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Effects of Molar Ratios Between Surfactant and Aniline in Synthesis of Polyaniline

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Abstract. Conductive polymers are widely used in many applications such as sensors, solar cells, diodes, electrodes, and actuators. Among of conductive polymers, Polyaniline (PANI) has gained more interests due to high environmental stability, electrical conductivity, easy processability, and low cost. Synthesis of PANI with different molar ratios between Dodecylbenzenesulfonic acid (DBSA) and Aniline (An) ([DBSA]/[An]) at 0.5, 1.0, and 1.5 were investigated. The increased molar ratio of surfactant affects to improvement in higher electrical conductivity of 18.91×10^{-2} S/m. This is due to the increasing of doping in PANI-DBSA which can be obtained by Fourier Transform Infrared Spectroscopy (FTIR). At high molar ratio, thorn-like structure and smooth surface of PANI are observed compared to irregular structure at low molar ratio. Moreover, the chemical structures of PANI-DBSA are investigated by Solid-state Nuclear magnetic resonance spectroscopy (NMR).

1. Introduction

Conductive polymer is an organic based polymer which can act as a conductor or a semiconductor due to their conjugated polymeric chains in form of polarons or bipolarons [1]. Among conductive polymers, Polyaniline (PANI) is widely studied because of ease of synthesis, low cost, good environmental stability, and good electrical conductivity [2, 3]. PANI has been used in many applications such as rechargeable batteries, shielding of electromagnetic interference, microwave and radar absorbing materials, sensors and indicators, membranes, electrochemical capacitors (supercapacitors), and solar cells [3, 4].

In general, conducting polymer is not dissolved by common organic solvents, this is because of their large intermolecular interfacial tension. Therefore, addition of functionalized protonic acids with long alkyl chain such as dedecylbenzene sulfonic acid (DBSA), sodiumdodecylsulfate (SDS), sodiumdodecylbenzenesulfonate (SDBS), and camphor sulfonic acid (CSA) could increase the solubility of PANI [1]. Commonly, emulsion polymerization is carried out with hydrophobic monomer



accumulated in the center of micelles with surrounding hydrophobic tails of emulsifiers, which providing suitable environment for para-directed coupling of monomer and leads to formation of conducting PANI [5, 6]. The aim of the present work is to investigate the effect of molar ratio between DBSA and aniline in PANI polymerization, effect of DBSA doped PANI at different molar ratio were carried out and characterized in this study.

2. Experimental study

2.1 Materials

Aniline ($C_6H_5NH_2$, 99% of purity) and Ammonium peroxodisulfate ($(NH_4)_2S_2O_8$, APS) were purchased from Wako, Japan. Dodecylbenzenesulfonic Acid (DBSA with >95% of purity) was purchased by Tokyo Chemical Industry Co., Ltd. APS and DBSA are used as oxidant and surfactant in the polymerization, respectively.

2.2 Synthesis of PANI

4 mmol of Aniline was mixed with DBSA and 90 ml of distilled water, solution was stirred 3 h. 5 mmol of APS was mixed with 10 ml of distilled water, solution was stirred 1 h. Next, APS solution was dropped with low speed into Aniline solution, the polymerization was carried out at 20 °C for 24 h. After polymerization is done, the dark green precipitates are obtained. 100 ml of Methanol was added into the solution to stop the polymerization, the precipitates were filtered, washed with methanol and distilled water until the pH of washing liquid reached pH 7.0. Finally, precipitates were dried in vacuum at 60 °C for 24 h, and the sample was pulverized into powder form.

2.3 Characterizations

Samples were characterized using Fourier Transform Infrared Spectroscopy (FTIR) (Perkin Elmer FT-IR Spectroscopy Frontier), 20 scans were used with scan range from 4000 cm^{-1} to 400 cm^{-1} . Nuclear Magnetic Resonance Spectroscopy (NMR) by JEOL (ECA400) was used to identify the chemical structure of the samples. PANI power was formed into pellet form with diameter of 13 mm at 700 MPa of pressure. The resistance of PANI pellets was tested by Prostat Resistance Meter (PRS-812), which the resistance was converted into electrical conductivity. Microstructures of PANI were observed by Scanning Electron Microscopy (SEM) (JCM-6000).

3. Results and discussion

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectrum of PANI-DBSA at various molar ratio between DBSA and aniline is illustrated in Figure 1. Main absorbances are observed at 1567 cm^{-1} , 1493 cm^{-1} , 1445 cm^{-1} , 1298 cm^{-1} , and 1136 cm^{-1} , these peaks are assigned to C=N stretching vibration of quinoid ring, C=C stretching vibration of benzenoid ring, C=C stretching of aromatic ring, C-N stretching of secondary aromatic amine, and NH⁺ stretching mode which indicates the degree of electron delocalization and its characteristic of conductivity, respectively [7-11]. In addition, relatively intensity of peak at 1136 cm^{-1} compared to peak at 1298 cm^{-1} is considerably increased in doped sample at high molar ratio, which result in higher conductivity of PANI-DBSA [11]. Besides, peaks at 1245 cm^{-1} , 1033 cm^{-1} , 1007 cm^{-1} are associated to C-N stretching in benzenoid unit, S=O stretching of DBSA, and C-H stretching of benzenoid ring in DBSA molecule, accordingly [10, 12, 13]. In addition, H-bonded of NH vibration and aliphatic C-H stretching are located at 3233 cm^{-1} , and region of 2800 - 3000 cm^{-1} , which C-H stretching is depending on long alkyl of DBSA [10]. Molar ratio of 1.5 exhibits the obvious peaks in the region of 2800-3000

cm^{-1} due to the higher content of DBSA. Small peaks at 823 cm^{-1} and 667 cm^{-1} are assigned to C-H out of plane bending vibration of 1,4-disubstituted benzene ring and S-O stretching vibration of DBSA [8, 14].

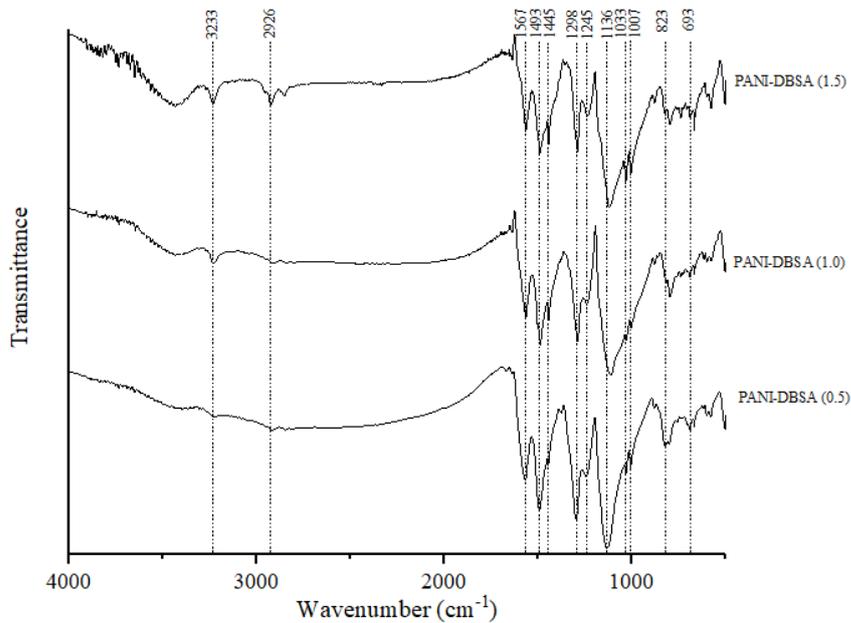


Figure 1. FTIR spectrum of PANI-DBSA at 0.5, 1.0, and 1.5 of molar ratio

3.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

The chemical structures of PANI and DBSA, and NMR spectra of PANI-DBSA are illustrated in Figure 2 and 3, respectively. Sharpest peaks at 128 and 124 ppm are associated to C-2 and C-3 position in benzenoid structure, respectively. Besides, non-protonated carbon C-1, protonated carbon C-4 and C-5 in benzenoid part, and C-8 in quinoid part are observed at 148, 140, and 137 (shoulder), accordingly. Small peak at 163 ppm is assigned to C-7 non-protonated carbon in quinoid part, while peak at 114 (shoulder) ppm in the spectra is associated with C-6 in benzenoid part. Several peaks of aliphatic carbon region between 10-50 ppm is arisen solely from aliphatic DBSA chains [15, 16]. In addition, presence of peaks at 180 and 96 ppm are referred to the cross-linking of well-ordered structures [17].

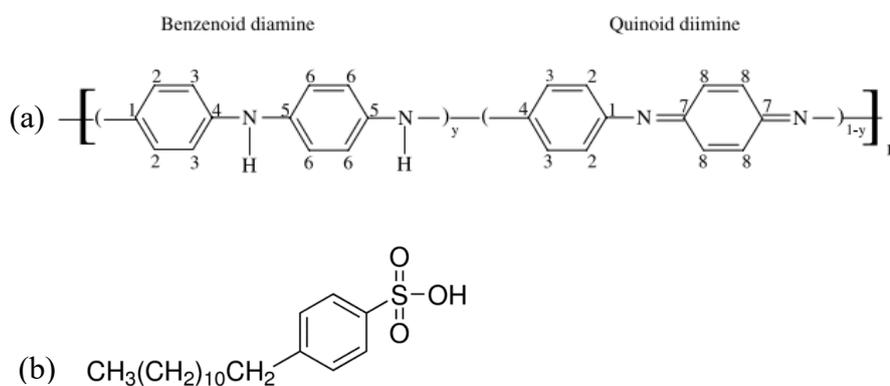


Figure 2. Chemical structure of (a) PANI and (b) DBSA

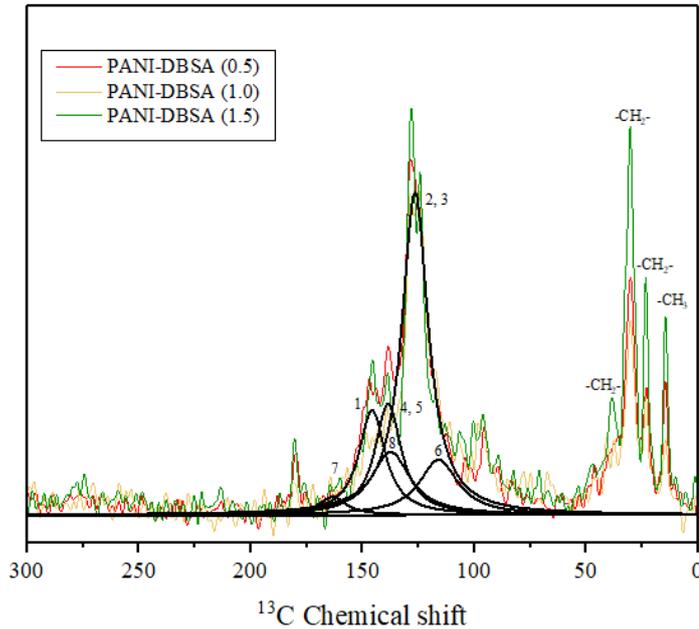


Figure 3. Comparison of ^{13}C NMR spectrum of PANI-DBSA at 0.5, 1.0, and 1.5 of molar ratio

3.3 Electrical conductivity

Electrical conductivities of PANI-DBSA at different molar ratios are illustrated in Figure 4. Low molar ratio of [DBSA]/ [An] at 1.25:0.5 exhibit the lowest electrical conductivity of 1.167×10^{-6} S/m. However, high molar ratio of 1.5 shows the highest electrical conductivity of 18.91×10^{-2} S/m. It is observed that increasing of molar ratio between DBSA and aniline influences on electrical conductivity of PANI-DBSA. This is due to addition of protonic acid as dopant. This doping agent is source of charge compensation which increases the conjugation length without protonation [16, 18].

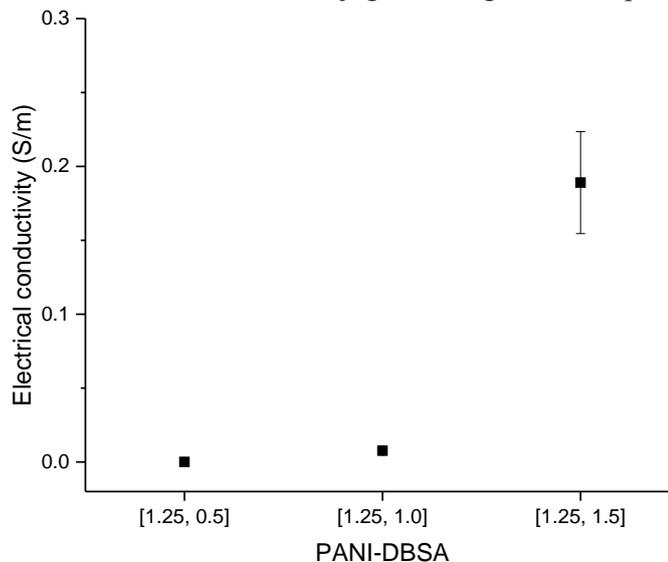


Figure 4. Electrical conductivity of PANI-DBSA at different molar ratio [DBSA]/ [An]

3.4 Scanning Electron Microscopy (SEM)

Figure 5 illustrates the microstructures of PANI-DBSA at different molar ratios between [DBSA]/[An]. At molar ratios of 0.5 (Figure 4a) and 1.0 (Figure 4b), PANI-DBSA microstructures are agglomerated and formed irregular rock-like shape. However, at molar ratio of 1.5 (Figure 4c), thorn-like structure and smooth surface are observed in PANI-DBSA microstructure. This is due to the changes in molar ratio causes the transition of micellar shape [19].

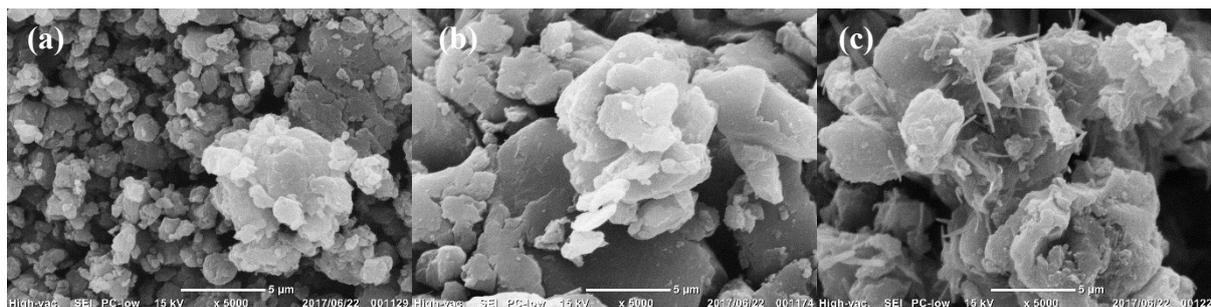


Figure 5. SEM images of PANI-DBSA at (a) [1.25, 0.5], (b) [1.25, 1.0], and (c) [1.25, 1.5] of [DBSA]/[An] molar ratios

4. Conclusion

DBSA doped PANI was polymerized at different molar ratios between DBSA and Aniline. High molar ratio of 1.5 exhibits the highest electrical conductivity of 18.91×10^{-2} S/m compared to the electrical conductivity at low molar ratios of 1.167×10^{-6} S/m. This is due to increasing of doping in PANI-DBSA at high molar ratio of 1.5. Besides, the morphology of high molar ratio illustrates the smooth surface and thorn-like structure, while low molar ratio exhibits the irregular agglomerated structure.

Acknowledgement

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