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A Water-Soluble and Self-Doped Conducting Polypyrrole Graft Copolymer

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Polypyrrole (PPY) is one of the most studied conducting polymers because of its high conductivity, thermal and environmental stabilities, and relative ease of synthesis.[1−6] Nevertheless, a few applications have been reported because conducting polymers based on PPY exhibit poor physical and mechanical properties and are not soluble in common solvents. Several methods have been developed to improve its solubility: (1) Polypyrrole becomes soluble in organic solvent when it is synthesized from monomers appropriately substituted at the β-position of pyrrole ring. For instance, n-alkyl substituents have been utilized for that purpose, and the resulting poly(n-alkylpyrrole)s become soluble in organic solvent only under neutral condition.[7,8] (2) Polypyrrole also becomes soluble when it is dissolved in organic solvents in the presence of surfactants, such as dodecylbenzenesulfonic acid, camphorsulfonic acid, and sodium dodecyl sulfate.[9,10] However, the polypyrrole still shows poor solubility in protic organic solvents and water. (3) Polypyrrole becomes dispersed in an aqueous media to form colloidally stable PPY particles when polypyrrole is dissolved in water in the presence of polymeric stabilizers and surfactants. However, the water-dispersed polypyrrole exhibits a very low conductivity (10^{-3}−10^{-8} S/cm).[11−14] (4) A water-soluble conducting polypyrrole was obtained when sulfonated pyrrole is polymerized.[15] For instance, a water-soluble polypyrrole was synthesized first by preparing a monomer, sodium 4-(3-pyrrolyl)butanesulfonate, and then by oxidative polymerization of the monomer. Synthesis of such a substituted pyrrole monomer is not a simple reaction, and therefore the cost of the monomer becomes expensive. When the polypyrrole is combined with collagen to yield a hybrid biomaterial, its conductivity is 10^{-2} S/cm.

In our previous paper,[16] we reported a novel water-soluble and self-doped polyaniline graft copolymer (PSSA-*g*-PANI), and the advantages of the graft copolymer were listed therein. Since it is known that the electrical conductivity of PPY is roughly 10 times higher than that of polyaniline (PANI), it motivates us to synthesize a water-soluble and self-doped polypyrrole graft copolymer by following the synthetic route similar to but different from the polyaniline graft copolymer; that is, poly(sodium styrenesulfonate-*co*-pyrrolylmethylstyrene) (P(SSNa-*co*-PMS)) was used as the precursor for the graft polymerization of pyrrole while poly(sodium styrenesulfonate-*co*-BOC-amonistyrene) (P(SSNa-*co*-BOC-AMS)) was used as the precursor for the graft polymerization of aniline. Here, we report the synthesis and conducting properties of a water-soluble (not a colloidal) and self-doped conducting polypyrrole graft copolymer (PSSA-*g*-PPY). Our synthetic method is described in Figure 1. In this route, when two oxidants, ammonium persulfate and $FeCl_3$, are used for graft copolymerization and their catalytic functions are compared with each other, it is found that ammonium persulfate is more effective than $FeCl_3$ for preparation of water-soluble polypyrrole graft copolymer. The molecular weight and its distribution are 33 000 and 1.54, respectively, when it is measured by size exclusion chromatography using water/DMF (v/v = 9.5/0.5) + 0.05 M NaOH as an eluant.

The PSSA-*g*-PPY so obtained is completely soluble in water and polar solvent such as DMSO as well. When aqueous solutions (1, 2, 4, 8, 15, 20 wt %) are centrifuged at 10 000 rpm for 2 h in a Beckman/XL-90 centrifuge, the solution remains clear without any dark black sediment on the wall of sample tube except for the 20 wt % solution, indicating that PSSA-*g*-PPY is completely soluble in water at lower concentrations and that the maximum solubility of PSSA-*g*-PPY in water is about 15 wt %, which is much higher than that of PSSA-*g*-PANI (4 wt %).

Figure 2 shows ^{1}H NMR spectra of PMS, P(SSNa-*co*-PMS), and PSSA-*g*-PPY. As can be seen in Figure 2a, the spectrum of PMS as purified by column chromatography shows the characteristic peaks of PMS. The content of PMS unit in a sample copolymer is estimated ca. 4.2 mol % from the ratio of the peak area at 5.1 ppm to the peak area at 1.0−2.0 ppm in Figure 2b, which is coincident with the result of elemental analysis (4.0 mol %) of P(SSNa-*co*-PMS). When the spectrum of PSSA-*g*-PPY (Figure 2c) is compared with that of P(SSNa-*co*-PMS) (Figure 2b), the spectrum in water ($D_2O + H_2O$) of PSSA-*g*-PPY has multiple peaks at 7.0−7.2 ppm, which are assigned to hydrogens in PPY rings. This confirms that PPY is successfully grafted onto P(SSNa-*co*-PMS). Since PSSA-*g*-PPY is not soluble in D_2O but soluble in $D_2O + H_2O$ solution due to different hydrogen-bonding character, the NMR spectrum of PSSA-*g*-PPY was obtained in D_2O/H_2O (v/v = 2/1) solution. A broad and strong peak at 3.5−6.0 ppm is attributed to water. The PPY content in the copolymer is estimated ca. 35 mol % from integration of peaks in Figure 2b,c. This is also very coincident with the result of elemental analysis of PSSA-*g*-PPY, which gives the S/N atomic ratio of 1.78, corresponding to ca. 36 mol % of PPY.

The FTIR spectrum of P(SSNa-*co*-PMS) shows that the characteristic peaks of PMS are observed at 1629, 1565, and 1396 cm^{-1} ($\nu_{C=C}$, $\nu_{C=C}$, and δ_{C-N}), which are absent in the spectrum of PSSNa. The FTIR spectrum of PSSA-*g*-PPY shows the characteristic absorption peaks of doped PPY at 1547, 1450, 1403, 1324, and 896 cm^{-1} ($\nu_{C=C}$, ν_{C-N}, $\nu_{C=C}$, δ_{C-N}, and δ_{C-H}).

When we used another backbone, poly(sodium styrenesulfonate-*co*-BOC-aminostyrene) (P(SSNa-*co*-BOC-AMS), which was used for the backbone of aniline grafting in our previous report,[16] for graft copolymerization of PY, the product was partially soluble in an

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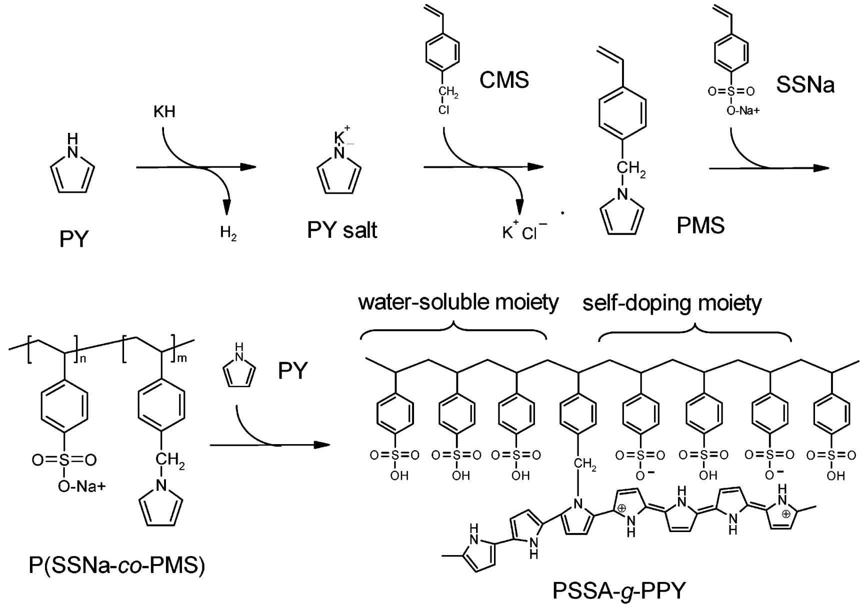

Figure 1. Synthetic route for PSSA-*g*-PPY. PY = pyrrole, CMS = chloromethylstyrene, PMS = pyrrolylmethylstyrene, SSNa = sodium styrenesulfonate, P(SSNa-*co*-PMS) = poly(sodium styrenesulfonate-*co*-pyrrolylmethylstyrene).

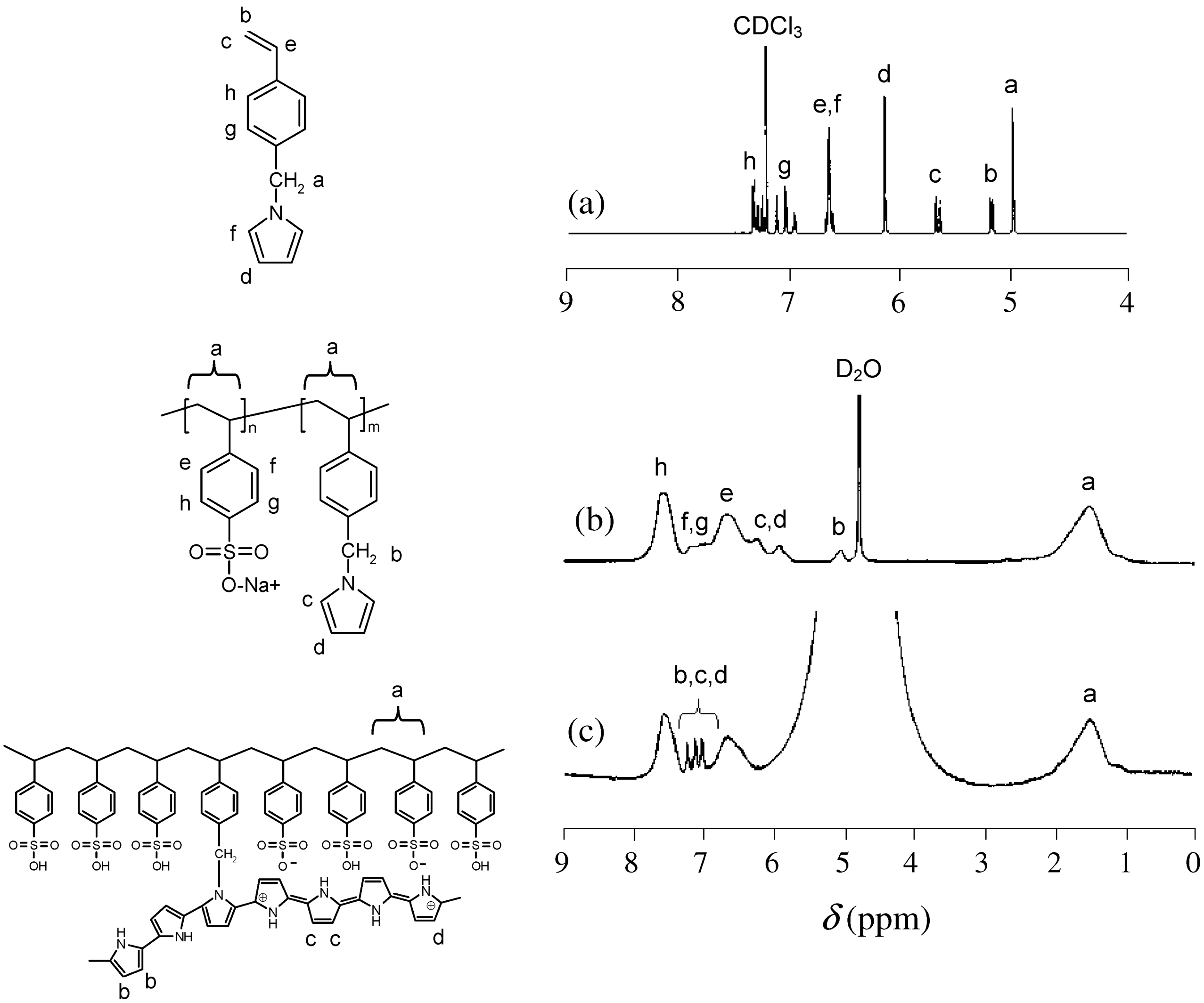

Figure 2. ^1H NMR spectra of (a) PMS in $CDCl_3$, (b) P(SSNa-*co*-PMS) in D_2O, and (c) PSSA-*g*-PPY in $D_2O + H_2O$.

aqueous media. When the water-soluble and -insoluble parts of the product are analyzed, it reveals that only P(SSNa-*co*-BOC-AMS) is soluble in water and the insoluble one is polypyrrole homopolymer, indicating that pyrrole monomers are not successfully grafted onto the P(SSNa-*co*-BOC-AMS).

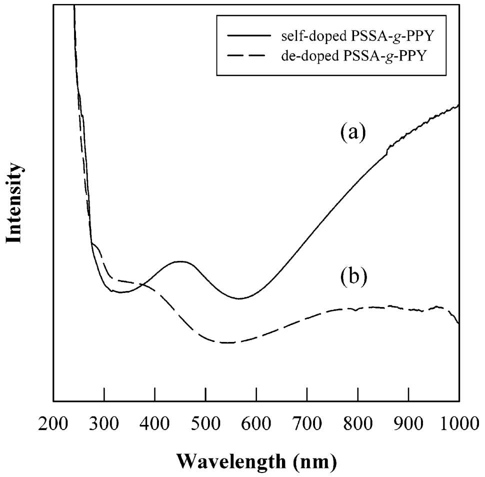

Figure 3. UV−vis spectra of PSSA-*g*-PPY: (a) self-doped state in aqueous solution and (b) dedoped state in aqueous NH_4OH (1 M) solution.

When the electrical conductivity was measured in a compressed pellet form at room temperature after the sample was dried in a vacuum at 30 °C over 24 h, the conductivity (σ) of PSSA-*g*-PPY copolymer was 4.8×10^{-1} S/cm, which is higher than that of PSSA-*g*-PANI ($\sigma = 1.2 \times 10^{-1}$ S/cm). This higher conductivity of PSSA-*g*-PPY as compared to that of PSSA-*g*-PANI is very significant when the contents of conducting units in graft copolymers (36 mol % PPY in PSSA-*g*-PPY vs 54 mol % PANI in PSSA-*g*-PANI) are taken into account. Details of the experiment for measuring the electrical conductivity are described elsewhere.[17] The X-ray diffraction (XRD) pattern shows that PSSA-*g*-PPY is amorphous, indicating that the conductivity is not related to its crystallinity.

The UV−vis spectrum of PSSA-*g*-PPY shows that the sample has a bipolaron absorption at 473 nm and a free carrier tailing in the near-IR region with a maximum above 1000 nm, as shown in Figure 3a. This indicates that PSSA-*g*-PPY is in a self-doped state. After dedoping of PSSA-*g*-PPY in 1 M NH_4OH aqueous solution, both the bipolaron absorption and the free-carrier tailing disappear, as shown in Figure 3b.

The structural change of PSSA-*g*-PPY chain before and after dedoping is examined by measuring the intrinsic viscosity of samples. The intrinsic viscosities of PSSA-*g*-PPY solution before and after dedoping (in water and in 1 M NH_4OH aqueous solution, respectively) are 0.23 and 0.12 dL/g, respectively, indicating that the chain conformation of PSSA-*g*-PPY in solution depends on the doping state. In other words, when grafted PPY chains are self-doped with polymeric dopant (PSSA), PSSA-*g*-PPY chains have an extended chain conformation in water, whereas the chains have a collapsed coil conformation in 1 M NH_4OH aqueous solution. The extended conformation in the doped state is not surprising because the conducting polymer in the doped state is more rigid than that in the dedoped state.[18] In the dedoped state, the aromatic structure has much more freedom of movement and can coil more easily.[18] It is believed that the extended chain conformation of PSSA-*g*-PPY in the doped state is attributed to incorporating strands of the extended chain of PPY and PSSA intertwined or otherwise closely associated, since it has been reported that polyaniline and PSSA are intertwined or otherwise closely associated with from complex when the two polymers are mixed in water.[13] Furthermore, when grafted PPY chains are dedoped at high pH, it is expected that the chains have more freedom of movement in dedoped state and thus are easily collapsed in hydrophilic aqueous medium, with formation of the core−shell structure (core: hydrophobic PPY; shell: hydrophilic PSSA), as schematically shown in Figure 4. The electrical conductivity of dedoped PSSA-*g*-PPY was 6.7×10^{-6} S/cm.

When aqueous solution of PSSA-*g*-PPY was spin-coated on glass, a very smooth and uniform film was obtained. The film is smooth enough to be used for electronic devices due to its inherent properties, particularly the absence of detectable defects.

In summary, we report here the synthesis, characterization, and electrical properties of a novel self-doped

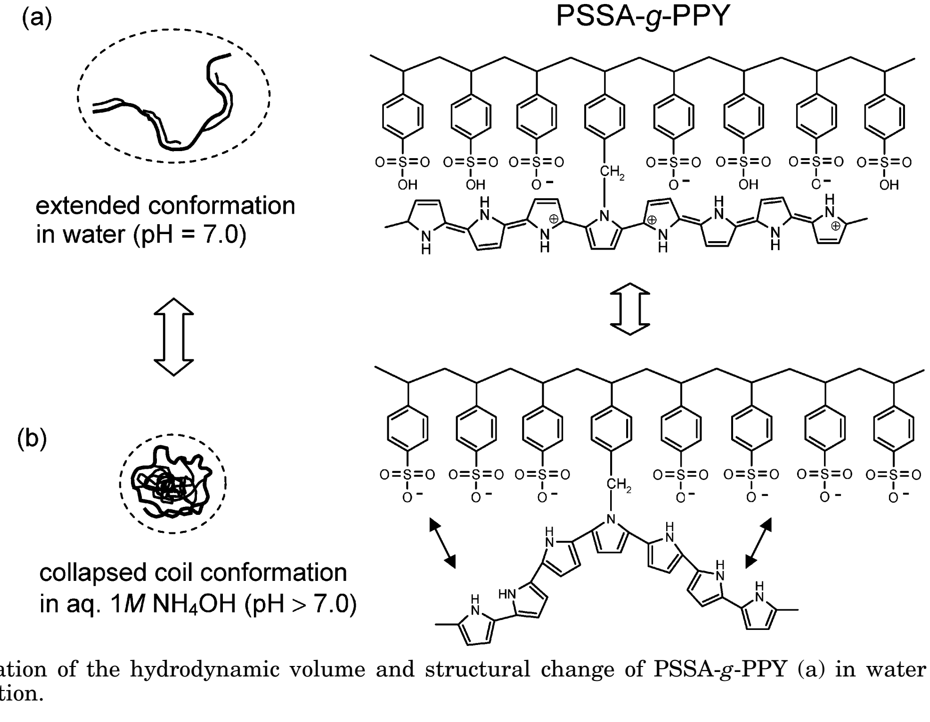

Figure 4. Illustration of the hydrodynamic volume and structural change of PSSA-*g*-PPY (a) in water and (b) in aqueous NH_4OH (1 M) solution.

conducting polypyrrole graft copolymer, which is soluble in both water and polar organic solvents. PSSA-*g*-PPY shows better solubility in water and higher conductivity than PSSA-*g*-PANI. Therefore, it could be widely applied to aqueous coating for EMI shielding, preparation of organic–inorganic hybrid for batteries, and solution blending with other water-soluble commodity polymers.

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Supporting Information Available: Text giving experimental procedures and characterizations, including FTIR spectra, GPC profile, XRD patterns, and FESEM micrograph. This material is available free of charge via the Internet at http://pubs.acs.org.

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