Electro-reticulation for the Production of Transparent Conducting Polymers

Poopathy Kathirgamanathan

Unit for Speciality Electronic Polymers, Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, UK

Electrocrystallisation of conductive adducts within the matrix of microporous membranes results in reticulated conducting polymers that are transparent; production, characterisation and conductivity data are presented.

Transparent conducting polymers with conductivities in the range 10^{-4} to 10 S cm^{-1} have eluded the industrialist for a long time. Conducting polymer films have widespread applications, for example in preventing static electrification and shielding electrical devices. The reticulated doping of polymer films is a technique which enhances the conductivity of commercially available polymers by many orders of magnitude.[1]

The preparation of conducting reticulated polymer films reported by Jeszka *et al.*[1] involves dissolving a conductive adduct (*e.g.* TTT–TCNQ) (TTT = tetrathiotetracene; TCNQ = tetracyanoquinodimethane) into a polymer–solvent system and casting a film onto a substrate (*e.g.* glass) by evaporating off the solvent at an elevated temperature under controlled conditions. As the solvent is evaporated off, the concentration of charge transfer complex increases to supersaturation and crystallisation commences. The conductivity of the resultant film is dependent on the morphology of the crystal network within the polymer matrix.

Control of the conditions employed to produce reproducible materials for commercial applications is very cumbersome and the use of organic solvents has environmental implications.

This paper reports a novel electrochemical method for producing conducting reticulated polymers where solvent evaporation is not involved. The method can be used to produce large quantities of reticulated polymers using a partially immersed cylindrical horizontally revolving electrode.

The method involves (*i*) positioning an electrode with a porous polymer film, solvent-swellable polymer film, or non-woven polymer fibre network mounted thereon or adjacent thereto in an electrochemical cell containing a counter-electrode and electrolyte, which consists of at least one charge-transfer donor or acceptor dissolved in a solvent, and, if not provided by the solvent, a source of counter-ions; (*ii*) the passage of an electric current (two-electrode system, galvanostatic mode) or application of a potential (three-electrode system, potentiostatic mode) for a sufficient time for a network of the conducting charge-transfer adduct to be formed in the pores of the polymer film or non-woven polymer fibre network. Suitable polymers, which may be formed into cast films include poly(vinyl chloride) (PVC); partially hydrolysed poly(vinyl acetate), poly(bisphenol A), poly(bisphenol B) *etc.* Microporous materials based on poly(ethylene), poly(propylene), poly(ethylene terephthalate) and poly(urethane)(s) may be used. Suitable non-woven polymer fibre networks are poly(ethylene terephthalate) poly(ethylene) and poly(propylene). Polymer films of porosity 40–70% (v/v) are preferred.

Table 1 Conductivity data for TTF(NO_3)0.55–PVC films

Electro-reticulation time/min	Conductivity/S cm^{-1} (4 probe)
0	$<10^{-12}$
10	3.7×10^{-8}
20	3.7×10^{-7}
30	6.7×10^{-6}
60	1.0×10^{-5}
90	1.0×10^{-4}

A thin film of PVC (ICI, Corvic grade C/47/488) of 20 μm thickness was cast onto a square glass-backed Pt foil electrode by submersing the foil in a 5% solution of PVC in tetrahydrofuran. The electrode was then air-dried in a fume cupboard for 1 h before being immersed in nitromethane (25 ml) containing tetrathiafulvalene (TTF; and 0.25 mmol) and tetrabutylammonium nitrate (2.5 mmol). A bare Pt electrode of identical size was positioned parallel to the PVC-coated electrode at a distance of 2 cm.

The cell was secured from vibrations and then electrolysed at various current densities using the coated electrodes as anodes. The anode was then rinsed with nitromethane and air-dried for 12 h. The electrolysis was carried out at current densities of 400, 500 and 700 μA cm^{-2} for 1 h and red-brown crystals were observed to be formed in the pores of the PVC films. From X-ray diffraction data, the crystals were identified as TTF(NO_3)$_{0.55}$. Some unoxidised TTF was also observed. It was concluded from optical microscopic examination that the

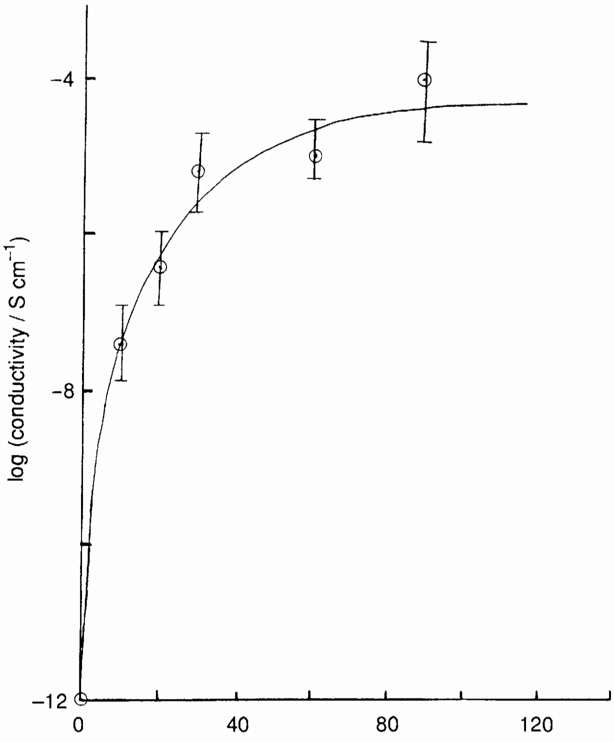

Fig. 1 Conductivity *vs.* time for electro-reticulation of TTF(NO_3)$_{0.55}$ into PVC

Table 2 Conductivity data for TTFX$_n$ reticulated PVC films

Anion	Potential,[a] *E*/V *vs.* Ag/AgCl	*t*/min	Conductivity/S cm^{-1} (4-probe)
NO_3^-	0.30	60	9.0×10^{-4}
NO_3^-	0.35	60	1.0×10^{-3}
SCN^-	0.35	40	5.0×10^{-4}
I^-	0.35	30	1.0×10^{-3}

[a] Potential sufficient to cause the oxidation of TTF to TTF$^{\bullet +}$.

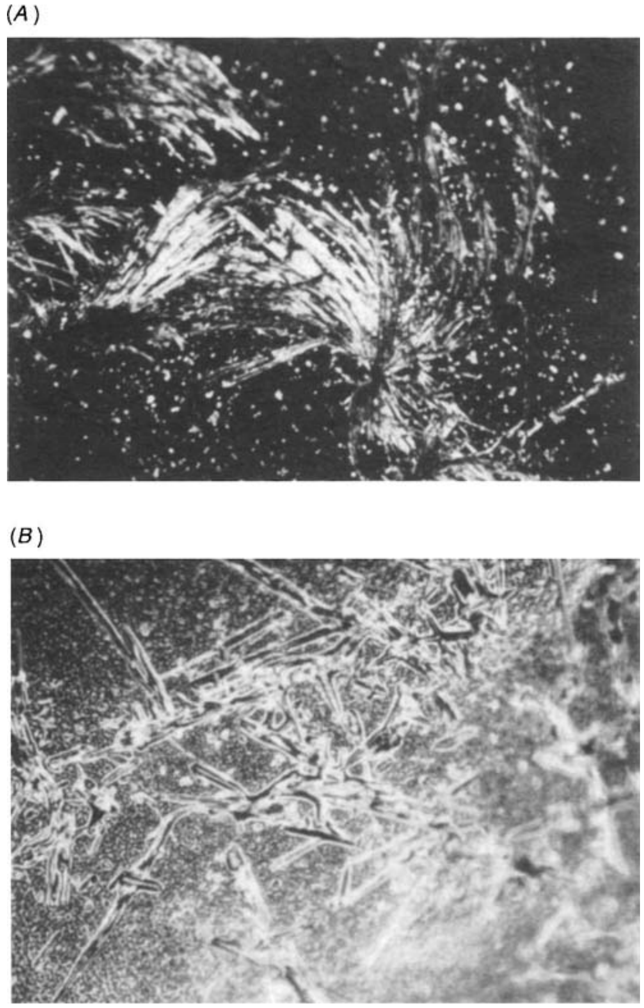

Fig. 2 (*A*) Solvent-cast reticulated polymer; (*B*) electro-reticulated polymer

most connected network of crystals was formed at 500 μA cm^{-2}.

Table 1 gives the conductivity of $TTF(NO_3)_{0.55}$-impregnated PVC films produced at 500 μA cm^{-2} at various time of electrolysis (*i.e.* various loading levels). As the time of electrolysis increases the conductivity increases as expected. Fig. 1 illustrates the conductivity *vs.* time plot, which is diagnostic of percolation behaviour[2] and similar to that observed in the solvent-casting method.[1] The initial dramatic rise in conductivity is observed as the crystallites start touching and any further increase in the content of crystals merely increases the extent of conduction pathways. The optical photographs (Fig. 2) show, however, that the morphology of the crystal network is different. The solvent-cast reticulated films have a fibrous network whereas the electrochemical method yields needle-shaped crystals.

Table 2 gives the conductivity data obtained under potentiostatic electroreticulation conditions for different anions NO_3^- SCN^- and I^-. It is clear from Table 2 that the percolation time for $TTFI_{0.70}$ is much shorter than that for $TTF(SCN)_{0.50}$ which in turn is shorter than for $TTF(NO_3)_{0.55}$. This may in part be explained on the basis of the fact that the rate of crystal growth on a bare Pt electrode is $I^- > SCN^- > NO_3^-$ and the same order appears to hold for PVC derivatised electrodes.

The electro-reticulated films are transparent (transmission 50–80% in the range 400–800 nm) and thus provide the first examples of electro-reticulated transparent conducting polymers which can be produced on a continuous basis.

The technique should be versatile. Virtually any compatible donors or acceptors can be used provided they can be dissolved in a solvent which does not attack the polymer base within the time scale of the electrolysis.

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