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Electrochemical Polymerization and Characterization of Conducting Copolymers from Pyrrole and PSCMS

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The electroactive copolymer of poly(styrene-co-chloromethylstyrene) and polypyrrole can be synthesized by the electrochemical polymerization using a polymer precursor which contains pyrrole moiety in its backbone. The polymer precursor was synthesized chemically with styrene-chloromethylstyrene copolymer and potassium pyrrole salt and characterized using FT-IR and ¹H-NMR spectroscopy.

Keywords: conducting copolymer; polypyrrole; potassium pyrrole salt.

INTRODUCTION

Conducting polymers and their derivatives have attracted the interest of many scientific researchers in recent years. These materials have wide range of applications^[1], such as plastic batteries, EMI shielding and anti-static materials. Although they have good electrical properties, most of them exhibit poor physical and mechanical properties. A lot of research groups studied composites of conducting polymers, but most of them lose their conductivity gradually by ageing^[2]. In this work, we attempted to prepare a copolymer of

poly(styrene-co-chloromethylstyrene) (PSCMS) and polypyrrole using a polymer precursor which contains pyrrole moiety in its backbone.

EXPERIMENTAL

The precursor matrix, PSCMS was copolymerized from styrene and chloromethylstyrene (with 5% and 10% feeds) using 2,2'-azobisisobutyronitrile (0.1 mol%) as an initiator in toluene for 36 hours at 75 °C under N₂ atmosphere, subsequently, the copolymer solution was precipitated by pouring it to methanol. Tetrahydrofuran (THF) solution of PSCMS added to the flask which contains potassium pyrrole salt^[3] in THF at -30 °C. The reaction was continued for 24 hours from -30 °C to room temperature under N₂ to obtain poly(styrene-co-pyrrolylmethylstyrene) (PSPMS).

Dichloromethane solution of PSPMS was spin coated on the Pt disc electrode. Constant potential was applied to the electrode. The electrolytic solution consisted of pyrrole monomer, LiClO₄, and a mixture solvent of acetonitrile and dichloromethane with varying composition ratios. A standard 3-electrode cell with SCE as a reference electrode was used. Overall scheme of this work was presented in Fig. 1.

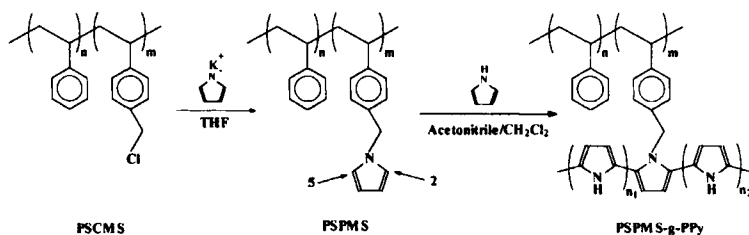


FIGURE 1 Overall experimental scheme.

RESULTS AND DISCUSSION

FT-IR spectra of polystyrene, PSCMS(10% of chloromethylstyrene feed) and PSPMS film were compared to identify the addition of pyrrolylmethyl group. PSCMS showed a peak at 1267cm^{-1} for chloromethyl group but PSPMS showed the reduced peak at 1267cm^{-1} and a new peak at 1081cm^{-1} due to the C-N bonds of pyrrolylmethyl group. This fact means that some of chloromethyl groups in PSCMS converted into pyrrolylmethyl groups. $^1\text{H-NMR}$ spectra of PSCMS(10%) and PSPMS are shown in Fig. 2. The peak at 4.4ppm indicated the presence of the chloromethyl groups and the peak at 4.9ppm indicated the existence of the pyrrolylmethyl groups. The integration of the area under each peak exhibited that 73% of chloromethyl groups have converted into pyrrolylmethyl groups, and the total content of pyrrolylmethyl groups in PSPMS was 8.0%.

Fig. 3. shows chronoamperograms of PSCMS, PSPMS(10%) and PSPMS(5%) at the constant potential of 0.8V. On considering the swelling and the electroactivity of PSPMS, the optimum dichloromethane content of acetonitrile and dichloromethane mixture solvent was 20%. In PSPMS(10%)

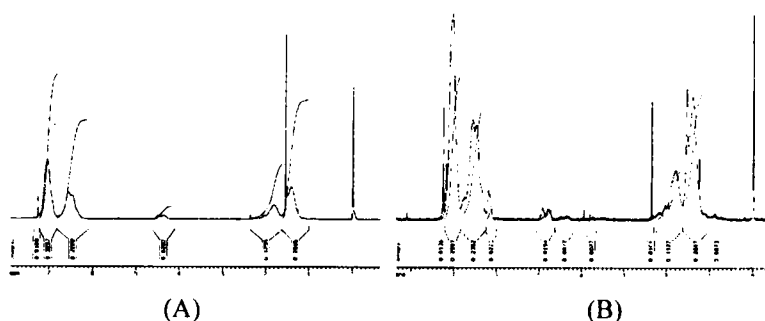


FIGURE 2 $^1\text{H-NMR}$ spectra of PSCMS (A) and PSPMS (B).

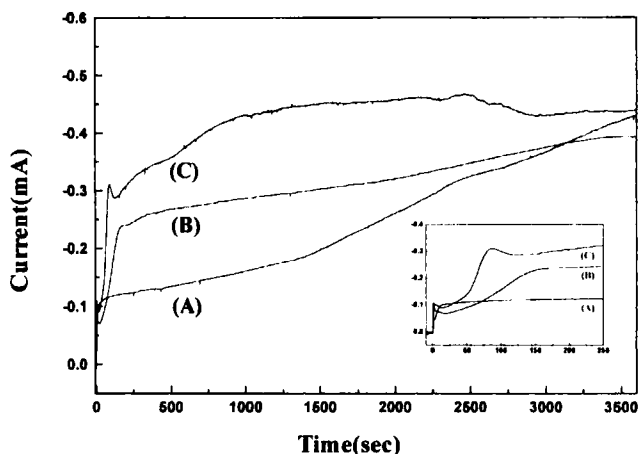


FIGURE 3 Chronoamperograms of PSCMS(A), PSCMS(5%)(B) and PSPMS(10%)(C).

and PSPMS(5%), the increasing rates of the current respond to the applied potential were fairly large compared with PSCMS at earlier stage (see insert of fig. 3.). This fact means that the pyrrolylmethyl groups in PSPMS film act as the nuclei of the growth of polypyrrole, and promote the polymerization of pyrrole at earlier stage.

Acknowledgment

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