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Preparation and Characterization of Polyheterocycle/Polyelectrolyte Molecular Composites

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INTRODUCTION

The ability to electrochemically prepare electrically conductive blends and molecular composites of polyheterocycles with a variety of carrier polymers has led to multi-component materials with enhanced mechanical and electrochemical properties. The ultimate properties of the materials are a result of the mechanical and chemical nature of both the carrier polymer and the polyheterocycle utilized. In-situ electropolymerization in thermoplastic matrices represented the first materials of this class.¹⁻³ Electropolymerization has also been carried out within ionomeric membranes, such as Nafion, in order to induce an ionically conductive medium.⁴⁻⁸ An extremely versatile technique for the preparation of these conductive molecular composites is heterocycle electropolymerization in the presence of a solubilized polyelectrolyte.⁹⁻¹¹ In addition to the structure of the respective polymeric components, the direct electropolymerization/deposition method has a number of variables which can be used for controlling material properties. For example, Wegner et al.⁹ have used the polarity of the electrochemical medium to control the solution properties of the polyelectrolyte which then directly affects the final materials electrical conductivity.

In this report we describe a facile derivatization of the polyaramid poly(p-phenylene terephthalamide), Kevlar, to form a highly water soluble polyelectrolyte. This represents the first report of a water soluble derivative of Kevlar, where previous Kevlar derivatizations^{12,13} resulted in the grafting of side chains onto the polyaramid backbone. It should be pointed out that rigid chain water soluble and lyotropic polyaramids have been directly prepared using sulfonated aromatic diamines.¹⁴⁻¹⁶

We have used this polyelectrolyte in the electrochemical synthesis of a conducting molecular composite with polypyrrole. In addition to high conductivity, this composite exhibits enhanced thermal stability when compared with typical polypyrroles. The electropolymerization/deposition process and ion transport properties of polyheterocycle/polyelectrolyte blends have been examined using the electrochemical quartz crystal microbalance. Studies on polypyrrole/poly(styrene sulfonate) molecular composites show these membranes to exhibit cation specific transport during electrochemical switching.

EXPERIMENTAL

Poly(p-phenyleneterephthalamide propane sulfonate) (PPTA-PS) was prepared by the treatment of Kevlar pulp (Du Pont) with 1 equivalent per repeat unit of NaH in DMSO or DMAc at 40-50 °C. A dark red, viscous, PPTA anion solution forms which is subsequently treated with 1 equivalent per repeat unit of 1,3-propane sultone (Aldrich). PPTA-PS is isolated by precipitation into THF followed by washing and drying. 100% sulfonated sodium polystyrene sulfonate (Polysciences Inc.) and tetraethylammonium tosylate (Aldrich) were used as received. Pyrrole was

purified prior to electropolymerization by passage over neutral alumina until clear.

Large scale electrochemical syntheses were carried out, in a two electrode configuration, on 100 cm² amorphous carbon plates (Atomergics Inc.) using either distilled CH₃CN or H₂O as solvent. The electrochemical quartz crystal microbalance (EQCM) technique and apparatus have been described previously.¹⁷

Infrared spectroscopy (diffuse reflectance and transmission) was carried out on a Digilab FTS-40 spectrophotometer. NMR on a Bruker 300-MSL and thermal analyses on a DuPont 9900 TA system equipped with TGA, DSC and DMA.

RESULTS AND DISCUSSION

Poly(p-phenyleneterephthalamide propane sulfonate).

The preparation of PPTA-PS is shown schematically in Figure 1. The polymer is obtained as a yellow powder that

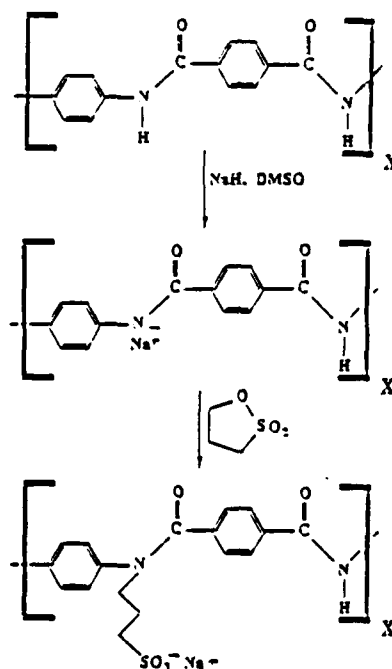


Fig. 1. Synthesis of PPTA-PS.

can be dissolved in water in concentrations up to 20 weight percent. Diffuse reflectance infrared spectroscopy shows major peaks at 3292, 3120, 3047, 2974, 1635, 1512, 1408, 1319, 1203, 1049, 860, 733, and 613 cm⁻¹. The low energy portion of the spectrum overlays with that of the Kevlar pulp except for the peaks at 1203 and 1049 cm⁻¹ which result from the S=O stretching vibrations as compared to similar peaks at 1220 and 1064 cm⁻¹ for benzene sulfonic acid, and at 1207 and 1050 cm⁻¹ for butane sulfonic acid.

NMR studies suggest the structure to be somewhat more complicated than the simple N-propyl sulfonate substitution shown. Integration of the carbonyl resonances, using a long delay time of 15s indicates approximately 60% of the nitrogen atoms along the polymer backbone are alkyl sulfonated. There is also some evidence of O-alkylation though the contribution to the overall composition is small.

Viscosity studies of the polymer in H₂O determined at 30°C indicate an intrinsic viscosity of 1.2 dl/g. The polymer is soluble to greater than 20 weight %. To date we have observed no indication of lyotropic behavior in these solutions.

A 1 % by weight solution of PPTA-PS (0.025 M assuming a weight of 411 g/repeat unit for 60% sulfonated Kevlar) and 0.20 M pyrrole in water, purged with N₂ for several minutes, was used in the electrochemical preparation of the conductive molecular composites. Amorphous carbon plate electrodes were placed horizontally into an electrochemical cell and the conductive films prepared at current densities of 1-2 mA cm⁻² for 4 hours. The resulting black shiny polymer films of polypyrrole/poly(phenyleneterephthalade propane sulfonate) (PP/PPTA-PS), ca. 150 μm in thickness, are quite strong though somewhat more brittle than poly(pyrrole tosylate). They are easily removed from the electrodes using a razor blade and exhibit four probe conductivities up to 1 Ω⁻¹ cm⁻¹.

One of the benefits of using a derivatized Kevlar dopant ion is the possibility of improving the thermal stability of the conductive polymer. TGA analysis under N₂ shows thermal stability of PP/PPTA-PS to greater than 300°C, with 90% weight retention to 400°C. This thermal stability is better than that observed for poly(pyrrole tosylate) as shown in Figure 2.

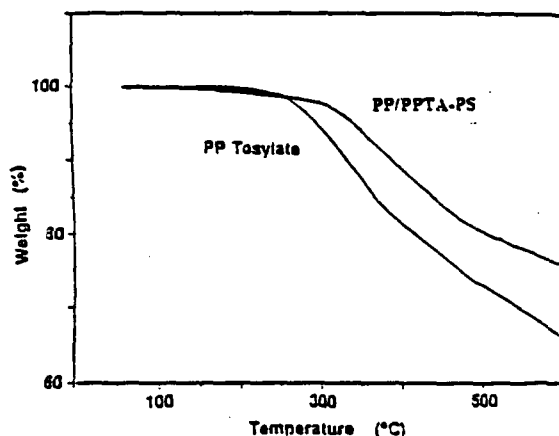


Fig. 2. TGA thermograms for PP/Tosylate and PP/PPTA-PS.

Electropolymerization/Deposition of Conductive Molecular Composites.

The electropolymerization/deposition of conductive polypyrrole films is generally accepted to proceed via an electrochemically activated step-growth coupling mechanism. The first step of this reaction is the oxidation of the monomer to give a radical-cation which may couple with another radical cation to form a dimer species. This dimer species can then lose two protons and rearomatize to yield a stable pyrrole dimer. The pyrrole dimer can be oxidized at lower potentials than that of the monomer and thus may participate in additional oxidation/radical coupling reactions to form oligomers and eventually polymer. Simultaneous incorporation of anions from the electrolyte, in this case polymeric anions, yield the resultant electrically conductive material having the general structure shown in Figure 3 for PP/PPTA-PS.

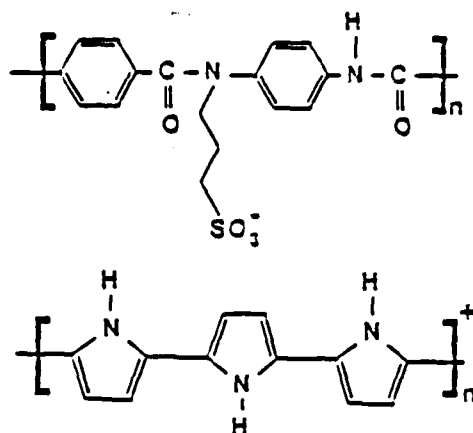


Fig. 3. General structure for PP/PPTA-PS.

In order to understand the effect of the chemical and electrochemical variables on composite formation and properties, we have utilized the EQCM. Our initial work in this area involved the electrosynthesis of poly(pyrrole tosylate) in acetonitrile and propylene carbonate.¹⁷ In this work we center on the formation of polypyrrole in the presence of sodium poly(styrene sulfonate) and PPTA-PS to form the conductive molecular composites we call PP/PSS and PP/PPTA-PS respectively.

A complete analysis of the deposition of PP/PSS shows the formation of nucleation sites in the early stages of deposition and subsequent three dimensional growth of the conducting surface phase. Electropolymerization efficiencies, measured by the effective *n*-value derived from Faraday's law, show approximately 2.35 electrons/pyrrole overall as expected when using applied potentials near that of the monomer oxidation potential. In the initial phases of electrodeposition we find the process to be overefficient. A large amount of mass is sensed by the EQCM per unit charge. This can be explained by the trapping of PSS chains in the PP/PSS nucleation sites as shown in Figure 4. As film growth continues these chains become completely embedded in the matrix and stoichiometric balance is attained. Similar results are seen for the deposition of PP/PPTA-PS.

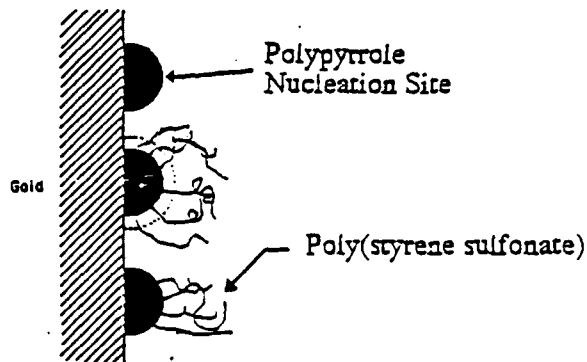


Fig. 4. Schematic of the nucleation sites formed on the electrode surface during the initial stages of pyrrole polymerization.

Chronogravimetry of PP/PSS.

The use of a polyelectrolyte, in which the dopant ion is bound to a polymer chain, closely associated with the polypyrrole matrix offers a means of preparing a system in which only one mobile species, the cation, is present. This ion specific behavior offers possibilities in the development of practical membranes as well as being an excellent model for use in detailed studies of electroactive and conducting polyheterocycle films. The use of PSS as the polyanionic dopant ion is attractive because it is chemically inert and contains an aromatic sulfonate as a pendant group on the polymer backbone. In addition, the polystyrene based polyanion system enhances the mechanical, and possibly, the morphological properties of the resulting films. The use of the EQCM gives us the unique ability to characterize and to identify the moving ionic species by the direction, magnitude and rate of the mass change associated with the redox switching of the electroactive polyheterocycle.

The films used to study the redox activity of the PP/PSS composite system were prepared by potentiostatic polymerization at 0.8 V (vs. Ag/Ag⁺) from an aqueous solution of 0.1M pyrrole and 0.1M Na⁺PSS⁻. The resulting films were then rinsed thoroughly with water to remove excess monomer and placed in a monomer free aqueous solution of Na⁺PSS⁻. To avoid overoxidation, the films were equilibrated at a rest potential (-0.25 V) below that of polymerization but higher than necessary to fully oxidize the polypyrrole. The potential was then stepped from the rest potential to a reductive potential at -1.0 V and subsequently returned. Again, both the chronocoulometric and chronogravimetric responses were monitored. The frequency/time response for a typical experiment for four consecutive potential steps are shown in Figure 5 and correlates well with the charge/time response.

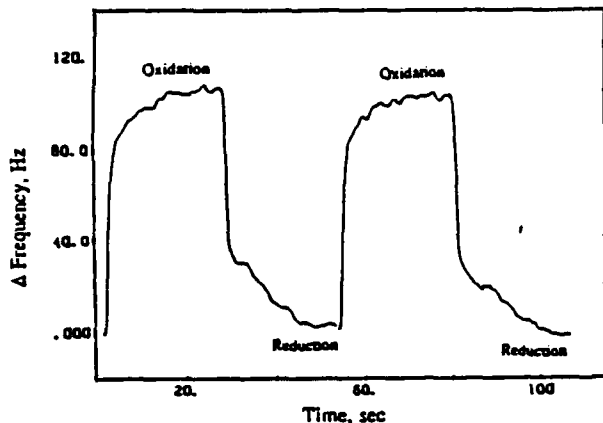


Fig. 5. The frequency vs. time response obtained from 4 consecutive potential steps on a 300 nm thick polypyrrole/poly(styrenesulfonate) composite film.

The frequency/time response shows that upon oxidation there is a mass decrease corresponding to the movement, or diffusion and migration of solvated Na⁺ ions out of the polymer film. The driving force for this movement is the necessity that the positive charge, created on the polypyrrole backbone through the removal of p-electrons, be stabilized by the styrene sulfonate anion units. This releases the Na⁺ from ionic interactions allowing them to leave the film. Upon the subsequent reduction, there is a mass increase associated with a movement of ions back into

the film in order to compensate the charge associated with the anionic styrene sulfonate sites which are no longer serving as dopant ions. The similar shape of chronogravimetric and chronocoulometric curves serves to demonstrate the analogous and complimentary information which can be obtained from these experiments as well as the relationship between the transport of charge and movement of ions in electroactive conducting polymers.

CONCLUSIONS

The electropolymerization of a heterocyclic monomer to a conducting polymer in the presence of a polyelectrolyte is a useful method for the formation of conductive blends or molecular composites. A range of properties can be attained via the chemical and electrochemical properties of the component polymers. In this work we have demonstrated improvement of thermal stability, using a thermally stable polyelectrolyte, and specific ion transport.

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