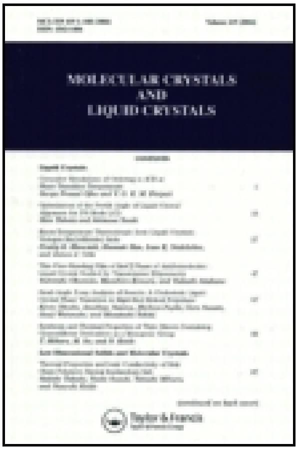

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Comparison of electrical and electrochemical properties between poly(vinyl chloride) and poly(vinyl methylaniline) composites with polyaniline

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To cite this article: Yun Park & Kye Yang (2004): Comparison of electrical and electrochemical properties between poly(vinyl chloride) and poly(vinyl methylaniline) composites with polyaniline, Molecular Crystals and Liquid Crystals, 425:1, 223-229

To link to this article: http://dx.doi.org/10.1080/15421400490506856

Mol. Cryst. Liq. Cryst., Vol. 425, pp. 223/[501]–229/[507], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490506856

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COMPARISON OF ELECTRICAL AND ELECTROCHEMICAL PROPERTIES BETWEEN POLY(VINYL CHLORIDE) AND POLY(VINYL METHYLANILINE) COMPOSITES WITH POLYANILINE

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The modified PVC with bulky functional groups, namely poly(vinyl methylaniline) (PVMA) was synthesized, and the PVMA/Polyaniline (PANI) composite was prepared electrochemically to compare its electrical and electrochemical properties with those of PVC/PANI composite. The synthesized PVMA was characterized using FT-IR and ^{1}H-NMR spectroscopy. To prepare composite, PVC and PVMA were spin-coated on a Pt disc electrode. After the pre-coated films were swelled in DMF/water mixture with 1.0 M sulfuric acid, the electrochemical polymerization of PANI on PVC or PVMA coated Pt electrode was performed by the constant-potential and potential-cyclic method, respectively. The electroconductivity, cyclic voltammetry, and chronoamperometry of PVMA/PANI composite were investigated comparing with those of PVC/PANI composite.

Keywords: electrochemical polymerization; polyaniline; poly(vinyl chloride); poly(vinyl methylaniline)

INTRODUCTION

Conductive polymers such as polyacetylene, polyaniline, polypyrrole, and polythiophene, have attracted so much research interest in wide range applications such as rechargeable battery [1], electrochromic display device [2], EMI shielding [3], and gas separation membranes [4]. Of these, polyaniline (PANI) has been extensively studied because of its environmental stab-

Received 1 October 2003; accepted 8 March 2004.

The Korea Science and Engineering Foundation through the Hyperstructured Organic Materials Research Center supported this work. We acknowledge this support with thanks.

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ility in a conducting form, easiness and low cost of synthesis, unique redox properties, and high conductivity [5]. Nevertheless, not so many applications have been reported because PANI exhibits poor mechanical properties. It is, therefore, of great interest to prepare composites of PANI with commodity polymers showing improved mechanical properties and electrical stabilities [6]. Among various commodity polymers, PVC is known as a highly versatile polymer with an excellent balance of properties and numerous applications, as water pipes, packaging and construction materials, and medical devices. PVC also can be used as an interesting starting membrane material for gas separation when the polymer is chemically modified [7,8].

In this study, we synthesized poly(vinyl methylaniline) (PVMA) which has more bulky group than PVC and prepared the PVMA/PANI composite electrochemically to compare its electrical and electrochemical properties with those of PVC/PANI composite.

EXPERIMENTAL

Chemicals used in this study were ACS grade. PVC (Aldrich) with the molecular weight of 62,000 and *n*-methylaniline (Aldrich) were used without further purification, and potassium hydride (Aldrich) was used after removing mineral oil. Aniline (Aldrich) and *N*,*N*-Dimethylformamide (DMF) (Aldrich) were purified by vacuum distillation. Other chemicals were used without further purification. PVMA was synthesized as follows: potassium methylaniline salt was synthesized by the reaction of methylaniline with potassium hydride for 12 hrs at 80°C under N_2 in DMF. DMF solution of PVC was added to a flask that contained potassium methylaniline salt in DMF. The reaction was continued for 24 hrs at 75°C under N_2. The product solution was poured into methanol for the precipitation of PVMA. The precipitate was filtered and dried under vacuum. The structure of PVMA was investigated using FT-IR (Perkin-Elmer, Spectrum 2000) and ^{1}H-NMR spectroscopy (Varian, 500 NB). The precursor film, PVMA, was spin-coated on a Pt disc electrode. The electrochemical polymerization of aniline onto PVMA was performed by applying intended potential to the electrode using potentiostat (EG&G, 273 A). 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. 0.1 *M* aniline was added to the electrolytic solution consisting of 1.0 *M* sulfuric acid in DMF/water mixture. The potential range for electrochemical polymerization and the scanning rate are $-0.2 \sim 1.0$ V (vs. SCE) and 50 mV/sec, respectively. The electrical conductivity of the product film was measured by using a four-probe method (Fluke, 45 multimetry). The synthetic routes of PVMA and PVMA/PANI composite are shown in Figure 1.

RESULTS AND DISCUSSION

Figure 2 shows FT-IR spectra of the reaction product, PVMA and PVC. The spectrum of PVMA compared to that of PVC shows the new peaks at 1604–1580 cm^{-1} due to $C = C$ stretching, which indicates that chlorine groups in PVC backbone were substituted with methylaniline.

^{1}H-NMR spectrum of PVMA is shown in Figure 3. The peaks at $\delta = 6.6 - 7.5$ ppm, due to aromatic protons in PVMA indicate the successful grafting of methylaniline.

Figure 4 shows the cyclic voltammograms obtained while PVC/PANI and PVMA/PANI composites were synthesized in 0.1 *M* aniline and 1.0 *M* sulfuric acid. For the preparation of PVC/PANI and PVMA/PANI composite films, DMF/water mixture solution is chosen for medium because DMF loosens the compact PVC and PVMA structures and thus the penetration of aniline monomer into PVC and PVMA becomes easier. By

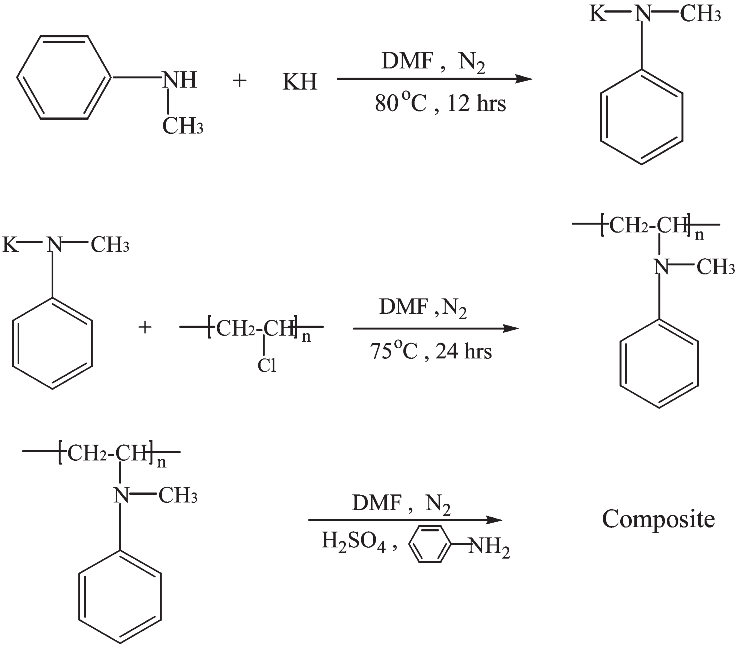

FIGURE 1 The synthetic routes for PVMA and PVMA/PANI composites.

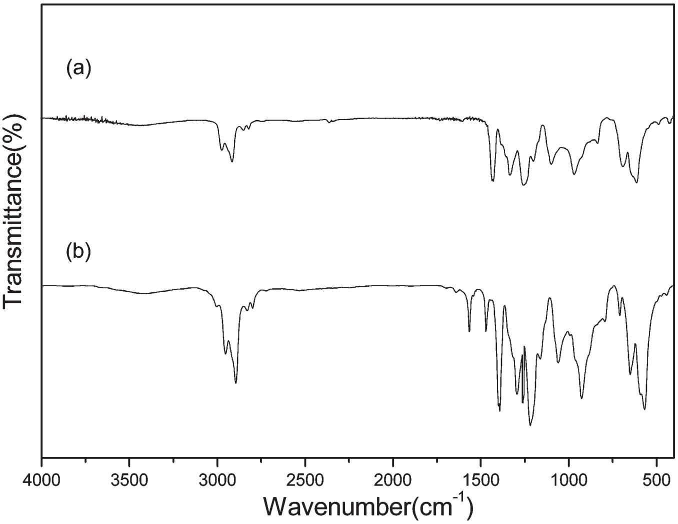

FIGURE 2 FT-IR spectra of (a) PVC and (b) PVMA.

comparison of cyclic voltammograms recorded during the preparation of PVC/PANI and PVMA/PANI composites, it can be seen that the current peaks of PVMA/PANI composite are higher than those of PVC/PANI composite.

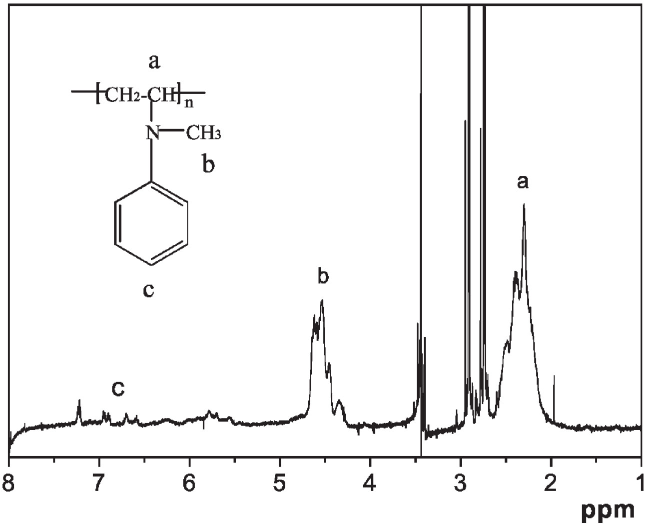

FIGURE 3 ^{1}H-NMR spectrum of PVMA.

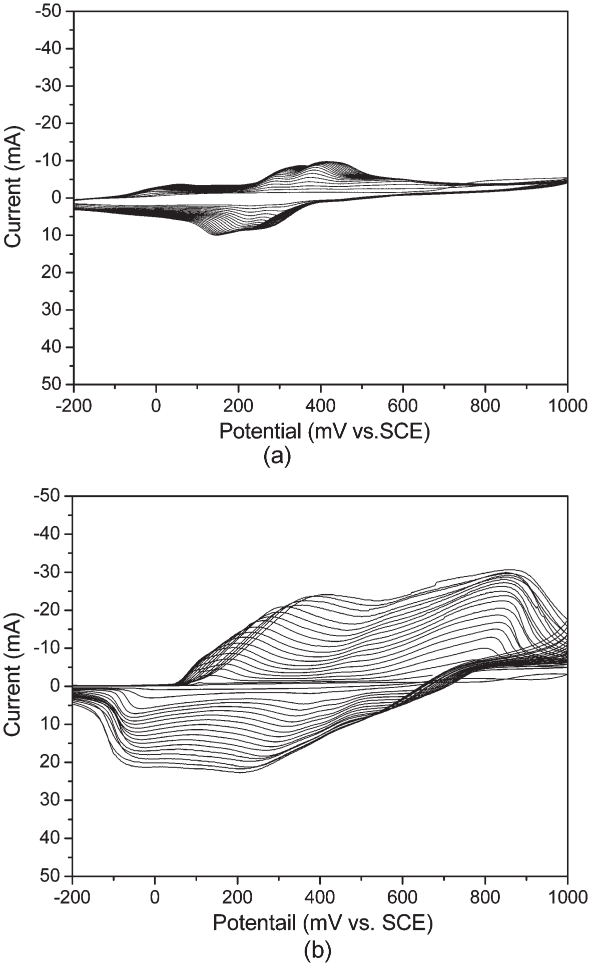

FIGURE 4 Cyclic voltammograms of (a) PVC/PANI and (b) PVMA/PANI composites on a Pt electrode in 1.0 *M* H_2SO_4 electrolyte containing DMF, water and 0.1 *M* aniline at 50 m V/sec scan rate.

Figure 5 shows chromoamperograms of PVC/PANI and PVMA/PANI composites that were polymerized with aniline for 1 hr under the constant potential of 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 V using PVC and PVMA as a matrix film, respectively. During the preparation of the PVC/PANI composite under the constant potential of 0.4 V, there is little oxidation current as shown in Figure 4(a). In the case of the potential of 0.5 V, we could see that the amount of oxidation current increased greatly as time went on and black spots that were big enough to be observed with the naked eye

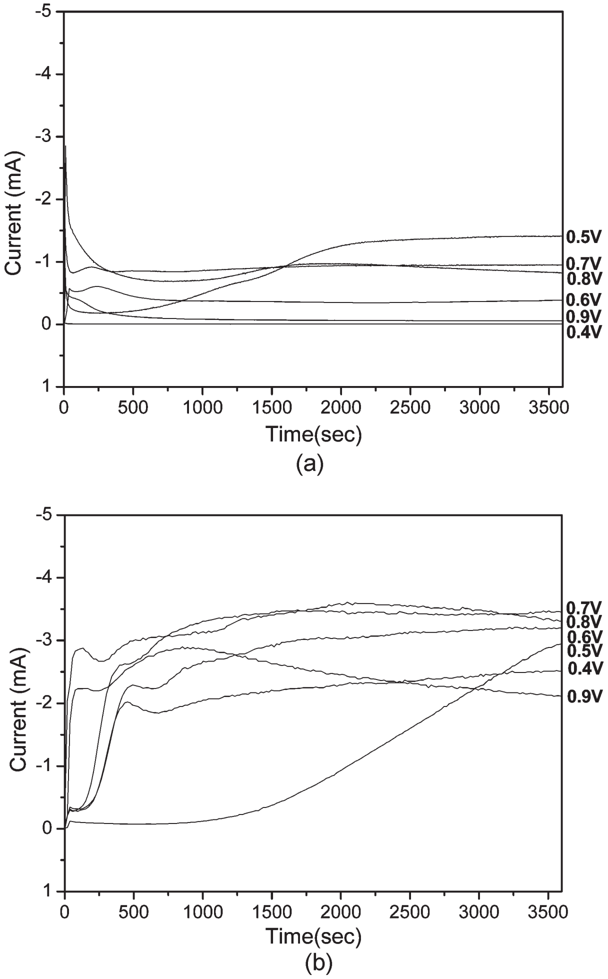

FIGURE 5 Chronoamperograms of aniline polymerization on (a) PVC and (b) PVMA coated Pt electrode at a constant potential of 0.50, 0.60, 0.70, 0.80, and 0.90 V for 1 hr.

appeared on both sides of the PVC film. However, when we use PVMA as a matrix film as shown in Figure 4(b), the oxidation current flows much more and polymerization occurs more rapidly at the same potentials when compared to PVC as a matrix film. The PVMA/PANI composite showed higher electrochemical activity compared to that of PVC/PANI composite.

The conductivities of electrode side and solution side of PVC/PANI and PVMA/PANI composites prepared for 1 hr under the constant potentials of

0.50 V were measured. The conductivities of electrode side and solution side of PVC/PANI were 1.0×10^{-2} and 9.5×10^{-3} S/cm, respectively. The conductivities of electrode side and solution side of PVMA/PANI were 1.5×10^{-2} and 1.1×10^{-2} S/cm, respectively. The PVMA/PANI composite has higher conductivity than the PVC/PANI composite. A possible reason for this could be that the incorporation of large bulky methylaniline group to PVC offers more sites for the penetration of aniline and the formation of PANI through the matrix film, resulting in higher conductivity.

CONCLUSION

The PVMA/PANI composite prepared by electrochemical method showed higher electrochemical activity and higher electrical conductivity when compared to PVC/PANI composite. This is because PVMA has the bulky functional groups that weaken the interaction between PVMA chains and thus, offer more vacant sites for the penetration of aniline and the formation of PANI through the PVMA matrix film.

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