Macromolecules **2000,** *33,* 8117−8118

Synthesis of New Water-Soluble Self-Doped Polyaniline

Hsien-Kuang Lin and Show-An Chen*

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

Received April 14, 2000
Revised Manuscript Received September 7, 2000

Polyaniline, a low cost intrinsically conductive polymer, is stable under ambient conditions. Because of its low solubility in most common solvents, the industrial application of polyaniline is limited. For the purpose of improving its solubility in water and to prevent dopant migration, polyaniline has been modified in the self-doped form by introducing protonic acids into the side chains. For example, a sulfonic acid group was introduced into the benzenoid ring to give sulfonated polyaniline (SPAN)[1] obtained by reacting the emeraldine base with fuming sulfonic acid; an alkyl sulfonic acid group or an alkylbenzenesulfonic acid group was grafted on the amine nitrogen to give poly(aniline-*co*-*N*-propanesulfonic acid aniline) (PAPSAH)[2,3] by reaction of the emeraldine base with sultones or to give poly(aniline-*co*-*N*-propylbenzenesulfonic acid aniline)[4] by reaction with *p*-(3-bromopropyl)benzenesulfonic acid sodium salt. However, SPAN is only soluble in aqueous alkaline solution ($NH_4OH_{(aq)}$ and $NaOH_{\mathbf{(aq)}}$) but insoluble in pure water, while an aqueous solution of PAPSAH has to be purified by dialysis of its sodium salt further by treatment with an H^+-type ion-exchange resin. To obtain an aqueous solution of SPAN,[5] it is necessary to follow the same treatment as for PAPSAH. Both polymers become insoluble in water after drying from their aqueous solution.

Another method attempting to produce water-soluble polyaniline is to polymerize protonic-acid moiety-containing aniline derivatives, such as aminobenzylphosphoric acid, to give poly(*o*-aminobenzylphosphoric acid) (PABPA, yield 30%)[6] or to copolymerize aniline with similar monomers, such as *N*-(4-sulfophenyl)aniline and *o*-anthranilic acid to yield poly(aniline-*co*-*N*-(4-sulfophenyl)aniline) (PASPA, yield 19−70%)[7] and poly(aniline-*co*-*o*-anthranilic acid) (PAAA, yield 22−84%),[8] respectively. However, the two copolymers are only partially soluble in water, while the homopolymer PABPA is only soluble in alkaline aqueous solution. Very recently, a new water-soluble self-doped polyaniline has been proposed by grafting polyaniline onto a water-soluble polymer having pendant aniline dimers and sulfonic acid groups to obtain poly(aniline-*co*-2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPANI).[9]

In the synthesis and purification of all the above-mentioned polyaniline derivatives the use of an inorganic acid, hydrochloric or sulfonic acid, cannot be avoided. Thus, additional purification steps are necessary for removing the free acids. For the N-substituted polyanilines, a substitution of amine hydrogen with sodium by reaction of polyaniline with sodium hydride is required prior to the grafting step. In this communication, we report the synthesis of a new water-soluble self-doped polyaniline derivative, poly(aniline-*co*-*N*-benzoylsulfonic aniline) (PABSAH), by direct reaction of polyaniline with *o*-sulfobenzoic anhydride. This synthetic route has no need of an inorganic acid in the synthesis or purification steps. Yet, PABSAH so obtained is completely soluble in water and can be redissolved after drying from its aqueous solution. It has a conductivity of 4.7×10^{-4} S/cm without external doping.

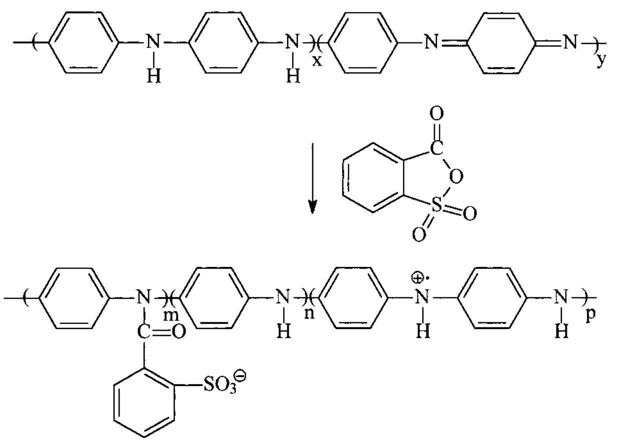

Figure 1. Reaction scheme.

The polyaniline of emeraldine base form was synthesized by the oxidation method[10] with ammonium persulfate as the oxidizing agent and has an oxidation level of about 0.5 as determined previously.[2] The emeraldine base (3.62 g, 0.04 equiv) was dissolved in 200 mL of *N*-methyl-2-pyrrolidone under a nitrogen stream. A 7.36 g (0.04 equiv) sample of *o*-sulfobenzoic anhydride was added, and the solution was kept at room temperature. After 24 h, 30 mL of H_2O was added to terminate the reaction. The resulting polymer solution was precipitated in 400 mL of acetone. The dark-green precipitate, after being filtered and washed twice with 200 mL acetone, was dissolved in 100 mL of deionized water to yield an aqueous PABSAH (I) solution. The reaction scheme is shown in Figure 1.

To remove residual *o*-sulfobenzoic acid, PABSAH (I) was undoped in 2% $NaOH_{(aq)}$ and purified by dialysis through a semipermeable membrane (Specrta/Por 3 membrane, molecular weight cutoff, 3500) in deionized (DI) water, which was replaced with fresh DI water frequently for 3 days. The excess NaOH was removed, and the pH of the polymer solution was reduced from about 12.5 to below 9.0. The aqueous solution of the poly(aniline-*co*-sodium *N*-benzoylsulfonate aniline) (PABSANa) was further treated with H^+-ion-exchange resin (IR 120H resin from Rohm and Haas Co.) to recover to its original doped form (PABSAH (II)). The dilute aqueous solution of PABSAH (II) about 2 wt % was further concentrated to about 10 wt % in a rotatory evaporator. The resulting viscous solution was stable, and no precipatation was observed for a prolonged period of time.

Following the same synthetic procedure of PABSAH (I) but replacing *o*-sulfobenzoic anhydride by *o*-sulfobenzoic acid (SBA), a SBA-doped polyaniline (PAn/SBA) dispersion was obtained. However, this dispersion was unstable, and the doped polymer precipitated within a

---

* Corresponding author: e-mail sachen@che.nthu.edu.tw.

10.1021/ma000660o CCC: \$19.00

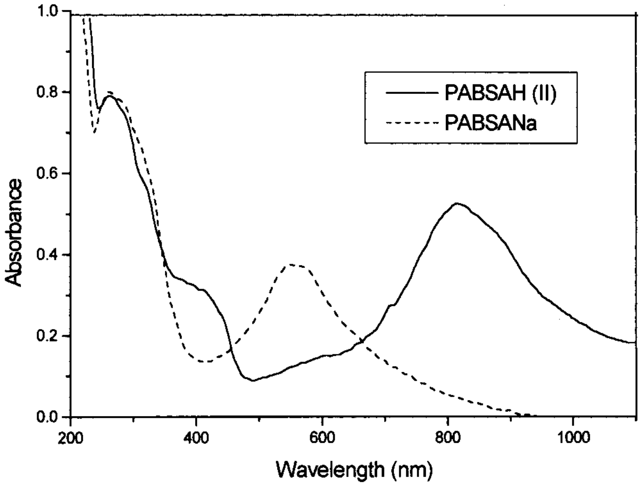

Figure 2. UV/vis spectra of dilute PABSAH (II) and PABSANa aqueous solutions.

few hours, indicating that the grafting of the acid group in PABSAH is necessary to obtain the solubility.

The electrical conductivity of compressed pellets of PABSAH (I) and PABSAH (II) measured with a four-point-probe method was 7.3×10^{-4} and 4.7×10^{-4} S/cm, respectively. Further doping of PABSAH (II) by the external dopant, camphor sulfonic acid (the equivalent ratio of camphor sulfonic acid to nitrogen atom on PABSAH is 0.3), provides only a slight increase in the conductivity (1.0×10^{-3} S/cm) close to that for PABSAH (I) in which some residual *o*-sulfobenzoic acid was still retained.

The IR spectrum of PABSAH (II) shows the characteristic absorption peaks: 1587, 1501, and 1320 cm^{-1} due to the quinoid ring, benzenoid ring, and $C_{aromatic}-N$ stretching.[11] The additional absorption at 1145 and 1018 cm^{-1} characteristic of asymmetric and symmetric $O=S=O$ stretching vibrations, respectively, and those at 800−600 cm^{-1} characteristic of stretching modes of C−S and S−O groups indicate the presence of a $-SO_3$ group in PABSAH (II).[12] The presence of the absorption at 820 cm^{-1} characteristic of the C−H out-of-plane bending of the 1,4-disubstituted benzene ring indicates the absence of ring substitution. The absorption peaks at 1640 cm^{-1} characteristic of C=O stretching vibration reveal the presence of amide groups and the attachment of sulfobenzoyl groups to the main chain.

The ^{13}C NMR spectrum of PABSANa in D_2O shows a broad peak in the range of 126−132 ppm due to the carbon atoms in the aromatic ring of main chains or side chains, peaks at 138−141 ppm due to the two carbon atoms in the aromatic rings on the side chains near $-C=O$ and $-SO_3Na$ groups, and a peak at 170 ppm due to the carbon atoms at the amide groups. This absorption shifts upfield by about 5 ppm as compared to that of the carbon atom on the carboxyl group of sodium *o*-sulfobenzoate, resulting from the lower electron negativity of the amide nitrogen in the main chain. The ^1H NMR spectrum of PABSANa in D_2O shows a broad peak in the range of 7.0−8.0 ppm, in which the aromatic hydrogens of the main chain and side chain are located.

The UV/vis spectrum of a dilute aqueous solution of PABSAH (Figure 2) has absorption peaks at 263 nm due to the $\pi-\pi^*$ transition[13] of the benzenoid ring in the *o*-sulfobenzoyl group and at 420 and 805 nm due to the polaron/bipolaron band transition,[14] indicating that PABSAH (II) in aqueous solution is in the doped state. As PABSAH (II) is converted to the salt form, PABSANa, by neutralization with 2% $NaOH_{(aq)}$, its UV/vis spectrum (Figure 2) shows the disappearance of polaron/bipolaron bands at 420 and 805 nm and the appearance of an absorption peak at 553 nm due to exciton transition of the quinoid ring. (The corresponding absorption of polyaniline in 1-methyl-2-pyrrolidone and as pure solid film is at 640 nm.[15]) The blue shift of the exciton transition could have resulted from the steric hindrance provided by the bulky side chain[16] of PAPSANa in its aqueous solution.[3] After additions of camphor sulfonic acid as external dopant to the dilute solution of PABSAH (the equivalent ratios of camphor sulfonic acid to nitrogen atom on PABSAH are 0.3−3.0), no obvious increase in the intensity of the absorption due to polarons around 805 nm was observed.

Elemental analysis for PABSAH (II) gives C, 59.23; H, 4.60; N, 8.20; S, 5.59; O, 22.38 (oxygen by difference), which yields a S/N atomic ratio of 0.3, indicating a grafting ratio of about 30%.

The ESR spectrum of PABSAH (II) in powder form gives a symmetric ESR signal with ΔH_{pp}, *g*-factor, and spin density of 2.02 G, 2.002 980, and 1.28×10^{20} spin/g, respectively, which are close to those of HCl-doped polyaniline ($g = 2.002\ 868$ and spin density $= 2.2 \times 10^{20}$ spin/g) and PAPSAH as film ($\Delta H_{pp} = 0.9$ G, $g = 2.002\ 865$, and spin density $= 6.2 \times 10^{19}$ spin/g).[3] These results indicate the presence of polarons in this substituted polyaniline and, in conjunction with the above results, that the PABSAH is a self-doped conducting polymer.

PABSAH can also form a stable solution when blended with other conventional polymers in water, for example, poly(vinyl alcohol), polyacrylamide, and poly(acrylic acid), gelatin, and hydroxyethylcellulose. The films after drying are transparent and green in color.

Acknowledgment. We thank the National Science Council of ROC for financial aid through Project NSC 88-2216-E-007-008.

References and Notes

(1) Yue, J.; Epstein, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 2800.
(2) Chen, S. A.; Hwang, G. W. *J. Am. Chem. Soc.* **1994**, *116*, 7939.
(3) Chen, S. A.; Hwang, G. W. *J. Am. Chem. Soc.* **1995**, *117*, 10055.
(4) Hwa, M. Y.; Su, Y. N.; Chen, S. A. *Polymer* **2000**, *41*, 813.
(5) Chen, S. A.; Hwang, G. W. *Macromolecules* **1996**, *29*, 3950.
(6) Chan, H. S. O.; Ho, P. K. H.; Ng, S. C.; Tan, K. L. *J. Am. Chem. Soc.* **1995**, *117*, 8517.
(7) Nguyen, M. T.; Kasai, P.; Miller, J. L.; Diaz, A. F. *Macromolecules* **1994**, *27*, 3625.
(8) Nguyen, M. T.; Diaz, A. F. *Macromolecules* **1995**, *28*, 3411.
(9) Yin, W.; Ruckenstein, E. *Macromolecules* **2000**, *33*, 1129.
(10) Chiang, J. C.; MacDiarmid, A. G. *Synth. Met.* **1986**, *13*, 193.
(11) Tang, J.; Jing, X.; Wang, B.; Wang, F. *Synth. Met.* **1988**, *24*, 231.
(12) Nakanishi, K.; Solomon, P. H. *Infrared Absorption Spectroscopy*, 2nd ed.; Nankodo: Tokyo, 1977; pp 50−51.
(13) Lu, F. L.; Wudl, F.; Nowak, M.; Heeger, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 8311.
(14) 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.
(15) Chen, S. A.; Lee, H. T. *Macromolecules* **1993**, *26*, 3254.
(16) Zheng, W. Y.; Levon, K. *Macromolecules* **1994**, *27*, 7754.

MA000660O