

# A Water-Soluble Self-Doped Conducting Polypyrrole-Based Copolymer

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**ABSTRACT:** A water-soluble self-doped conducting polypyrrole-based copolymer was synthesized via the grafting of pyrrole onto the *p*-aminodiphenylamine moieties of a water-soluble copolymer. The conductive copolymer exhibited a conductivity as large as 3.4 S/cm. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 86–89, 2001

**Key words:** polypyrrole; water-soluble polypyrrole copolymer; self-doped polypyrrole copolymer

## INTRODUCTION

Polypyrrole (PPy) has been considered as one of the most promising conducting polymers because of its high conductivity, thermal and environmental stabilities, and the low oxidative potential of its monomer.<sup>1,2</sup> Since the late 1970s, there has been a genuine interest in preparing materials possessing the electronic and optical properties of semiconductors or metals, attractive mechanical properties, and processing advantages.<sup>3</sup> Because PPy is insoluble and infusible, several strategies have been developed to increase its solubility: (1) Soluble polypyrroles could be prepared via the electrochemical polymerization of alkyl substituted pyrroles.<sup>4–6</sup> The substituted polypyrroles were soluble in  $\text{CHCl}_3$  or *o*-dichlorobenzene and the conductivity was  $10^{-2}$ – $10$  S/cm.<sup>4</sup> (2) Soluble polypyrrole could be also obtained via a counterion-induced processibility<sup>7,8</sup> by using, for instance, dodecylbenzene sulfonic acid. Sarac et al. developed a new class of water-soluble polypyrroles by the oxidative polymerization of pyrrole with  $\text{Ce}(\text{SO}_4)_2$  in the presence of poly(acrylic acid),

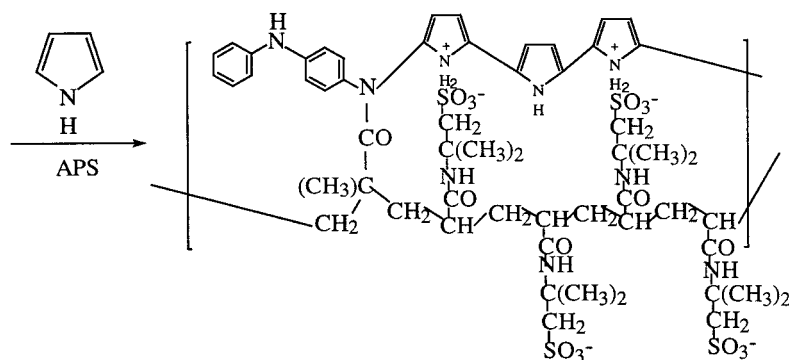
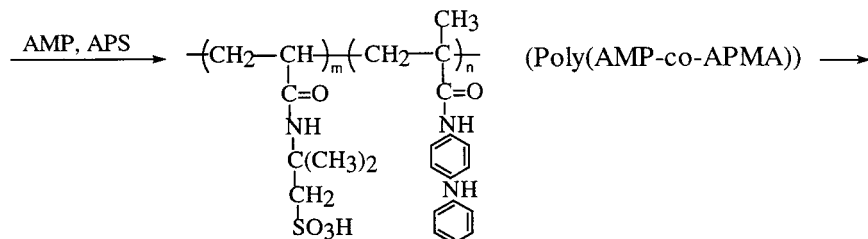
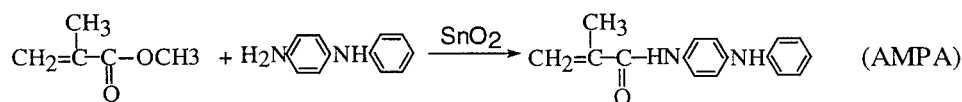
poly(vinyl pyrrolidone), or their copolymers.<sup>9</sup> However, the water-soluble polypyrroles obtained exhibited a very low conductivity ( $10^{-3}$  to  $10^{-8}$  S/cm). (3) Havinga<sup>10</sup> and Heeger et al.<sup>11</sup> prepared a water-soluble polypyrrole by the electrochemical polymerization of sulfonyl-substituted pyrrole. The monomer was prepared from *N*-protected pyrrole by acylation, reduction and treatment with  $\text{Na}_2\text{SO}_3$ , followed by *N*-deprotection with a base. The resulting water-soluble self-doped conducting polymer exhibited a conductivity of 0.18 S/cm. Li<sup>12</sup> prepared a water-soluble self-doped conducting polypyrrole, starting from a butane sulfonyl-substituted pyrrole as monomer. This polymer was combined with collagen to obtain a hybrid biomaterial whose electrical conductivity was  $10^{-2}$  S/cm. The above water-soluble self-doped conducting polypyrroles were synthesized by first preparing a substituted pyrrole monomer, followed by the oxidative polymerization of the monomer. Generally, the synthesis of the substituted pyrrole monomer is a complex process that increases the cost of the conducting polymer.

In this article, a novel approach is suggested to synthesize a new water-soluble self-doped PPy copolymer. The main idea was to prepare a highly water-soluble copolymer containing sulfonic moi-

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P(PY-co-AMP-co-AMPA)

Scheme I

eties that can dope the pyrrole, namely, poly(2-acrylamido-2-methyl-1-propanesulfonic acid-co-N-(4-anilinophenyl)-methylacrylate), [Poly(AMP-co-AMPA)], and then to graft pyrrole onto the copolymer. Because of the presence of the *p*-aminodiphenylamine moiety in AMPA, the latter has a low oxidative potential, and this stimulates the grafting of pyrrole onto the copolymer. A water-soluble self-doped PPy copolymer, poly(pyrrole-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-N-(4-anilinophenyl)-methylacrylate) P(PY-co-AMP-co-AMPA) was thus obtained (Scheme I).

## METHOD OF PREPARATION

AMPA was synthesized via the catalytic aminolysis reaction between methyl methacrylate and *p*-aminodiphenylamine (the detailed preparation

was described in our previous paper<sup>13</sup>). The AMPA obtained exhibited the following characteristics: mp  $107 \pm 1^\circ\text{C}$ ,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  ppm relative to  $\text{Me}_4\text{Si}$ ): 2.0 (s,3H), 5.4 (s,1H), 5.8(s, 1H), 5.9(s,1H), 6.9–7.4 (m,9H), 7.5 (s,1H); MS (m/e): 252.2 ( $\text{M}^+$ ), 183.2, 69; Fourier transform infrared (FTIR) ( $\text{cm}^{-1}$ ): 3353 (N—H), 3100–3059 ( $=\text{CH}$ ), 1663 (C=O in amide), 1608 (C—NH def.).

Poly(AMP-co-AMPA) was prepared via a surfactant free emulsion polymerization in water using ammonium persulfate (APS) as initiator as described previously.<sup>13</sup> FTIR ( $\text{cm}^{-1}$ ): 3345–3245 (N—H); 1662 (CO—NH—alkyl); 1640 (CO—NH—aromatic); 1190 and 1054 (O=S=O, asymmetric and symmetric stretchings.);  $^1\text{H NMR}$  ( $\text{D}_2\text{O}$ , ppm): 1.3 (s,  $\text{CH}_3$ ), 1.8–2.0 (m,  $\text{CH}_2$ ), 3.0–3.4 (m,  $\text{CH}_2\text{—SO}_3$  and  $\text{CH—CO}$ ), and 7.0–7.4 (m, aromatic hydrogen).

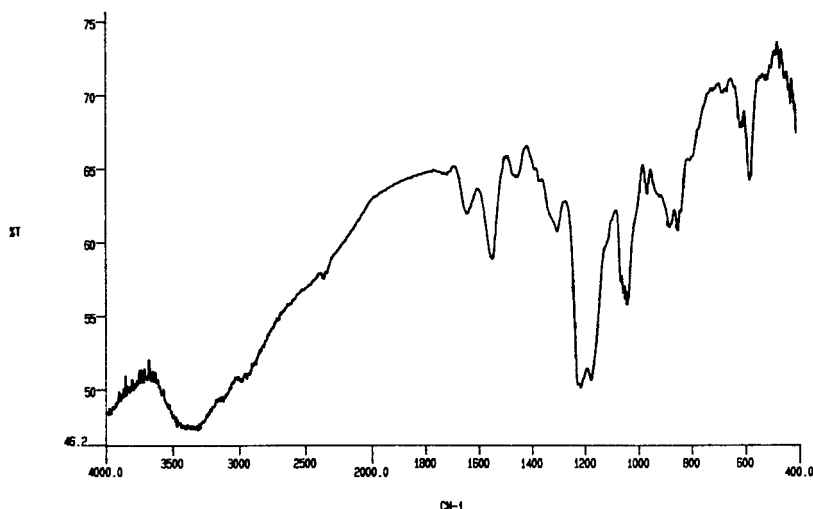


Figure 1 FTIR spectrum of P(PY-co-AMP-co-AMPA) copolymer.

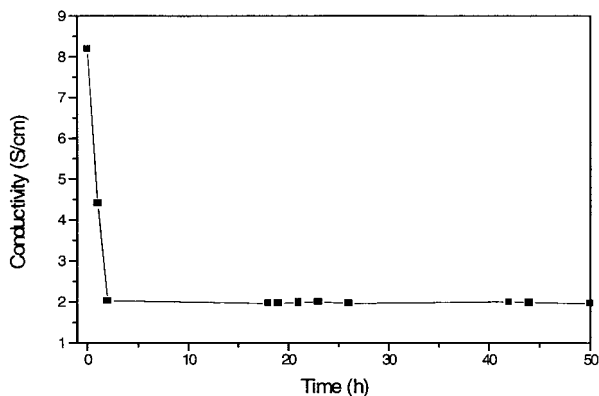
The grafting of pyrrole onto poly(AMP-co-AMPA) was carried out in an aqueous solution as follows: 0.4 g of poly(AMP-co-AMPA) was dissolved in 20 g distilled water with stirring. The amounts of 0.3 g of APS and 0.2 g of pyrrole were dissolved each separately in 5 g H<sub>2</sub>O and added dropwise to the above solution. The reaction was carried out first in an ice bath for 10 h and then at room temperature for 15–16 h. On the completion of the reaction, the solution was filtered and this was followed by purification [using a H<sup>+</sup> exchange resin column (IR 1200H resin from Aldrich) neutralized with polypyrrole to avoid its reacting with the copolymer] to remove the inorganic salt. The P(PY-co-AMP-co-AMPA) solution was concentrated in a vacuum evaporator and a film was obtained by casting from solution.

## RESULTS AND DISCUSSION

The FTIR spectrum of P(PY-co-AMP-co-AMPA) (Fig. 1) exhibits peaks at 1192 and 1053 cm<sup>-1</sup>, which can be assigned to the asymmetric and symmetric O=S=O stretching vibrations, respectively, and indicate the existence of SO<sub>3</sub><sup>-</sup> groups.<sup>15</sup> The peaks at 3465, 1208, 1050, 858, and 699 cm<sup>-1</sup> indicate the presence of the pyrrole ring. The broad peak at 1656 cm<sup>-1</sup>, which can be assigned to the C=O stretching vibration, is due to the —CO—N in AMP and the —CO—N< in AMPA. This spectrum is compatible with the structure of P(PY-co-AMP-co-AMPA) presented in Scheme I. Because after casting a film from a

solution of P(PY-co-AMP-co-AMPA) and drying, the copolymer could hardly be redissolved in water, we could not obtain suitable <sup>1</sup>H NMR results. Additional support for the structure in Scheme I is brought by the following observations. The copolymer P(PY-co-AMP-co-AMPA) is water soluble. However, when P(AMP-co-AMPA), which, because of the *p*-aminodiphenylamine moieties, possesses sites for the grafting of pyrrole, was replaced with P(AMP), which does not have such sites, and the polymerization conditions were kept the same, the pyrrole could no longer be grafted; instead, it polymerized separately as PPY, which, being insoluble, generated a suspension. The film obtained by casting from the P(PY-co-AMP-co-AMPA) solution was homogeneous, while that obtained from the suspension was heterogeneous because of the two distinct polymers involved.

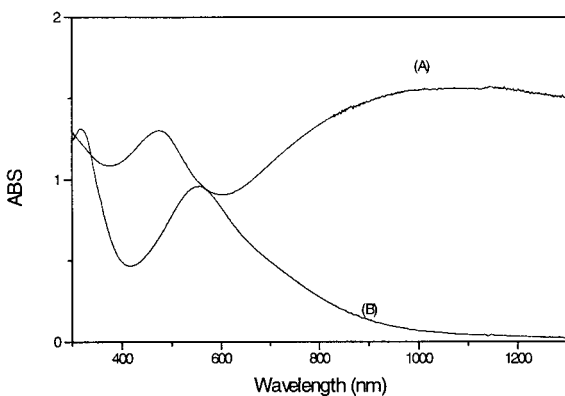
After drying in vacuum, the P(PY-co-AMP-co-AMPA) film had a conductivity of 1.96 S/cm (Fig. 2), while P(PY-co-AMP-co-AMPA)-NH<sub>4</sub> film [cast from P(PY-co-AMP-co-AMPA) 1M NH<sub>4</sub>OH solution] had a conductivity of 10<sup>-6</sup> S/cm. This indicates that P(PY-co-AMP-co-AMPA) was self-doped with its protons. A color change from dark blue in the doped state [P(PY-co-AMP-co-AMPA)] to yellow in the undoped state [P(PY-co-AMP-co-AMPA)-NH<sub>4</sub>] was observed. That P(PY-co-AMP-co-AMPA) is self-doped could be further substantiated by the electronic spectrum of its aqueous solution (Fig. 3), which exhibits a bipolaron absorption at 475 nm and a free-carrier tailing in the near-IR region with a maximum at about



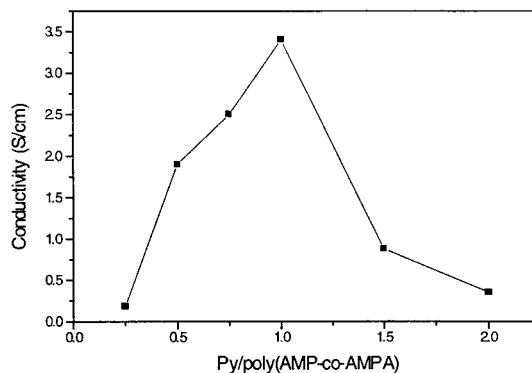
**Figure 2** Conductivity vs the drying (in vacuum) time of a thin film (first the film was dried in air for 24 h after which it was dried in vacuum).

1100 nm. When P(PY-co-AMP-co-AMPA) was converted to P(PY-co-AMP-co-AMPA)-NH<sub>4</sub> by its reaction with a 1M NH<sub>4</sub>OH solution, the bipolaron and free-carrier absorption disappeared and a strong excitation transition of the pyrrole and quinoid rings at 557 nm appeared.

The effect of pyrrole /poly(AMP-co-AMPA) wt ratio on the conductivity is presented in Figure 4, which shows a maximum conductivity of 3.4 S/cm for a ratio of 1:1. The change in the conductivity occurs because (1) at a low feed ratio of pyrrole/poly(AMP-co-AMPA), conducting PPY segments are hardly formed; and (2) at a high feed ratio, the effective conjugation length is small due to the



**Figure 3** UV/vis spectra of P(PY-co-AMP-co-AMPA): (A) aqueous solution and (B) 1M NH<sub>4</sub>OH solution.



**Figure 4** Effect of PY/poly(AMP-co-AMPA) wt ratio on the conductivity of the copolymer film.

low dopant/pyrrole ratio. As a result, the conductivity exhibits a maximum.

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