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Electrochemical Preparation of Polypyrrole Copolymer Films from PSPMS Precursor

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ABSTRACT: The electronically conductive copolymer of PSPMS-*g*-PPy (poly(styrene-*co*-pyrrolylmethylstyrene)-*g*-polypyrrole) was synthesized by the electrochemical method. In this copolymerization, a processable polymer film that has pyrrole moiety in its backbone was used as a copolymer precursor. The precursor was obtained by modifying PSCMS (poly(styrene-*co*-chloromethylstyrene)) with potassium pyrrole. ^{1}H NMR spectroscopic analysis indicated that 4.7% of the styrene units in the precursor have pyrrole substituents. Electrolysis of the spin-coated precursor film on platinum electrodes showed optimum copolymerization in a mixture electrolyte consisting of acetonitrile, dichloromethane (80:20 by volume), 0.1 M pyrrole, and 0.1 M lithium perchlorate. Constant potential electrolysis showed that pyrrole groups in the precursor were oxidized to form PPy; that is, they acted as grafting centers at which the PPy grew. SEM results and conductivity measurements supported the formation process of PPy copolymer. The maximum conductivity of the final products was in the range of 10^{-2} S/cm.

Introduction

Since the introduction of high electronic conductivity to the polymers, these materials have attracted significant interest and have become a popular basic material for advanced applications including plastic batteries, electrochromic displays, and sensors.[1−4] The doping-induced reversible changes in electrical and optical properties can be adopted for advanced optoelectronic applications. On the other hand, their characteristics as a conductor can be utilized for microchip circuits, electromagnetic interference shielding, and antistatic materials. A lot of research papers regarding these applications have been reported.[5,6] However, not many real applications are reported these days because these polymers exhibit poor physical and mechanical properties and are not soluble in common solvents. The recent work involving soluble PPy seems to overcome the solubility problems, but it still shows weak mechanical properties when it is in the conducting state.[7] In this view, composite formation or copolymerization of conducting polymers becomes a main issue in the applications of conducting polymers. Many research groups, including this group, suggested the composite formation method of conducting polymers and succeeded in improving the mechanical and physical properties.[8,9] However, most of these polymers lose their conductivity gradually by aging. Copolymerization could be an alternative in this regard, because the chemical bond between the matrix and the conducting polymer can solve the aging problem.[10]

In this work, we tried to show that the electrochemical method can be applied to polymer chemistry, especially to the copolymerization. The precursor preparation started with copolymerization of poly(styrene-*co*-chloromethylstyrene) (PSCMS) from styrene and chloromethylstyrene with 2,2′-azobis(isobutyronitrile) (AiBN). The chlorines in PSCMS were substituted with pyrrole using potassium pyrrole. The resulting product containing pyrrolyl groups was used for the precursor of the final copolymer PSPMS-*co*-PPy. The precursor polymer synthesized in this work is soluble to common organic solvents, and it can be fabricated into various shapes with reasonable mechanical properties. When the spin-coated precursor films are electrolyzed in the solution containing pyrrole monomers, the PPy is copolymerized at the pyrrolyl groups of the precursor. PPy is a well-known conducting polymer having simple structure, high electronic conductivity, long-term stability, and good applications, especially in copolymers with polypyrrole branches. An overall scheme of this work is presented in Figure 1.

Experimental Section

Styrene monomer and chloromethylstyrene monomer were purified by distillation under reduced pressure at 25 and 47 °C, respectively, after removing inhibitor with 5% sodium hydroxide solution and distilled water three times. The initiator AiBN was purified by recrystallization in methanol using an ice/salt mixture. Toluene, pyrrole, and acetonitrile were dried by distillation with calcium hydride. THF was distilled with sodium and benzophenone. Dichloromethane and lithium perchlorate were used without further purification.

The starting material PSCMS was synthesized as follows: A set of mixtures of styrene and chloromethylstyrene in different feed ratios were refluxed in toluene for 36 h at 75 °C under dried N_2 atmosphere. AiBN (0.1 mol %) was used as an initiator in this copolymerization reaction. After refluxing, the reacted solution was poured into methanol to make the product precipitate. Subsequently, the product was filtered and dried under vacuum for 24 h at 70 °C. This product was dissolved in $CDCl_3$ for NMR analysis. THF solution of PSCMS precipitate was directly added to a flask that contains potassium pyrrole salt in THF at −30 °C. The reaction was continued

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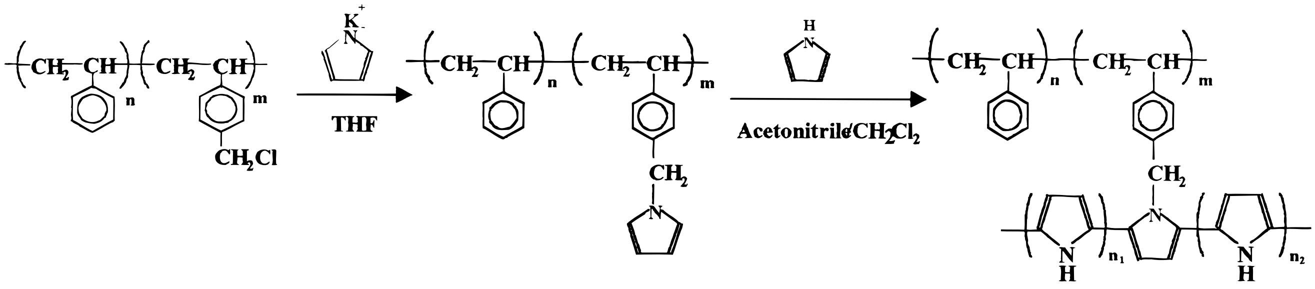

PSCMS PSPMS PSPMS-*g*-PPy

Figure 1. Overall preparation processes of polypyrrole copolymer.

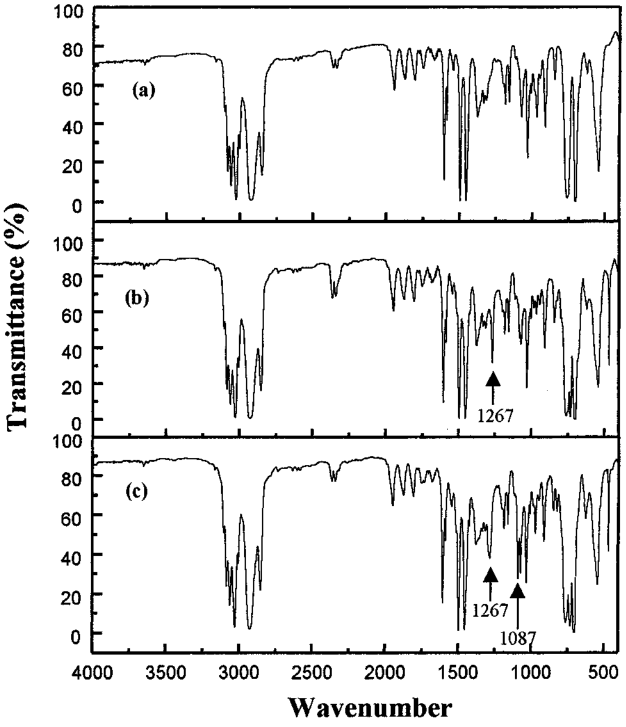

Figure 2. FT-IR spectra of polystyrene (a), PSCMS (b), and PSPMS (c).

for 24 h at room temperature under N_2 atmosphere to obtain PSPMS. The product solution was also poured into methanol to obtain PSPMS precipitate. The precipitate was filtered and dried under vacuum. The PSPMS was analyzed with FT-NMR. Samples for FT-IR were thin free-standing films prepared from toluene solutions.

A dichloromethane (DCM) solution of PSPMS was spin-coated on a platinum disk electrode. After dipping the electrode into solutions with different compositions of acetonitrile (ACN) and DCM, linear sweeping or constant potential was applied to the electrode. All electrolytic solutions contained 0.1 M pyrrole monomer and 0.1 M $LiClO_4$ as a supporting electrolyte. In this electrolysis, a standard three-electrode cell, without any cell partition, using a platinum plate counter electrode and a SCE as a reference electrode was employed. A potentiostat (EG&G 273A) was used for applying intended potential to the electrode. For comparison, the Pt electrodes covered with PSCMS films were electrolyzed in the same manner. Solubility of the copolymer film prepared at 0.85 V was examined using a solvent extraction technique. SEM images were obtained for the electrolyzed films after removal from the Pt electrodes. Conductivity was measured using a four-point probe with Keithley 236 source and measure unit.

Results and Discussion

The reaction products were identified by IR and NMR analysis. Figure 2 shows FT-IR spectra of polystyrene

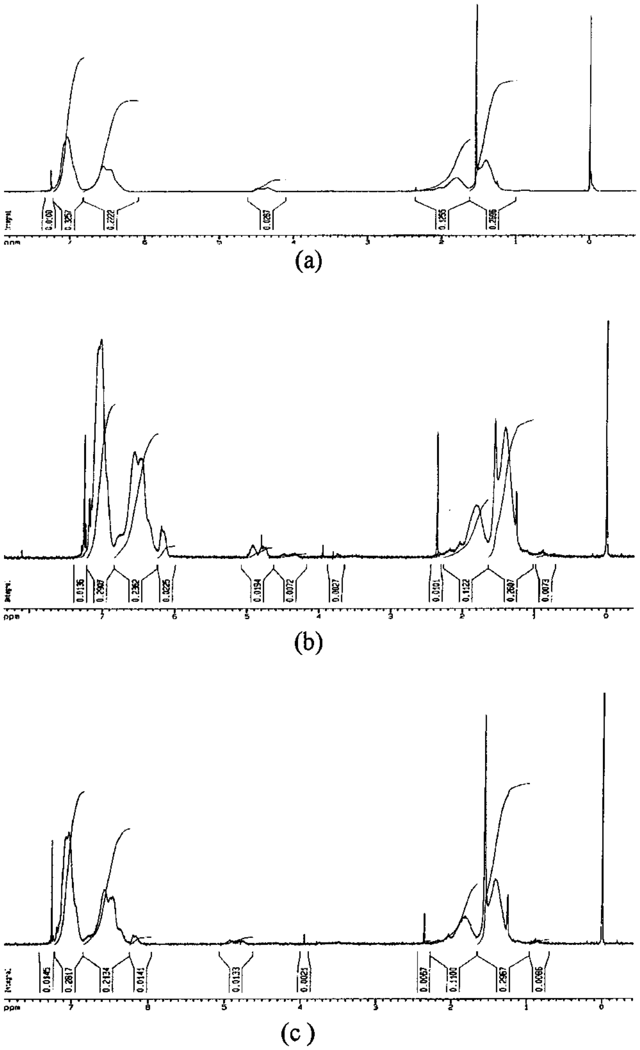

Figure 3. ^{1}H NMR spectrum of (a) PSCMS (monomer feed ratio; styrene:chloromethylstyrene = 9:1), (b) PSPMS (monomer feed ratio; styrene:chloromethylstyrene = 9:1), and (c) PSPMS (monomer feed ratio; styrene:chloromethylstyrene = 9.5:0.5).

film in (a), PSCMS (chloromethylstyrene, 10% feed) in (b), and PSPMS in (c). All of these spectra were obtained from solution-cast free-standing films. PSCMS shows a characteristic peak at 1267 cm^{-1}, ascribed to ν(C−Cl) of a chloromethyl group which has not appeared in polystyrene (a). PSPMS also shows the peak at the same position with lower intensity as in (c). A new peak has also appeared at 1081 cm^{-1} due to ν(C−N) of the pyrrolylmethyl group. This fact implies that a part of the chloromethyl groups in PSCMS converted into pyrrolylmethyl groups by the substitution reaction.

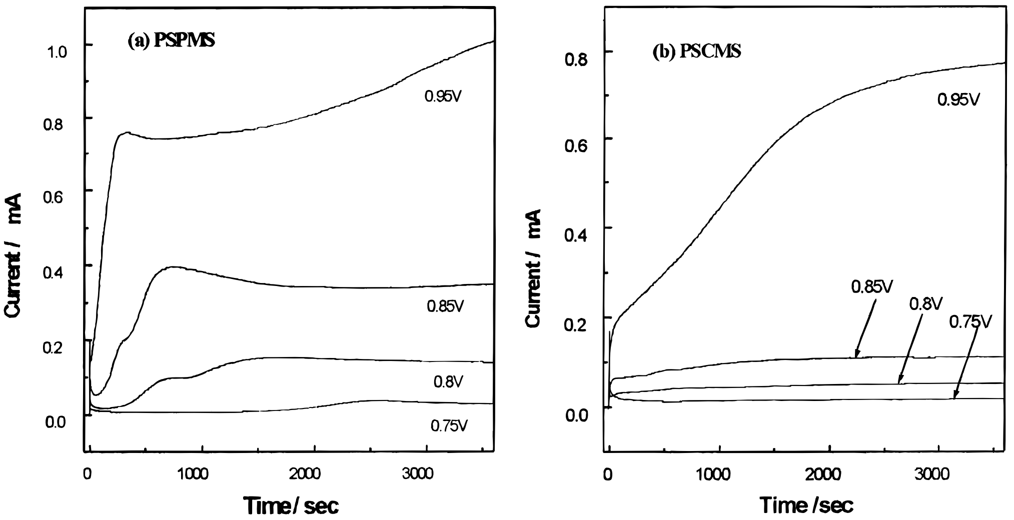

Figure 4. Chronoamperograms of pyrrole polymerization on the (a) PSPMS and (b) PSCMS-coated Pt electrode at the constant potential of 0.75, 0.8, 0.85, and 0.95 V.

Table 1. Result of Electrochemical Polymerization Current in Different Mixture Solutions (Potential Cycle between −1.0 and +0.9 V, at 50 mV/s)

mix. ratio (ACN/DCM)[a]	E_{pol} (mV)	E_{red} (mV)	E_{ox} (mV)	I_{pol} (μA)	I_{red} (μA)	I_{ox} (μA)
100/0						
90/10	575	−100	375	−50	24	−24
80/20	600	−150	350	−274	75	−87
75/25	600	−150	350	−475	112	−137

[a] ACN = acetonitrile, DCM = dichloromethane by volume ratio.

^{1}H NMR spectra in Figure 3 show the pyrrolyl substitution ratio clearly. The PSCMS (chloromethylstyrene, 10% feed) spectrum in (a) shows a pair of peaks at 4.4 ppm due to the resonance of protons on the chloromethyl group of PSCMS. This implies that 10.9% of all styrene units have chloromethyl groups. The spectrum shown in (b) was taken for the PSPMS obtained from PSCMS and potassium pyrrole. A pair of new peaks appear at 4.7 ppm which is attributed to pyrrolyl protons in addition to that of 4.4 ppm. The area ratio analysis gives 73% of all the chloromethyl groups were substituted with pyrrolyl groups. With these results we have deduced that only 8% of styrene units of PSCMS (chloromethylstyrene, 10% feed) have pyrrolyl groups. The NMR spectrum of PSPMS synthesized with PSCMS (chloromethylstyrene, 5% feed) is shown in (c). In this case all the chloride groups are substituted with pyrrolyl groups. The substitution ratio was calculated with the peak area at 1.4 and 1.8 ppm. It is identified that 4.7% of styrene units have pyrrolyl groups. The PSPMS (chloromethylstyrene, 5% feed) with 4.7% pyrrolyl substitution was used throughout the rest of this work, because this does not have any chloride in its structure.

The possibility of electrochemical polymerization of the precursor was tested with cyclic voltammetry. Potential cycles were applied to the platinum electrode covered with the precursor film, and the current information was obtained as in Table 1.

The precursor film is inactive electrochemically in ACN. So we have used several different mixture solvents, and the polymerization effect is compared in Table 1. We have chosen the mixture solvent of ACN 80/DCM 20 as an optimum electrolyte mixture solvent which provides the maximum polymerization current. The mixture solvent of ACN 75/DCM 25 provides more polymerization and redox current, but the precursor dissolves slightly in this solution. In the rest of this work, we adopted the ACN 80/DCM 20 mixture as an electrolytic solvent. In this solvent, the constant potential electrolysis of PSPMS and PSCMS films (20 μm thick) shows polymerization current responses as in Figure 4. The potential-dependent current transients of PSPMS are shown in (a). As the applied potential increased, the total current response increased. Each curve shows a quick decaying of initial charging current followed by an induction time; consequently, a current maximum and a plateau appear in a later step. This type of transient strongly implies that two different species are involved in the polymerization process. For example, after the induction time, the potential of 0.75 V is able to oxidize only the pyrrole species between Pt electrode and PSPMS film and makes the formation of PPy growing centers. As the growing centers expand and coalesce, the current reaches a maximum and decays as usual $t^{-1/2}$ behavior.[11] Potentials higher than 0.75 V are able to form the grafting centers at pyrrolyl groups of the precursor in addition to PPy formation at the interface region, and their transients show both a current plateau and a maximum. On the other hand, PSCMS transients in (b), except 0.95 V, show a broad maximum due to the formation of PPy at the interface. When the applied potential was increased to 0.95 V, PSCMS showed a very rapid increase of current because PPy has grown directly out of the film with this high potential. The formation of the copolymer using PSPMS precursor film was examined using solvent extraction technique. It was found that the weight difference between before and after 24 h extraction in DCM was hardly recognized for the copolymer film synthesized at 0.85 V.

Results from SEM and conductivity measurements support the above explanation. The SEM image in Figure 5A shows that PSPMS film prepared at 0.75 V has small black spots irregularly distributed underneath the film. When the potential is increased, the black spots of growing centers are formed at the interface and inside of the precursor. As the polymerization proceeds, the growing centers coalesce and grow further three-

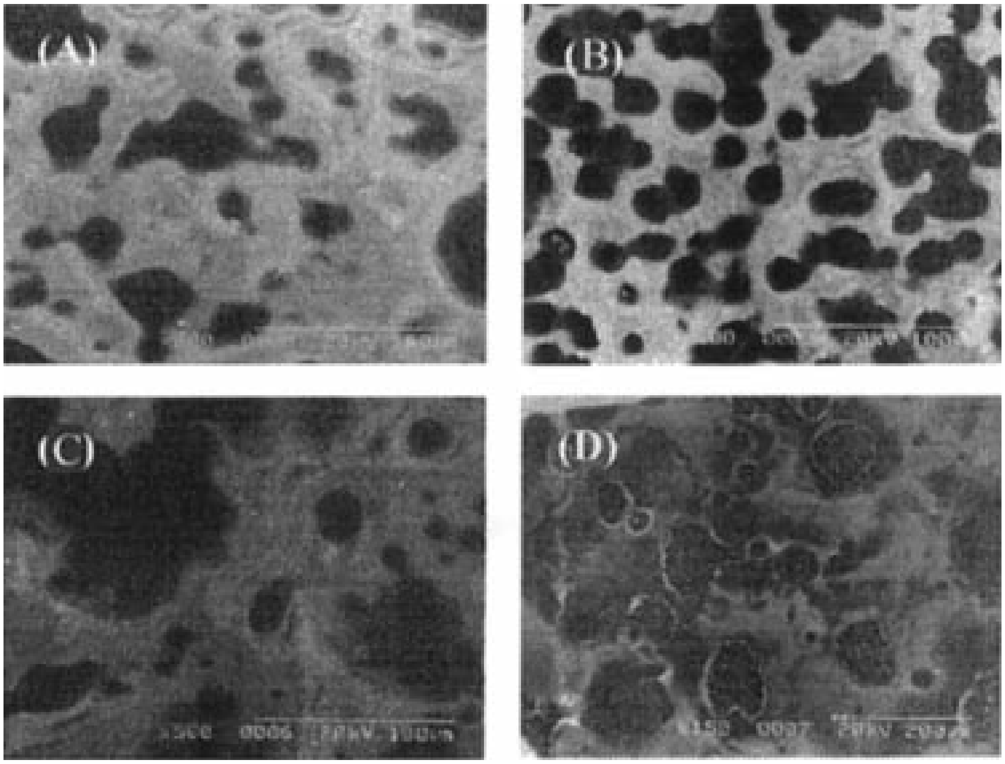

Figure 5. SEM images of samples prepared with (A) PSPMS at 0.75 V, (B) PSPMS at 0.85 V, (C) PSCMS at 0.8 V, and (D) PSCMS at 0.95 V.

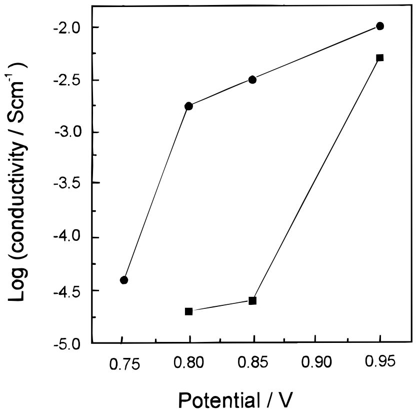

Figure 6. Solution side conductivity of the PSPMS (●) and PSCMS (■) at different electrolytic potentials.

dimensionally. On the other hand, the composite film prepared with PSCMS matrix films at 0.75, 0.8, and 0.85 V show the PPy centers at interfaces only as in (C). Applying the highest potential of 0.95 V to PSCMS induces PPy to grow directly out of the matrix films as in (D). This interpretation can be supported by the conductivity measurements.

The conductivity changes of the electrolyzed PSPMS and PSCMS are compared in Figure 6 as a function of polymerization potential. The conductivity in PSPMS increases abruptly at low potential region due to the existence of the copolymerized PPy. A comparable conductivity is developed only at 0.95 V in PSCMS, and this implies that PPy has been formed at the interface region only. The conductivity of electrode side is about 10 times greater than that of solution side.

Conclusion

We have prepared the PSPMS precursor which has pyrrole moieties in its backbone. The pyrrole content was controlled by the monomer feed ratio in PSCMS synthesis. Using PSPMS precursor film, copolymerized PPy was formed through the precursor film, resulting in a conductivity of around 10^{-2} S/cm. The SEM and conductivity measurements support a copolymerization process. In this paper we have demonstrated the electrochemical method can be used in graft copolymerization of pyrrole.

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