

Electroactive Conducting Composites from Poly(3-methylthiophene) and Poly(methylmethacrylate)

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Electrically conducting composites from poly(3-methylthiophene) and poly(methylmethacrylate) showing interesting spectroelectrochemical properties have been obtained in a one-step electrosynthesis.

In the last few years, there has been increasing interest in polyheterocyclic conducting polymers obtained by electrochemical synthesis, *e.g.* polypyrrole and polythiophene.¹ However, some practical applications of these polymers, such as their use as anti-static coatings are still restricted by their poor mechanical properties. In order to improve these mechanical properties, the preparation of composite materials containing a conducting polymer alloyed with a classical non-conducting polymer has been proposed. This idea has been successfully applied to polyacetylene,² and more recently, composite materials containing an electropolymerizable conducting polymer like polypyrrole and non-conducting polymers like poly(vinyl chloride) (PVC)³ or poly(vinyl alcohol) (PVA)⁴ have been described. Although attempts to improve the synthesis have been reported,⁵ these composites have been obtained, until now, by means of a two-step synthesis involving as a preliminary step the dip-coating of the working electrode with PVC followed by the electropolymerization of pyrrole within the PVC matrix. In this communication, we show for the first time that a five membered heterocycle like 3-methylthiophene (MeT) can be electropolymerized in a solution containing a dissolved polymer like poly(methylmethacrylate) (PMMA) and that the resulting composites films show interesting spectroelectrochemical properties together with high electrical conductivity.

The PMeT-PMMA films have been prepared in galvanostatic conditions on indium-tin oxide (ITO) in a single

compartment cell containing 0.2 M methylthiophene, 0.035 M tetrabutylammonium perchlorate, and 50 g l⁻¹ PMMA in 50/50 methylene chloride/nitrobenzene. The counter electrode was an aluminium foil, and a saturated calomel electrode (s.c.e.) was used as reference. A cursory study of the effect of PMMA molecular weight showed that the best results were obtained with high molecular weight PMMA (MW = 310 000). After electropolymerization, the working electrode was dried at 50 °C in air and rinsed with distilled water. The resulting flexible composite film was then easily removed from the electrode for electrical conductivity measurements or left on the electrode for spectroscopic and electrochemical analysis.

Owing to its composition, the reaction medium acts at the same time as a dip-coating solution and as an electropolymerization electrolyte and this has two consequences. On the one hand, when low charge densities (Q/S) are used for the electropolymerization of MeT, the thickness of the films depends mainly on PMMA concentration and increase of the film thickness occurs only when $Q/S > 500$ mC cm⁻². On the other hand, electrical conductivity measurements show that the two sides of the film are very dissimilar. Whereas the conductivity of the electrode side of the films increases steadily with polymerization time, the electrolyte side of the films shows much lower and less reproducible conductivities. We found the homogeneity and electrical conductivity of the composite films to be very dependent on the electrical conditions applied for the electropolymerization. Microscopic examination of the films shows that at low current density (2 mA cm⁻², 2.35 V/s.c.e.) PMeT grows on disconnected preferential sites within the PMMA matrix and the electrical conductivity of the electrode side of the films is in the range 0.1–1 S cm⁻¹. Increasing the current density leads to more homogeneous films and the electrical conductivity increases reaching values of 20–30 S cm⁻¹ for three minutes polymerization at 5 mA cm⁻² (3.5 V/s.c.e.) (Figure 1). With such

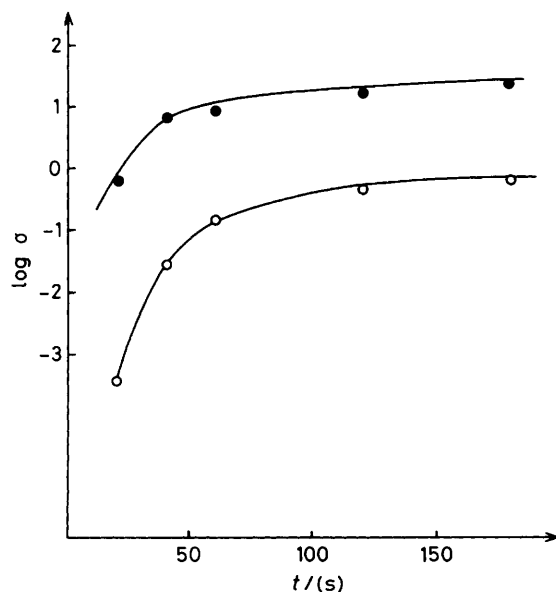


Figure 1. Plots of the electrical conductivity of PMeT-PMMA composite films vs. polymerization time (current density: 5 mA cm⁻²). ● Electrode side, ○ electrolyte side.

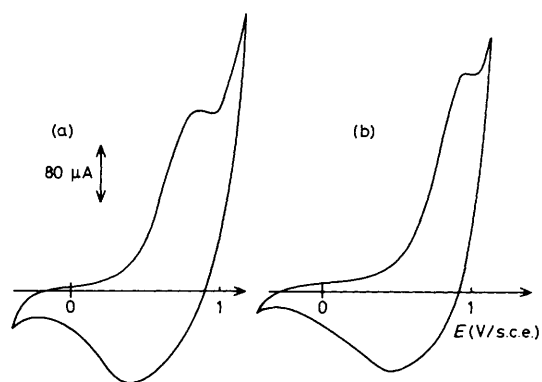


Figure 2. Cyclic voltammograms recorded in H₂O-LiClO₄ 0.1 M. Sweep rate 20 mV s⁻¹. (a) PMeT-PMMA film 80 mC cm⁻² on ITO, (b) PMeT film 80 mC cm⁻² on ITO.

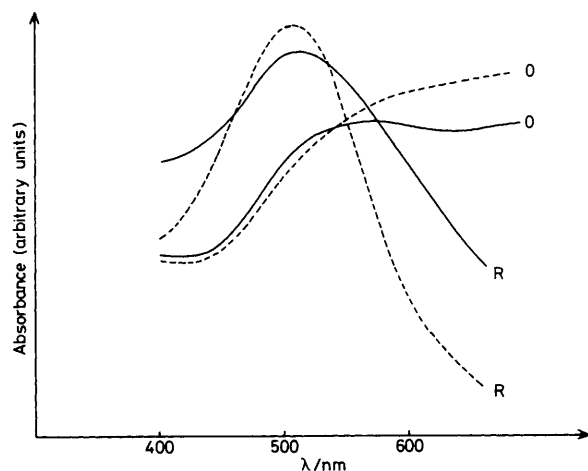


Figure 3. Visible absorption spectra of thin polymer films on ITO electrodes. - - - PMeT film O: oxidized at +1 V/s.c.e.; R: reduced at -0.4 V/s.c.e. ——— PMeT-PMMA composite film O: oxidized at +1 V/s.c.e.; R: reduced at -0.4 V/s.c.e.

charge density ($Q/S = 1 \text{ C cm}^{-2}$) the films are quite dark, but the optical transmittance can be controlled over a wide range using lower charge densities, thus a charge density of 80 mC cm^{-2} leads to blue semi-transparent films of $5 \mu\text{m}$ thickness with 40% transmittance at 633 nm and an electrode side conductivity of $1\text{--}2 \text{ S cm}^{-1}$. As PMeT films of the same optical density are only 2000 \AA thick and consequently cannot be removed from the electrode, this thickness difference clearly confirms the presence of PMMA in the composite films. Despite the lower conductivity of the electrolyte side surface, the composite films present interesting electrochemical properties. Figure 2 shows the cyclic voltammograms recorded in $\text{H}_2\text{O-LiClO}_4$ 0.1 M of a $5 \mu\text{m}$ PMeT-PMMA film obtained using 80 mC cm^{-2} on ITO compared with a PMeT

film synthesized in the same conditions, but in the absence of PMMA. Surprisingly, we found that the amounts of charge exchanged during the redox cycles were very close (4 mC cm^{-2} in both cases) showing that the PMeT part of the composite film is entirely electroactive. As for PMeT films, this redox behaviour is accompanied with reversible changes of the absorption spectrum of the film from blue (oxidized form) to red (reduced form)⁶ (Figure 3), with however slower response time to potential steps.

In summary, we have shown that PMeT derived composite films can be prepared in one step electrosynthesis. This synthesis method which can be generalized to other conducting/non-conducting polymer systems allows a wide control of the electrical and optical properties of the composites by the synthesis conditions. The new PMeT-PMMA composite materials described in this work exhibit interesting electrical and optical properties and they can be electrochemically switched from oxidized to reduced form. This latter result could be of particular interest for the design of electrochromic devices or of modified electrodes based on these materials.

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