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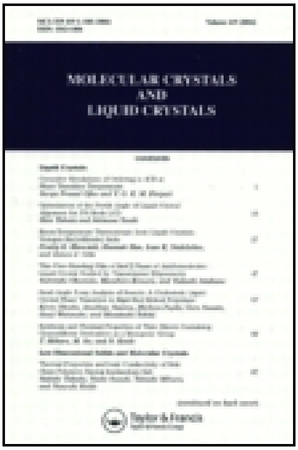

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Synthesis and Characterization of Electroactive Polymers Based on Pyrrole

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A novel method for polymerizing pyrrole has been identified which utilizes aqueous KI_3 solutions. This new synthesis technique enables a controlled method for incorporating pyrrole into composite systems to produce new electrically active polymers and to provide process control. Two electroactive systems were synthesized by this technique and characterized for their morphological and electrical properties. Electromembranes were fabricated from polypropylene and polycarbonate membranes and exhibited virtually no pore size restriction. Stable conductive coatings composed of ethylene-vinylacetate (EVA) copolymer and polypyrrole (PPy) were also developed.

INTRODUCTION

In the last decade, various electrically conductive polymers have been studied extensively. A considerable volume of work on polyheterocyclic polymers such as polypyrrole and polythiophene has been produced as they present a number of important advantages. They show high electrical conductivity associated with high stability when exposed to ambient conditions, and they can be conveniently synthesized via both electrochemical[1,2] and chemical oxidation[3,4] polymerization techniques. In contrast to chemically oxidized polymers, PPy prepared by electrochemical methods are relatively stable and have higher levels of conductivity. Insulating PPy films, with low oxidation levels, have been synthesized chemically in the presence of an acid peroxide initiator. These initially insulating films can be subsequently doped with halogens to achieve stable conductivities on the order of $10^{-5}\ \Omega^{-1}\text{cm}^{-1}$. Oxidized PPy films with conductivities on the order of 1 to 10 $\Omega^{-1}\text{cm}^{-1}$ have also been synthesized in the presence of Lewis acid catalysts, such as $FeCl_3$. Kang *et al.*[5] reported a one-step method for the simultaneous chemical polymerization and oxidation of pyrrole by halogens, such as iodine. The resulting PPy-halogen charge transfer complexes showed remarkable stability under ambient conditions and in aqueous environments.

Some important limitations of these polymers are their poor mechanical properties and their lack of solubility, which restrict some of their practical applications.

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To improve the processability of conductive polymers, several approaches have been adopted. Electropolymerization of conductive polymers on electrodes covered with insulating polymers provides conductive composite films. Polypyrrole was mostly used in these composite systems due to its high conductivity and good film forming property. Poly vinylchloride (PVC), copolymer of vinylidene fluoride and trifluoroethylene,[6] poly vinylalcohol,[7] and others[8] were used as host polymers to provide better mechanical properties. Lindsey and Street[9] have demonstrated that polypyrrole can be deposited within the matrix of several swellable polymers to form conducting composites. For instance, polypyrrole sulfate can be electrochemically deposited from an aqueous electrolyte solution into a poly vinylalcohol film which had been spun onto a metal electrode and then partially crosslinked to reduce its solubility while still permitting it to swell. Thin film of this composite polymer material had conductivities as high as 10 $\Omega^{-1}\text{cm}^{-1}$ and excellent mechanical properties which allowed these films to be folded and creased without cracking. Chemical synthesis of other conducting composites has been reported.[10,11] Transparent, electrically conductive composite films were obtained by vapor-phase polymerization of pyrrole into a PVC matrix containing $FeCl_3$.[12] It is proposed that the reaction mechanism involves the coupling reaction between pyrrole cation radicals and is similar to the electropolymerization of pyrrole.

In this paper, we present a novel method for the fabrication of polypyrrole composites using aqueous KI_3 solutions. Electromembranes and conductive coatings are prepared as two of many possible applicable forms of these new polymer systems. Electromembranes have potential uses in applications such as drug release control systems and separation processes. Conductive coatings can be used for antistatic finishes. Performance aspects of these systems are currently being developed for membrane transport, conductive coatings, and thermal and dielectric behavior.

EXPERIMENTAL

For the electromembranes, polycarbonate (Nuclepore) and polypropylene (Celanese, Celgard-2500) membranes were selected as the starting materials. Potassium iodide (Mallinckrodt, analytical reagent) and iodine (Aldrich) were used as received. Pyrrole monomer (Aldrich, 99%) was distilled before use. Conductive membranes were prepared by first soaking the membranes in a mixture of chloroform (Aldrich, HPLC) and pyrrole. The soaked membranes were then removed from the solution and exposed to air to remove the residual solvent. After drying in air, they were oxidized by dipping into KI_3 (0.1M I_2, 0.2M KI) aqueous solutions. This led to both polymerization and oxidative doping of the pyrrole embedded in the membrane. The oxidation time was controlled to obtain optimal properties. The treated membranes were washed with water and vacuum dried at 60°C for two hours.

For the conductive coatings, ethylene-vinylacetate copolymer (USI, Vynathene, EY 904-25) solution containing pyrrole monomer was cast on a substrate. The substrate was dipped into KI_3 solutions. Polymerization and doping of pyrrole occurred simultaneously. The samples were washed with water and dried under vacuum.

Surface resistivities were measured by using the four-probe method. Morphologies of the polypyrrole composites were investigated using scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Figure 1 shows surface resistivity as a function of time subsequent to polymerization for polypyrrole coated conducting membranes. The conducting membranes remained stable after the initial loss of conductivity. The Nuclepore polycarbonate membranes exhibited higher conductivities than the selected polypropylene membranes. It is believed that the electromembrane conductivity is related to the amount of the deposited conductive polymer and its deposition uniformity. The average pore structure in the Nuclepore membrane is much larger than that in the polypropylene membrane. This larger pore structure, correlating to smaller surface area within the membrane, leads to thicker and more uniform conducting polymer coatings in the polycarbonate microporous structure. Therefore, control of the conductive polymer impregnation concentration is responsible for determining the conductivity of the fabricated membrane.

The resultant electromembrane pore structure (Figure 2) was dependent on the starting material. The Nuclepore membrane had approximate micron size cylindrically shaped pores. This geometry allowed excellent fluid flow and complete coverage with no pore constriction (Figure 2a). The PP membrane possessed a net-like pore structure with an effective pore size of ~0.04 μm. The smaller, net-like

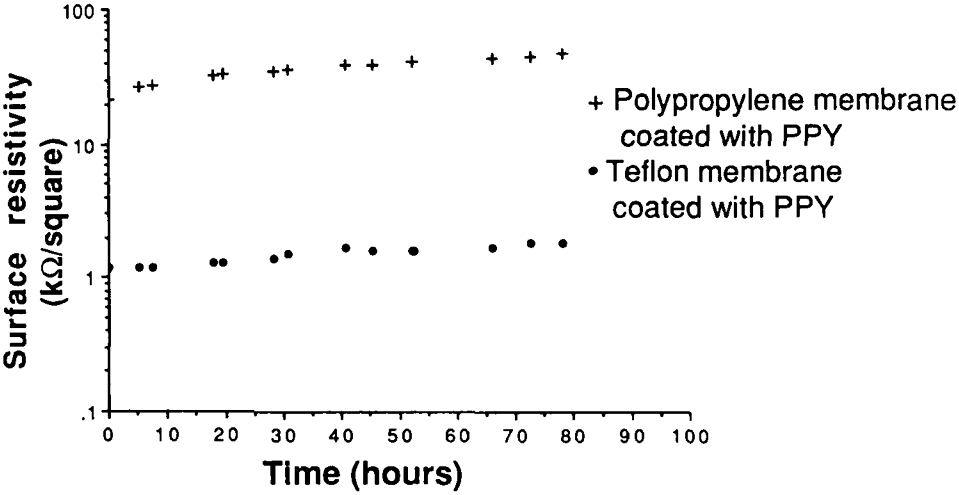

FIGURE 1 Surface resistivity as a function of time subsequent to polymerization for polypyrrole coated conducting membranes.

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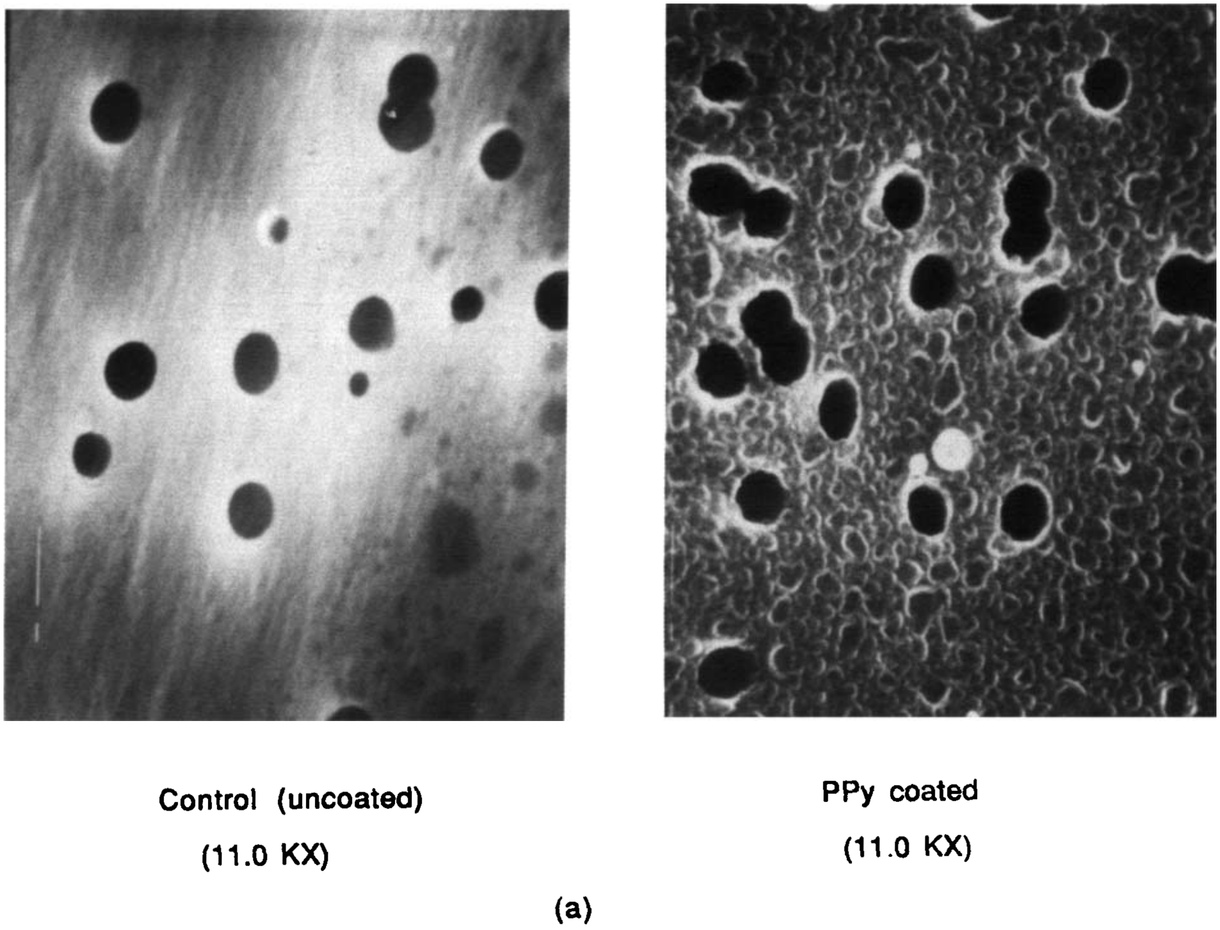

Control (uncoated)
(11.0 KX)

PPy coated
(11.0 KX)

(a)

FIGURE 2 Surface morphology of control and polypyrrole coated membranes. (a) Nuclepore polycarbonate membranes. (b) Polypropylene membranes.

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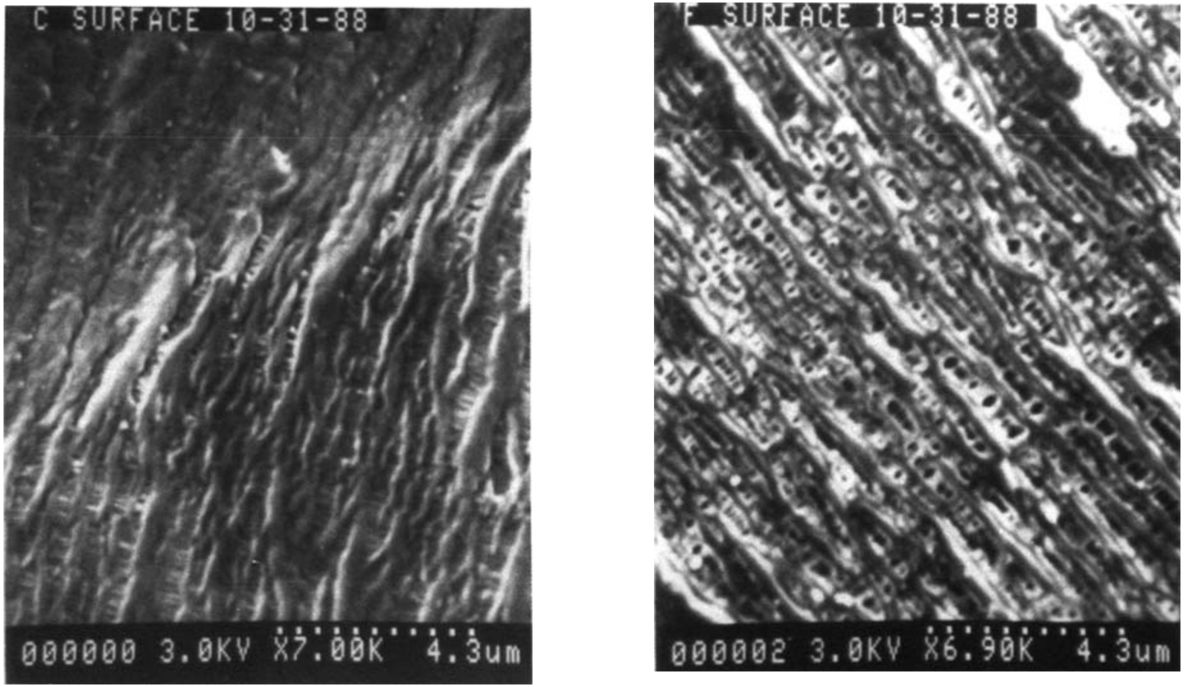

Control (uncoated)

PPy coated

(b)

FIGURE 2 (*continued*)

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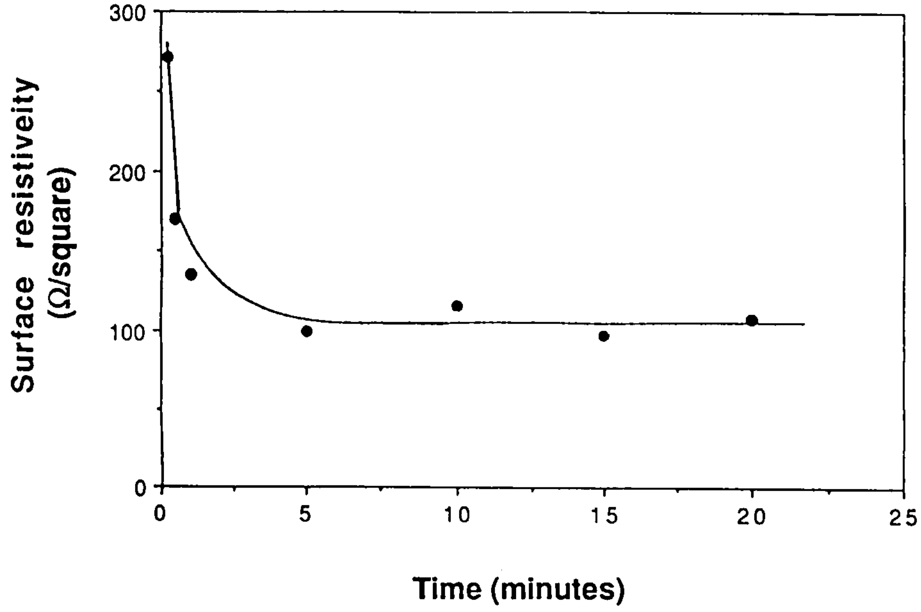

FIGURE 3 Surface resistivity of conductive coatings vs. reaction time.

pore geometry provided agglomeration sites for the PPy which led to pore constriction and, in some cases, blockage (Figure 2b).

Figure 3 shows the surface resistivity of the conductive coatings versus reaction time. It indicates that the surface resistivity of the composite film decreases with reaction time and reaches its saturation value within three minutes.

Initial investigations indicate that the reaction between pyrrole and KI_3 solution is almost instantaneous while the reaction between pyrrole and $FeCl_3$ takes longer time to complete. This indicates that the reaction between pyrrole and KI_3 is an electron transfer enhanced oxidation-reduction reaction. A reaction mechanism similar to electropolymerization of pyrrole is probably involved.

The surface morphologies of the conductive coatings are shown in Figure 4. EVA can be dissolved in pyrrole monomer without using a co-solvent and forms a viscous solution. The films (Figure 4a) prepared from this solution possessed rough surfaces with nonuniform coating thickness. Using chloroform as a co-solvent, a lower viscosity solution is formed which provides better flow properties for casting or spin coating. The surfaces of the conductive coatings are smooth but contain numerous holes (Figure 4b). These holes are due to the evaporation of the co-solvent during processing. The hole size in the surface can be controlled by washing with chloroform (Figure 4c).

CONCLUSION

A new technique for processing and polymerizing pyrrole has been utilized to fabricate new electroactive polymers. These polymers were analyzed for their elec-

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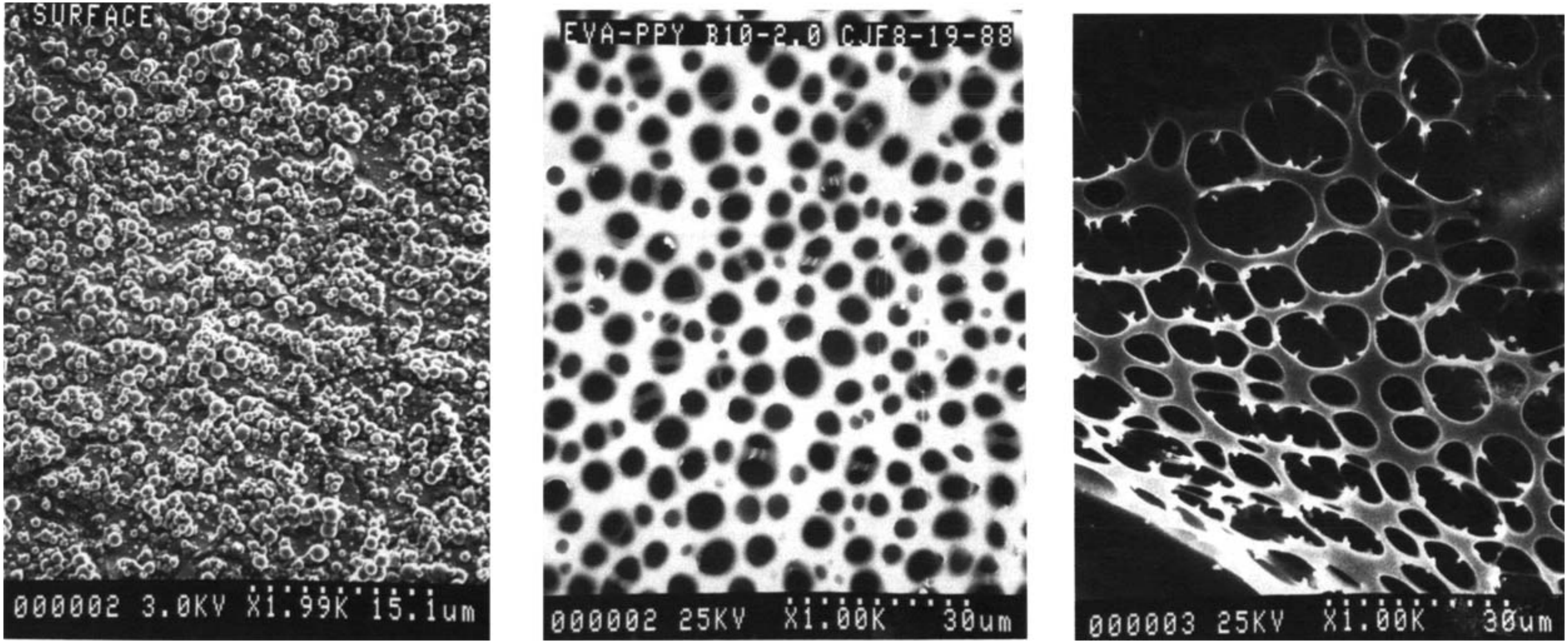

(a) (b) (c)

FIGURE 4 Surface morphology of conductive coatings. (a) Without using a co-solvent. (b) Using chloroform as a co-solvent in the EVA solution. (c) Washing with chloroform.

trical and morphological properties and found to be of excellent quality. Performance criteria for these systems are currently being developed to demonstrate potential use for commercial applications.

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