Flexible and Heat-processable Conductive Films of Polypyrrole

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The electro-oxidation of pyrrole in the presence of anionic polyelectrolytes produces characteristic conductive black films of polymerically doped polypyrrole whose physical properties depend on those of the polyelectrolyte material.

Many conjugated polymer systems exhibit electronic conductivity following suitable doping reactions, but practical applications of these materials have been limited by their unsatisfactory mechanical properties in the conductive doped forms. Several recent attempts have been made to address this problem without unacceptable losses in conductivity, employing a general approach in which improved mechanical properties derive from the introduction of an additional component into the system.

The specific strategies depend upon the natures of the conducting polymers. Thus block and graft copolymers and blends of polyacetylene have been prepared;[1] thermally stable polyphthalocyanines have been melt-blended with conventional high-performance polymers;[2] and polypyrrole, which may be obtained by electro-oxidation as a thin film coating the anode, has been strengthened by the use of anodes pre-coated in porous films of non-conducting but mechanically superior polymers.[3]

In this communication we report the formation of elastic and melt-processable conductive films of polypyrrole by another route, in which the doping behaviour of this class of polymers is exploited. Polypyrrole and related electro-oxidatively formed conductive polymers such as polythiophene, polyaniline, and polyazulene are obtained directly in stable doped forms in which the dopant† is an anionic species derived from the electrolyte.[4] Our approach was to employ as dopants anionically derivatised polymers. Improved mechanical properties derive from the chain structure of the dopant. This approach differs from those mentioned above because the strengthening member is an intrinsic part of the conducting polymer matrix.

Our strategy was initially to show that such materials would function adequately as dopants and allow the formation of free-standing films of polypyrrole. For this purpose commercially available polymeric sulphonic and carboxylic acids and their salts were employed. Comparison of the mechanical properties of the resultant films with those of the pristine polyelectrolytes then provided a basis for the manipulation of film properties by tailoring of the polymeric dopant. In these cases synthesis of specific materials was required.

Electrolyses were performed in a 2-electrode single-compartment cell equipped for vigorous stirring. Anodes were of platinum foil or stainless steel sheet. Cathodes were of platinum or stainless steel gauze, held at a distance of only ~5 mm from the anode to minimise resistive losses. With this arrangement, constant current densities of 1—10 mA cm^{-2} were obtained at overall cell voltages of up to 60 V. Polymeric anions were employed as free acids and solvents were selected according to solubility criteria. The passage of 1—2 C cm^{-2} produced characteristic black films which could be peeled from the electrode and were of thicknesses ranging from 0.03 to 0.5 mm.

Table 1 lists electrolysis data and film properties for electro-oxidations of pyrrole with a representative sample of film-forming polymeric dopants. Samples 1—3 are commercially available polyelectrolytes; samples 4—6 were synthesised separately. All the films were tough and flexible when wet, but upon drying all but samples 3 and 6 became brittle, reflecting the brittleness of the majority of polyelectrolyte starting materials. It was possible to measure the electronic conductivities of the dry films by the 4-point probe method; the values so obtained were lower than those for polypyrrole doped with small monomeric anions (~50 S cm^{-1} for BF_4^-), but were within the conductivity range encompassed by polymers of simple functionalised polypyrroles such as poly(*N*-methylpyrrole) (~10^{-3} S cm^{-1} for BF_4^-).[5]

Of the commercially available polyelectrolytes, only hydrolysed chlorosulphonated polyethylene exhibited elastomeric properties, and the carrying-over of these into polypyrrole film 3 prompted us to synthesise dopants 4, 5, and 6 by conventional sulphonation or copolymerisation procedures.[6] However, of these materials only no. 6, a sulphonated tri-block copolymer of styrene/(hydrogenated) butadiene, proved to be elastomeric in its pristine form. This polyelectrolyte required specific solvent properties for electrolysis. It was soluble in CH_2Cl_2 and tetrahydrofuran (THF), but electro-oxidation in CH_2Cl_2 produced a particulate film of poor physical properties, while electrolysis in THF was hindered by poor solution conductivity of <1 μS cm^{-1}. The addition of up to 20% nitrobenzene to the THF solution increased the conductivity to 10 μS cm^{-1}. It appears that CH_2Cl_2 solvates the aliphatic blocks of the copolymer whereas THF–$PhNO_2$ solvates the styrene sulphonate blocks. Electrolysis in THF–$PhNO_2$ produced a tough and flexible film which retained these properties in the dry state. Extended electrolysis times produced a laminated film owing to electrophoretic build-up of the polyelectrolyte at the electrode which inhibited further pyrrole oxidation.

The laminate was conductive on its face adjacent to the electrode, but insulating on the other face, providing in one step an asymmetric polymeric conduction system.

Film 6 could be heat processed to a homogenous structure without loss of conductivity or of mechanical properties. Table 2 gives data for this film before and after moulding at 125 °C under pressure, contrasted with data from polypyrrole films doped with toluene-*p*-sulphonate and tetrafluoroborate which cannot be heat processed in this way. The polymer dopant produces a considerable improvement in ultimate elongation, and the film is generally more robust, being greatly resistant to tearing under sideways twisting motion. The principle has been extended to 3,4-dimethylpyrrole,[7] employing as dopant hydrolysed chlorosulphonated polyethylene. Electrolysis in acetonitrile solvent produced a black film with a dry conductivity of 3×10^{-3} S cm^{-1}, which was elastomeric when dry and which retained its flexibility after storage for several months.

The electrochemical properties of thin polymerically doped films were found to be not unlike those of polypyrrole films doped with small monomeric anions.[8] Cyclic voltammetry of thin films on platinum in both acetonitrile and aqueous electrolyte systems showed reduction currents during cathodic

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† Throughout this communication the term 'dopant' refers to the counterion required for charge neutrality following redox reactions of the polymer chain.

Table 1. Polymeric dopants in polypyrrole.

Sample	Polymeric dopant	Electrolysis solvent	Current density /mA cm^{-2}	Thickness /mm	Dry conductivity /S cm^{-1}
1	Poly(2-acrylamido-2-methylpropanesulphonic acid)	MeCN–H_2O (80%)	5	0.03	4 × 10^{-2}
2	Poly(methacrylic acid)	MeOH–H_2O (43%)	10	0.09	1.70
3[a]	Hydrolysed chlorosulphonated polyethylene (S, 1.1 wt.%)	THF–H_2O (2%)	1	0.09	1 × 10^{-3}
4	Poly(acrylamide, co-2-acrylamido-2-methyl-propanesulphonic acid) (S, 9.0 wt.%)	MeOH	1	0.06	0.10
5	Sulphonated poly(vinyl alcohol) (S, 13.4 wt.%)	DMF–H_2O (27%)[b]	10	0.24	2.60
6[a]	Sulphonated styrene/(hydrogenated) butadiene tri-block copolymer (S, 4.8 wt.%)	THF–$PhNO_2$ (20%)	1	0.4	9 × 10^{-3}

[a] These films retained flexibility in the dry state. [b] DMF = dimethylformamide.

Table 2. Mechanical and electrical properties of doped polypyrrole films.

Dopant	Film thickness /mm	Ultimate elongation (%)	Failure stress/ /MPa	Dry conductivity /S cm^{-1}
Sample 6 before hot pressing	0.40	410	18	8 × 10^{-3}
Sample 6 after hot pressing at 125 °C	0.27	390	32	5 × 10^{-3}
Tetrafluoroborate	0.20	2	20	34
Toluene-*p*-sulphonate	0.30	20	33	42

sweeps, in association with colour changes from dark to pale-coloured.

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References

1 G. L. Baker and F. S. Bates, *Macromolecules,* 1984, **17**, 2619; M. E. Galvin and G. E. Wnek, *ACS Polymer Preprints,* 1984, **25**(2), 229; M. F. Rubner, S. K. Tripathy, J. Georger, Jr., and P. Cholewa, *Macromolecules,* 1983, **16**, 870; K. I. Lee and H. Jopson, *Makromol. Chem. Rapid Commun.*, 1983, **4**, 375.

2 T. Inabe, J. W. Lyding, and T. J. Marks, *J. Chem. Soc., Chem Commun.*, 1983, 1084.

3 M-A. De Paoli, R. J. Waltman, A. F. Diaz, and J. Bargon, *J. Chem. Soc., Chem. Commun.,* 1984, 1015; O. Niwa and T. Tamamura, *ibid.,* 1984, 817; S. E. Lindsey and G. B. Street, *Synth. Metals,* 1984, **10**, 67.

4 J. Bargon, S. Mohmand, and R. J. Waltman, *IBM J. Res. Develop.*, 1983, **27**, 330.

5 A. F. Diaz, J. Castillo, K. K. Kanazawa, J. A. Logan, M. Salmon, and O. Fajardo, *J. Electroanal. Chem.,* 1982, **133**, 233.

6 Details are given in U.K. Patent GB 2 124 635 A, assigned to Raychem Ltd.

7 D. O. Cheng, T. L. Bowman, and E. LeGoff, *J. Heterocycl. Chem.*, 1976, **13**, 1145.

8 S. Kuwabata, H. Yoneyama, and H. Tamwa, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2247; A. F. Diaz, J. I. Castillo, J. A. Logan, and W-Y Lee, *J. Electroanal. Chem.,* 1981, **129**, 115.