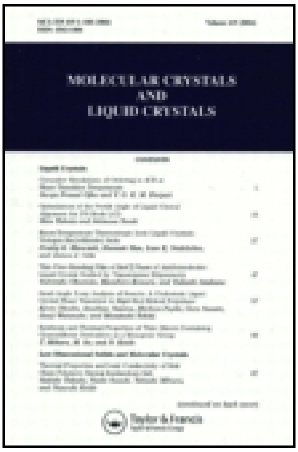

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Electrochemical Polymerization and Characterization of Conducting Copolymers from Pyrrole and Poly(acryloyl chloride)

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Electrochemical Polymerization and Characterization of Conducting Copolymers from Pyrrole and Poly(acryloyl chloride)

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The electroactive copolymer of poly(acryloyl chloride)(PAC) and polypyrrole(PPy) was synthesized by the electrochemical polymerization using a polymer precursor which contains pyrrole moiety in its side chain. Poly(acryloyl pyrrole)(PAP) was synthesized by the addition polymerization of monomer obtained by the reaction with acryloyl chloride and potassium pyrrole salt and characterized using FT-IR and ^{1}H-NMR spectroscopy. The electrochemical property and morphology of PAC-g-PPy copolymer was investigated comparing with those PAC/PPy composite.

Key words: conducting copolymer; polypyrrole; Chronoamperogram

INTRODUCTION

Conducting polymers and their derivatives have attracted the interest of many scientific researchers in recent years. These materials have wide range of applications[1,2], such as plastic batteries, Light Emitting Diode(LED), EMI shielding. Although they have good electrical properties, most of them exhibit poor environmental stability, brittleness, low elongation, and poor processibilities[3]. In order to improve these problems, the modification of the monomers[4] of conducting polymers or the synthesis of composites[5] and copolymers[6] is reported.

In this work, the authors have prepared a new conducting graft copolymer of poly(acryloyl chloride)(PAC) and polypyrrole(PPy), PAC-g-PPy, by using a precusor polymer, poly(acryloyl pyrrole)(PAP) which is processable and has desirable mechanical properties.

EXPERIMENTAL

PAC was synthesized as follows: 2,2'-azobisisobutyronitrile(AIBN) as an initiator was added into the 2-neck flask which contains THF solution of acryloyl chloride. The reation was continued for 1 hour at 70℃. PAP was synthesized as follows: THF solution of acryloyl chloride was added to a flask which contains THF solution of potassium pyrrole salt at 0℃. The reaction was continued for 4 hours at room temperature. After AIBN was added, the reaction was continued for 8 hours at the temperature of 70℃. All reactions were carried out under nitrogen atmosphere. The product solution was poured into ether for the precipitation of PAP. DMF solution of PAP was spin-coated on a platinum disc electrode and the precursor polymer was electrochemically graft-copolymerized on PAP coated electrode in the electrolytic mixture solution consisting of acetonitrile as a solvent, 0.1M pyrrole monomer, and 0.1M lithium perchlorate as a supporting electrolyte. In this electrolysis, a standard 3-electrode cell was used without any cell partition with a platinum plate as a counter electrode and a saturated calomel electrode as a reference electrode.

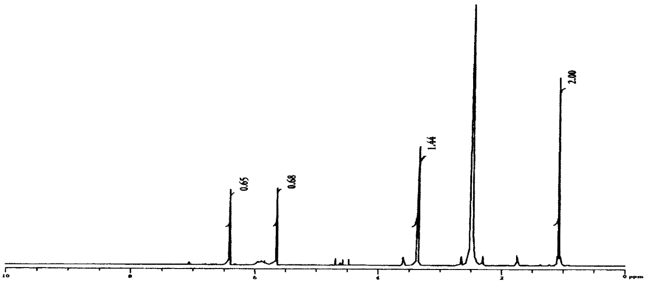


FIGURE 1 ^{1}H-NMR spectrum of PAP

RESULTS AND DISCUSSION

Synthesized PAC showed characteristic peaks at 740cm^{-1} responsible for ν(C-Cl) and 1780cm^{-1} responsible for ν(C=O). But PAP showed the peak at 740cm^{-1} responsible for ν(C-Cl) with decreased intensity and a new peak has also appeared at 1066cm^{-1} due to ν(C-N) of pyrrolyl group. This fact implies that a part of chloride in PAC converted into pyrrolyl group by the substitution reaction.

^{1}H-NMR spectrum of PAP in Figure 1 shows the pyrrolyl substitution ratio clearly. The peak at 1ppm indicates the presence of the proton in backbone and a pair of peaks at 5.6ppm indicate the existence of the pyrrole. From the area integration under the peaks the total content of pyrrolyl groups in PAP was calculated to be 34%.

Figure 2 shows chronoamperograms of PAC/PPy composite and PAC-g-PPy copolymer that were synthesized with pyrrole for 1 hour under the constant potential of 0.80V using PAC and PAP as matrix film, respectively. when we use PAP as a matrix film, the oxidation current flows much more and the copolymerization occurs more rapidly compared to the homopolymerization of pyrrole in PAC matrix film. This fact means that the pyrrolyl groups in PAP film act as the nuclei of the growth of polypyrrole, and promote the polymerization of pyrrole at earlier stage.

Figure 3 shows the atomic force microscopes(AFMs) of PAC-g-PPy copolymer and PAC/PPy composite films which were synthesized for 1 hour under a constant potential of 0.80V. In case of PAC/PPy composite, RMS value was measured to be 52.854nm and in case of PAC-g-PPy copolymer film, 0.687nm. It is noted that the scale of Z axis

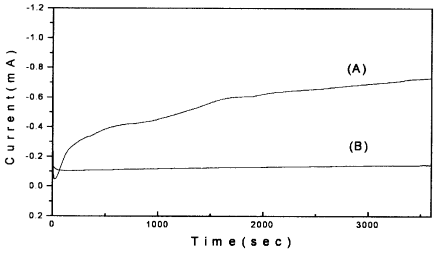
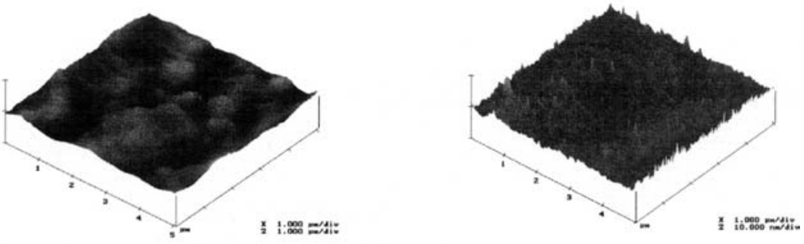


FIGURE 2 Chronoamperograms of (A)copolymer and (B)composite



(A) (B)

FIGURE 3 AFMs of (A)composite and (B)copolymer

of copolymer in Figure 3-(B) is magnified by 100 times of that of composite in Figure 3-(A). As a result, we could know that PAC-g-PPy copolymer film has more smooth surfaces compared with composite film.

Acknowledgements

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