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A novel water-soluble and self-doped conducting polyaniline graft copolymer†

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A water-soluble and self-doped conducting polyaniline graft copolymer, poly(styrenesulfonic acid-*g*-aniline) (PSSA-*g*-PANI), was first synthesized and its electrical properties were investigated.

Polyaniline (PANI) has been extensively studied for its environmental stability in the conducting form, easiness and low cost of synthesis, unique redox properties,[1] and high conductivity.[2] Nevertheless, few applications have been reported because conducting polymers based on polyaniline exhibit poor physical and mechanical properties and are not soluble in common solvents. Numerous methods have been developed to overcome these shortcomings: blending PANI with a commodity polymer,[3] the incorporation of side groups into the main chain,[4] grafting of the conducting polyaniline chain onto a non-conductive polymer[5] and electrochemical polymerization of aniline in a polymer matrix.[6]

Development of water-soluble polymers becomes important because environmental concerns have recently imposed restrictions on the commercial use of many organic solvents. As for PANI, two methods were reported to prepare water-soluble or dispersive PANI. One was to graft sulfonic or phosphoric acid groups onto the benzene ring or nitrogen atom in PANI.[7] However, the film prepared from the grafted PANIs, after removal of residual moisture by dynamic vacuum pumping, becomes insoluble in water.[8] The other was to synthesize colloidal polyaniline particles in the presence of a water-soluble polymeric stabilizer.[9,10]

Here we report the synthesis and conducting properties of a water-soluble (not a colloidal) and self-doped conducting polyaniline graft copolymer (PSSA-*g*-PANI). Our synthetic method, as described in Fig. 1, has several advantages as below:

1. Water-soluble backbone moieties (sulfonic acid groups), which do not participate in self-doping, make the polymer soluble in water or polar organic solvents such as dimethyl sulfoxide (DMSO).
2. The polymeric dopant (backbone poly(styrenesulfonic acid)) is so structurally stable in wide range of pH that phase separation by dopant migration can be prevented, since the dopant is covalently bonded.
3. Higher conductivity ($\sim 10^{-1}$ S cm^{-1}) is achieved compared to any other benzene ring or nitrogen atom-substituted water-soluble PANI[7,11,12] because our synthetic procedure does not modify the structure of the PANI backbone whereas other methods involve the substitution of sulfonic acid or phosphoric acid groups onto the phenyl ring or nitrogen atom in PANI which results in a decrease of conductivity due to electron localization and structural disorder.

The PSSA-*g*-PANI so obtained is completely soluble in water and polar solvents such as DMSO. When the aqueous solution was centrifuged at 10 000 rpm for 2 h in a Beckman/XL-90 centrifuge, the solution was clear without any dark green sediment on the wall of sample tube, indicating that PSSA-*g*-PANI is perfectly soluble in water

Fig. 2 shows ^{1}H NMR spectra of P(SSNa-*co*-BOC-AMS), P(SSA-*co*-AMS), and PSSA-*g*-PANI. As can be seen in Fig. 2(a) and (b), the peak at 1.5 ppm (–CH_3) disappears from the spectrum of P(SSA-*co*-AMS) (Fig. 2(b)) as the BOC group is removed from P(SSNa-*co*-BOC-AMS) (Fig. 2(a)). When the spectrum (Fig. 2(c)) of PSSA-*g*-PANI is compared with that

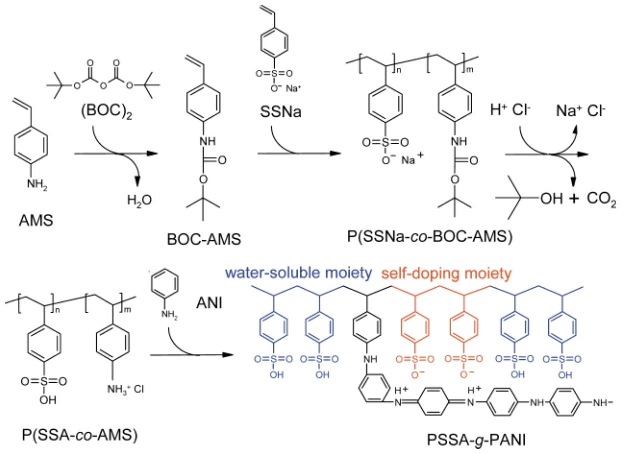

Fig. 1 Synthetic route for PSSA-*g*-PANI. AMS = *p*-aminostyrene, (BOC)$_2$ = di-*tert*-butyl dicarbonate, ANI = aniline, BOC-AMS = BOC-*p*-aminostyrene, SSNa = sodium styrenesulfonate, P(SSNa-*co*-BOC-AMS) = poly(sodium styrenesulfonate-*co*-BOC-*p*-aminostyrene), P(SSA-*co*-AMS) = poly(styrenesulfonic acid-*co*-*p*-aminostyrene).

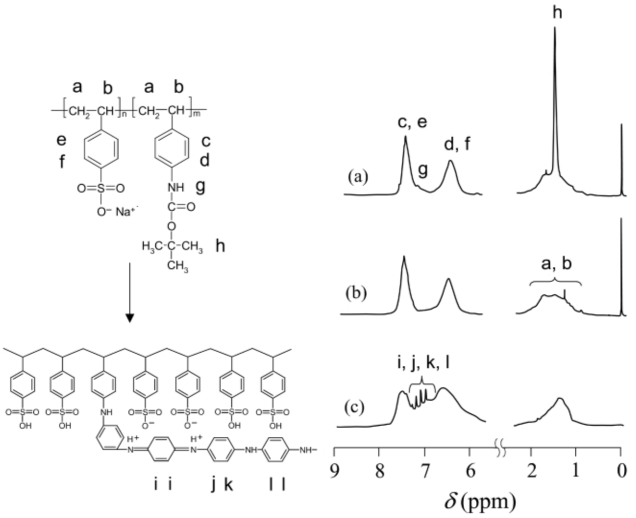

Fig. 2 ^{1}H NMR spectra of (a) P(SSNa-*co*-BOC-AMS), (b) P(SSA-*co*-AMS) in DMSO-d_6 and (c) PSSA-*g*-PANI in D_2O.

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† Electronic supplementary information (ESI) available: schematic diagrams; XPS and FTIR spectra; GPC profile. See http://www.rsc.org/suppdata/cc/b3/b309346h/

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(Fig. 2(b)) of P(SSA-*co*-AMS), the spectrum in D_2O of PSSA-*g*-PANI has multiple peaks at 7.0, 7.1, 7.2 and 7.3 ppm, which are assigned to hydrogens in phenyl and quinoid rings of PANI. This confirms that PANI is successfully grafted onto P(SSA-*co*-AMS). The PANI content in the copolymer is estimated as *ca.* 53 mol% from integration of the peak areas in Figs. 2(b) and (c). This is very coincident with the result of elemental analysis for PSSA-*g*-PANI (S/N atomic ratio = 0.85), from which the PANI content is estimated as *ca.* 54 mol%.

FTIR spectra (see ESI†) show that the characteristic peaks of BOC group (1718, 1539, 1369 cm^{-1}) disappear, instead a new peak at 2618 cm^{-1} due to NH_3^+ stretching vibrations is observed as the BOC group is removed from P(SSNa-*co*-BOC-AMS). The FTIR spectrum of PSSA-*g*-PANI shows the characteristic absorption peaks of doped PANI: 3325, 1561, 1481, 1301, 1148, 802, 511 cm^{-1}. The peak at 2618 cm^{-1} due to NH_3^+ stretching vibrations in P(SSA-*co*-AMS) almost disappears in PSSA-*g*-PANI, indicating that PANI is successfully grafted onto P(SSA-*co*-AMS). It has been reported that the oxidation level of PANI can qualitatively be estimated by the intensity ratio of the IR absorption peak at 1560–1600 cm^{-1} (quinoid ring stretching) to that at 1460–1500 cm^{-1} (benzenoid ring stretching).[13] Based on the intensity ratio of these two characteristic peaks, the oxidation level of our sample is estimated to be about 0.5.

We also prepared a PSSA/PANI blend by the same procedure‡ as PSSA-*g*-PANI except for use of PSSNa instead of P(SSNa-*co*-BOC-AMS), in order to compare its properties with those of PSSA-*g*-PANI. When the PSSA-*g*-PANI copolymer and PSSA/PANI blend were de-doped in NH_4OH aqueous solution, the de-doped PANI in PSSA/PANI blend was precipitated from the solution, whereas the de-doped PSSA-*g*-PANI changed color from dark green to blue violet without precipitation. This also leads us to conclude that ANI is successfully grafted onto the P(SSA-*co*-AMS) backbone. The number average molecular weight and polydispersity of PSSA-*g*-PAN determined by size exclusion chromatography are 34 000 and 1.54, respectively (see ESI†).

When the electrical conductivity was measured in compressed pellet form at room temperature after the sample was dried under vacuum at 30 °C over 24 h, the conductivities of the PSSA-*g*-PANI copolymer and PSSA/PANI blend were 1.2×10^{-1} and 7.7×10^{-2} S cm^{-1}, respectively. Details of the experiment for measuring electrical conductivity were described in our earlier paper.[14]

The UV-visible spectrum of PSSA-*g*-PANI shows that the polaron band transitions take place at 420 and 770 nm, as shown in Fig. 3(a), which indicates that the PSSA-*g*-PANI is in a self-doped state. After de-doping of PSSA-*g*-PANI, the two peaks at 420 and 770 nm disappear and a new strong absorption peak appears at 550 nm due to the π–π* transition of the quinoid rings in PANI,[8] as shown in Fig. 3(b).

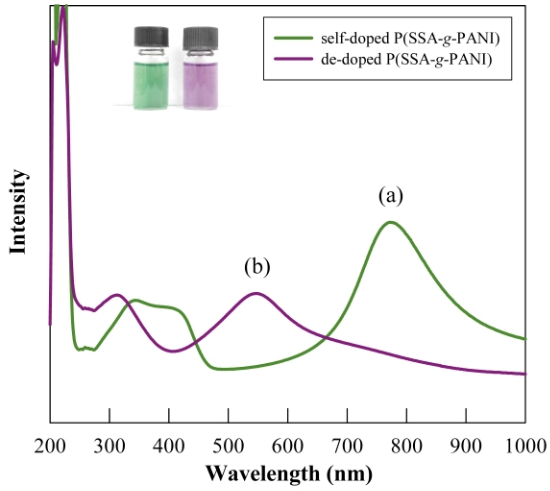

Fig. 3 UV-visible spectra of PSSA-*g*-PANI: (a) self-doped state in aqueous solution and (b) de-doped state in aqueous NH_4OH (1 M) solution.

In summary, we report here the synthesis, characterization, and electrical properties of a novel conducting polyaniline graft copolymer, which is soluble in both water and polar organic solvents. Particularly, it is noted that our synthetic procedure is simple and straightforward as compared with others, because de-protection, ion-exchange and aniline grafting could be conducted in an acidic bath by a one-batch process. Furthermore, our polymer is, to our knowledge, the first conducting PANI that is soluble in both water and organic solvents. Therefore, it would be widely applicable to aqueous coatings, preparation of exfoliated clay nanocomposites, and solution blending with other commodity water-soluble polymers.

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Notes and references

‡ 5 ml of vacuum-distilled AMS (0.042 mol) was dissolved in 100 ml of dioxane and placed into a 250 ml three-necked round-bottom flask equipped with a reflux-condenser, a thermometer and mechanical stirrer, and cooled with a water/ice bath. Then, 75 ml of $(BOC)_2$ solution (0.055 mol) in dioxane were slowly added to the AMS solution under N_2 atmosphere. After the solution was stirred for 10 h, 200 ml of ethyl acetate and 200 ml of water were added in sequence. The organic phase was then separated and washed with water several times. Finally, the solvent was evaporated under reduced pressure. The crude BOC-AMS was recrystallized from *n*-hexane to yield a white crystalline solid (yield 40%). P(SSNa-*co*-BOC-AMS) was synthesized by copolymerizing SSNa and BOC-AMS by using AIBN as an initiator. SSNa (5 g), BOC-AMS (0.5 g), and AIBN (0.1 g) were dissolved in 60 ml of DMSO and polymerized at 80 °C for 15 h under N_2 atmosphere. After polymerization, the product was precipitated with acetone, filtered, washed several times with acetone, and dried in a vacuum oven at 60 °C for 24 h. ^1H NMR (DMSO-d_6): δ 1.5 (s, 9H, –CH_3), 0.8–2.2 (br, 3H, –CH_2–C*H*–), 6.6 and 7.5 (br, 4H, Ar–*H*). FTIR spectrum of P(SSNa-*co*-BOC-AMS) shows the characteristic absorption peaks: 1718 cm^{-1} (C=O stretching), 1539 cm^{-1} (N–H bending), 1369 cm^{-1} (–$(CH_3)_3$ deformation). Elimination of the BOC group from P(SSNa-*co*-BOC-AMS) and ion-exchange of Na^+ with H^+ were carried out under acidic conditions. P(SSNa-*co*-BOC-AMS) (0.8 g) was added to 30 ml of HCl aqueous solution (1 M) at 30 °C for 1 h under stirring to yield P(SSA-*co*-AMS), and then the solution temperature was lowered to 0 °C. For graft copolymerization of ANI onto P(SSA-*co*-AMS), ANI (0.2 g) was first added to the above copolymer solution for 0.5 h during stirring, and then 20 ml of ammonium persulfate (0.49 g)/HCl aqueous solution (1 M) was dropwise added at 0 °C. After 6 h of reaction, a dark green solution was obtained and then filtered. The filtered solution was further purified by dialysis using a semipermeable membrane (molecular weight cutoff, 3500). The chemical structure of PSSA-*g*-PANI was identified by ^1H NMR (in D_2O).

1 W. W. Focke, G. E. Wnek and Y. Wei, *J. Phys. Chem.*, 1987, **91**, 5813.
2 R. P. Kingsborough and T. M. Swager, *Adv. Mater.*, 1998, **10**, 1100.
3 W. J. Bae, W. H. Jo and Y. H. Park, *Synth. Met.*, 2003, **132**, 239.
4 L. H. Dao, M. Leclerc, J. Guay and J. W. Chevalier, *Synth. Met.*, 1989, **29**, E377.
5 Y. H. Park, H. C. Shin, Y. Lee, Y. Son and D. H. Baik, *Macromolecules*, 1999, **32**, 4615.
6 Y. H. Park and C. R. Park, *Synth. Met.*, 2001, **118**, 187.
7 X. L. Wei, Y. Z. Wang, S. M. Long, C. Bobeczko and A. J. Epstein, *J. Am. Chem. Soc.*, 1996, **118**, 2545.
8 S. A. Chen and G. W. Hwang, *J. Am. Chem. Soc.*, 1995, **117**, 10055.
9 S. P. Armes and M. Aldissi, *J. Chem. Soc., Chem. Commun.*, 1989, 88.
10 S. Maeda, D. B. Cairns and S. P. Armes, *Eur. Polym. J.*, 1997, **33**, 245.
11 H. K. Lin and S. A. Chen, *Macromolecules*, 2000, **33**, 817.
12 K. Takahashi-, K. Nakamura, T. Yamaguchi, T. Komura, S. Ito, R. Aizawa and K. Murata, *Synth, Met.*, 2002, **128**, 27.
13 Y. Cao, S. Li, Z. Xu e and D. Guo, *Synth. Met.*, 1986, **16**, 305.
14 Y. H. Park, Y. K. Kim and D. S. Lee, *J. Appl. Polym. Sci.*, 1990, **40**, 1487.