Electrochemical Copolymerization of Bithiophene and Aniline in Aqueous-Organic Mixed Solution

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Polybithiophene (PBTh) and polyaniline (PAn) have been synthesized electrochemically in an aqueous-organic mixed solvent containing perchloric acid and acetonitrile. By using the mixed solvent system, the difference between the oxidation potentials of the two monomers is substantially reduced to 0.17 V from 0.55 V in pure acetonitrile organic medium. This enables the electrosynthesis of copolymer of bithiophene and aniline. Raman and absorption spectra were compared.

Polythiophene (PTh) and polyaniline are by far the most studied conjugated polymers due to attractive applications.[1-3] Recently, attention has been paid to electrosynthesis of copolymers based on aniline derivatives and thiophene derivatives.[4,5] Nevertheless, limited work was reported on electrochemical copolymerization of aniline with thiophene derivatives.[6] The main difficulty is the large difference in the electro-oxidation potentials between the two types of monomers. For example, the onset oxidation potentials of aniline, bithiophene and thiophene are 0.65, 1.2 and 2.4 V respectively. So far copolymers of thiophene or bithiophene with aniline were mainly synthesized *via* conventional multistep chemical methods.[7-9]

Whilst there are some reports on electrochemical study of thiophene in aqueous solutions,[10,11] bithiophene is insoluble in water. In order for copolymerization to occur, it is very important to have a suitable solvent/electrolyte system in which both monomers, e.g., bithiophene and aniline, dissolve readily. Also it is desirable the two monomers should have similar oxidation potentials. This would allow the possibility of electrogeneration of the cationic free radical intermediates of the two monomers simultaneously, which is believed to be crucial for well-controlled copolymerization to occur. Results show that bithiophene and aniline can dissolve in the mixed solution of aqueous perchloric acid and acetonitrile. Copolymers of bithiophene and aniline can be deposited electrochemically in this mixed solution system.

2,2'-Bithiophene (97%, Aldrich), aniline (99%, Aldrich), acetonitrile (HPLC, J.T. Baker) and perchloric acid (70% in water, Univar) were used as received. An EG&G 273 potentiostat was used for the electrochemical study. Electropolymerization was carried out at room temperature in a three-electrode system in 1 M perchloric acid solution in water and acetonitrile mixture. Platinum foil, Ag/AgCl and ITO glass were used as counter, reference and working electrode respectively. Spectroscopic study was conducted using a Renishaw Raman (with HeNe laser) and a HP spectrometer.

Cyclic voltammetry experiments also revealed that the current density for electropolymerizing bithiophene is generally much higher than that for aniline at a given potential. This indicates a faster reaction rate of bithiophene. Therefore, concentrations of bithiophene and aniline used for copolymer deposition were 0.002 and 0.1 M respectively. Figure 1 displays first-cyclic voltammograms of aniline, bithiophene and a mixture of the two monomers in a mixed solution with volume ratio of water to acetonitrile of 3:1. The difference between the onset oxidation potentials in the mixed solvent is much lower than that of in the organic solvent acetonitrile. The onset oxidation potential of the monomer mixture is 0.82 V which is in between 0.9 V for bithiophene and 0.73 V for aniline. Also the current density is not the simple sum of the values for the two monomers measured individually. These observations suggest interaction between the monomers and that the intermediates of the two monomers may have reacted to form copolymer. The development of the doping and dedoping peaks at 0.32 and 0.18 V can be seen in the multiple cyclic voltammograms of the

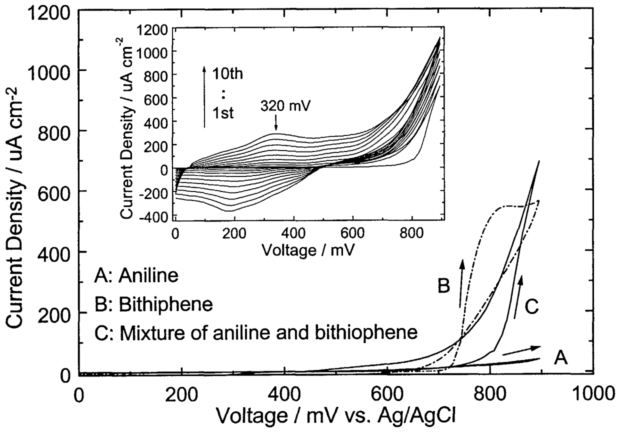

Figure 1. First cyclic votammograms (scan rate: 10 mV/s) of aniline, bithiophene and their mixture in $HClO_4$/Acetonitrile solution with water to acetonitrile ratio of 3:1. The inset shows multiple-cyclic votammograms of the monomer mixture.

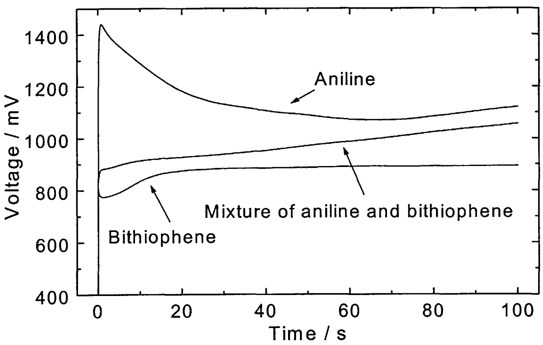

Figure 2. Chronopotentiograms of aniline, bithiophene, and their mixture obtained at constant anodic current densities of 0.5 mA/cm^2.

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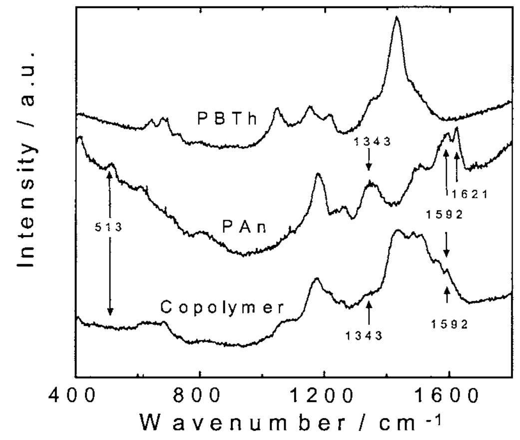

Figure 3. Raman spectra of PBTh, PAn and a copolymer of bithiophene and aniline.

monomer mixture (inset of Figure 1). This indicates that the copolymer deposited is electroactive. It should be pointed out that these multiple cyclic voltammograms of copolymer deposition are very different from those of polyaniline and polybithiophene homopolymers (not shown). Figure 2 shows chronopotentiograms of aniline, bithiophene, and their mixture obtained at constant anodic current densities of 0.5 mA/cm^2 in the same mixed solution. It can be seen that the potential trace of mixture is located between those of two monomers. The potential versus time trace of copolymerization is distinctively different from those of homopolymerization of the two individual monomers. The onset oxidation potentials observed in the chronopotentiograms agree well with those observed in the cyclic voltammograms given Figure 1.

Figure 3 shows the Raman spectra of PBTh, PAn and a bithiophene-aniline copolymer electrodeposited on ITO glass. The thickness of the polymer films was about 0.2-0.3 μm. It can be seen that the Raman spectra of the copolymer is quite different from those of PAn and PBTh homopolymers. The bands at 1620 and 1343 cm^{-1}, assignable to phenyl ring stretching and C=N-C in PAn respectively,[12,13] appear in PAn but not in the copolymer. However, the aniline units must exist due to the retaining of bands at about 1590 and 1170 cm^{-1} in the copolymer spectrum. Perhaps, it is worth noting that the band at 513 cm^{-1} in PAn, assignable to N-C=O,[12] is also absent in the copolymer spectrum.

Additional evidence for copolymerization is from the absorption spectroscopy. Figure 4 shows the UV-Vis absorption spectra of electrochemically synthesized PBTh, PAn and a bithiophene-aniline copolymer in dedoped states. It can be seen that the copolymer spectrum is clearly not a simple mixture of those of PBTh and PAn homopolymers. It is important to point out that the absorption spectrum of the electrochemically deposited copolymer studied here is remarkably similar to the reported spectrum of the copolymer synthesized *via* conventional chemical oxidation method.[7]

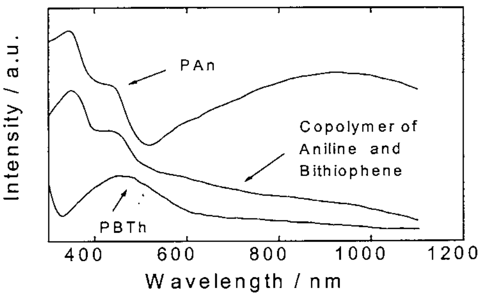

Figure 4. Absorption spectra of dedoped films of electrochemically synthesized PBTh, PAn, and bithiophene-aniline copolymer.

Although further study is necessary in order to reveal more detailed structure and properties of the copolymer, the following conclusions can be drawn from the above analysis. Copolymer of bithiophene and aniline was synthesized *via* electrochemical method in an aqueous-organic mixed solution system. More balanced or matched oxidation potential of the two monomers can be achieved by utilizing the mixed solution system. Copolymerization could thus be better controlled owing to the reduced difference of the oxidation potentials of the two monomers. Results from Raman and absorption spectroscopy supported the prediction of copolymerization.

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