ELSEVIER

Polymer 41 (2000) 813–815

polymer

Polymer Communication

Water-soluble self-acid-doped conducting polyaniline: poly(aniline-*co*-*N*-propylbenzenesulfonic acid-aniline)

M.-Y. Hua[1], Y.-N. Su, S.-A. Chen*

Chemical Engineering Department, National Tsing-Hua University, Hsinchu, Taiwan 30013, ROC

Received 18 January 1999; received in revised form 8 June 1999; accepted 11 June 1999

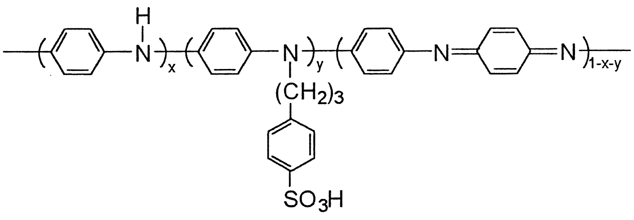
Abstract

The new water-soluble self-acid-doped conducting polyaniline, poly(aniline-*co*-*N*-propylbenzenesulfonic acid-aniline) (PAPBSAH), is synthesized, in which 47% of total nitrogen is linked with $-(CH_2)_3-$$-SO_3H$ groups as determined by elemental analysis. The protons in the pendent acid groups are capable of doping the nitrogen atoms in the quinoid units. The conductivity of the cast film (at 25°C, 8.5×10^{-5} S cm^{-1}) increases with temperature and reaches the maximum at 125°C (4.7×10^{-4} S cm^{-1}); it then decreases with temperature to 160°C (1.7×10^{-4} S cm^{-1}). This polymer has better thermal stability than its parent polymer, poly(aniline-*co*-*N*-propanesulfonic acid-aniline), in which the pendent group is $-(CH_2)_3-SO_3H$ and its maximum conductivity is located at 110°C. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Water-soluble self-acid-doped conducting polymer; Poly(aniline-*co*-*N*-propylbenzenesulfonic acid aniline)

1. Introduction

Polyaniline (PAn) is an important conjugated conducting polymer because of its good environmental stability [1,2]. It can be doped to conducting form without changing the number of π-electrons through protonation by exposure to an appropriate protonic acid in aqueous solution [3]. The aqueous solutions of self-acid-doped polyanilines have been prepared by reactions of emeraldine base with fuming sulfuric acid [4–6] to give ring-substituted polyaniline (SPAN) and with NaH and then propanesulfone to give poly(aniline-*co*-*N*-propanesulfonic acid-aniline) (PAPSAH) [7,8]; both followed with neutralization, purification and then exchanging Na^+ for H^+ using H^+-type ion-exchange resin to give their solutions in water. The thermal stability of the former is better than that of the latter, the maximum conductivity is located at 190°C, higher than that at 110°C for the latter. In an attempt to improve the thermal stability of PAPSAH, here we introduce a benzene ring between the $-SO_3H$ and $-(CH_2)_3-$ groups attached to the amine nitrogens in the PAn to give a new water-soluble self-acid-doped polyaniline, poly(aniline-*co*-*N*-propylbenzenesulfonic acid-aniline) (PAPBSAH, compound **I**). It can be cast into free-standing film and has higher thermal stability than PAPSAH, but lower conductivity.



(I)

2. Experimental section

The emeraldine base form of polyaniline (PAn) with an oxidation level of 47% was synthesized by a chemical oxidation method similar to that of MacDiarmid and co-workers [3]. The dried PAn (2.26 g, 2.5×10^{-2} mol) solution in dried DMSO was then reacted with excess NaH (0.9 g, 3.75×10^{-2} mol) at about 45°C under a dried nitrogen atmosphere for 2 h to give a dark green solution, in which the hydrogen atoms on the amine nitrogens in the original emeraldine base were substituted by sodium atoms. The solution was subsequently reacted with excess *p*-(3-bromopropyl)benzenesulfonic acid sodium salt (15 g,

---

* Corresponding author. Tel./fax: +886-3-5710733.
E-mail address: sachen@che.nthu.edu.tw (S.-A. Chen)

[1] Present address: Chemical Engineering Department, Chang Gung University, Kwei-San, Tao-Yuan, Taiwan 33302, ROC.

PII: S0032-3861(99)00452-8

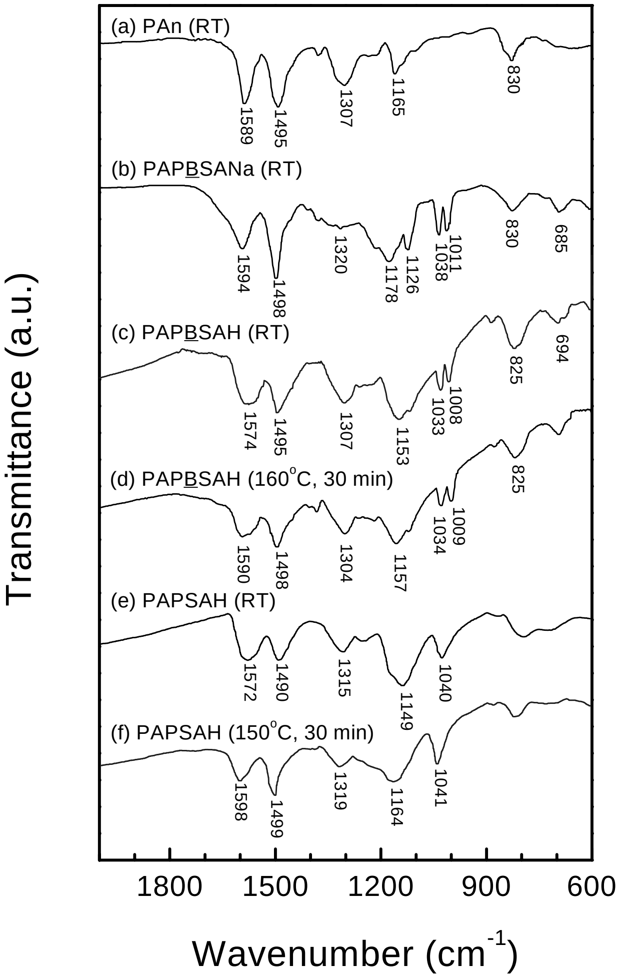


Fig. 1. IR spectra of: (a) the emeraldine base form of PAn; (b) PAPBSANa at room temperature (RT); (c) PAPBSAH at RT; (d) PAPBSAH after thermal treatment by heating at 160°C for 30 min under nitrogen atmosphere; (e) PAPSAH at RT; and (f) PAPSAH after thermal treatment by heating at 150°C for 30 min under nitrogen atmosphere.

5.0×10^{-2} mol) for 24 h at room temperature to give a dark blue solution. The resulting solution was precipitated with 1 M HCl aqueous solution, and the dark green precipitate (HCl-doped PAPBSAH) after filtration was washed by a large amount of acetonitrile. Then, it was undoped with 1 N NaOH aqueous solution to yield a blue solution, followed with a purification by dialysis with semipermeable membrane (Spectra/Por3 membrane, molecular weight cutoff, 3500) in de-ionized (DI) water for 3 days, which was replaced with fresh DI water frequently. The PAPBSAH aqueous solution so obtained and the solid film casts therefrom were then subjected to characterization and property measurements using methods similar to those reported previously by us [8].

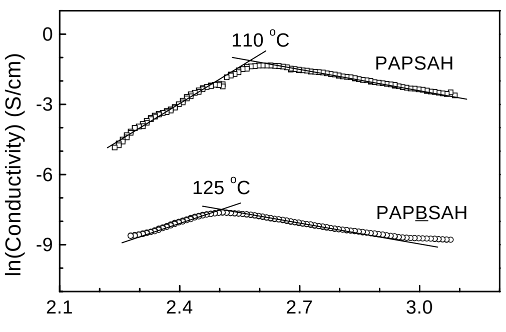


Fig. 2. Results of conductivity versus temperature for PAPSAH and PAPBSAH solid films coated on glass plates.

3. Results and discussion

Electronic spectra of PAPBSAH solution in water and as solid film exhibit three absorption bands at 314, 410 and 1015 nm for aqueous solution and 1021 nm for solid film; the first peak can be assigned to the $\pi-\pi^*$ transition [9], and the second and third peaks to the polaron band [10,11]. These results are similar to those of its parent polymer, PAPSAH [7,8].

Elemental analysis for the PAPBSAH sample gives an S/N atomic ratio of 0.47, which implies that 47% of the total nitrogens in the polymer are linked with the propylbenzenesulfonic acid as a side chain.

Infrared spectra of the emeraldine base form of PAn, PAPBSAH and its sodium salt, poly(aniline-*co*-sodium *N*-propylbenzenesulfonate-aniline) (PAPBSANa) are shown in Fig. 1 (curves (a)–(c), respectively). For PAPBSANa, the presence of the absorption peaks at 1178, 1038 and 1011 cm^{-1} characteristic of asymmetric and symmetric O=S=O stretching vibrations, respectively, and the presence of the absorption bands at 800–600 cm^{-1} characteristic of stretching modes of C–S and S–O groups indicate the existence of SO_3^- groups [12]. The presence of the absorption peak at 830 cm^{-1} (as in the emeraldine base) characteristic of the C–H out-of-plane bending vibrations of the l,4-disubstituted benzene ring [12], 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-substituted PAn), indicates that no ring substitution occurs in the present PAn derivative. For PAPBSAH, the bands of the benzeneoid ring and the quinoid ring shift to lower frequencies at 1495 and 1574 cm^{-1}, respectively, and the $C_{aromatic}$–N stretching shifts to lower frequency by about 13 cm^{-1} (from 1320 to 1307 cm^{-1}), which implies that the self-acid-doping also undergoes a polaron separation to yield a polaron lattice after disassociation of bipolaron into two polarons, similar to those observed in the PAPSAH [8,13].

After the solid film of PAPBSAH was subjected to thermal treatment by heating at 160°C for 30 min under nitrogen atmosphere, the 1574, 1495 and 1153 cm^{-1} bands shift to higher energies 1590, 1498 and 1157 cm^{-1} (Fig. 2, curve (d)), respectively, indicating that PAPBSAH was thermally undoped and lost majority of the polarons [8,14]. For comparison purposes, the IR spectrum of the solid film of PAPSAH at 25°C and that by heating at 150°C for 30 min under nitrogen atmosphere have also been recorded as shown in Fig. 2, curves (e) and (f), respectively. The absorption intensity ratio of the peak at 1304 cm^{-1} to that at 1499 cm^{-1} for PAPBSAH is larger than that at 1319 to that 1499 cm^{-1} for PAPSAH, indicating that the extent of thermal-undoping for PAPBSAH is lower than that of PAPSAH after the thermal treatment. The TGA thermogram of PAPBSAH in dry nitrogen atmosphere shows a weight loss starting at about 125°C and that of PAPBSAH at 110°C due to the elimination of some sulfonic acid groups [8], since the intensities of S=O and S–O stretching bands in the IR spectra (Fig. 2, curves (d) and (f)) decrease. Thus, the thermal stability of PAPBSAH is better than that of PAPSAH.

The temperature dependence of the conductivity for PAPBSAH and PAPSAH is shown in Fig. 2, in which the logarithm of conductivity is plotted against inverse temperature 1000/T from 50 to 160°C. The plots exhibit conductivity maxima at 125 and 110°C for PAPBSAH and PAPSAH, respectively, below which both plots are fairly linear, indicating that the charge transport follows the polaron hopping model (i.e. conductivity variation with temperature follows the Arrhenius law) [15]. The activation energy calculated from the slope is 0.332 eV/mol for PAPBSAH, which is higher than that of the PAPSAH, 0.315 eV/mol [8]. This result indicates that the barrier for polaron hopping in the former is larger than that in the latter due to the longer and more bulky side chain. The temperatures at conductivity maxima are the same as the onset temperatures of weight loss of these two polymers. Thus the conductivity drops above these temperatures must be due to the loss of $-SO_3H$ groups by thermal decomposition. The lower conductivity of PAPBSAH than that of PAPSAH below the optimum temperature is due to the lower doping level and higher barrier for charge hopping; while the higher thermal resistance of PAPBSAH is due to the electron donating characteristic of the benzene ring attaching to the $-SO_3H$ groups.

Acknowledgements

We wish to thank the National Science Council of ROC for financial aid through the project, NSC 85-2216-E-007-047 and NSC 86-2216-E-007-044.

References

[1] Huang WS, Humphrey BD, MacDiarmid AG. J Chem Soc, Faraday Trans 1 1986;82:2385.

[2] Chen S-A, Fang W-G. Macromolcules 1991;24:1242.

[3] Chiang JC, MacDiarmid AG. Synth Met 1986;13:193.

[4] Yue J, Epstein AJ. J Am Chem Soc 1990;112:2800.

[5] Yue J, Wang ZH, Cromack KR, Epstein AJ, MacDiarmid AG. J Am Chem Soc 1991;113:2665.

[6] Chen S-A, Hwang G-W. Macromolcules 1996;29:3950.

[7] Chen S-A, Hwang G-W. J Am Chem Soc 1994;116:7939.

[8] Chen S-A, Hwang G-W. J Am Chem Soc 1995;117:10055.

[9] Lu FL, Wudl F, Nowak M, Heeger AJ. J Am Chem Soc 1986;108:8311.

[10] Epstein AJ, Ginder JM, Zuo F, Bigelow RW, Woo H-S, Tanner DB, Richter AF, Huang W-S, MacDiarmid AG. Synth Met 1987;18:303.

[11] Furukawa Y, Ueda F, Hyodo Y, Harada I, Nakajima T, Kawagoe T. Macromolcules 1988;21:1297.

[12] Nakanishi K, Solomon PH. Infrared absorption spectroscopy, 2nd ed. Tokyo: Nankodo, 1977. p. 19–21,33,50,51.

[13] Tang T, Jing X, Wang B, Wang F. Synth Met 1988;24:231.

[14] Chen S-A, Hua M-Y. Macromolcules 1996;29:4919.

[15] Epstein AJ. AC conductivity of polyacetylene: distinguishing mechanisms of charge transport. In: Skotheim TA, editor. Handbook of conducting polymers, vol. 2. New York: Marcel Dekker, 1985. p. 1050.