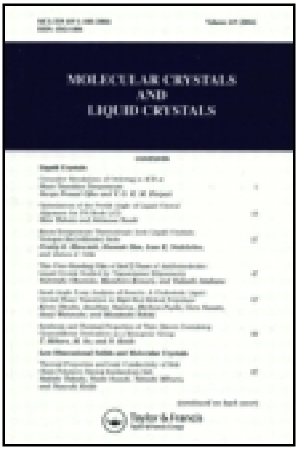

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Comparison of Electrochemical Properties of Poly(vinyl phenylmethylamine)/ Polyaniline Composite with those of Poly(vinyl benzylmethylamine)/ Polyaniline Composite

Kye Yong Yang [a] [b] , Yun Heum Park [a] [b] & Kyung Chan Go [a]

[a] School of Applied Chemistry and Chemical Engineering, Sungkyunkwan University, Suwon, Korea
[b] Hyperstructured Organic Materials Research Center, Seoul, Korea

Version of record first published: 23 Aug 2006

To cite this article: Kye Yong Yang, Yun Heum Park & Kyung Chan Go (2006): Comparison of Electrochemical Properties of Poly(vinyl phenylmethylamine)/ Polyaniline Composite with those of Poly(vinyl benzylmethylamine)/Polyaniline Composite, Molecular Crystals and Liquid Crystals, 445:1, 71/[361]-80/[370]

To link to this article: http://dx.doi.org/10.1080/15421400500367041

Mol. Cryst. Liq. Cryst., Vol. 445, pp. 71/[361]–80/[370], 2006
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500367041

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Kye Yong Yang
Yun Heum Park
School of Applied Chemistry and Chemical Engineering,
Sungkyunkwan University, Suwon, Korea and Hyperstructured Organic Materials Research Center, Seoul, Korea

Kyung Chan Go
School of Applied Chemistry and Chemical Engineering,
Sungkyunkwan University, Suwon, Korea

Poly(vinyl phenylmethylamine) (PVPMA) and poly(vinyl benzlmethylyamine) (PVBMA) were chemically synthesized and PVPMA/polyaniline (PANI) and PVBMA/PANI composites were electrochemically prepared for the investigation of the effect of different bulky side groups of matrix polymers on the electrochemical properties of the polymer composites. The cyclic voltammertry, chronoamperomtry, and conductivity were investigated.

Keywords: electrochemical polymerization; electrochemical properties; polyaniline

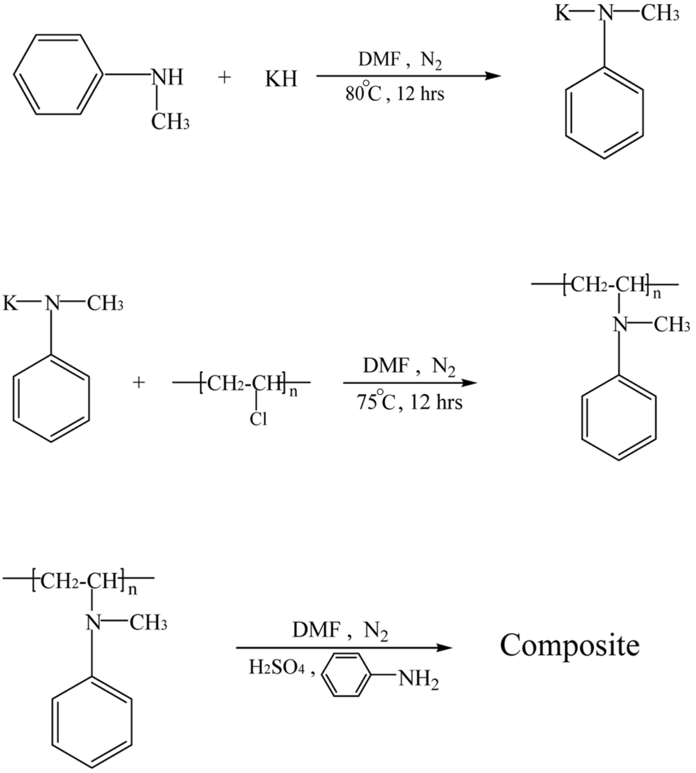
INTRODUCTION

The properties of most polymers, distinguishing them from metals, are their inability to carry electricity. However, a new class of organic polymers has been devised with the striking ability to conduct electrical current. Polyaniline (PANI) of conductive polymer has been extensively studied because of its environmental stability in a conducting form, easiness and low cost of synthesis, unique redox properties [1],

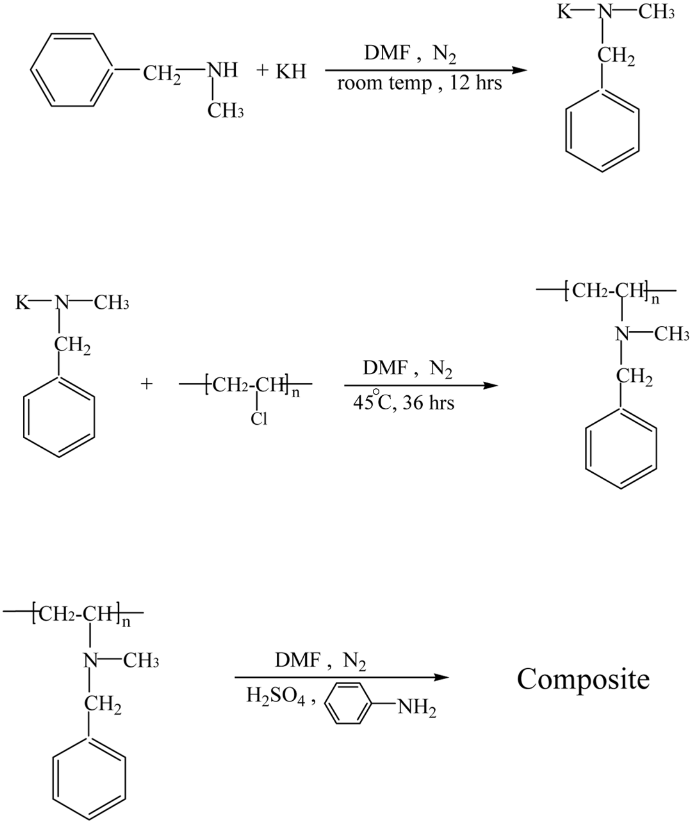
The Korea Science and Engineering Foundation through the Hyperstructured Organic Materials Research Center supported this work. We acknowledge this support with thanks.

Address correspondence to Yun Heum Park, School of Applied Chemistry and Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea. E-mail: yhpark@skku.edu

and high conductivity [2]. On the other hand, PANI is mechanically weak and its processability is poor. It is, therefore, of great interest to prepare composites of PANI [3–6] showing improved mechanical properties [7] and electrical stabilities [8]. In this study, we synthesized poly(vinyl phenylmethylamine) (PVPMA) and poly(vinyl benzylmethylamine) (PVBMA) with each different bulky group, PVPMA/PANI and PVBMA/PANI composites were electrochemically prepared to compare their electrical and electrochemical properties. In this paper, we have studied the optimum condition for the preparation of PVPMA/PANI and PVBMA/PANI composites. We have investigated an appropriate polymerization medium based on the analysis of electrochemical properties. The synthetic routes for PVPMA and PVBMA composites are shown in Scheme 1 and Scheme 2, respectively.



SCHEME 1 The synthetic routes for PVPMA and PVPMA/PANI composite.



SCHEME 2 The synthetic routes for PVBMA and PVBMA/PANI composite.

EXPERIMENTAL

PVPMA was synthesized as follows: potassium phenylmethylamine salt was synthesized by the reaction of phenyl methylamine with potassium hydride in DMF for 12 h at 80°C under N_2 in DMF. PVC solution in DMF was added to a flask containing potassium phenyl methylamine salt in DMF. The reaction was continued for 24 h at 75°C under N_2. PVBMA was synthesized as follows: potassium benzyl methylamine salt was synthesized by the reaction of benzyl methylamine with potassium hydride for 12 h at room temperature under N_2 in DMF. PVC solution in DMF was added to a flask containing potassium benzyl methylamine salt in DMF. The reaction was continued for 36 h at 45°C under N_2. The product solutions were poured into methanol for the precipitation of PVPMA and PVBMA, respectively.

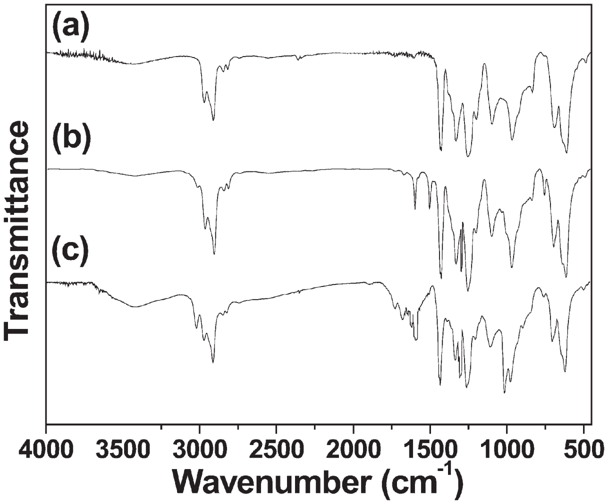


FIGURE 1 FT-IR spectra of (a) PVC, (b) PVPMA, and (c) PVBMA.

The precipitations were filtered and dried under vacuum. For the preparation of PVPMA/PANI and PVBMA/PANI composite films, electrochemical polymerization was carried out in a simple cell chamber of 100 ml capacity using a three-electrode system, i.e., a disc-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. The electrolyte solution consists of 0.1 M aniline and 1.0 M sulfuric acid in DMF 65%/water 35% (v/v) mixture (D 65/W 35), D 50/W 50, and D 35/W 65, respectively. The potential range for electrochemical polymerization and scanning rate are −0.2 to 1.0 V (vs. SCE) and 50 mV, respectively. Unless otherwise stated all data are for above-mentioned experimental conditions. The details of the experimental technique are reported in an earlier article [8,9].

RESULTS AND DISCUSSION

The structures of PVPMA and PVBMA were analyzed using FT-IR (Perkin-Elmer, Spectrum 2000) and ^{1}H-NMR (Varian, 500 NB) spectroscopy. Figure 1 shows FT-IR spectra of PVC, the reaction product, PVPMA and PVBMA. All of these spectra were obtained from KBr pellets. The spectra of Figure 1(b) and 1(c) compared to that of Figure 1(a) show new peaks at 1604–1580 cm^{-1} and 1598–1550 cm^{-1} due to aromatic $C=C$ stretching, respectively. This result implies that some chlorine groups in PVC chain were substituted with phenyl methylamine and benzyl methylamine groups. ^{1}H-NMR spectra of PVPMA and PVBMA were shown in Figure 2. As shown in Figure 2(a) the peaks at $\delta = 6.6$–7.5 ppm, due to aromatic protons were observed, which indicates successful grafting of phenyl methylamine on PVPMA backbone. Aromatic protons of PVBMA were also observed at around $\delta = 6.7$–7.6 ppm, as shown in Figure 2(b). For the preparation of PVPMA/PANI and PVBMA/PANI PANI composites, D/W mixture is chosen as a medium because DMF

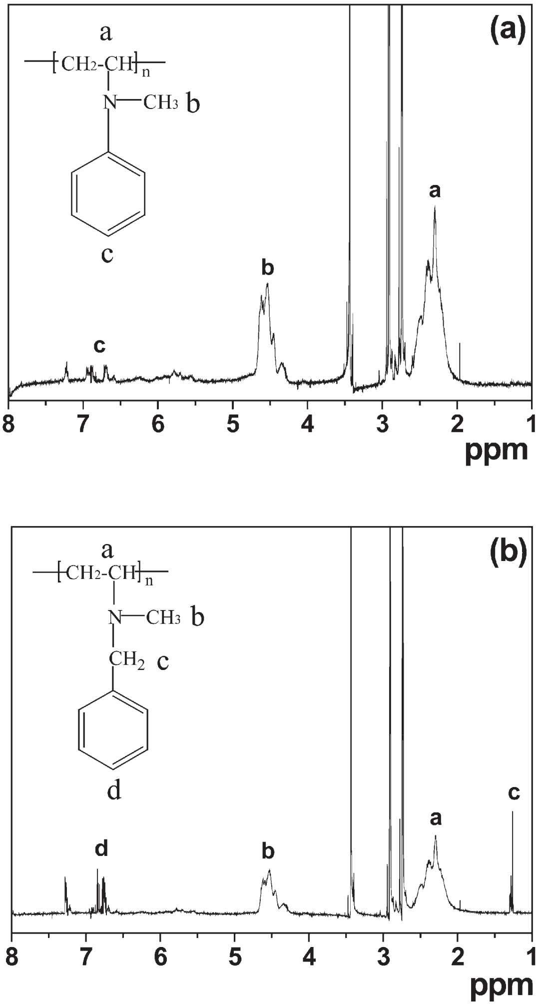


FIGURE 2 ^{1}H-NMR spectra of (a) PVPMA and (b) PVBMA.

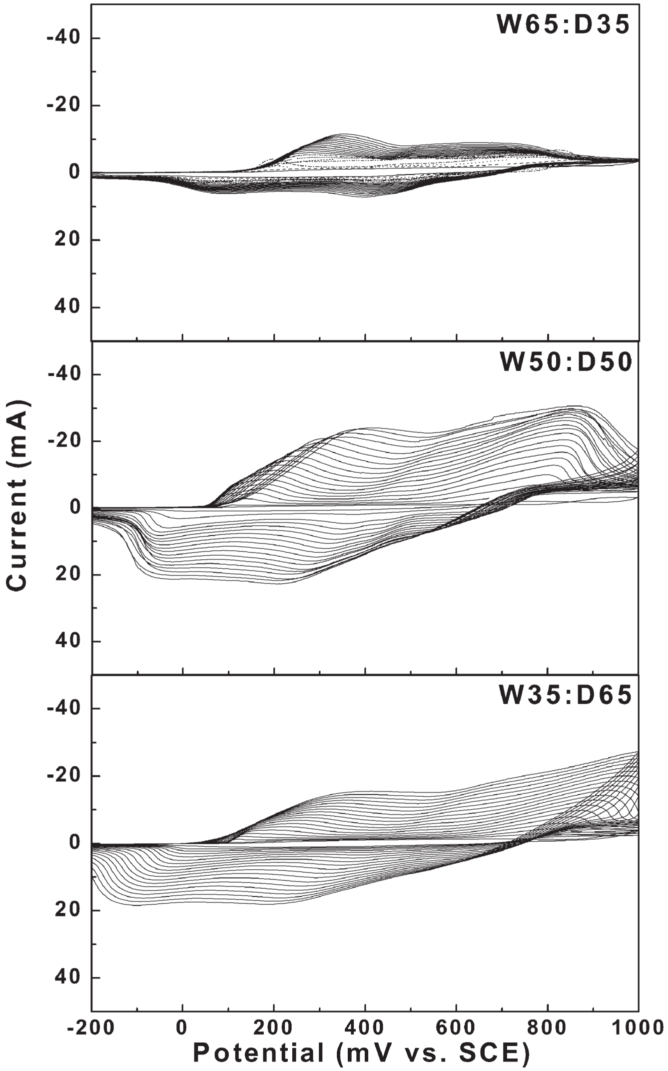


FIGURE 3 Cyclic voltammograms of aniline polymerization on a PVPMA-coated Pt electrode in (a) DMF 65/water 35, (b) D 50/W 50, and (c) D 35/W 65 containing 0.1 M aniline and 1.0 M sulfuric acid at 50 mV/s.

loosens the compact PVPMA and PVBMA structures and thus the penetration of aniline monomer into PVPMA and PVBMA becomes easier.

The electrochemical polymerization of aniline onto PVPMA and PVBMA, respectively was performed by applying intended potential

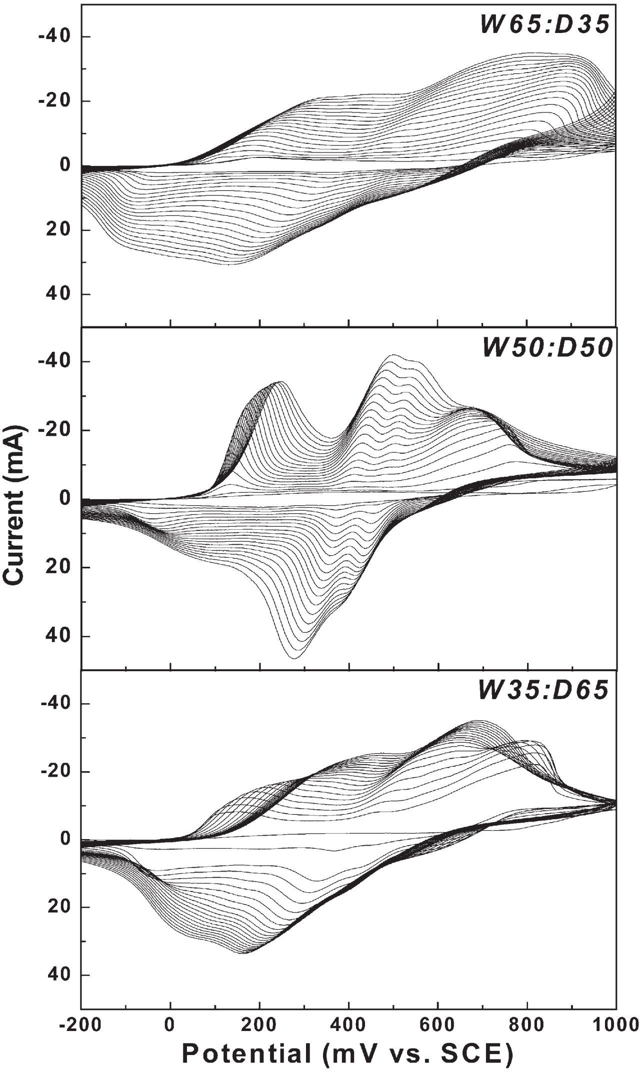


FIGURE 4 Cyclic voltammograms of aniline polymerization on a PVBMA-coated Pt electrode in (a) DMF 65/water 35, (b) D 50/W 50, and (c) D 35/W 65 containing 0.1 M aniline and 0.1 M sulfuric acid at 50 mV/s.

to the electrode using potentiostat (EG&G, 273 A). Figures 3 and 4 show the cyclic voltammograms according to the mixture composition of medium. PVPMA/PANI and PVBMA/PANI composites were synthesized with 0.1 M aniline and 1.0 M sulfuric acid. As cyclic

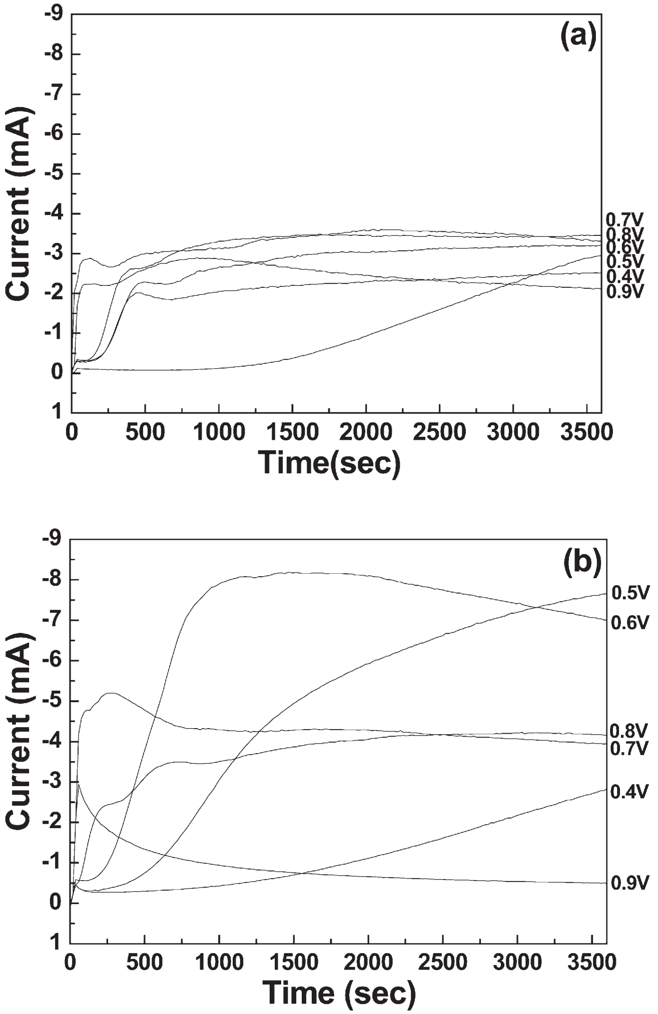


FIGURE 5 Chronoamperograms of aniline polymerization on (a) PVPMA and (b) PVBMA coated Pt electrode at a constant potential of 0.40, 0.50, 0.60, 0.70, 0.80, and 0.90 V for 1 h.

voltammograms were recorded during the preparation of PVBMA/PANI composite, it can be seen that the current peaks of PVBMA/PANI composite are higher than those of PVPMA/PANI composite as show in Figures 3 and 4, respectively. The PVPMA/PANI and PVBMA/PANI composites with highest redox current were obtained when they were prepared in D 50/W 50 medium. We speculate that the optimum DMF content in DMF/water mixture is determined by the relative competition between the structure loosening of PANI by DMF and the acid dissociation by water.

Figure 5 shows chromoamperograms of PVPMA/PANI and PVBMA/PANI composites recorded under the constant potential of 0.4, 0.50, 0.60, 0.70, 0.80, and 0.90 V for 1 h using PVPMA and PVBMA as matrix film, respectively. During polymerizing under the constant potential of 0.4 and 0.9 V, very low oxidation currents occur as shown in Figure 5(a). In case of the potential of 0.7 V, we could see that the amount of oxidation current increased as time went on and black spots that were grown big enough to be observed with the naked eye appeared on both electrode and solution sides of the PVPMA film. However, when we use PVBMA as a matrix film as shown in Figure 5(b), the oxidation current flows much more and polymerization occurs more rapidly at the same potentials than when PVPMA as a matrix film. The PVBMA/PANI composite showed higher electrochemical activity compared to PVBMA/PANI composite.

The electrical conductivity of composite films was measured by using a four-probe method (Fluke, 45 Multimetry). The samples were taken off from the Pt electrode and were dried thoroughly under 60°C over 24 hrs for the electrical conductivity measurement. The conductivities of electrode and solution side of PVPMA/PANI and PVBMA/PANI composites prepared under the constant potentials of 0.5 V for 1 h were measured. The conductivities of electrode and solution side of PVPMA/PANI were 1.5×10^{-2} and 1.1×10^{-2} S/cm, respectively. The conductivities of electrode and solution side of PVBMA/PANI were 2.6×10^{-2} and 2.0×10^{-3} S/cm, respectively. The PVBMA/PANI composite has higher conductivity than the PVPMA/PANI composite. A possible reason for this could be that the incorporation of large bulky benzyl methylamine group to PVC offers more sites for the penetration of aniline and the formation of PANI through the matrix film; resulting in higher conductivity.

CONCLUSIONS

PVPMA/PANI and PVBMA/PANI composites were successfully prepared by electrochemical method in the medium of DMF/water mixture. In D 50/W 50 the composites with highest redox currents were prepared. The PVBMA/PANI composite showed higher electrochemical activity and higher electrical conductivity when compared to the PVPMA/PANI composite. This is because PVBMA has the larger bulky groups that weaken the interaction between PVBMA chains and thus, offer more vacant sites for the penetration of aniline and the formation of PANI through the PVBMA matrix film. This result was consistent with our previous reports [10].

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