-Elmer, Eden Prairie, 1979
38 Kishi, K. and Ikeda, S. *J. Phys. Chem.* 1974, **78**, 107
39 Lyons, A. M., Pearce, E. M., Waszdzak, J. V. and Vasile, M. J. *Macromolecules* 1988, **21**, 3125
40 Pfluger, P., Krounbi, M., Street, G. B. and Weiser, G. *J. Chem. Phys.* 1983, **78**, 3212