Synthesis of Polyaniline in the Presence of Physiological Active Compounds

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Abstract: Synthesis of polyaniline (PANI) in the presence of physiological active materials is reported. Infrared absorption, electron spin resonance, and UV-Vis optical absorption spectroscopy measurements for the resultants were carried out. Scanning electron microscopy (SEM) observations revealed the surface structures of the polymer.

Introduction

Polyaniline (PANI) has been studied for over a century [1-5]. Polyaniline has various advantages such as simple synthetic process, low cost, good stability in the air, and relatively high electrical conductivity. Polymerization mechanism [6-8], surface structure [9-18], synthesis of nano-composite [19-21], and chiroptical properties of polyaniline [22] have been studied. Polymerization of aniline under different conditions allows formation of various fine surface structures [23]. Sensor function of polyaniline for medical applications was examined [24].

Sugars and polysaccharides have been used as pharmaceutical materials, foods, molecular motors [25], and water purification [26]. Properties of polysaccharide such as oxidative reaction [27], and 3-D structure have been studied [28]. Carbon nanotubes/alginate acid [29], and PANI/polysaccharides composites have been developed [30]. Polysaccharides were employed as templates for the synthesis of polyaniline, and biocomposites was synthesized [31].

In this paper, we report synthesis of PANI in the presence of low-molecular weight physiological active compounds such as polysaccharides. Optical properties and surface structures of the PANIs thus prepared are discussed. This can be a first attempt of combination of PANI and pharmaceutical compounds in the polymerization reaction.

Experimental

Materials

Aniline (Wako Chemical, Japan) was purified by distillation. Acetic acid, adipic acid, L-ascorbic acid, cholesterol hydrogen phthalate, streptomycin, *N*-methyl pyrrolidone (NMP) (Tokyo Chemical Industry, Japan), stearic acid, retinoic acid (Wako Chemical, Japan), and ammonium persulfate (APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$) (Kanto chemical, Japan) were used as received.

Instruments

Infrared (IR) absorption spectra of the polymers were obtained by using a JASCO IR 550 Fourier transform spectrometer (Japan) with the KBr method. Ultraviolet-visible (UV-Vis) optical absorption spectra were recorded on a JASCO V-630 spectrophotometer. Electron spin resonance (ESR) measurements and electrical conductivity were carried out using a Bruker EMX-T ESR (USA) spectrometer and Loresta GP (measurement range: 10^3 – 10^{-7} (S/cm)) (Japan), respectively.

Scanning electron microscopy (SEM) observations and energy dispersive X-ray spectrometry (EDS) were performed with a JEOL JSM-521 (Japan).

Pure-polyaniline

A solution of aniline (120 mM), sulfuric acid (60 mM), and hydrochloric acid (1 M) were stirred in an Erlenmeyer flask at ca. 0 °C. Then, APS (96 mM) was added to the flask, and further stirred for 24 h at ca. 0 °C. The mixture was filtered, and washed with a large volume of water/methanol for several times. After filtration, the product was collected and dried in a vacuum for 6 h. The resultant sample is abbreviated as pure-PANI.

Polyaniline/physiological active compounds

Aniline and the physiological active compounds (acetic acid, adipic acid, L-ascorbic acid, stearic acid, retinoic acid, cholesterol hydrogen phthalate, or streptomycin) were added to ultrapure water in an Erlenmeyer flask (aniline: 120 mM, the physiological active compound: 60mM). The water solution was stirred for 3 h and cooled to ca. 0 °C. APS was then added into the flask (96 mM), and stirred for 24 h at 0 °C. The mixture was filtered, and washed with a large volume of water/methanol for several times. After filtration, the crude product was collected and dried in a vacuum for 6 h. Thus, seven samples with different additives were obtained. The samples are abbreviated as P1 (acetic acid), P2 (adipic acid), P3 (L-ascorbic acid), P4 (stearic acid), P5 (retinoic acid), P6 (cholesterol hydrogen phthalate), and P7 (streptomycin).

Results and Discussion

IR absorption spectra

Fig. 1 shows IR spectra of as-prepared pure-PANI, a series of PANIs (P1-P7), and PANI-base as a reference. All of the samples showed characteristic absorptions derived from structure of the PANI. The peaks in the IR are attributed to out of plane bending (γ_{CH} : 796 cm^{-1}), in plane bending (δ_{CH} : 1133 cm^{-1}), stretching vibration (ν_{CN} : 1297 cm^{-1}), and stretching vibration from quinonoid ring (ν_Q : 1571 cm^{-1}) and benzenoid ring (ν_B : 1490 cm^{-1}) of the PANIs.

Figure 1. Infrared (IR) absorption spectra of pure-PANI, P1-P7, and PANI-base (emeraldine base).

Figure 2. Electron spin resonance (ESR) spectra of pure-PANI, P1-P7, and PANI-base (emeraldine base).

ESR spectra

Polyaniline (doped form) has radical cation units along with the main-chain as polarons. Polyaniline forms several redox states. All of the samples showed ESR signal due to unpaired electrons of the radical cations in the polarons [32], Fig. 2. The g -values of P1-P7 are to be 2.0039 (Table 1). Line-width (ΔH_{pp}) and spin concentrations are summarized in Table 1. Electrical conductivities of P1-P7 are lower than that of the pure-PANI. This may be due to the fact that spin concentrations of P1-P7 are lower than that of pure-PANI. In other words, low charge carrier density in the composite results in low conductivity (charge carrier density $\propto$ conductivity). PANI-base shows no conductivity ($< 10^{-7}$ S/cm).

Table 1. ESR measurement results.

	g -Value	ΔH_{pp} (mT)	N_s (spins/g)	Conductivity (S/cm)
Pure-PANI	2.00390	0.195	2.77×10^{20}	2.237×10^{-2}
P1	2.00390	0.215	9.63×10^{19}	6.052×10^{-4}
P2	2.00392	0.205	1.72×10^{20}	8.048×10^{-4}
P3	2.00390	0.210	5.52×10^{19}	1.775×10^{-3}
P4	2.00391	0.220	1.32×10^{20}	3.226×10^{-4}
P5	2.00391	0.239	3.25×10^{19}	2.474×10^{-4}
P6	2.00392	0.215	1.41×10^{20}	3.654×10^{-4}
P7	2.00391	0.220	6.48×10^{19}	2.773×10^{-4}
PANI-base	2.00392	0.323	1.86×10^{20}	—

UV-Vis absorption spectra

Fig. 3 displays UV-Vis optical absorption spectra of pure-PANI and P1-P7 in NMP solution. All of the samples exhibited good solubility in NMP. The absorption bands of the samples are corresponding to that of PANI-base form. The absorption band at 320-326 nm is ascribed to π - π^* transition of benzene ring, and absorption band at 630-636 nm is due to doping band.

Figure 3. UV-Vis optical absorption spectra of pure-PANI and P1-P7 in *N*-methylpyrrolidone (NMP) solution (0.05 g/L). All of the samples were pre-treated with sonification for 30 min and stirred for 3 h.

Figure 4. Scanning electron microscopy (SEM) images of pure-PANI and P1-P7.

SEM observation

Fig. 4 shows SEM images of the fine surface structure of pure-PANI and P1-P7, showing low magnification (a), high magnification (b) of the samples. The granular structure consists of tiny particles. P1, P2, P4, P5, and P7 display fiber/network structure. According to the previous research, acidity of solution of aniline in the polymerisation is the key factor to form nano-fiber/tube/rod structures of PANI. Energy Dispersive x-ray Spectroscopy (EDS) measurement evaluates that elements ratio of C, N, O, and S (Table 3) for the samples are almost the same, Table 2. The fine structure may come from process of phenazine nucleus stacking. In the polymerization process, an aniline monomer becomes low molecular aniline derivative such as phenazine-type anilinium ion (Fig. 5), and the phenazines nucleus form various fine structure [33,34]. The polymerization of aniline mechanism based on the nuclei was previously studied [35-37]. In this study, the polymerization of aniline proceeds in this mechanism on the molecular substrates.

Figure 5. Phenazine-type anilinium ion structure.

Table 2. Abundance ratio of P1-P7 obtained with EDS.

	Abundance ratio, %			
	C	N	O	S
PANI	71.2	14.9	12.7	1.2
P1	70.0	16.9	11.6	1.5
P2	69.2	17.5	11.8	1.5
P3	70.0	18.0	10.9	1.1
P4	70.6	16.9	11.3	1.3
P5	70.4	16.7	11.7	1.2
P6	71.0	16.0	11.9	1.1
P7	69.3	16.8	12.5	1.4

Conclusion

Polyanilines were synthesized in the presence of low-molecular mass physiological active compounds. SEM observations revealed that the resultant PANI showed bulky fine structure or fiber/network structure. PANI/physiological active compound may function as biological active products.

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