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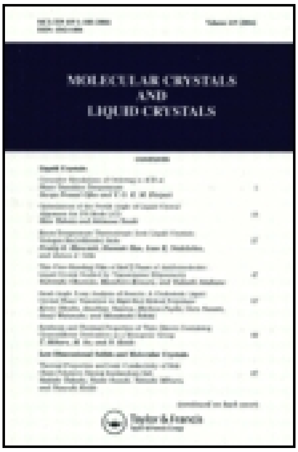

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Electrochemical Synthesis of Conducting Poly(methyl methacrylate-co-pyrrolylmethylstyrene)-g-Polypyrrole Copolymer

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Electrochemical Synthesis of Conducting Poly(methyl methacrylate-co-pyrrolylmethylstyrene)-g-Polypyrrole Copolymer

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The conducting poly(methylmethacrylate-co-pyrrolylmethylstyrene)-g-poly pyrrole (PMMAPMS-g-PPy) was synthesized by the electrochemical reaction with PMMAPMS and pyrrole in the electrolyte solution containing lithium perchlorate and a mixture solvent of acetonitrile and dichloromethane. The precursor PMMAPMS was synthesized by the reaction with poly(methyl methacrylate-co-chloromethylstyrene) (PMMCMS) and potassium pyrrole salt.

Keywords: conducting copolymer; polypyrrole; electrochemical polymerization.

INTRODUCTION

In recent years, there has been growing interest in conducting polymers because of their wide range of potential applications in the areas such as EMI shielding [1], electrochromic display devices[2], and so on. Electrochemically prepared polypyrrole(PPy) has limited practical applications due to its poor mechanical properties and processibilities. Recently, some methods to compensate these deficiencies have been reported. Synthesis of PPy composites[3,4] was an effective

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way to improve mechanical properties at the expense of electrical conductivity. Another way of improving mechanical properties was to synthesize PPy copolymer[5,6]. In other to compensate poor mechanical properties, we synthesized electrochemically a new conducting graft copolmer by using the precursor polymer, poly(methylmethacrylate-co-pyrrolylmethylstyrene)(PMMAPMS) which has excellent processibility.

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EXPERIMENTAL

Methyl methacrylate(MMA) and chloromethylstyrene(CMS) were purified by shaking in 5% aqueous NaOH, washing with distilled water, drying over $CaCl_2$, and finally distilling under reduced pressure. The initiator 2.2'-azobisisobutyronitrile(AIBN) was recrystallized from methanol. Pyrrole was dried over CaH_2 and distilled under reduced pressure before using. Acetonitrile and benzene were also dried over CaH_2 and fractionally distilled under nitrogen atmosphere. Dichloromethane and lithium perchlorate were used without further purification.

Poly (methylmethacrylate -co- chloromethylstyrene) (PMMACMS) was synthesized by copolymerizing MMA and CMS using 0.1 mol % AIBN in benzene for 36 hours at 60℃ under N_2 atmosphere. The synthesized copolymer was precipitated by pouring its solution to methanol. PMMAPMS was synthesized by adding THF solution of PMMACMS to the flask which contains THF solution of potassium pyrrole salt at –30℃ and the reaction was continued for 24 hours at room temperature under N_2 atmosphere. PMMAPMS dissolved in THF was spin coated on the platinum disc electrode and the graft copolymerization was carried out with 0.1 M pyrrole in the electrolytic mixture solution containing 0.1M $LiClO_4$ and a mixture solvent of acetonitrile (Ac) and dichloromethane (Dm). A standard 3-electrode cell with saturated calomel electrode as a reference electrode and Pt plate as a counter electrode was used.

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FT-IR spectrum was obtained using a Perkin Elmer 2000 FT-IR spectrophotometer and ^{1}H-NMR spectrum was acquired on a 500MHz ^{1}H-NMR spectrometer using DMSO as a solvent. Cyclic voltammetry was carried out using an EG&G model 273A potentiostat.

RESULTS and DISCUSSION

The formation of PMMACMS and PMMAPMS was characterized by FT-IR analysis. PMMACMS showed the absorption peak of benzene ring existing in CMS at 710cm-1. PMMAPMS showed the absorption peak of pyrrole ring at 721cm^{-1} and the absorption peak of C-N bonds of pyrrolylmethyl groups at 1084cm^{-1}. ^{1}H-NMR spectra of PMMACMS and PMMAPMS were also investigated. The presence of chloromethyl groups was identified by the peak at 4.7ppm in PMMACMS. The substitution of the chloromethyl groups into the pyrrolylmethyl groups was identified by the peak at 5.1ppm in PMMAPMS. The feasibility of electrochemical copolymerization of pyrrole with the precursor, PMMAPMS was tested by cyclic voltammetry.

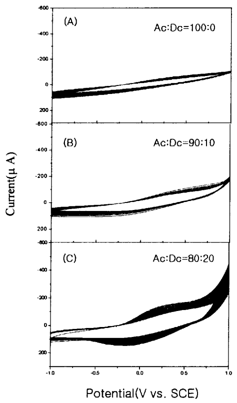

Fig 1. Cyclic voltammograms of PMMAPMS-g-PPy for various compositions of mixture solvent.

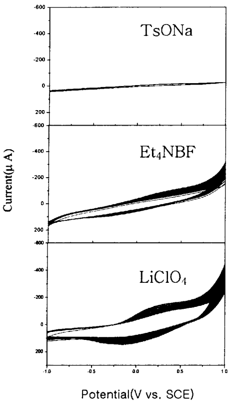

Fig 2. Cyclic voltammograms of PMMAPMS-g-PPy for various electrolytes.

Fig 1 shows the cyclic voltammograms according to the composition ratio of the mixture solvent of acetonitrile and dichloromethane in the preparation of PMMAPMS-g-PPy. As shown in Figure 1-(A), the redox current scarecely flows in Ac,

that is, the conductive copolymer has not been formed. But as the content of Dm in the mixture solvent increased, the redox current increased and the highest redox current was obtained in the mixture solvent of Ac:Dm = 80:20. However, in case that the content of Dm was over 20%, the copolymer film could not be obtained because of the dissolution of precursor PMMAPMS film. The rationalization of these results is given by the following arguments: as the content of Dm in the mixture solvent increases, the accessibility of pyrrole monomer to the pyrrolyl groups in the precursor film becomes much easier due to the structure loosening of the precursor film by Dm. Fig 2 shows the cyclic voltammograms for the electrochemical polymerization of pyrrole on PMMAPMS-coated Pt electrode by varying the type of electrolyte. In case of NaTsO, the flow of redox current is negligible. In case of Et_4NBF_4, the maximum redox current is lower than that in case of $LiClO_4$. A plausible explanation is that the movement of ClO_4- into the precursor film becomes more easier due to the smaller size of ClO_4- than these of BF_4- and TsO- and thus the higher redox current flows.

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