Characterization of Conducive polyaniline synthesized in presence of [2,2azobis{2-(2-imidazolin-2-yl)propane} dihydrochloride] (VA-044)

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1. INTRODUCTION

Polyaniline (PANi) is the most attracting conducting polymer because of its good environmental stability with excellent electrical, magnetic and optical properties. The important applications of PANi include secondary batteries, electromagnetic interference shielding, molecular sensors, non-linear optical devices, electrochromic displays and macroelectronic devices, anti-corrosion coatings, ion-exchanger for water purification especially for softening drinking water, welding (joining) of thermoplasics and thermosets. Emeraldine salt is the most conductive form of PANi, which can be obtained by protonation of emeraldine base and oxidation of leucoemeraldine base. Besides the emeraldine, leucoemeraldine, and pernigraniline; nigraniline has also been reported. Soluble polypyrrole and soluble polyaniline have been introduced recently. Good stability is essential for the characterization and application of polymers. Polyaniline is insoluble in common solvents because of stiffness of chain and inerchain interaction. Structural modification of PANi by incorporation of flexible alkyl chains into PANi through an N-alkylation method with leucoemeraldine base is another successful approach towards solubility of PANi in common organic solvents [1-5].

In the present work, we have focused on the chemical synthesis of PANi using Azo-initiator VA-044 [2,2-azobis{2-(2-imidazolin-2-yl)propane}dihydrochloride] which decomposes at higher temperature (half life at 44oC is 10 hrs) with liberation of molecular nitrogen and free-radicals as shown in Figure 1; and initiates free-radical polymerization; polyvinylpyrrolidone (PVP) as a steric stabilizer, ammonium peroxodisulphate (APS) as oxidant. The structure and properties thus obtained PANi were investigated.

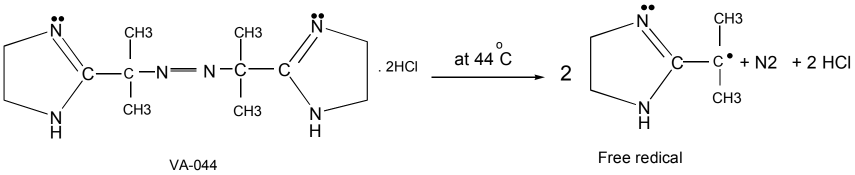


Figure 1. Structure and decomposition of VA-044.

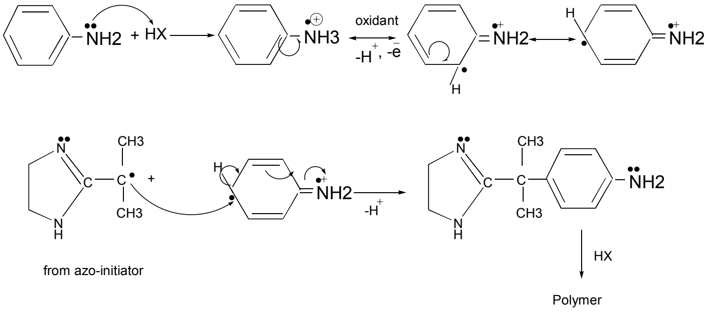
2. EXPERIMENTAL

Aniline(Junsei, Japan), VA-044(Wako, Japan) ammonium peroxodisulphate (APS,,98.5%), Toluene sulfonic acid (TSA)(98.5%), HBr (48%) and Polyvinylpyrrolidone (PVP) (Aldrich) were used without further purification. 0.93gm

(0.01 mole) of aniline was dissolved in 30 ml of aqueous acid or acid mixture (50/50, v/v) (dopants). Then 0.5 gm of initiator followed by 1.0gm of PVP were added to the beaker containing stirring mixture of aniline monomer and dopant(s). VA-044 was not used in sample no.1 and 5; and PVP was not used in sample no.3. The reaction mixture was transferred into three-naked reaction flask (100 ml) and was stirred for 24 hrs at 440C. 2.28 gm APS oxidant (0.01 mole, same in all cases) was dissolved in 30 ml mixture of TSA and HBr (equivolume) for experiments from 1 to 3 and in 20 ml for experiments 4 and 5. The oxidant solution was added slowly to the stirring solution (1drop/sec). The well-dispersed composite solutions was dropped on thin PET sheet cleaned by methanol and was coated by moving and pressing scroll bar in one direction. The coated film was dried in oven (80o C) for 5 minutes and surface resistivity was measured by SM-8220 (DKK.TOA Co., Japan) instrument. For dedoping process, the prepared composite was poured over glass slide and allowed to dry in dust free environment for 1 day. The film of glass was dipped on concentrated ammonia solution for 12 hours, washed several times by distilled water and dried in drying oven at 80o C for 24 hours. The electronic spectra of PANi composite dispersions in situ-polymerization were recorded in UV-VIS spectrophotometer (JASCO-550).

3. RESULTS AND DISCUSSION

The possible mechanism of polymerization is shown in Scheme I. The key of our investigation is thus obtained free radical attacks on anilinium ion and hence polymerization proceeds.



Scheme I. Proposed mechanism of Polymerization.

The surface resistivity of PET film coated by polyaniline is listed in Table 1. To obtain well dispersion in aqueous solution was the main goal of the present work. PANi/PVP/VA-044 composite is more stable than PANi/PVP composites. This may be, of course, due to H-bonding between (i) N-atom of VA-044 bonded with PANi chain and NH- of another PANi chain or H-of protic solvent (ii) NH groups of VA-044 attached with PANi chain and O-atom of PVP or solvent containing O-atoms (iii) NH group of PANi chain and O-atom of PVP or solvent (eg. water, ethanol etc). However, the macroscopic precipitation of PANi/PVP is disappeared on stirring. Moreover, the PANi doped by H2SO4 is more dispersed than PANi doped by TSA or TSA and HBr. This is because two O-atoms of H2SO4 may form H-bond with NH- group of PANi or H-atom of solvent. The surface resistivity of PANi/PVP/VA-044 was found 4 to 5 Ohm/square, particles were not seen by naked eye, no aggregation was taken place even after long time.

Table 1. Surface resistivity of PANi synthesized in different condition.

Sample No.	Surface Resistivity
PANi-1	10^8 Ω/㎠
PANi-2	$10^{4.5}$ ~ 10^5 Ω/㎠
PANi-3	$10^{6.5}$ ~ 10^7 Ω/㎠
PANi-4	10^4 ~ 10^5 Ω/㎠
PANi-5	$10^{4.5}$ Ω/㎠

The UV-Vis spectra of PANi were taken in situ-polymerization without any purification. UV-VIS spectra of PANi-4 are shown in Fig.2. The broad peak at 785 nm (Emeraldine Salt) can be assigned to localized polaron structure. When emeraldine salt was dedoped by concentrated ammonia solution, the peak at 331 nm and 575 nm were appeared. These peaks are due to * transition of benzoid ring [6] and benzoid-quinoid structure respectively. The peak at latter (575 nm) differs with different dedoping agent [7-9]. UV-VIS spectra of PANi-5 were also taken but there was no characteristic difference, therefore they are not shown here.

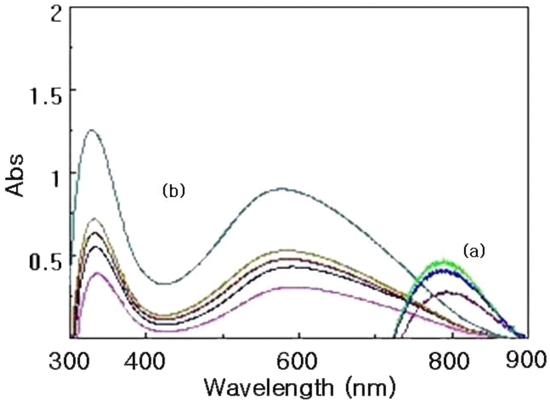


Figure 2. UV-Vis spectra of H2SO4- doped and NH4OH dedoped-polyaniline(PANi-4). **(a)** The intensity of peak of PANi (salt) is increasing with oxidation time (5 mins, 2 hrs, 3 hrs from bottom to top) **(b)** The intensity of peak of PANi (EB) is increasing with dedoping time (1 min, 30 min, 4 hrs, 5 hrs, 24 hrs; from bottom to top).

4. CONCLUSIONS

The PANi composites have been synthesized in aqueous acid medium. The characterization of PANi composites by using UV-VIS indicates the formation of polyaniline. The dispersion and surface resistivity of different samples of Polyaniline synthesized in one acid or mixture of inorganic and organic acid using PVP and azo-initiator are higher than PANi without VA-044. The well dispersion of PANi only with azo-initiator indicates that it must have done some role. It reveals that azo-initiator plays a multiple-role: dispersion agent by forming H-bonds, initiator and controller for polymerization.

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