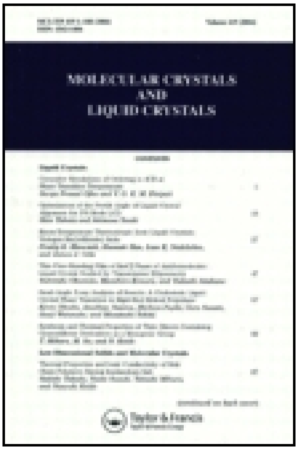

Molecular Crystals and Liquid Crystals

PREPARATION AND ELECTROCHEMICAL PROPERTIES OF POLY(VINYL CHLORIDE)-g-POLY(ANILINE) COPOLYMER

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PREPARATION AND ELECTROCHEMICAL PROPERTIES OF POLY(VINYL CHLORIDE)-g-POLY(ANILINE) COPOLYMER

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The electroconductive graft copolymer, Poly(vinyl chloride)-g-poly(aniline) (PVC-g-PANI) was prepared by the electrochemical polymerization using a precursor as follows: The precursor polymer, poly(vinyl 1,4-phenylene-diamine)(PVPD) dissolved in DMF was spin coated on a platinum electrode and polymerized electrochemically in the electrolytic mixture solution consisting of DMF, water, 0.1 M aniline, and 1.0 M electrolyte such as H_2SO_4, HCl, or HNO_3. PVPD was synthesized chemically with PVC and potassium 1,4-phenylenediamine salt and characterized using FT-IR and ^{1}H-NMR spectroscopy. The electrochemical properties such as cylclic voltammetry and chronoamperogram of PVC-g-PANI were investigated comparing with those of PVC/PANI composite.

Keywords: electrochemical properties; graft copolymer; polyaniline

INTRODUCTION

Polyaniline(PANI) has attracted considerable interest as a conducting polymer. It is studied extensively for a variety of applications, including rechargeable batteries [1], EMI shielding [2], and biosensors [3], but PANI is mechanically weak and its processability is poor. It degrades before melting, is insoluble in common organic solvents, soluble only in concentrated sulfuric acid [4] under the specific condition, and also limitedly soluble in organic solvents like N-methylpyrrodidone and tetrahydrofuran [5]. In order to improve these problems, the author [6] and other workers [7,8] have utilized the method of synthesizing composites and copolymers.

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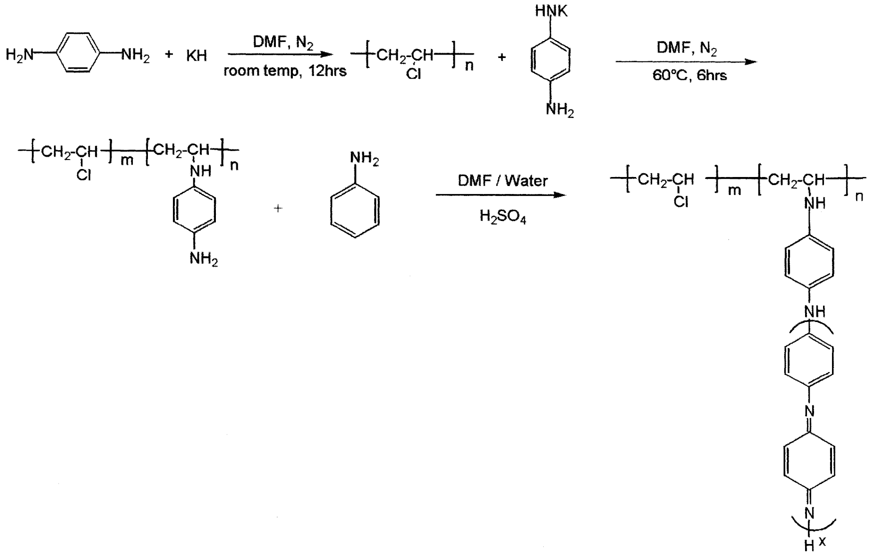
In this work, we have prepared a new conducting graft copolymer of PVC-g-PANI by electrochemical method using a precursor polymer, poly(vinyl 1,4-phenylenediamine)(PVPD) which is processable and has desirable mechanical properties. The electrochemical properties of graft copolymer are compared with those of PVC/PANI composites. PVC is used for the backbone polymer because it can provide good mechanical properties and has reactive chlorine atoms for graft sites even though their reactivity are low. The route of the preparation of PVC-g-PANI is shown in Scheme 1.

The systematic investigations including electrical properties, thermal properties, and morphological studies of this novel copolymer in comparison with composite are in progress and we shall no doubt be reporting our findings in the near future.

EXPERIMENTAL

Chemicals used in this study were ACS grade. PVC(Aldrich) with the molecular weight of 62,000 and 1,4-phenylenediamine(Aldrich) were used without further purification and potassium hydride(Aldrich) was used after removing mineral oil. Aniline(Aldrich) and Dimethylformamide (DMF)



SCHEME 1 The overall preparation route of PVC-g-PANI copolymer.

(Aldrich) were purified by vacuum distillation. Other chemicals were used without further purification. PVPD was synthesized as follows: potassium 1,4-phenylenediamine salt was prepared by the reaction of 1,4-phenylenediamine with potassium hydride in DMF for 12 hrs at room temperature under N_2 atmosphere. DMF solution of PVC was added to a flask that contained potassium 1,4-phenylenediamine salt in DMF. The reaction was continued for 6 hrs at 60°C under N_2 atmosphere. The product solution was poured into methanol for the precipitation of PVPD. The precipitate was filtered and dried under vacuum. PVPD was characterized using FT-IR and ^{1}H-NMR spectroscopy. The precursor, PVPD was spin-coated on a Pt disc electrode. The electrochemical graft polymerization of aniline onto PVPD was performed by applying intended potential to the electrode using potentiostat (EG&G 273A). In this electrolysis, a standard three-electrode cell, without any cell partition, using a disk-type Pt working electrode (diameter, 1 cm), a plate-type Pt counter electrode, and an aqueous sodium chloride saturated calomel electrode (SCE) as a reference electrode was employed. The electrolyte solution consists of 0.1 M aniline and 1.0 M sulfuric acid in DMF/Water mixture. The potential range for electrochemical polymerization and the scanning rate were $-0.5 \sim 1.0$ V (vs. SCE) and 50 mV/sec, respectively.

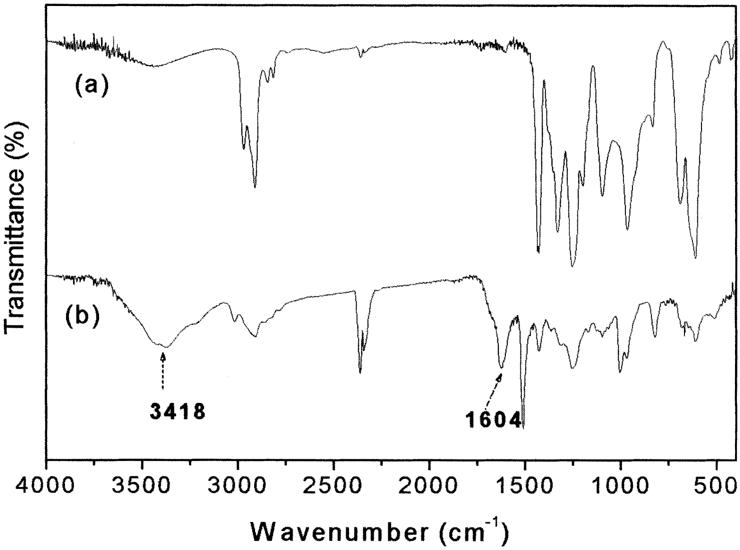


FIGURE 1 FT-IR spectra of (a) PVC and (b) PVPD.

RESULT AND DISCUSSION

Figure 1 shows FT-IR spectra of the reaction product, PVPD and PVC. All of these spectra were obtained from KBr pellets. In comparison with Figure 1(a) and Figure 1(b), Figure 1(b) shows the new peak at 3418 cm^{-1} due to N-H stretch and 1604 cm^{-1} due to C=C stretch. This result implies that some chlorine groups in PVC chain were substituted with phenylenediamine groups.

Figure 2 shows ^{1}H-NMR spectrum of PVPD. The occurrence of the peaks at $\delta = 6.5$ and $\delta = 7.0$ indicates that phenylenediamine has been bonded to PVC.

Figure 3 shows the cyclic voltammograms obtained when PVC-g-PANI copolymer and PVC/PANI composite are synthesized with 0.1 M aniline and 1.0 M sulfuric acid. For the preparation of PVC-g-PANI copolymer and PVC/PANI composite, DMF/Water mixture solution is chosen as a medium because DMF loosens the compact PVC and PVPD structures and thus the penetration of aniline monomer into PVPD and PVC becomes easier. In comparison with Figure 3(a) and Figure 3(b), both CV's show well developed redox peak pairs during the potential cycling. The CV in Figure 3(a) shows large monomer oxidation current response at 0.9 V for the initial scan that is getting smaller for subsequent scans. This may be due to

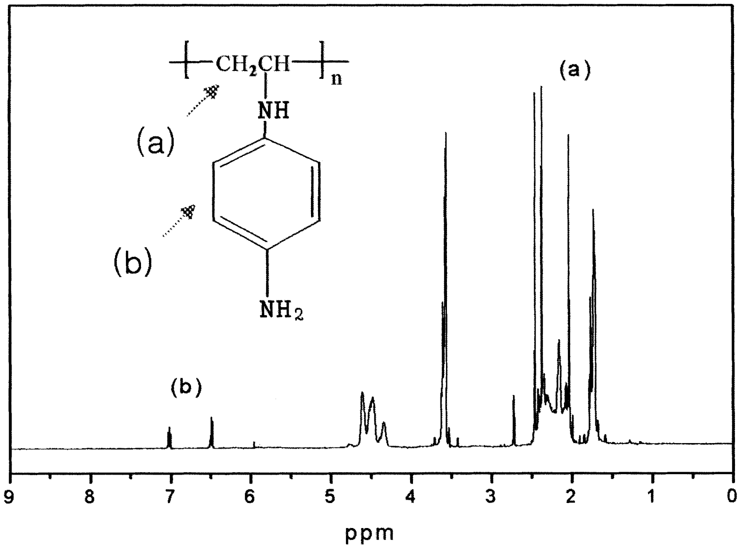


FIGURE 2 ^{1}H-NMR spectrum of PVPD.

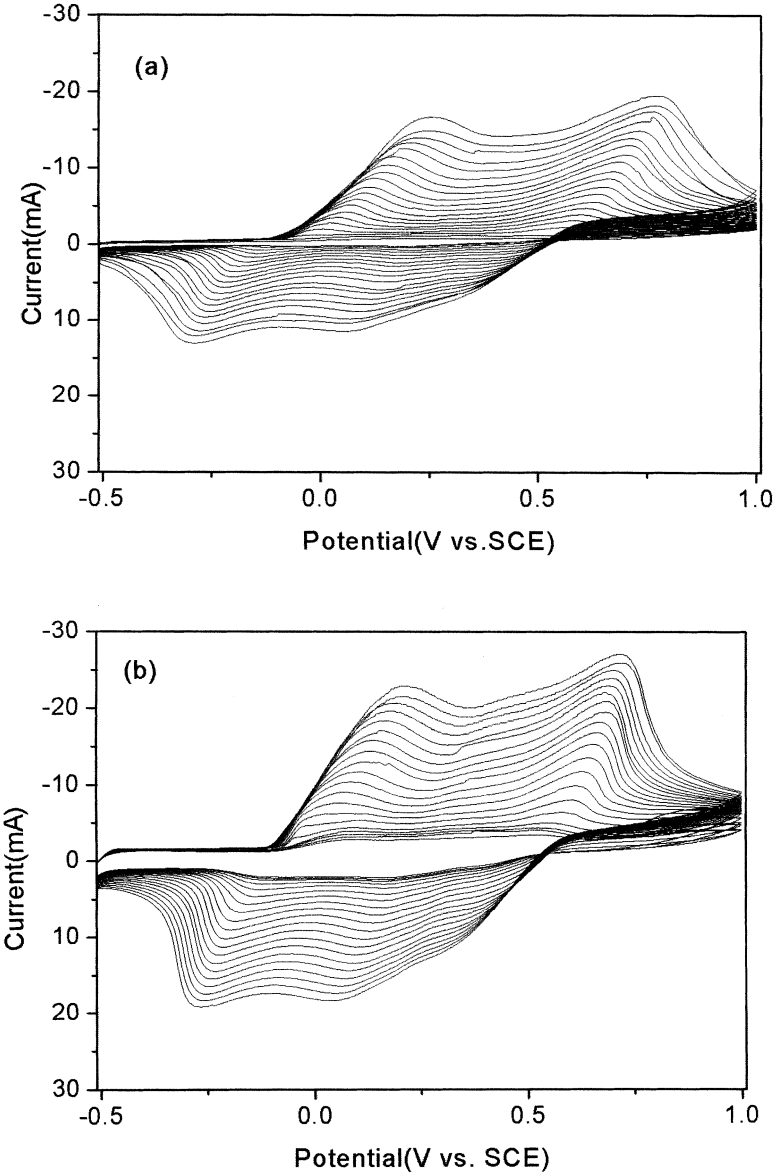


FIGURE 3 Cyclic voltammograms of (a) PVC/PANI composite and (b) PVC-g-PANI copolymer on a Pt electrode in 1.0 M H_2SO_4 electrolyte containing DMF/Water and 0.1 M aniline at 50 mV/sec scan rate.

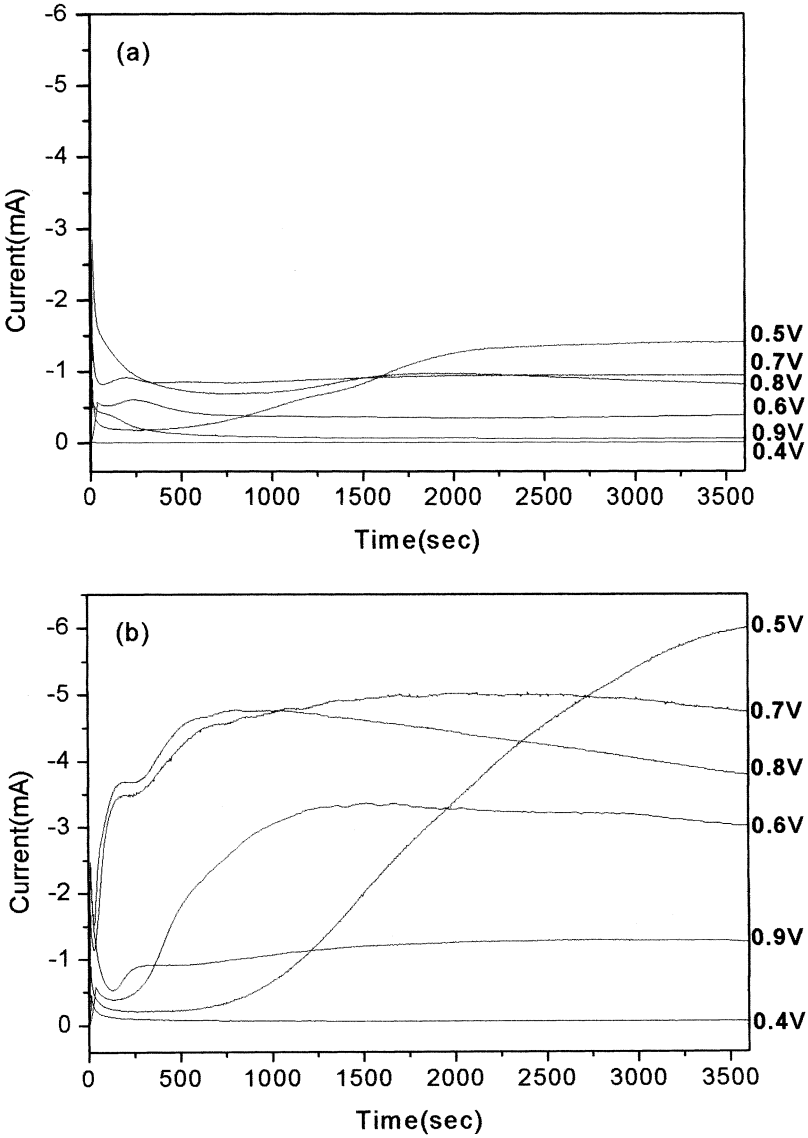


FIGURE 4 Chronoamperograms of aniline polymerization on (a) PVC and (b) PVPD coated Pt electrode at a constant potential of 0.50, 0.60, 0.70, 0.80, and 0.90 V for 1 hr.

depletion of monomer that has diffused into the PVC film. The amount of current flow in the composite (Figure 3(a)) is much lower than that in the copolymer (Figure 3(b)). This result suggests that it is difficult for the aniline monomer to diffuse into the matrix PVC film. Only the monomers near the electrode surface have chance to be electropolymerized and adsorbed on the working electrode surface. On the other hand, the CV in Figure 3(b) shows a similar behavior of aniline polymerization on bare Pt electrode because phenylenediamine moieties in the precursor, PVPD start to be oxidized for polymerization. The redox peak has broad shape and its position is shifted to higher potential region. The polymerization current is growing continuously as the potential cycling proceeds. This shifting implies that the PANI formation is started at the phenylenediamine moieties at the inner side of the precursor film. As the polymer grows the ohmic conduction occurs between the electrode and the phenylenediamine moieties at outer side of the precursor so that polymerization rate continuously increases for the subsequent potential cycles. In this way, the PANI is grafted to the precursor PVPD chain.

Figure 4 shows chronoamperograms of PVC/PANI composite and PVC-g-PANI copolymer that were polymerized with aniline for 1 hr under the constant potential of 0.50, 0.60, 0.70, 0.80, and 0.90 V using PVC and PVPD as matrix and precursor, respectively. Polymerizing under the constant potential of 0.4, there is little oxidation current as shown in Figure 4(a). But under the potential of 0.5 V, the amount of oxidation current increased greatly as time went by and black spots that were big enough for us to observe with the naked eyes appeared on both sides of the PVC film. Under the potential of above 0.5 V, the amount of oxidation current decreased. These results indicate that polymerization and the degradation reactions occur competitively [9]. However, when PVPD was used as a precursor film, the oxidation current flows much more and polymerization occurs more rapidly at the same potentials compared to the use of PVC as a matrix film. This fact means that the phenylenediamine groups in the PVPD film act as nuclei for the growth of PANI, and promote the polymerization of aniline at an earlier stage.

CONCLUSIONS

We have prepared PVC-g-PANI copolymer by the electrochemical method as a conducting polymer that carries improved mechanical properties. In order to prepare PVC-g-PANI copolymer, we used precursor polymer, PVPD which has been synthesized by the chemical reaction of PVC and potassium 1,4-phenylenediamine. The PVC-g-PANI copolymer showed better electrochemical activity compared to that of PVC/PANI composite.

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