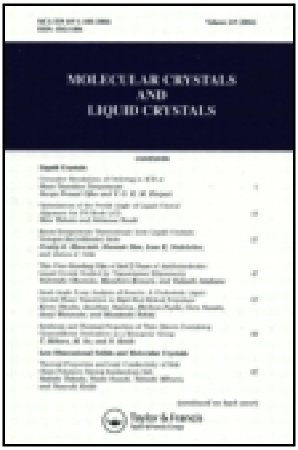

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Electrochemical Preparation of Conductive Copolymer Pvc-g-Ppy

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ELECTROCHEMICAL PREPARATION OF CONDUCTIVE COPOLYMER PVC-*g*-PPy

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Abstract A graft copolymer of polyvinyl chloride and polypyrrole, PVC-*g*-PPy, has been electrochemically synthesized. Potassium pyrrole was used to prepare the polymerization precursor PVC-Py. ^{1}H NMR data implies that every 27 repeating unit of the PVC has one pyrrole branch. The copolymer film was prepared by elctrochemical polymerization of pyrrole using the precursor film. This copolymer shows good electrochemical activity and maximum conductivity of 3.2 $(\Omega\ \mathrm{cm})^{-1}$.

INTRODUCTION

A group of organic polymers having conjugated double bond on their backbone is known as a conducting polymer class. The π-electron structure in this class allows the enhanced electric conductivity at a certain oxidation state. They have attracted so much research interest, mainly, because of their possible applications to electronic device such as redox switching devices, electrochromic displays, sensor applications, smart window, rechargeable batteries, and nonlinear optical materials [1-6]. The leading idea of these scenarios is based on the reproducible fast redox reaction of the π-electron system. Several chemical [7] and electrochemical [8] polymerization routes have been reported. The former is suitable for preparing massive product under controlled condition and the latter is good for preparing highly conductive and electrochemically active films. The advantages of the electrochemical method may be due to the finer morphology [9] which is very important in application systems.

In these days, real devices of conducting polymer are rarely found. One of the reasons is that good physical property and electrochemical activity are complementary each other. Some of recent studies show enhanced processibility of chemically synthesized conducting polymers using soluble chain attachment [10,11], blending [12],

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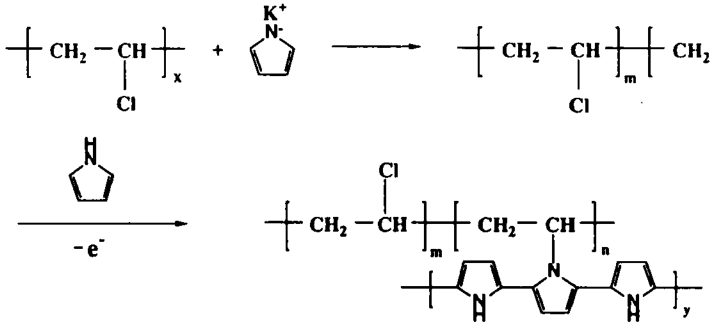
copolymerization[13]. These new systems, however, hardly show reproducible electrochemical activity, thus their applications are limited. A new method of preparing the material having electrochemical activity is necessary.

In order to make a conducting polymer having desirable mechanical properties and electrochemical activity, a graft copolymer system of polyvinyl chloride (PVC) and polypyrrole (PPy), PVC-*g*-PPy, was designed in this work. PVC is used for the matrix polymer in order to provide good mechanical properties. The route of the preparation of PVC-*g*-PPy is shown in scheme 1.



[Scheme 1]

In this article, we like to present the preliminary results of our experimental work of preparing polymer precursor and electrochemical preparation of PVC-*g*-PPy.

EXPERIMENTAL

Potassium metal (Aldrich, ACS) was used as received after removing mineral oil. Pyrrole (Aldrich, ACS) was purified by using Al_2O_3 column. Polyvinyl chloride (Aldrich, 18958-8) was purchased from Aldrich and used as received. THF (Mallinckrodt) was freshly distilled before use. Acetonitrile was distilled over CaH_2 before use and ACS grade lithium perchlorate was used without further purification.

Potassium pyrrole was synthesized by the reaction of pyrrole with potassium metal at -30C under nitrogen. Pyrrole is attached to PVC chain by the substitution reaction of the potassium pyrrole for the Cl of PVC in THF at -20C under nitrogen. IR spectrum of this product, PVC-Py, was obtained using Mattson 5000 FT-IR(Unicam) and NMR spectra were recorded using Unity 300MHz FT-NMR (Varian) spectrometer.

The precursor film was spin-casted on a Pt disc electrode with the surface area of

0.78 cm^2. After dipping the electrode into a pyrrole solution, the potential of the electrode was cycled between 1.0V and -1.0V using BAS 100W potentiostat. All the potentials in this article are based on a house made Ag/AgCl (saturated KCl) reference electrode. The counter electrode is a Pt plate with the surface area of 8cm^2. The electric conductivity of the product film was measured with a four-probe.

RESULTS AND DISCUSSION

Figure 1 shows IR spectrum of the reaction product, PVC-Py, compared to that of pyrrole and PVC. An absorption band at 3400cm^{-1} due to N-H vibration of pyrrole is disappeared and a new absorption band due to the C-N bond is appearing at 1066cm^{-1}.

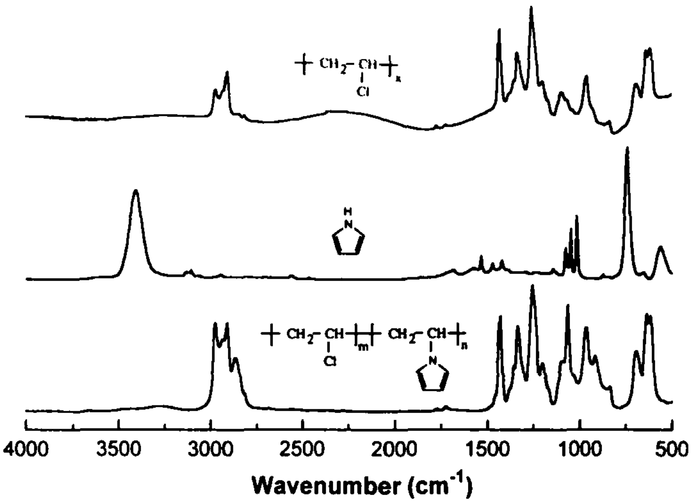


Figure 1. IR absorption spectra of PVC/KBr pellet, pyrrole liquid, PVC-Py/KBr pellet

Examination of these spectra tells that the chlorine of the PVC chain was substituted with the potassium pyrrole resulting in a new C-N bond formation. The substitution ratio was calculated from ^{1}H NMR spectrum shown in figure 2. In order to prepare a sample for NMR spectrum, 15 mg of the product were dissolved in 1 ml duterated THF. ^{1}H NMR spectrum of PVC-Py shows a new doublet peak at δ=6 which is due to the olefinic site of pyrrole. Simple algebraic calculation of integrated area for each proton indicates that every 27 PVC repeating units has one pyrrole unit.

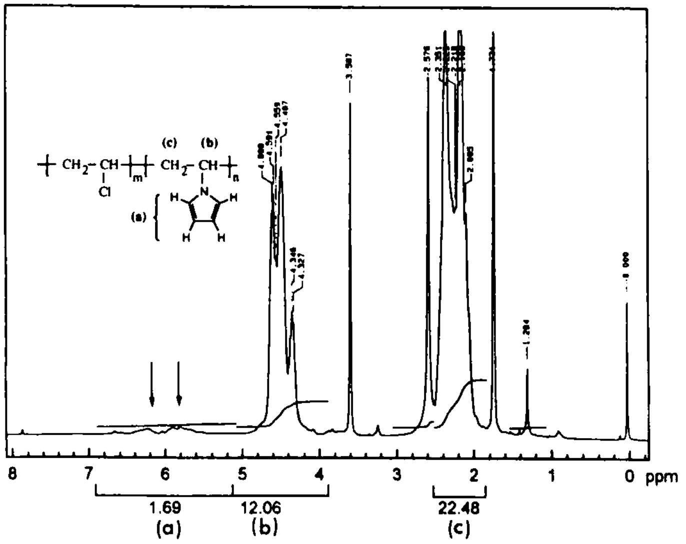


Figure 2. NMR spectrum of the precursor PVC-Py

The product of the reaction was purified by repeated precipitation into methanol to remove any unreacted pyrrole moiety. The purified PVC-Py was dissolved in THF (8 wt %) and spin-casted at 3000 rpm on the platinum electrode described earlier. In order to prepare PVC-*g*-PPy, the electrode subsequently dipped into an acetonitrile solution of 0.1M lithium perchlorate and 0.1M of pyrrole monomer. After 10 min, The potential of the electrode was cycled between -1.0V and 1.0V. Figure 3 shows polymerization cyclic voltammograms (CV) for PVC-Py covered electrode in (a) and PVC covered electrode in (b). The films were ca. 0.8 μm thick. The potential scan rate was 50 mV/sec for both electrodes. Both CV's show well developed redox peak pairs during the potential cycling. CV in (b) shows large monomer oxidation current response at 0.9Vfor the initial scan which is getting smaller for consequent scans. This may be due to depletion of monomer which have diffused into the PVC film. The CV also shows a redox peak pair at -0.25V responsible for the redox reaction of small amount of polypyrrole adsorbed on the electrode. The decreasing in monomer oxidation rate coincides with the change of growing rate of the redox peak at -0.25V, because the polymer formed at 0.9V is to be reduced at -0.25V and oxidized at the same potential on the next scan. In other words, the growing rate of the redox current response of the polymer is getting smaller and has almost constant value after 9th cycle. The decrease in current of pyrrole monomer at 0.9V suggests that the monomer can not diffuse into the matrix PVC film in this time scale. Only the monomers near the electrode surface have chance to be electropolymerized and adsorbed on the platinum electrode surface.

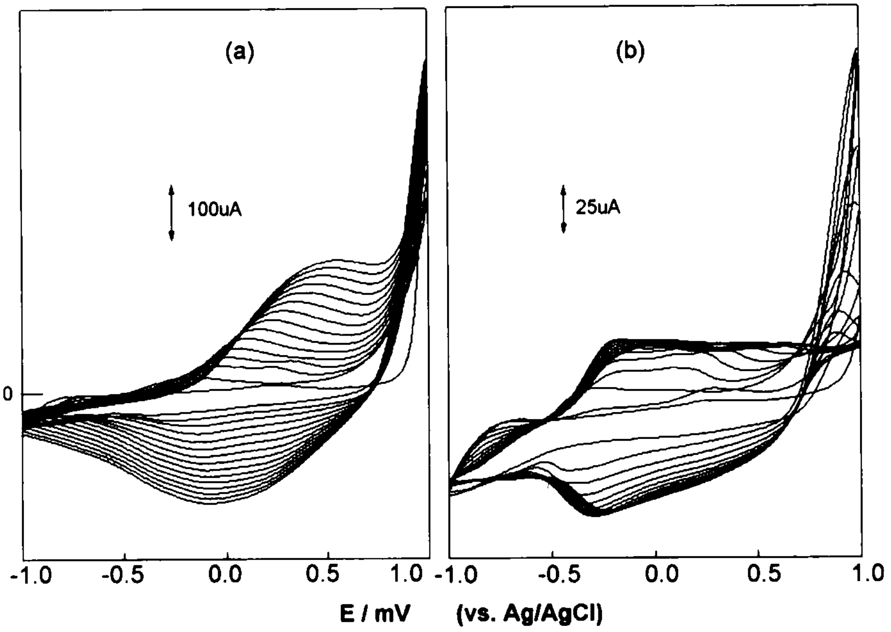


Figure 3. Polymerization CV's (a) precursor PVC-Py, (b) PVC on Pt electrodes

On the other hand, the CV in (a) shows the formation of PVC-*g*-PPy. The oxidation current of pyrrole monomer at 0.9V is growing as the cycling proceeds. This is a similar behavior of pyrrole polymerization on bare Pt electrode except the appearence of small oxidation peaks at 0.25V for first four scans[14]. Because pyrrole moieties in the PVC matrix start to be oxidized for polymerization. A redox peak pair of polymerized product is also appearing at about -0.2 V. The peak has broad shape and its position is shifted to higher potential region. The polymerization current is growing continuously as the potential cycling proceeds. The shifting implies that the PPy formation is started at the pyrrole moieties at the inner side of the matrix film. As the polymer grows the ohmic conduction occurs between the electrode and the pyrrole moieties at outer side of the matrix so that polymerization rate continuously increases for the consequent potential cycles. In this way the polypyrrole is grafted to the PVC matrix chain[15]. The final PVC-*g*-PPy polymer are easily peeled off the electrode and used for conductivity measurements. The four-probe methode produces maximum value of 3.2 $(\Omega cm)^{-1}$.

CONCLUSION

We have shown the electrochemical method of copolymerization of PVC-*g*-PPy as a conducting polymer which carries an improved mechanical properties in addition to its original functions. This copolymer also shows better electrochemical activity compared to that of simple PVC/PPy composite. The measured conductivity is 3.2 $(\Omega cm)^{-1}$. which is ca. 10 times higher than that of the composite. This may be an important implication to the device application of conducting polymers. Further investigation about this system is continuing in this laboratory

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