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Electrochemical Copolymerization of Pyrrole and Styrene

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ABSTRACT: A semiconducting pyrrole−styrene block copolymer film was electrochemically synthesized in nitromethane. The product polymer was confirmed to be a copolymer of pyrrole and styrene and not a composite or a blend of PPy and PSt through electrochemical, spectral, and dissolving experiments.

Introduction

Since metallic electric conductivity of iodine-doped polyacetylene was discovered,[1] conjugated polymers have received a great deal of attention because of their potential applications such as biosensors, electrochromic windows and displays, nonlinear optics, solid-state batteries, and semiconductor devices.[2−6] However, not many applications have been reported because of their poor mechanical properties and processability. In fact, most conjugated polymers are insoluble and nonfusible except for a few, such as poly(3-alkylthiophene)[7−9] and polyaniline.[10]

Several approaches have been taken to improve the mechanical properties and processability of conducting polymers and still exploit their electrical conductivity. A natural way is to introduce insulating polymers into them, because superb processability is one of the essential advantages of classical insulating polymers. This can be achieved by compounding, blending, and copolymerization.

To make composites or blends of conducting polymers and insulating polymers, conducting polymers have been incorporated into various matrix polymers. Electropolymerization, which has been used more widely than chemical oxidative polymerization, can be divided into two categories: one involving deposition of conjugated polymer within a polymer matrix deposited on an electrode surface and another involving the electropolymerization in the presence of a soluble polymeric electrolyte. Both methods succeeded in improving the mechanical and physical properties.[11−18] However, most of these composites and blends gradually lose their conductivity upon aging. Copolymerization could be a desirable alternative, because the chemical linkage between the matrix and the conjugated polymer can improve the aging properties.[19]

Copolymerization is often used to prepare a new polymer with properties different from homopolymers of the constituent monomers. Generally speaking, the physical and chemical properties of a copolymer are in the range of those of respective homopolymers but significantly distinct from those of a composite and a blend. Efforts have been made to combine the advantages of conjugated and insulating polymers by copolymerization. Galvin et al. reported first the synthesis of soluble styrene−acetylene block copolymer,[20] and since then several studies of the properties of that copolymer have been performed.[21−23] Francois et al. synthesized the block and graft copolymer of styrene and thiophene and found that that copolymer could depolymerize and yield polythiophene with a conductivity of 60 S cm^{-1}.[24] Li et al. grafted polyaniline onto poly(*p*-aminostyrene)[25] and obtained a copolymer, whose conductivity was in the range 0.01−1 S cm^{-1}. Graft and block copolymers of pyrrole and several kinds of insulating polymers also have been made[26−31] as well as the block copolymers of 3-hexylthiophene and styrene or methyl methacrylate.[32] However, the complicated synthesis methods and strict reaction conditions have limited the applications of these copolymers.

We carried out an electrochemical copolymerization of pyrrole and styrene directly on the surface of the electrode in nitromethane and obtained a satisfactory copolymer film.

Experimental Section

Chemicals. Pyrrole (Aldrich) and styrene were distilled under reduced pressure, and the distillates were collected at 70−71 °C (85 mmHg) and 83−84 °C (100 mmHg). Nitromethane had been dried for 24 h in the presence of anhydrous magnesium sulfate, filtered, distilled, and stored with activated molecular sieves. Bu_4NBF_4 was prepared from $NaBF_4$ and Bu_4NBr, recrystallized three times, and then dried under vacuum at 80 °C.

Electrochemical Experiments. Electrochemical polymerization and examinations were performed in a one-compartment, three-electrode cell with the use of a PARC M273 potentiostat under the control of a computer. To obtain a free-standing film, ITO glass plates (1 × 3 cm^2) were employed as working electrodes with a stainless steel sheets as counter electrode. Stainless steel electrodes were polished with abrasive paper (1200 mesh) and diamond paste (1.5 mm) and then cleaned in an ultrasonic acetone bath before use. Potentiostatic methods were utilized for electrochemical polymerization. Electrochemical measurements were carried out with a platinum disk (diameter 0.5 mm), polished, and cleaned as mentioned above before each experiment. All potentials were measured versus an Ag/AgCl (3.5 M KCl) reference. Nitromethane was used as the solvent and Bu_4NBF_4 (0.1 M) as the supporting electrolyte. Each solution was degassed by bubbling dry argon before the experiments, and a slight argon overpressure was maintained during the experiments.

Measurement of Conductivity. Having been washed well with acetone, the polymer films were stripped from the electrodes and dried under vacuum at room temperature. The conventional four-electrode cell was utilized to measure electrical conductivity of the films.

Spectroscopy Experiment. Washed and dried polymer films were ground with KBr and pressed into pallets for

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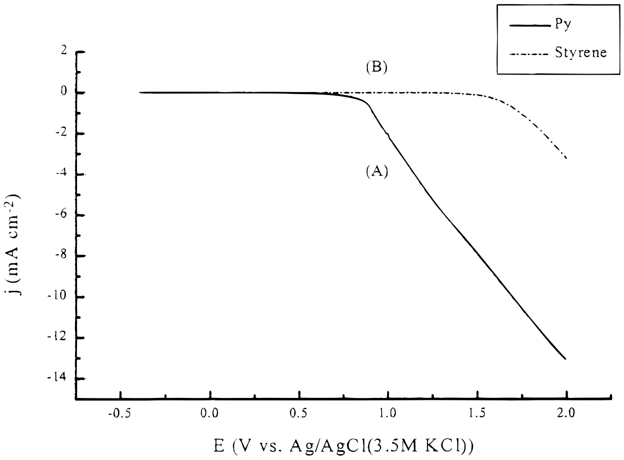


Figure 1. Anodic polarization curves of (A) 0.1 M pyrrole and (B) 1.0 M styrene both in nitromethane containing 0.1 M Bu_4NBF_4 at a scan rate of 10 mV s^{-1}.

vacuum transmission FT-IR measurements. The IR spectrometer is RFS-66V (Bruker).

DSC Experiment. The DSC curve was measured with a SDT 2960 simultaneous DTA-TGA instrument (TA Instruments).

Results and Discussion

Figure 1 shows the anodic polarization curves of pyrrole and styrene in nitromethane. When the anodic potential rises, pyrrole and styrene begin to polymerize at 0.9 and 1.8 V, respectively.

The IR spectrum of the product polymer prepared via potentiostatic deposition at 1.35 V from a pyrrole−styrene (1:10) nitromethane solution is shown in Figure 2B, compared with spectra of polypyrrole (PPy) and polystyrene (PSt). Figure 2C is the spectrum of PSt, which shows C−H stretching bands at 2849 and 2922 cm^{-1} and several benzene ring C−H stretching bands from 3000 to 3100 cm^{-1}. There is no strong band in the range 1000−1200 cm^{-1}. Figure 2A is the spectrum of PPy. There is no significant band between 2800 and 3100 cm^{-1}, but there are strong bands at 1084 and 1041 cm^{-1}, which are assigned to the in-plane deformation vibration of pyrrole ring. A skeletal vibration of pyrrole ring appears at 1544 cm^{-1}. In the spectrum of the product polymer, strong bands appear in the ranges 2800−3100 and 1000−1200 cm^{-1}, a skeletal vibration of benzene ring appears at 1601, 1493, and 1452 cm^{-1}, and a pyrrole ring skeletal vibration appears at 1544 cm^{-1}. This proves that the product polymer contained both styrene and pyrrole units.

If the electrochemical polymerization yielded a composite or a blend of PPy and PSt, the product polymer would not contain styrene units when the anodic potential is higher than the polymerization potential of pyrrole but lower than that of styrene. If a copolymerization induced by radical cations of pyrrole or its oligomer took place on the surface of the anode, the product should contain styrene units when the anodic potential is between the polymerization potentials of pyrrole and styrene. The potential applied in the experiment above (1.35 V) was far lower than the oxidation potential of styrene, so that polymerization of styrene could be initiated by the radical cations of pyrrole or its oligomer and form a copolymer. The product polymer cannot be a composite or a blend of PPy and PSt.

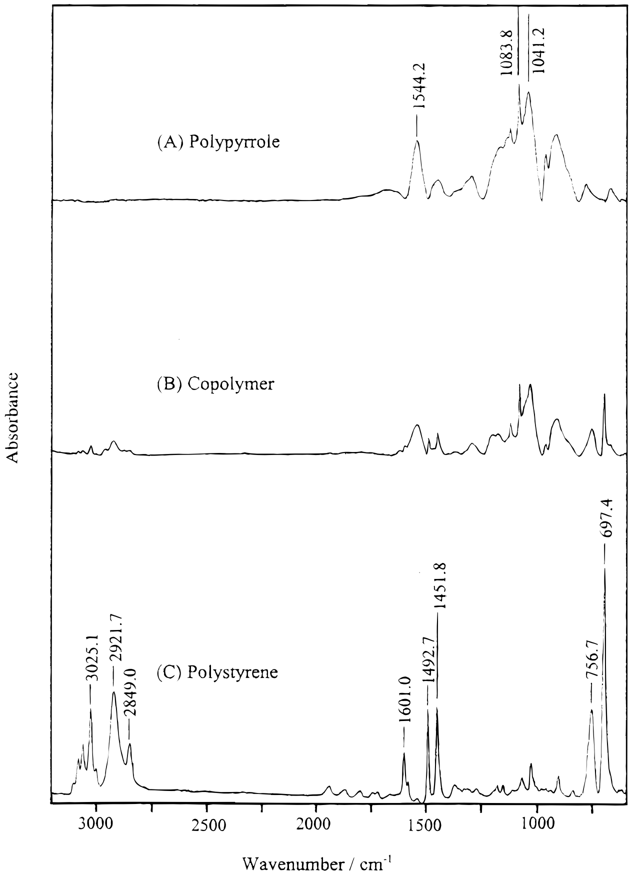


Figure 2. FT-IR spectra of polypyrrole, polystyrene, and pyrrole−styrene copolymer prepared all in nitromethane containing 0.1 M Bu_4NBF_4. (A) Polypyrrole: galvanostatic at 1 mA cm^{-2}, pyrrole 0.1 M. (B) Pyrrole−styrene copolymer: potentiostatic at 1.35 V, pyrrole 0.1 M and styrene 1.0 M. (C) Polystyrene.

After extraction with CH_2Cl_2 (a good solvent of PSt) for 2 days, the product polymer film prepared from pyrrole/styrene/nitromethane solution maintained its original form and did not dissolve perceptibly. The FT-IR analysis of the product before and after extraction did not show any change in the relative content of styrene units. Moreover, there was no PSt found in the CH_2Cl_2 after the extraction. All of these strongly suggest that the product is not a composite or a blend, but a copolymer.

The relative contents of pyrrole and styrene units of the product polymer at different polymerization potentials were studied, and the results are illustrated qualitatively in Figure 3. The 1084 cm^{-1} band assigned to C−H in-plane deformation vibration of pyrrole ring and the 697 cm^{-1} band assigned to C−H out-plane deformation vibration of monosubstituted benzene ring were utilized to compare the amount of pyrrole and styrene units. The intensity ratio of the 1084 cm^{-1} band to the 697 cm^{-1} band decreased when the polymerization potential rose from 1.2 to 1.8 V, which means that the population of pyrrole units fell off relative to that of styrene units.

Figure 4 is the DSC curve of the product polymer. There is a significant glass transition at 95 °C. PPy prepared electrochemically does not show glass transition due to the rigid chains and cross-linkage. Therefore, the presence of glass transition proved that the product polymer is not an alternating copolymer but a block copolymer with quite long PSt chains. According to

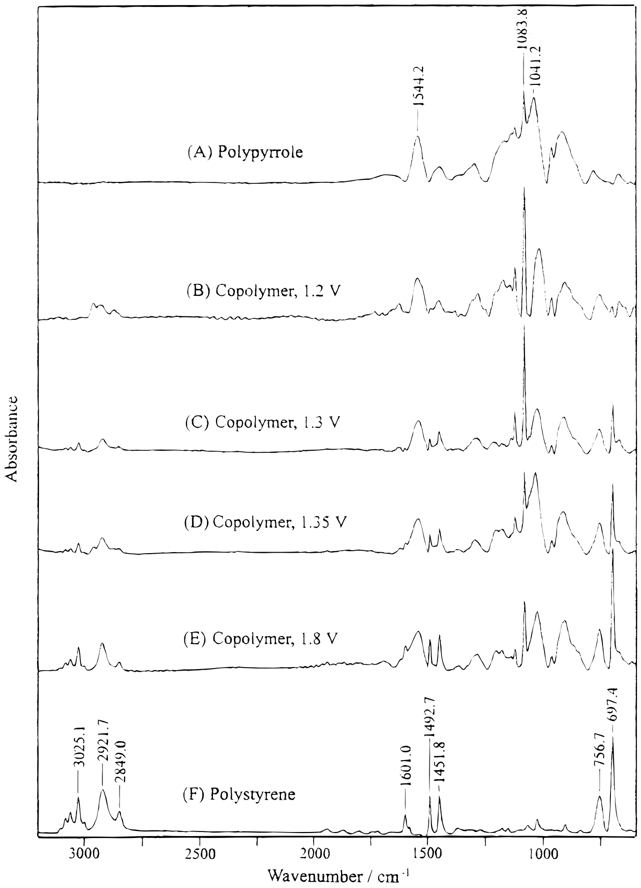


Figure 3. FT-IR spectra of PPy, PSt, and pyrrole−styrene copolymer prepared at different oxidization potentials in nitromethane containing 0.1 M Bu_4NBF_4. (A) PPy: galvanostatic at 1 mA cm^{-2}, pyrrole 0.1 M. (B−E) Pyrrole−styrene copolymer: potentiostatic at 1.2, 1.3, 1.35, and 1.8 V, respectively; pyrrole, 0.1 M; styrene, 1.0 M. (F) PSt = polystyrene.

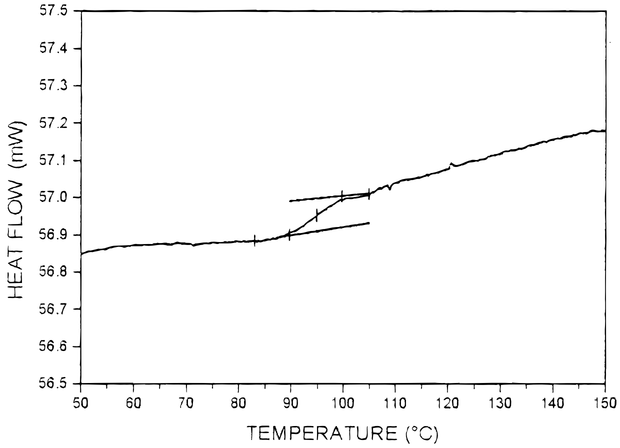
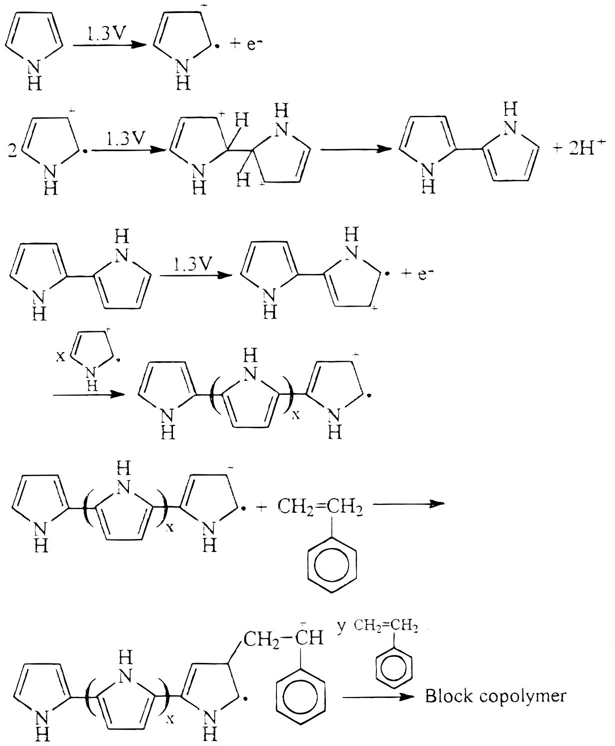


Figure 4. DSC curve of pyrrole−styrene copolymer prepared potentiostatically at 1.35 V from 0.1 M pyrrole and 1.0 M styrene in nitromethane containing 0.1 M Bu_4NBF_4.

available data of the dependence of T_g upon molecular weight, a T_g of 95 °C corresponds to a molecular weight of 3×10^4 of PSt.[33]

The possible mechanism of this electrochemical copolymerization of pyrrole and styrene in nitromethane has been studied and is illustrated in Scheme 1. It is generally known that electrochemical homopolymerization of pyrrole takes place and progresses through the formation of radical cations. Radical cations of pyrrole or its oligomer are the most likely species initiating the copolymerization. The monomer radical cations can react with a compound which forms a stable radical cations, i.e., a vinyl monomer with electron-donating substituents or/and a monomer with conjugated groups, e.g., styrene. Styrene molecules are attacked by radical cations of pyrrole or its oligomer and produce radical cation intermediates, which are stable because they are conjugated with the benzene rings. Monomers with electron-withdrawing substituting groups cannot be initiated by radical cations of pyrrole or oligomeric pyrrole. Electropolymerization of pyrrole in the presence of vinyl−acetic ester and acrylonitrile yielded no copolymer.

Scheme 1. Possible Mechanism of the Electrochemical Copolymerization of Pyrrole and Styrene in Nitromethane Containing 0.1 M Bu_4NBF_4



Properties of the solvent affect greatly the electrochemical copolymerization of pyrrole and styrene. A solvent with strong polarity and weak nucleophilicity is necessary. No copolymer was found when acetonitrile (a strong nucleophile with strong polarity) or dichloromethane (a weak nucleophile with weak polarity) was used as a solvent in the electropolymerization.

Our pyrrole−styrene copolymer was a free-standing film, and its composition and conductivity were found to vary with the ratio of pyrrole to styrene in the polymerization solution. When the concentration of styrene in the solution rose from 0.2 to 4.0 M while that of pyrrole was fixed at 0.1 M, the ratio of styrene units to pyrrole units in the copolymer increased from 1:7.5 to 5:1 and the conductivity decreased from 0.2 to 0.007 S cm^{-1}. Elemental analysis and conductivity data are listed in Table 1.

While having fair conductivity, the pyrrole−styrene copolymer films also displayed better mechanical properties and processability than those of polypyrrole. Further work on these films is in progress, and the results will be published in the near future.

Table 1. Composition (x^a) and Conductivity (σ) of Pyrrole−Styrene Copolymer Prepared Potentiostatically at 1.35 V in Nitromethane Containing 0.1 M Bu_4NBF_4

concn of monomers (mol L^{-1})		elemental analysis for the copolymers				
$C_{pyrrole}$	$C_{styrene}$	% C	% H	% N	x	σ (S cm^{-1})
0.1	0.2	48.53	5.03	11.17	7.5	0.2
0.1	0.5	57.66	5.38	8.67	2.1	0.1
0.1	2	82.79	7.28	2.63	0.24	0.01
0.1	4	85.04	8.24	2.13	0.19	0.007

[a] Composition of copolymer $[(Py)_xSt]_n$ calculated from the results of elemental analysis.

Conclusions

A semiconducting pyrrole−styrene block copolymer film was obtained successfully not via complex conventional synthesis paths but via convenient direct electrochemical polymerization. Through electrochemical, spectral, and dissolving experiments, the product polymer was shown to be a copolymer of pyrrole and styrene and not a composite or a blend of PPy and PSt.

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