Poly(phenylene sulfide−tetraaniline): The Soluble Conducting Polyaniline Analogue with Well-Defined Structures

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ABSTRACT: A novel conducting polymer poly(phenylene sulfide−tetraaniline) (PPSTEA), with tetraaniline (TA) and phenylene sulfide (PS) segments in its repeat unit, has been synthesized through an acid-induced polycondensation reaction of 4-methylsulfinylphenyl-capped tetraaniline. The new polymer, which represents the first soluble conducting polyaniline analogue with well-defined structure, has high molecular weight, good solubility in common solvents, and good film-forming properties. Its electrical property is analogous to polyaniline. The conductivity of preliminarily protonic-doping PPSTEA is up to 10^0 S/cm. This synthetic strategy appears to be general for developing novel well-defined polyaniline analogue containing much longer fixed conjugation length.

Nitrogen- and/or sulfur-containing polymers play an important role in electrically conducting polymers, such as polyaniline (PAn), polypyrrole (PPy), polythiophene (PTh), and poly(phenylene sulfide) (PPS).[1−5] Among them, PAn has important technological applications in many areas, owing to its excellent electrical properties, good environmental stability, facile synthesis, and low cost of the monomer.[6] To our best knowledge, although much efforts have been paid to investigate its synthesis, structure, property, and application, PAn, synthesized by chemical or electrochemical polymerization, usually exhibits an ill-defined structure feature. Nevertheless, there are still some unsolved problems concerning its structure and property due to its complexity in molecular structure and poor solubility in common organic solvents, which limits the investigation of the structure−property relationship and of the conducting mechanism to some extent.

It should be pointed out that the challenging research for synthetic aspect is to design the new polyaniline derivative with fixed conjugation length, as the model polymer for identifying the conducting mechanism of common PAn.

To gain a deeper insight into the question mentioned above, there is a need to develop a general synthetic strategy to design and synthesize novel soluble polyaniline analogues with well-defined structures. Recently, Müllen's group proposed the simple combination of PPS and PAn to give poly(phenylene sulfide−phenyleneamine) (PPSA), which is believed to be the first hybrid structure of PPS/PAn and has promising electronic, optical, and mechanical properties.[7] This synthetic concept was continuously extended toward the design and synthesis of poly(phenylene sulfide−phenyleneamine−phenyleneamine) (PPSAA) by the same group.[8] However, two alternating conjugated polymers (PPSA and PPSAA) could not be doped to be conductive by protonic acid, due to the short phenyleneamine segment in their repeat unit. Besides, we have also synthesized analogous polymer whose repeated unit contains one phenylene sulfide and three phenyleneamine segments by using this route. However, the result on its protonic acid doping test and conductivity measurement was disappointing.

In this paper, we report the result on the extension of this synthetic concept toward poly(phenylene sulfide−tetraaniline) (PPSTEA) containing one phenylene sulfide and four phenyleneamine segments in the repeat unit, for determining the shortest of conduction conjugation length of common PAn to be conductive. It is found that PPSTEA surprisingly exhibits analogous electronic properties to polyaniline, as expected.

The synthesis of PPSTEA is outlined in Scheme 1. The uncapped tetraaniline (TEA) was prepared in 90% yield from 4-aminodiphenylamine by oxidative coupling with ammonium persulfate in an acetone/HCl solution and reduction with phenylhydrazine.[9] The NH groups of TEA were subsequently protected by acetylation with acetic anhydride.[10] 4-Bromo(methylsulfinyl)benzene (**2** in Scheme 1) was obtained quantitatively by oxidizing 4-bromothioanisole with Br_2 in the presence of wet, powered silica gels.[11] A modified Ullmann reaction (K_2CO_3, CuI), followed by the base hydrolysis of the acetyl groups and subsequent reduction of the resulting quinoid diimine moieties with phenylhydrazine, afforded the fully reduced state of monomer **3** suitable for making PPSTEA (**4**).

In the ^{1}H NMR spectrum of **3**, four signals at $\delta = 7.77$, 7.84, 7.89, and 8.35 are assigned to the four amino protons. The signals at $\delta = 2.77$ are ascribed to the methylene proton linked with sulfinyl group. The NMR spectra, mass spectrum, IR spectroscopy, and elemental analysis all indicate the monomer to be 4-sulfinylmethylphenyl-capped tetraaniline.[12]

The monomer **3** was self-condensed according to the modified Tsuchida route.[13] It was added into methanesulfonic acid and stirred for 24 h at room temperature under argon. The resulting viscous mixture was poured into ice water, and the resulting green solids (95%) were washed with water. The polymer precursor was dissolved in pyridine, and the pyridine solution was refluxed for 10 h to afford a complete demethylation. After being precipitated in methanol and further treated with

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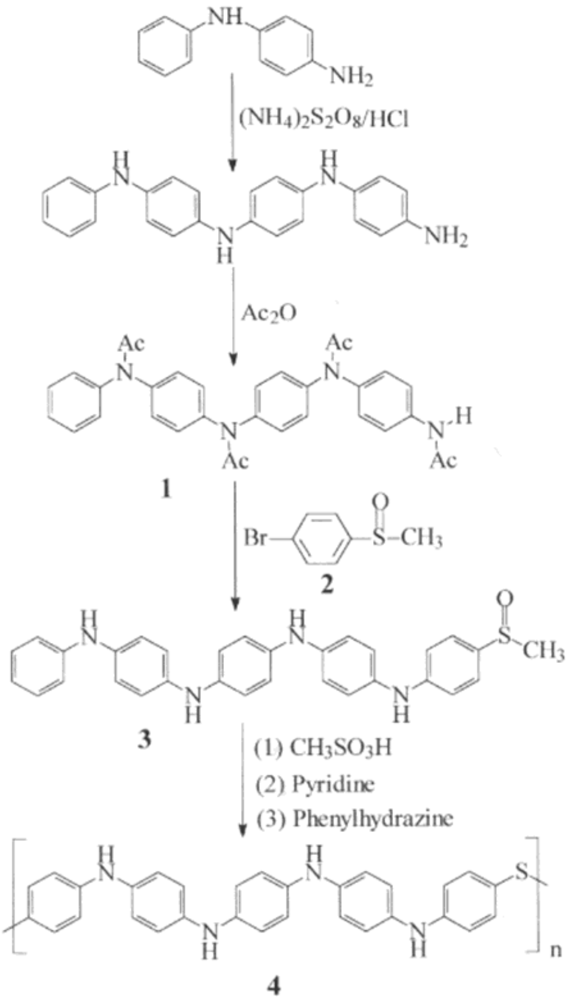
Scheme 1



phenylhydrazine to ensure its fully reduced state, the target polymer **4** was obtained as colorless solid in 90% yield after workup.

In contrast to PPS and PAn, PPSTEA (**4**) was extremely soluble in THF, DMF, DMSO, and NMP, implying much less crystallinity compared to the cases of PPS and PAn. A combination of ^{1}H NMR, ^{13}C NMR, IR, and elemental analysis reveals the formation of polymer **4**. A single strong IR band at 814 cm^{-1} in the region of aromatic C$-$H out-of-plane banding supports the 1,4-linkage of the phenylene units in PPSTEA.[14] No absorption bands attributed to the methyl, sulfoxide, and sulfone group are detected. The molecular weight ($M_w = 20\,900$, $M_n = 10\,600$, polydispersity index = 1.97) was determined by gel permeation chromatography (GPC) using tetrahydrofuran (THF) as eluent and polystyrene as standard. PPSTEA possessed a glass transition temperature (T_g) of 112 °C by differential scanning calorimetry (DSC) and a decomposition temperature (T_d) of 395 °C as assessed by thermogravimetric analysis for 5% weight loss in air. The X-ray diffraction pattern was composed a diffuse peak at $2\theta = 18°$, confirming its amorphous nature. By UV$-$vis spectroscopic analysis, there was a strong absorption at 320 nm (L1 in Figure 1), assignable to a $\pi-\pi^*$ transition of phenylene amine rings in neutral PPSTEA (**4**). When the fully reduced PPSTEA film was oxidized with iodine, its color changed gradually from colorless to light green to purple. Different colors were expected to correspond to different states of oxidation, i.e., fully reduced, partially oxidized, and fully oxidized states. Correspondingly, the UV$-$vis spectra of PPSTEA exhibited the following changes: the peak at 320 nm was weakened and shifted slightly to shorter wavelengths, there appeared a broad absorption at 580 nm for partially oxidized PPSTEA (L2 in Figure 1), and it moved to 530 nm for fully oxidized PPSTEA (L3 in Figure 1). It was interesting that when partially oxidized PPSTEA film was doped with hydrochloric acid, its color became from purple to green. As shown in Figure 1 (L4), there appears a new peak at about 420 nm and a very broad band centered at 800 nm. These behaviors are consistent with that of common polyaniline synthesized by chemical or electrochemical polymerization of aniline, indicating that three oxidative states of PPSTEA could be converted into each other and that PPSTEA could be doped to be conductive state by protonic acid.[15,16]

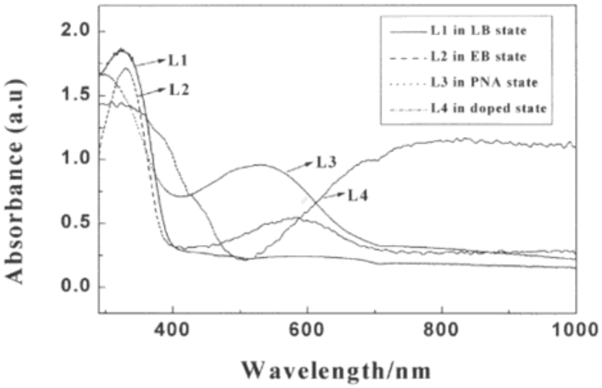


Figure 1. UV$-$vis spectra of PPSTEA in different oxidation states(20 °C, film coated onto Vycor): L1, in fully reduced state; L2, in partially oxidized state; L3, in fully oxidized state; L4, doped with HCl.

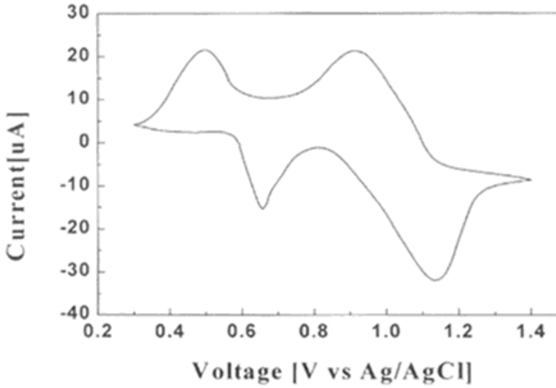


Figure 2. Cyclic voltammogram of a PPSTEA film: 20 °C, 0.1 M Bu_4NClO_4 in acetonitrile, voltage vs Ag/AgCl, scan rates 20 mV/s.

Cyclic voltammetry (CV) measurement was carried out in acetronitrile solution at room temperature with 0.1 M tetra-*n*-butylammonium perchlorate as supporting electrolyte. A three-electrode system was used; PPSTEA film coated with Pt working electrode (0.8 mm), a Pt wire as a counter electrode, and Ag/AgCl as a reference electrode. The CV curve of PPSTEA (Figure 2) showed two redox peaks at 0.46 and 0.92 V, respectively. After over 50 cyclic scans, the redox peaks remain unchanged, implying the electrochemical reversibility and stability.

Preliminary doping tests were carried out on freestanding films. The conductivity was determined by four-probe technique. The film of the fully reduced polymer doped with iodine had a conductivity of 10^{-2} S/cm. When the partially oxidized PPSTEA was doped with hydrochloric acid (HCl), its conductivity is estimated to be 10^{0} S/cm.

In conclusion, we have successfully synthesized a novel conducting poly(phenylene sulfide−tetraaniline) (PPSTEA) whose repeat unit is the combination of one phenyl sulfide and tetraaniline segments by using an acid-induced polycondensation of 4-methylsulfinylphenyl-capped tetraaniline. The new polymer PPSTEA, which represents the first soluble conducting polyaniline analogue with well-defined structures, has high molecular weight, good solubility in common organic solvents, and good film-forming properties. Its electronic property is analogous to polyaniline. From the results on its protonic-doping reaction and conductivity study, it is deduced that at least four phenyleneamine units (one benzenoid diamine and one quinoid diimine) are required for completing the insulator−conductor transition of common polyaniline by doing with protonic acid. This synthetic strategy appears to be general for developing novel well-defined polyaniline analogue containing much longer fixed conjugation length. Further studies in this regard are currently underway in our laboratory.

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Supporting Information Available: The synthetic procedure and the ^{1}H NMR and ^{13}C NMR spectra of monomer and polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Monomer **3**: mp 197 °C. ^{1}H NMR (400 MHz, 300 K, DMSO-d_6): δ [ppm] 2.77 (s, 3H, $SOCH_3$), 6.79−7.57 (m, 21H, aromatic H), 7.77 (s, 1H, NH), 7.84 (s, 1H, NH), 7.89 (s, 1H, NH), 8.35 (s, 1H, NH). ^{13}C NMR (400 MHz, 300 K, DMSO-d_6): δ [ppm] 43.07, 113.66, 114.59, 116.42, 117.45, 117.89, 118.23, 119.36, 120.61, 122.56, 125.56, 129.03, 129.16, 132.56, 132.70, 136.19, 137.61, 138.69, 140.63, 145.42, 148.63. FTIR (KBr, cm^{-1}): 3385 (NH), 1026 (S═O). Anal. Calcd for $C_{31}H_{28}N_4SO$: C, 73.81; H, 5.56; N, 11.11; S, 6.35. Found: C, 73.66; H, 5.77; N, 11.08; S, 6.32. *m*/*z* (MALDI-TOF MS): 505 (M^+).

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(14) ^{1}H NMR (400 MHz, 300 K, DMSO-d_6): δ [ppm] 6.84−7.13 (m, 20H, aromatic H), 7.63 (s, 2H, NH), 7.92 (s, 2H, NH). ^{13}C NMR (400 MHz, 300 K, DMSO-d_6): δ [ppm] 116.54, 118.68, 120.50, 122.94, 126.08, 133.83, 136.20, 139.08, 141.57, 146.79. FTIR (KBr, cm^{-1}): 3385 (NH), 814 (1,4-phenylene substitution). Anal. Calcd for $C_{30}H_{24}N_4S$: C, 76.27; H, 5.08; N, 11.87; S, 6.78. Found: C, 75.74; H, 5.20; N, 11.82; S, 6.75.

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