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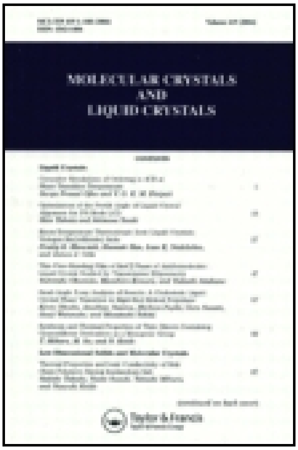

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Synthesis and Characterization of a Novel Conducting Graft Copolymer

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Synthesis and Characterization of a Novel Conducting Graft Copolymer

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The electrically conductive graft (g) copolymer, poly(dimethylolpropionic acid –co-adipoyl chloride)-g-poly(aniline) (PDMPAAC-g-PAni) was prepared by the electrochemical polymerization of aniline (Ani) using a precursor polymer, poly[(4-aminophenyl)-dimethylolpropionic amide-co-adipoyl chloride] (PADMPAAC). PADMPAAC was synthesized chemically by reacting PDMPAAC with 1,4-phenylenediamine. The electrochemical properties of graft copolymer are compared with those of PDMPAAC/PAni composites. Synthesis of PDMPAAC and PADMPAAC was characterized using ^{1}H-NMR, FT-IR spectroscopy. The electrochemical properties of the novel conducting copolymer were investigated using cyclic voltammetry (CV) and chronoamperometry (CA); thermal properties were investigated using thermogravimetric analysis (TGA). The electric conductivity was measured with four-probe method.

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

1. INTRODUCTION

In recent years, study of conducting polymers has become one of the most important areas of research in materials science [1]. Conducting polymers have attracted so much research interest in wide range applications such as in chemical sensor [2,3], light emitting diode [4],

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EMI shielding [5,6], electrochromic display device [7,8], rechargeable battery [9,10], photovoltaic cell [11] etc. Conducting polymers have good electrical properties, but they exhibit poor environmental stability, brittleness, low elongation, and poor processibilities. In order to improve these problems methods of reforming the monomers of the conducting polymers or synthesis of composites [12,13] and copolymers [14,15] are reported. Among conducting polymers, polyaniline (PAni) has been extensively studied for its environmental stability in the conducting form, easiness and low cost of synthesis, and high conductivity [16,17].

In this work, we have prepared a new conducting graft copolymer of poly(dimethylolpropionic acid-co-adipoyl chloride) (PDMPAAC) and PAni, PDMPAAC-g-PAni, by using a precursor polymer, poly[(4-aminophenyl)-dimethylolpropionic amide -co- adipoyl chloride] (PADMPAAC) which is processable and has desirable mechanical properties. The electrochemical polymerization method is used for the preparation of the novel conducting graft copolymer. The electrochemical properties of graft copolymer are compared with those of PDMPAAC/PAni composites. Synthesis of PDMPAAC and PADMPAAC was characterized using ^{1}H-NMR, FT-IR spectroscopy. The electrochemical properties of the novel conducting copolymer were investigated using cyclic voltammetry (CV) and chronoamperometry (CA); thermal properties were investigated using thermogravimetric analysis (TGA). The electric conductivity was measured with four-probe method. The route for the preparation of PDMPAAC-g-PAni is shown in Scheme 1.

2. EXPERIMENTAL

Chemicals

The chemicals used in this study were of ACS grade. Aniline (Ani) (Aldrich) and tetrahydrofuran (THF) (Aldrich) were dried over CaH_2 and distilled under reduced pressure. 1,4-phenylenediamine (Aldrich) was recrystallized from benzene. The other chemicals were purchased from Aldrich and used without further purification.

Synthesis of PDMPAAC

PDMPAAC was synthesized by copolymerizing dimethylolpropionic acid (DMPA) and adipoyl chloride (AC) for 24 hrs at 60°C under N_2 atmosphere in THF. The synthesized copolymer was precipitated by pouring its solution to methanol/water mixture solution. The precipitate was filtered and dried at 60°C under vacuum.

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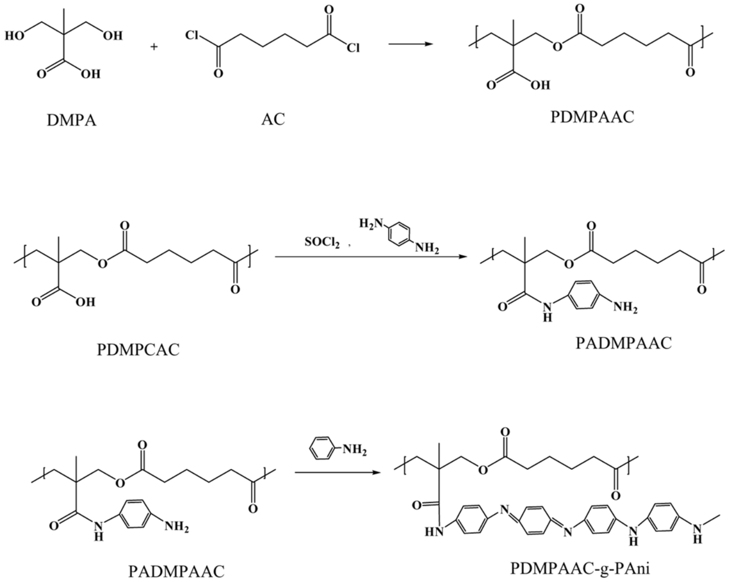

SCHEME 1 The route for the preparation of PDMPAAC-g-PAni.

Synthesis of PADMPAAC

PADMPAAC was synthesized as follows: Poly(dimethylolpropionic chloride –co-adipoyl chloride) (PDMPCAC) was synthesized by the reaction of PDMPAAC with $SOCl_2$ for 12 hrs at 40°C under N_2 atmosphere in $CHCl_3$. $CHCl_3$ solution of 1,4-phenylenediamine was added to a flask that contained PDMPCAC in $CHCl_3$. The reaction was continued for 12 hrs at 20°C under N_2 atmosphere. The product solution was poured into acetone for the precipitation. The precipitate was filtered and dried at 20°C under vacuum.

Electrochemical Polymerization of PDMPAAC-g-PAni

PADMPAAC dissolved in dimethyl sulfoxide (DMSO) was spin-coated on a platinum disc electrode. The electrochemical graft polymerization of aniline onto PADMPAAC 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 DMSO/water mixture. The potential range for electrochemical polymerization and the scanning rate were $-200 \sim 1000$ mV (vs. SCE) and 50 mV/sec, respectively.

Characterization

The structure of copolymers was characterized using FT-IR (Perkin-Elmer, Spectrum 2000) and ^{1}H-NMR (Varian, 500 NB) spectroscopy. TGA data were obtained under nitrogen atmosphere by using a Du Pont 2950 TGA at a heating rate of 20°C/min. The electrical conductivity was measured by using a four-probe method (Fluke, model 73 III multimetry).

3. RESULTS AND DISCUSSION

Figure 1 shows the FT-IR spectra of (a) PDMPAAC, (b) PDMPCAC and (c) PADMPAAC. All of these spectra were obtained from KBr pellets. In comparison with Figure 1(a) and Figure 1(b), the disappearance of the broad peak at 3200–3650 cm^{-1} in Figure 1(a) are due to chloridation of O–H. Figure 1(c) shows the new peaks at 1600 and 1500 cm^{-1} due to aromatic C=C stretching and 3200 and 3400 cm^{-1} due to –NH$_2$ stretching. The conversion yield of PDMPAAC into PADMPAAC is about 95%.

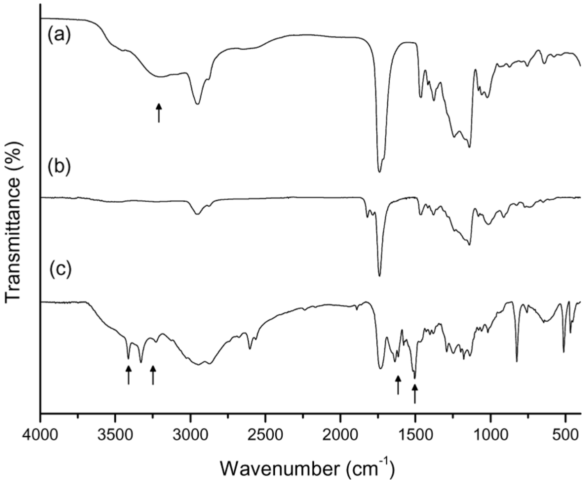

FIGURE 1 FT-IR spectra of (a) PDMPAAC, (b) PDMPCAC and (c) PADMPAAC from KBr pellets.

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Figure 2 shows the 1H-NMR spectra of (a) PDMPAAC, (b) PDMPCAC and (c) PADMPAAC. Figure 2(a) shows peaks at $\delta = 12.5$ ppm due to proton of carboxylic acide, which was disappeared in Figure 2(b). Figure 2(c) shows the new peaks at $\delta = 6.5$–7.2 ppm due to aromatic protons and $\delta = 7.8$ ppm due to proton of amide.

Figure 3 shows the cyclic voltammograms obtained from the synthesis of PDMPAAC-g-PAni copolymer and PDMPAAC/PAni composite with 0.1 M aniline and 1.0 M sulfuric acid. For the preparation of PDMPAAC-g-PAni copolymer and PDMPAAC/PAni composite, DMSO/water mixture is chosen as a medium because DMSO loosens the compact PADMPAAC and PDMPAAC structures and thus the penetration of aniline monomer into PADMPAAC and PDMPAAC becomes easier. By comparison of cyclic voltammograms recorded during the preparation of PDMPAAC-g-PAni copolymer and PDMPAAC/PAni composite, it can be seen that the current peaks of PDMPAAC-g-PAni copolymer are higher than those of PDMPAAC/PAni composite. The higher increase of maximum current and shifting of its peaks to higher potential imply that the PAni formation is started at the phenylenediamine moieties in the precursor film.

Figure 4 shows chronoamperograms of PDMPAAC-g-PAni copolymer and PDMPAAC/PAni composite that were polymerized with Ani for 1 hr under the constant potential of 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 V using PADMPAAC and PDMPAAC as precursor and matrix film, respectively. In comparison with Figure 4(a) and (b), when PADMPAAC was used as a precursor film, the oxidation current flows much more and polymerization occurs more rapidly at the same potentials as compared to the use of PDMPAAC as a matrix film. This fact implies that since the phenylenediamine group in PADMPAAC has lower oxidation potential than the free aniline monomer, PAni domains can be formed more easily in the graft copolymer.

TGA thermograms of PDMPAAC-g-PAni copolymer and PDMPAAC/PAni composite are given in Figure 5. In the case of PDMPAAC/PAni composite the weight loss occurs before 180°C with a weight loss of 4.0% which can be attributed to the expulsion of loosely bound water molecule from the polymer chain. Between 180°C and 370°C, a rapid weight loss occurs and PDMPAAC/PAni composite loses 56% of its weight. It can be attributed to the dopant loss, and the beginning of a chain degradation. Above this temperature range, a slower weight loss process assigned to main chain degradation occurs. In the case of PDMPAAC-g-PAni copolymer, however, the weight loss of 6.0% occurs before 150°C. It can be attributed to the expulsion of loosely bound water molecule from the polymer chain. Between 150°C and 380°C, a slower weight loss than in the cases of PDMPAAC/PAni

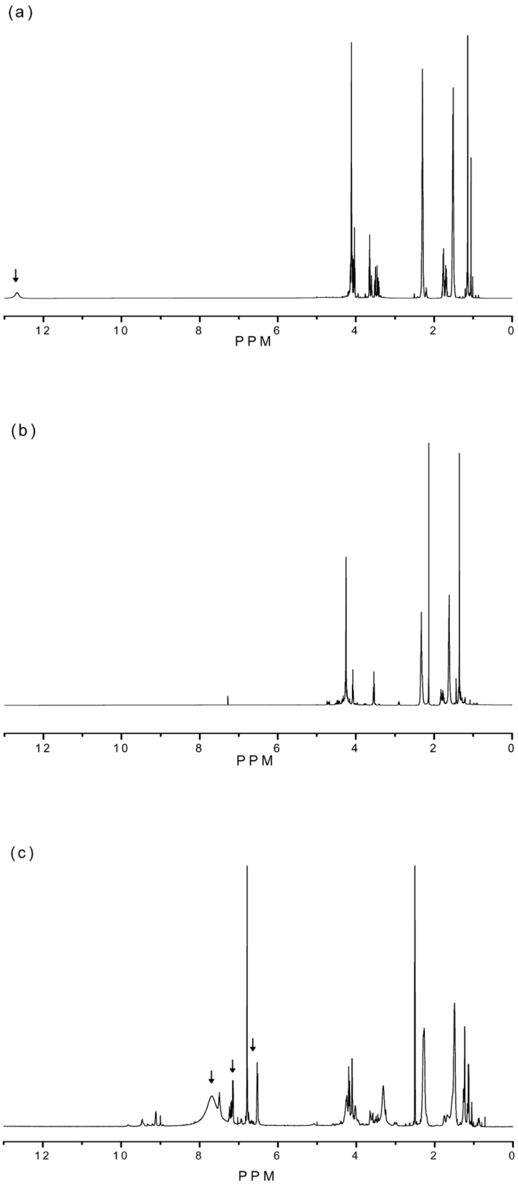

FIGURE 2 ^{1}H-NMR spectra of (a) PDMPAAC, (b) PDMPCAC and (c) PADMPAAC in DMSO-d_6.

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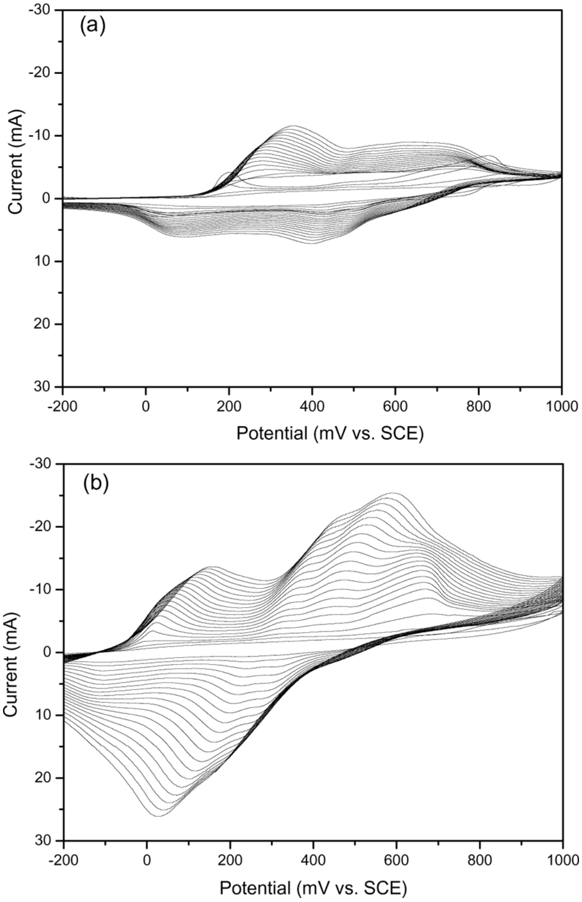

FIGURE 3 Cyclic voltammograms of aniline polymerization on (a) PDMPAAC-coated (PDMPAAC/PAni) and (b) PADMPCAC-coated (PDMPAAC-g-PAni) Pt electrode in DMSO/water containing 0.1 M aniline and 1.0 M sulfuric acid at 50 mV/s scan rate.

composite occurs. The weight loss reaches about 48%, which can be attributed mainly to dopant loss and the beginning of a chain degradation. Above this temperature range, the polymer presents very slow weight loss process assigned to main chain degradation. The relatively stable thermal degradation behavior of the copolymer above 370°C might be due to the grafted branch polymer.

The conductivities of PDMPAAC-g-PAni copolymer and PDMPAAC/PAni composite prepared for 1 hr under the constant potentials of

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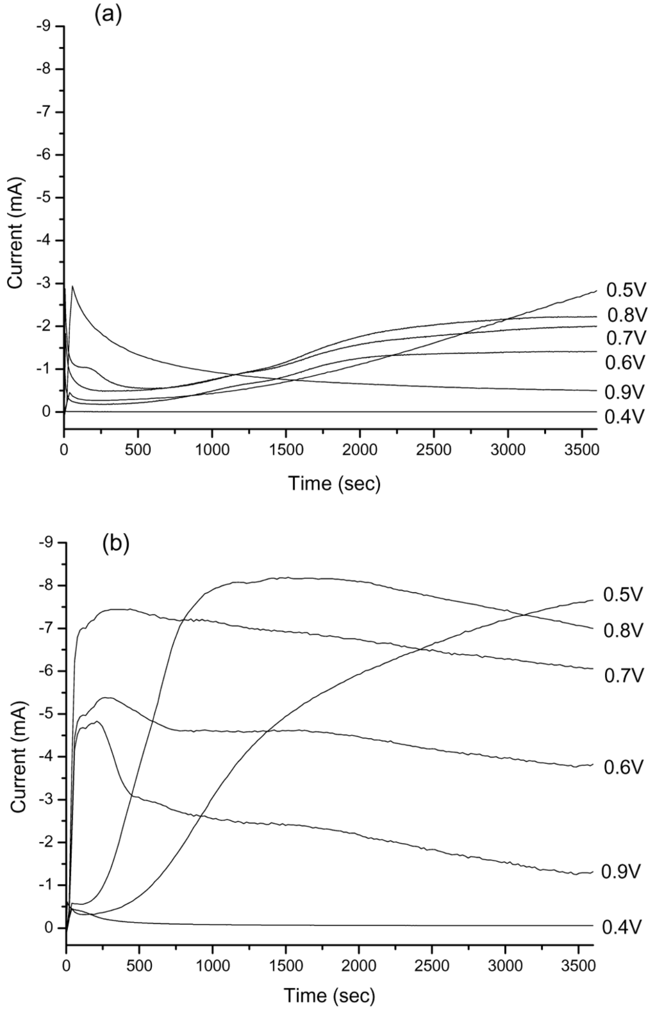

FIGURE 4 Chronoamperograms of aniline polymerization on (a) PDMPAAC-coated (PDMPAAC/PAni) and (b) PADMPCAC-coated (PDMPAAC-g-PAni) Pt electrode at a constant potential of 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 V for 1 hr.

0.5 V were measured. The conductivities of PDMPAAC-g-PAni copolymer and PDMPAAC/PAni composite were 2.2×10^{-1} and 1.9×10^{-2} S/cm, respectively. The PDMPAAC-g-PAni copolymer has higher conductivity than the PDMPAAC/PAni composite. A possible reason for this could be due to the presence of regularly repeated PAni

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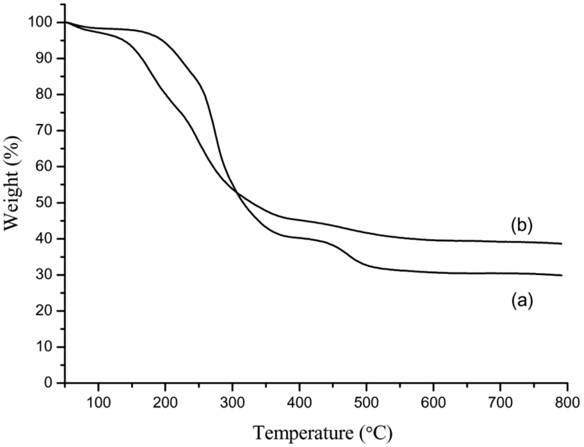

FIGURE 5 TGA thermograms of (a) PDMPAAC/PAni and (b) PDMPAAC-g-PAni.

branch of the PDMPAAC-g-PAni and the less uniform distribution of PAni of the PDMPAAC/PAni composite.

4. CONCLUSION

PDMPAAC-g-PAni copolymer can be prepared by the electrochemical method. For the preparation of PDMPAAC-g-PAni copolymer, the precursor polymer, PADMPAAC which has been synthesized by the chemical reaction of PDMPCAC with 1,4-phenylenediamine is utilized. The PDMPAAC-g-PAni copolymer showed higher electrochemical activity compared to that of PDMPAAC/PAni composite. The electrical conductivity of the copolymer was about 2.2×10^{-1} S/cm which is about one order of magnitude higher than that of the composite. The conductivity results support that the phenylenediamine moieties of PADMPAAC act as nuclei for the graft copolymerization reaction of Ani with PADMPAAC.

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