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Synthesis of Water-Soluble Self-Acid-Doped Polyaniline

Show-An Chen* and Gue-Wuu Hwang

Department of Chemical Engineering
National Tsing-Hua University
Hsinchu, Taiwan 30043, China

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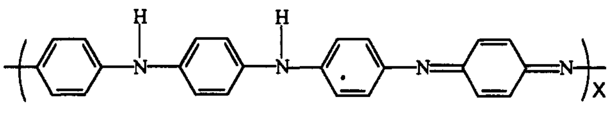
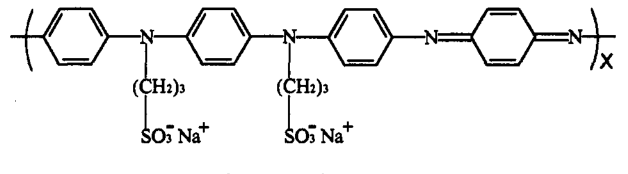
Polyaniline (PAn) is different from other conjugated conducting polymers in that it can be doped to a conducting form without the number of π-electrons being changed through protonation by exposure to an appropriate protonic acid in aqueous solution.[1] Yue and Epstein[2] have synthesized the protonic acid self-doped PAn by reaction of emeraldine base with fuming sulfuric acid to give a sulfonic acid ring-substituted PAn having a conductivity of 0.1 S/cm; however, it is insoluble in the acid form (doped) and can be made soluble only by its conversion to the salt form (undoped). Genies et al.[3] also have attempted to synthesize a self-doped PAn by reaction of emeraldine base directly with propane or butane sultone. However, the reaction product has a very poor solubility and low conductivity ($\sim 10^{-9}$ S/cm). So far, the reported self-acid-doped PAns are insoluble, and thus their applications are limited. Dao and co-workers[4] have synthesized a water soluble polyaniline, poly(aniline–propanesulfonic acid) (PAPSA), by reaction of leucoemeraldine base (the fully reduced PAn) with propanesultone. However, the PAPSA is supposed to have no imine nitrogen to allow self-acid-doping, although they have claimed the appearance of a strong absorption band at about 900 nm, which always appears for protonic acid-doped PAn. Here, we report a successful preparation of the first water-soluble self-acid-doped polyaniline, poly(aniline-*co*-*N*-propanesulfonic acid–aniline) (PAPSAH), and its sodium salt, which can be cast into free-standing films from their aqueous solutions. PAPSAH gives a conductivity of 1.5×10^{-2} S/cm without external doping.

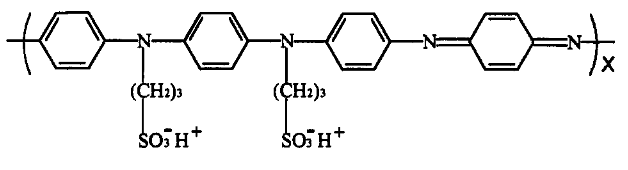
The emeraldine base form of polyaniline (PAn, compound I) was synthesized by a chemical oxidation method similar to that of MacDiarmid and co-workers,[1] and the emeraldine base so obtained has an oxidation level of about 0.5 as determined from its N(1s) core level spectrum obtained using X-ray photoelectron spectroscopy (XPS), which can be deconvoluted into two peaks with approximately equal areas, one centered at 398.3 ± 0.1 eV (due to the imine nitrogen[5]) and the other located at 399.4 ± 0.1 eV (due to the amine nitrogen[5]). Gel permeation chromatography (GPC) analysis with *N*-methyl-2-pyrrolidone (NMP) as eluent exhibits a bimodel molecular weight distribution. For the high-molecular-weight fraction, the weight average molecular weight is about 1×10^6, and for the low-molecular-weight fraction, about 1100, as compared with polystyrene standards. The dried PAn (2.26 g) was then reacted with excess NaH (0.9 g) in dired dimethyl sulfoxide (DMSO) at about 45 °C under a dried nitrogen atmosphere for 6 h to give a green-black solution, in which the original emeraldine base was probably converted to an emeraldine base without H on nitrogen (anionic nitrogen). The solution was subsequently reacted with excess 1,3-propanesultone (4.57 g) for 20 h at room temperature to give a blue-black solution. The resulting solution was precipitated with 1 M HCl aqueous solution, and the green precipitate (HCl-doped PAPSAH) after filtration was washed by a large amount of acetonitrile and then undoped with a NaOH aqueous soluton to yield a blue solution, which was then purified by dialysis with semipermeable membrane (Spectra/Por 3 membrane, molecular weight cutoff, 3500) in deionized (DI) water, which was replaced with fresh DI water frequently for 3 days. The poly(aniline-*co*-sodium *N*-propanesulfonate–aniline) (PAPSANa, compound **II**) aqueous solution so obtained was concentrated in a vacuum evaporator at a temperature below 40 °C. A PAPSANa film can be obtained by casting from this concentrated solution. The polymer, PAPSANa, was then converted to poly(aniline-*co*-*N*-propanesulfonic acid–aniline) (PAPSAH, compound **III**) by dissolving it in DI water and then exchanging Na$^+$ for H$^+$ using H$^+$-type ion-exchange resin (IR 120H resin from Rohm and Haas Co.) to give a PAPSAH aqueous solution green in color. A PAPSAH free-standing film can be obtained by casting from this green solution; however, the film is hard and brittle, since it is in the doped state.



Compound I



Compound II



Compound III

The IR spectrum of the PAPSANa shows that the ratio of the absorption intensity at 1589 cm^{-1} (due to the quinoid ring[6]) to that at 1498 cm^{-1} (due to the benzenoid ring[6]) is the same as the corresponding ratio in the emeraldine base before reacting with propanesultone, indicating an oxidation level of about 0.5. This also indicates that 1,3-propanesultone does not give an oxidation reaction during the synthesis of PAPSANa. The presence of the absorption peaks at 1172 and 1044 cm^{-1} characteristic of asymmetric and symmetric O═S═O stretching vibrations, respectively, and the absorption band at 800–600 cm^{-1} characteristic of stretching modes of C—S and S—O groups indicate the existence of SO_3^- groups.[7a] The presence of an absorption peak at 829 cm^{-1} (as in the case of the emeraldine base) characteristic of the C–H out-of-plane bending vibrations of the 1,4-disubstituted benzene ring, together with the absence of a splitting of this peak into the two peaks at 820 and 870 cm^{-1} (which occurs in the case of sulfonic acid ring-substituted PAn[2]), indicates that no ring substitution occurs in the present PAn derivative. The presence of an absorption peak at 1268 cm^{-1} characteristic of the $C_{aliphatic}$–N group,[7b] together with the presence of the SO_3^- group as stated above, shows that the alkanesulfonic acid groups are linked on the amine nitrogens.

The ^{1}H NMR spectrum of the PAPSANa shows a broad peak around 6.6 ppm, characteristic of the aromatic protons, a peak

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[1] Chiang, J. C.; MacDiarmid, A. G. *Synth. Met.* **1986**, *13*, 193–205.

[2] Yue, J.; Epstein, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 2800–2801. Yue, J.; Wang, Z. H.; Cromack, K. R.; Epstein, A. J.; MacDiarmid, A. G. *J. Am. Chem. Soc.* **1991**, *113*, 2665–2671.

[3] Hany, P.; Genies, E. M.; Santier, C. *Synth. Met.* **1989**, *31*, 369–378.

[4] Bergeron, J. Y.; Chevalier, J. W.; Dao, L. H. *J. Chem. Soc., Chem. Commun.* **1990**, 180–182.

[5] Kang, E. T.; Neoh, K. G.; Khor, S. H.; Tan, B. T. G. *J. Chem. Soc., Chem. Commun.* **1989**, 695–697.

[6] Tang, T.; Jing, X.; Wang, B.; Wang, F. *Synth. Met.* **1988**, *24*, 231–238.

[7] Nakanishi, K.; Solomon, P. H. *Infrared Absorption Spectroscopy*, 2nd ed.; Nankodo: Tokyo, 1977; (a) pp 50–51, (b) p 33.

0002-7863/94/1516-7939$04.50/0

at 3.6 ppm characteristic of the protons of the methylene of the $CH_2CH_2CH_2SO_3Na$ group bound to the nitrogen, and peaks at 2.0 and 2.9 ppm characteristic of the protons of the next methylene group and the methylene group bound to the sulfur atom, respectively. These results indicate the presence of alkanesulfonic acid groups in the resulting PAn derivative, which is consistent with the IR results.

Elemental analysis for PAPSAH[8] gives a S/N atomic ratio of 0.48, which implies that almost each amine nitrogen (about 50% of the total nitrogen) in the polymer is linked with a side chain of alkanesulfonic acid.

The free-standing film of PAPASNa has a conductivity of 1.3 × 10^{-6} S/cm, while the pressed pellet and thin film coated on a glass plate of the PAPSAH have conductivities of 1.5 × 10^{-2} and 3 × 10^{-2} S/cm in vacuum at room temperature, respectively. This PAPSAH is in the doped state, as can be confirmed by the electronic spectra of its aqueous solution and thin solid film coated on a glass plate (Figure 1, curves a and b), which exhibit a π–π^* transition of the benzenoid rings[9] at 330 nm and polaron/bipolaron band transitions[10] at about 400 and 860 nm for the solution and 420 and 910 nm for the film. As the PAPSAH aqueous solution was converted to PAPSANa by neutralization with ~2% of NaOH (aqueous), the polaron/bipolaron bands disappear and a strong exciton transition of the quinoid rings[11] at 573 nm grows at the same time (Figure 1, curve c). Furthermore, the electron spin resonance (ESR) measurement on the aqueous solution of PAPSAH gives an asymmetric ESR signal with a g value of 2.0042 and a peak-to-peak line width ΔH_{pp} of 10.8 G, and that on the film of PAPSAH gives a symmetric ESR signal with ΔH_{pp} = 0.9 G and a spin density of about 6.2 × 10^{19} spin/g and g = 2.002 865 (both values being rather close to those of HCl-doped PAn (2.2 × 10^{20} spin/g, g = 2.002 868)). The presence of free spins indicates that polarons exist in the self-doped PAPSAH in both aqueous solution and solid films. Thus, in the present self-doped polymer the alkanesulfonic acid bound on the side chain attached to the amine nitrogen protonates ("dopes") the imine nitrogen atom to make the polymer conducting.

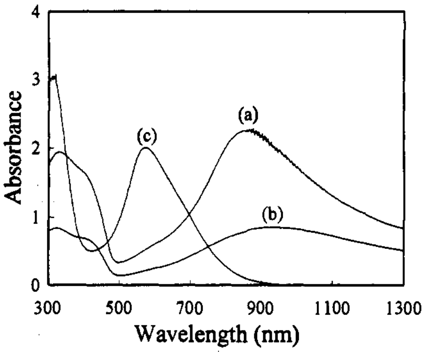

Figure 1. UV/vis spectra of PAPSAH: (a) aqueous solution, (b) thin solid film coated on a glass plate, (c) aqueous solution after neutralization with 2% NaOH (aqueous).

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[8] Elemental anal. Found for PAPSAH: C, 53.67; H, 5.64; N, 8.45; S, 9.3; O, 22.94. (Oxygen by difference).

[9] Lu, F. L.; Wudl, F.; Nowak, M.; Heeger, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 8311–8313.

[10] Stafstrom, S.; Breadas, J. L.; Epstein, A. J.; Woo, H. S.; Tanner, D. B.; Huang, W. S.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1987**, *59*, 1464–1467.

[11] Epstein, A. J.; Ginder, J. M.; Zuo, F.; Bigelow, R. W.; Woo, H.-S.; Tanner, D. B.; Richter, A. F.; Huang, W.-S.; MacDiarmid, A. G. *Synth. Met.* -1987, *18*, 303–309.