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Synthesis and Electrochemical Properties of Poly(vinyl carboxy ethyl ether)-g-poly(pyrrole) Copolymer

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A novel conducting graft copolymer (PVCEE-g-PPy) of poly(vinyl carboxy ethyl ether) (PVCEE) and polypyrrole (PPy) was prepared by electrochemical polymerization of pyrrole using a precursor, poly(vinyl pyrrolyl propanone ether) (PVPPE). For synthesis of the graft copolymer, PVCEE was first synthesized by reacting poly(vinyl alcohol) with 3-chloro propionic acid. The precursor PVPPE for PVCEE-g-PPy was then synthesized from PVCEE. The chemical structures of PVCEE and PVPPE were confirmed by FT-IR spectroscopy and ^{1}H-NMR. Electrochemical properties of the novel conducting graft copolymer were compared with those of the PVCEE/PPy composite using cyclic voltammetry (CV) and chronoamperometry (CA). It was confirmed that the pyrrolyl group of the precursor polymer can act as the nuclei for the graft polymerization of pyrrole into PVPPE.

Keywords: conducting graft copolymer; electrochemical polymerization; electrochemical properties; polypyrrole

1. INTRODUCTION

In recent years, conducting polymers have attracted interests of many researchers, since they have been applied to various fields such as in chemical sensor [1], light emitting diode [2], EMI shielding [3], electrochromic display device [4], rechargeable battery [5,6], photovoltaic cell etc. [7]. Conducting polymers have good electrical properties, but usually have poor environmental stability, physical properties, and

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processibility. To overcome these defects, various methods to reform the monomers of the conducting polymers or to synthesize copolymer [8,9] and composite [10] have been reported.

We have prepared a novel conducting graft copolymer (PVCEE-g-PPy) of poly(vinyl carboxy ethyl ether) (PVCEE) and polypyrrole (PPy), which is expected to show high electrochemical activities. Chemical structures of PVCEE and PVPPE were confirmed by FT-IR spectroscopy and ^{1}H-NMR. The electrochemical properties of the novel conducting graft copolymer were compared with those of PVCEE/PPy composite using cyclic voltammetry (CV) and chronoamperometry (CA).

2. EXPERIMENTAL

Chemicals

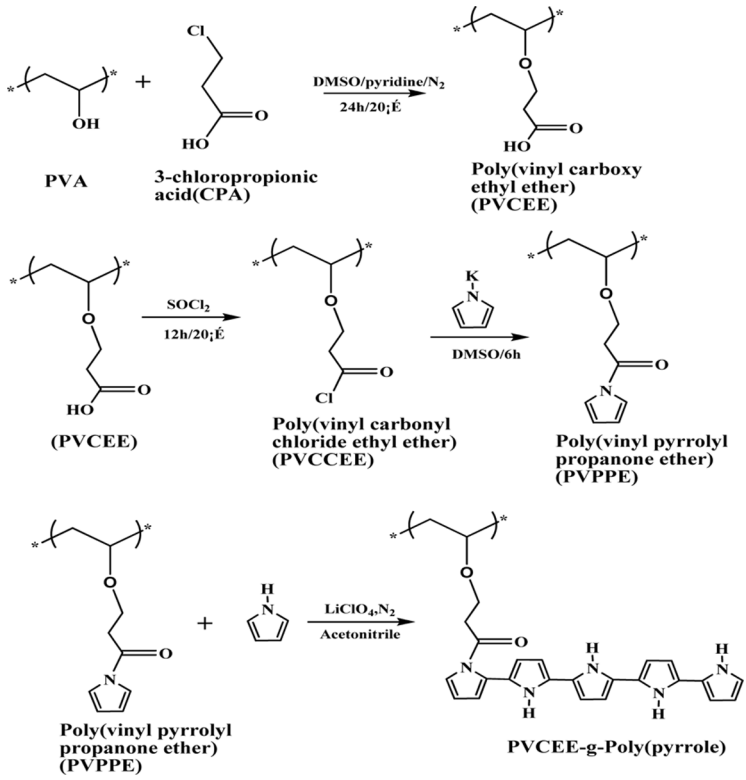
Pyrrole (Aldrich) and dimethyl sulfoxide (DMSO) (Aldrich) were dried over CaH_2 and distilled under reduced pressure. Poly(vinyl alcohol) (PVA) with the molecular weight of 50,000 g/mol (Aldrich) was used without further purification and potassium hydride (Aldrich) was used after removing mineral oil. Other chemicals were purchased from Aldrich and used without further purification.

Synthesis of PVCEE-g-PPy

PVCEE-g-PPy was synthesized following procedures as shown in Scheme 1.

PVCEE was first synthesized by reacting PVA with 3-chlolo propionic acid (CPA) for 24 hrs at room temperature under N_2 atmosphere in DMSO. PVCEE was precipitated by pouring the solution to methanol/water mixture solution. The precipitate was filtered and dried at 80°C under vacuum.

The precursor polymer, poly(vinyl pyrrolyl propanone ether) (PVPPE), was synthesized as following two steps from PVCEE. Poly (vinyl carbonyl chloride ethyl ether) (PVCCEE) was synthesized by reacting PVCEE with $SOCl_2$ for 12 hrs at room temperature under N_2 atmosphere in DMSO. The PVCCEE solution was then added to a flask which contains potassium pyrrole salt solution in DMSO at room temperature. The reaction was continued for 8 hrs at room temperature under N_2 atmosphere. PVPPE powder was obtained by precipitation in methanol and drying at 60°C under vacuum. The chemical structures of PVCEE and PVPPE were characterized using FT-IR (Perkin-Elmer, Spectrum 2000) and ^{1}H-NMR (Varian, 500 NB) spectroscopies.



SCHEME 1 Synthetic route to PVCEE-g-PPy.

PVCEE-g-PPy was finally synthesized on an electrode coated with PVPPE by applying intended potential using potentiostat (EG & G 273 A) in the electrolyte solution consisting of 0.1 M pyrrole monomer and 0.1 M lithium perchlorate in acetonitrile. In this electrolysis, a standard three-electrode cell was employed, where a square-type ($1 \times 1\,cm^2$) platinum working and counter electrodes and an Ag/AgCl reference electrode were used. The applied potential range for electrochemical polymerization was $-2 \sim 2\,V$ (vs. Ag/AgCl) and the scanning rate was 50 mV/sec. Electrical conductivity was measured by a four-probe method (Fluke, Model 73 III Multimetry).

3. RESULTS AND DISCUSSION

Figure 1 shows the FT-IR spectra of (a) PVCEE and (b) PVPPE. As shown in Figure 1(a), appearance of the peak at 1030–1080 cm^{-1} is

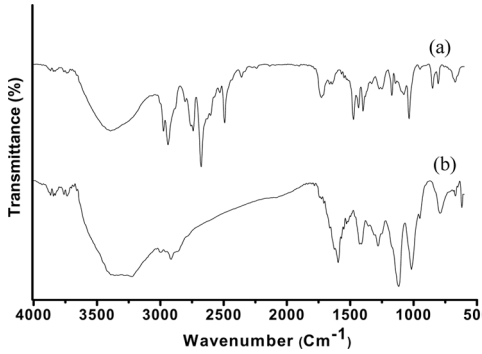


FIGURE 1 FT-IR spectra of (a) PVCEE and (b) PVPPE.

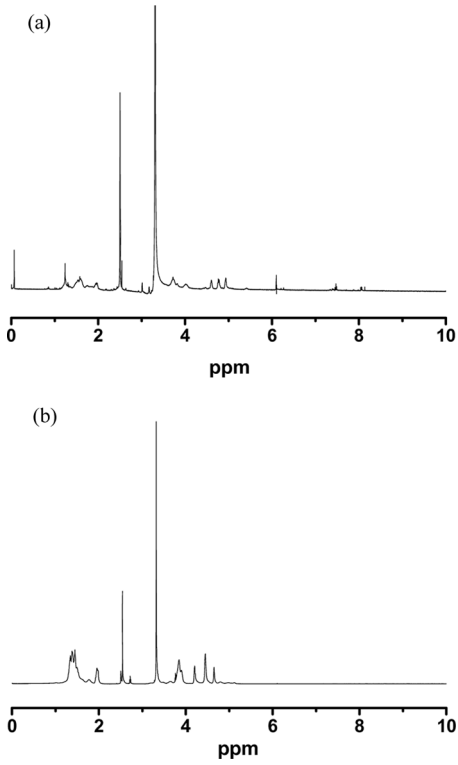


FIGURE 2 ^{1}H-NMR spectra of (a) PVCEE and (b) PVPPE.

due to ether bond of C−O−C, confirming synthesis of PVCEE by etherification between OH group of PVA and Cl of 3-chloropropionic acid. In Figure 1(b), the peaks at 1580–1630 cm^{-1} and 1130–1190 cm^{-1} are due to C=C and C−N stretch of the pyrrolyl group, respectively. This indicates PVPPE was synthesized with the desired structure. Figure 2 shows the ^{1}H-NMR spectra of (a) PVCEE and (b) PVPPE. In Figure 2(a) the peak at 7.5–8.5 ppm due to proton of O−H could be observed. However, in Figure 2(b), the peak at 7.5–8.5 ppm disappeared and a new peak at 4.2 ppm due to protons of pyrrolyl group appeared. These NMR results also confirm the desired chemical structure of PVPPE.

Figure 3 shows the cyclic voltammograms obtained during the preparation of PVCEE/PPy composite and PVCEE-g-PPy copolymer with

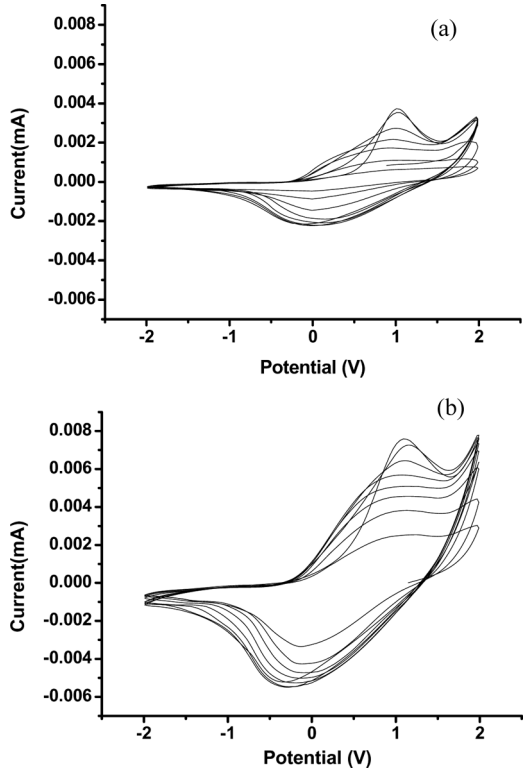


FIGURE 3 Cyclic voltammograms of (a) PVCEE/PPy composite and (b) PVCEE-g-PPy copolymer in 0.1 M pyrrole and 0.1 M lithium perchlorate electrolyte solution in acetonitrile at 50 mV/s scan rate.

0.1 M pyrrole and 0.1 M lithium perchlorate in acetonitrile. It can be seen in Figure 3 that the current peaks of PVCEE-g-PPy copolymer are higher than those of PVCEE/PPy composite. The higher maximum current in graft copolymer implies that PPy polymerization is more efficient in PVPPE precursor than in PVCEE, possibly because pyrrolyl groups in PVPPE may act as the nuclei for PPy polymerization.

Figure 4 shows chronoamperograms of PVCEE/PPy composite and PVCEE-g-PPy copolymer that were polymerized for 1 hr under the constant potential of 0.7, 0.9, 1.1, 1.3, and 1.5 V using PVCEE and PVPPE as the matrix and the precursor film. As shown in Figure 4, when PVCEE was used as the matrix film, the oxidation current flows much less and polymerization proceeds more slowly at the same potentials than when PVPPE was used as the precursor film. The higher oxidation current and faster polymerization of PPy in the

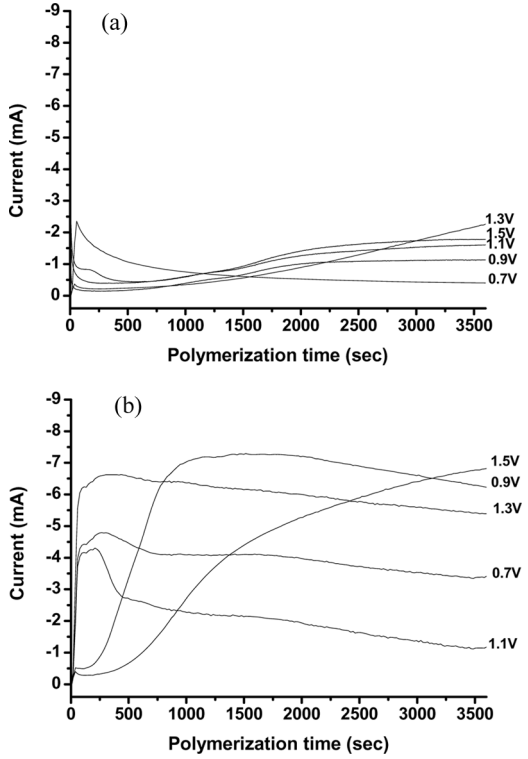


FIGURE 4 Chronoamperograms of (a) PVCEE/PPy composite and (b) PVCEE-g-PPy copolymer at constant potentials of 0.7, 0.9, 1.1, 1.3, and 1.5 for 1 hr.

precursor imply that the pyrrolyl moiety in PVPPE acts as the nuclei for PPy polymerization.

The conductivities of PVCEE-g-PPy copolymer and PVCEE/PPy composite prepared for 1 hr under the constant potentials of 0.5 V were 1.7×10^{-1} and 8.9×10^{-2} S/cm, respectively. N contents in the copolymer and composite obtained from elemental analysis were 7.152 and 7.268 mol%, respectively. This implies that almost same amounts of PPy were incorporated into the copolymer and composite. Therefore, higher conductivity of the copolymer may be due to the presence of more regularly grafted PPy along the main chain in the copolymer than in the composite.

4. CONCLUSION

PVCEE-g-PPy copolymer was synthesized by electrochemical polymerization of PPy using the precursor, PVPPE. The PVCEE-g-PPy copolymer showed higher electrochemical activities compared to those of PVCEE/PPy composite. The electrical conductivity of the copolymer was about 1.7×10^{-1} S/cm, which is slightly higher than that of composite. The higher electrochemical activity and conductivity confirmed that the pyrrolyl groups of PVPPE act as nuclei for the graft copolymerization reaction of pyrrole into PVPPE.

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