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Design, synthesis and characterization of novel nitrogen- and sulfur-containing polymers with well-defined conjugated length

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A series of novel nitrogen- and sulfur-containing conjugated polymers with well-defined conjugation length have been synthesized *via* an acid-induced self-polycondensation of functional monomers with methylsulfinyl groups. Synthesized polymers exhibit good solubility in common solvents, such as $CHCl_3$, THF, DMF, DMSO, and NMP. With increased numbers of aminophenyl groups, these polymers have shown similar electrical properties to polyaniline (PAn), and these are demonstrated by UV–vis spectroscopy and cyclic voltammetry (CV) measurements on the polymers. The conductivity of preliminarily protonic-doped poly[phenylene sulfide-*alt*-tetrakis(aniline)] (PPSTEA) is up to 10^{-1} S cm^{-1}.

Nitrogen- and/or sulfur-containing polymers are an important group of electrically conductive polymers, such as polyaniline (PAn), polypyrrole (PPy), polythiophene (PTh), and poly(phenylene sulfide) (PPS).[1–6] Among them PAn is especially attractive, owning to its unique electrooptical properties and market potential, good environmental stability, facility of synthesis (chemical or electrochemical oxidation of aniline), and cheapness of the monomer, *etc.*[7] Thus, PAn offers the promise of a relatively low-cost conducting (metallic) polymer that is both stable and processable. To the best of our knowledge, although much effort has been applied to investigating its synthesis, structure, properties, and application, PAn, synthesized by chemical or electrochemical polymerization, usually exhibits an ill-defined structure. Nevertheless, there still exist some unsolved problems concerning its structure and properties due to its complexity in molecular structure and poor solubility in common organic solvents, which limits in-depth investigations of the structure–property relationship and of the conducting mechanism to some extent.

It should be mentioned that a challenging synthetic research goal is to design new polyaniline derivatives with fixed conjugation length and well-defined structures, as the ideal polymer for identifying the conducting mechanism of common PAn.

Recently, one of the authors 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.[8] This synthetic concept was further extended to the design and synthesis of poly(phenylene sulfide–phenyleneamine–phenyleneamine) (PPSAA) by Müllen.[9] However, two alternating conjugated polymers (PPSA and PPSAA) could not be doped to be conductive by protonic acids, due to the too short iminophenylene segment in their repeat unit.

In this paper our efforts have focused on the extension of this synthetic concept towards poly(phenylene sulfide–trianiline) (PPSTRA) and poly(phenylene sulfide–tetraaniline) (PPSTEA), which containing one phenylene sulfide (PS) and three or four iminophenylene segments in the repeat units, for determining the shortest of conduction conjugation length of common PAn to be conductive (Scheme 1). It is found that PPSTEA exhibits remarkably close electronic properties to polyaniline, as expected. The conductivity of a preliminary protonic-doping test of PPSTEA is up to 10^{-1} S cm^{-1}. Herein we will report the details of synthesis and characterization for these new polyaniline-derived polymers.

Results and discussion

1. Polymer synthesis

The synthesis of these above polymers was based on the Tsuchida route toward sulfur-linked polymer *via* an acid-induced self-polycondensation of functional monomers with a methylsulfinyl group and an aromatic group, which is successful for the synthesis of PPSA and PPSAA.[10]

The synthesis of trianiline-containing monomer **15** was started from the commercially available 4-bromothioanisole (**8**) as shown in Scheme 2. 4-Bromo(methylsulfinyl)benzene (**9**) was synthesized quantitatively by oxidizing **8** with Br_2 in the presence of wet, powdered silica gels.[11] A modified Ullmann reaction (K_2CO_3, CuI), starting from condensation of **9** and *N*-acetylaniline (**10**), followed by the base hydrolysis of the acetyl groups yielded the PPSA monomer **11** (4-methylsulfinylphenyl(phenyl)amine). The iodo aromatic derivative **12** was prepared by iodination reaction of **11** with benzyltrimethylammonium dichloroiodate (BTMA.ICl_2). Compound **14** was obtained by the acetylation of 4-aminophenyl(phenyl)amine (**13**).[12] Condensation of **12** and **14** by a similar Ullmann reaction, base hydrolysis of the acetyl and reduction of the TRA segment by phenylhydrazine resulted in the fully reduced monomer **15**.

The synthesis of tetraaniline-containing monomer **18** is outlined in Scheme 3. The uncapped tetraaniline (TEA) **16** was prepared in 90% yield from **13** by oxidative coupling with ammonium persulfate (APS) in an acetone–HCl solution and reduction with phenylhydrazine.[13] Amine protected compound **17** was coupled with **9** and deprotection of the amino groups

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‡The IUPAC names for these polymers are as follows: PPSA = poly(phenylene sulfide-*alt*-aniline), PPSAA = poly[phenylene sulfide-*alt*-bis(aniline)], PPSTRA = poly[phenylene sulfide-*alt*-tris(aniline)] and PPSTEA = poly[phenylene sulfide-*alt*-tetrakis(aniline)].

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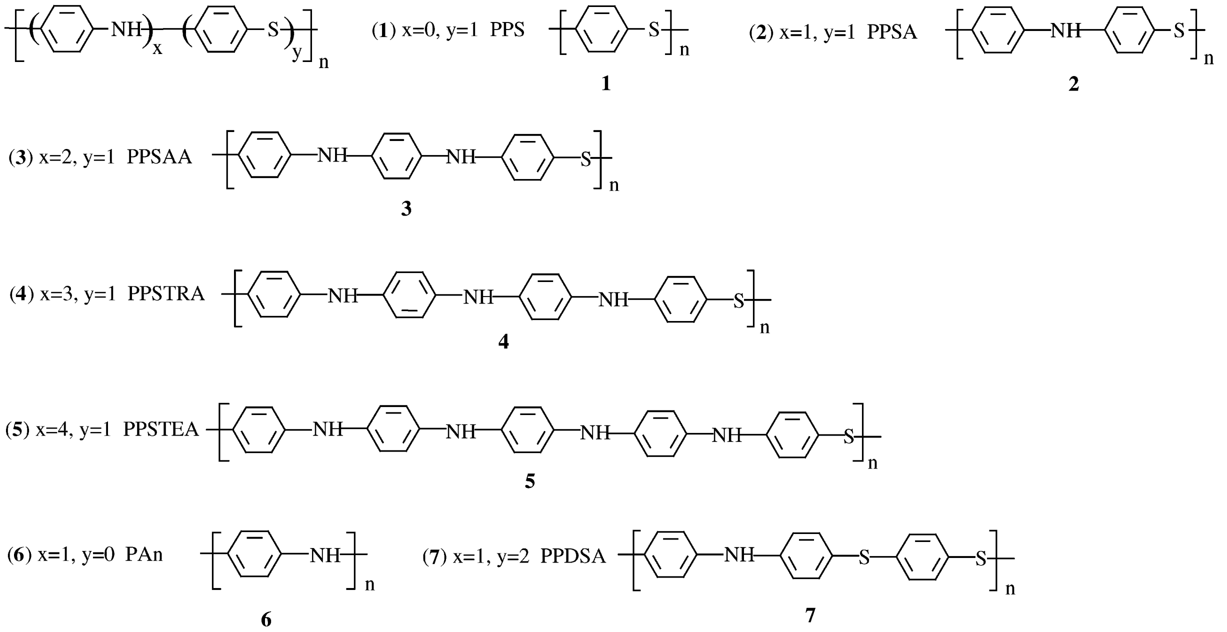
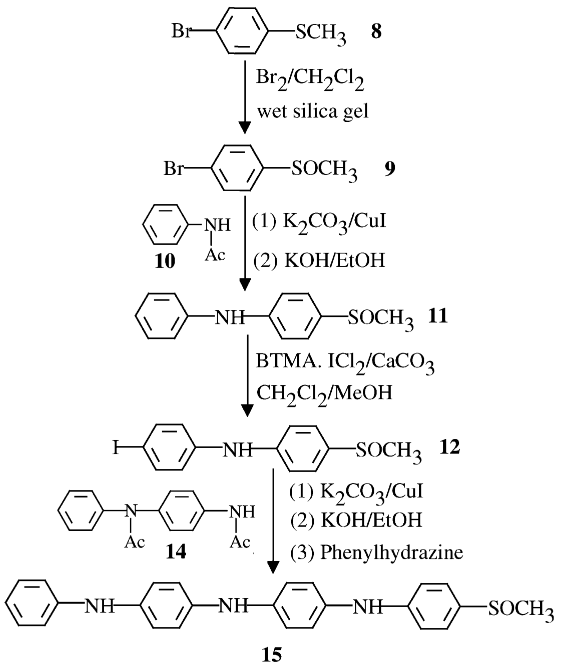
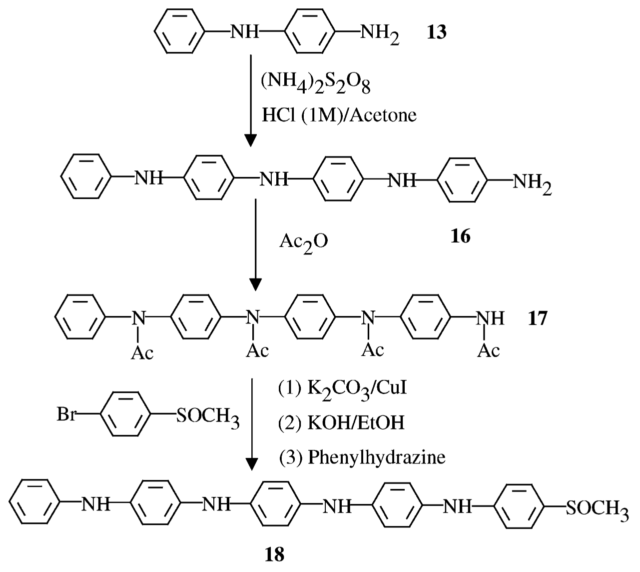


Scheme 1 Typical novel nitrogen- and sulfur-containing polymers.



Scheme 2 Synthesis of PPSTRA monomer **15**.

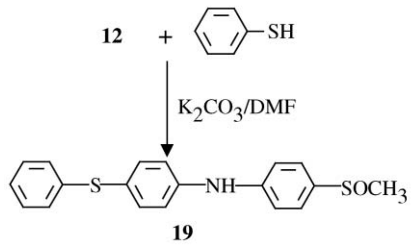


Scheme 3 Synthesis of PPSTEA monomer **18**.

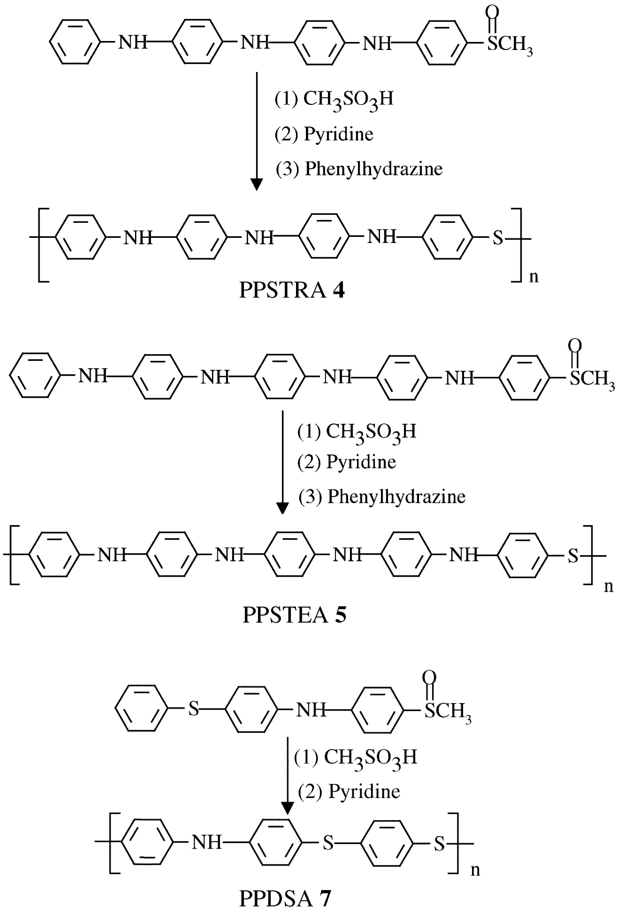
with basic aqueous ethanol and reduction of the TEA segment with phenylhydrazine gave the final fully reduced monomer **18** in good yield.

The diphenyl sulfide-containing monomer **19** was synthesized *via* a similar Ullmann reaction by the condensation of **12** and benzenethiol according to Scheme 4.

The above monomers were self-condensed, respectively, according to the modified Tsuchida route (Scheme 5).[8] They were added to methanesulfonic acid and stirred for 24 h at room temperature under argon. The resulting viscous mixtures were precipitated into an ice–water mixture and the resulting green solids were washed with water. The polymer precursors were dissolved in pyridine, and their pyridine solutions were refluxed for 10 h to afford complete demethylation. After being precipitated in methanol and further treated with phenylhydrazine to ensure the fully reduced state, the target polymers were obtained as colorless solids in 90% yield. By a similar polymerization procedure, PPDSA (**7**) was also prepared from the polymerization of monomer **19**.



Scheme 4 Synthesis of PPDSA monomer **19**.



Scheme 5 Acid-induced synthesis of PPSTRA (**4**), PPSTEA (**5**), and PPDSA (**7**).

2 Polymer characterization

NMR spectra and elemental analyses verified the proposed chemical structure of these synthesized monomers and polymers. The ^1H NMR spectrum of monomer **18** is given as an example (Fig. 1). Four signals at δ = 7.77, 7.84, 7.89, and 8.35 ppm are assigned to the four amino protons of **18**; one signal at 2.77 ppm is ascribed to the methyl proton linked with the sulfinyl group. The relative intensities of the signals around δ = 6.78–7.58 ppm allow estimation of the other expected splitting of the aromatic proton signals. In the ^{13}C NMR spectrum of **18** (Fig. 2), one signal at δ = 43.1 ppm and twenty signals at around δ = 113.7–148.6 ppm are ascribed to the methyl carbon and the other aromatic carbons, respectively.

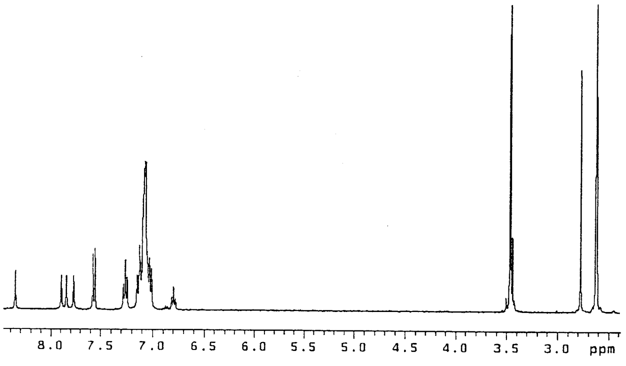


Fig. 1 ^1H NMR spectrum of tetraaniline-containing monomer **18**.

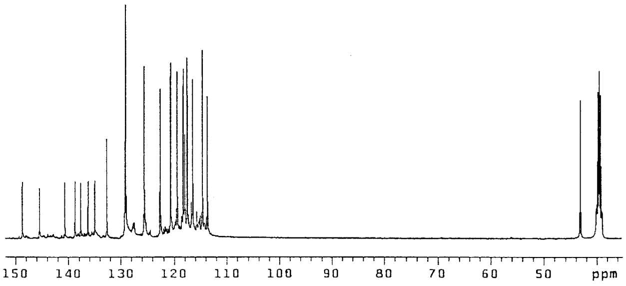


Fig. 2 ^{13}C NMR spectrum of tetraaniline-containing monomer **18**.

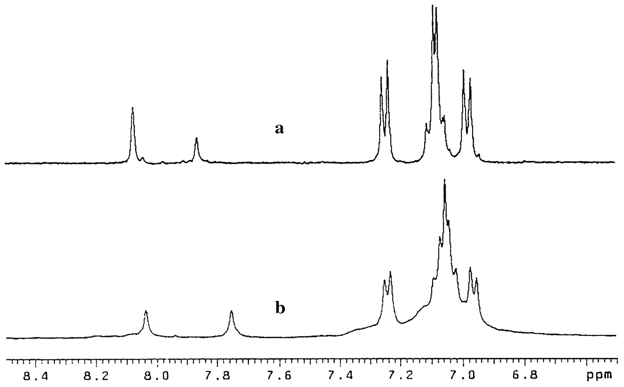


Fig. 3 ^1H NMR spectra of PPSTRA (**4**) (a) and PPSTEA (**5**) (b).

The ^1H NMR spectra of PPSTRA (**4**) and PPSTEA(**5**) are shown in Fig. 3. Two signals at δ = 7.87, 8.08 ppm (a) and δ = 7.76, 8.04 ppm (b) are attributed to the three and four amino protons of **4** and **5**, respectively. Furthermore, the other expected splitting of the aromatic proton signal is seen, demonstrating the well-defined structure of the two polymers. In Fig. 4 and Fig. 5 are shown the ^{13}C NMR spectra of **4** and **5**, where only eight and ten aromatic carbons are observed, as expected. A single strong IR signal at about 813 cm^{-1} in the region of aromatic C–H out-of-plane banding supports the 1, 4-linkage of the phenylene units in PPSTRA and PPSTEA. No absorption bands attributed to the methyl, sulfoxide and sulfone group are detected (see Fig. 6).

For the sake of comparison, we have also synthesized the other two nitrogen- and sulfur-containing polymer PPSA (**2**) and PPSAA (**3**), whose repeat units are combinations of PS and aniline or bis(aniline). In contrast to PPS and PAn, PPSTRA (**4**), PPSTEA (**5**), and PPDSA (**7**) were extremely soluble in

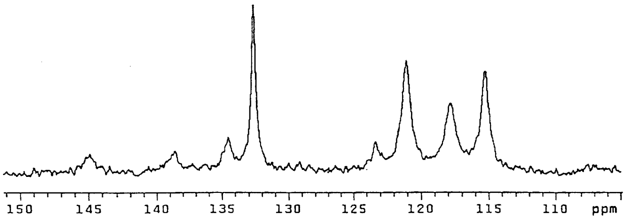


Fig. 4 ^{13}C NMR spectrum of PPSTRA (**4**).

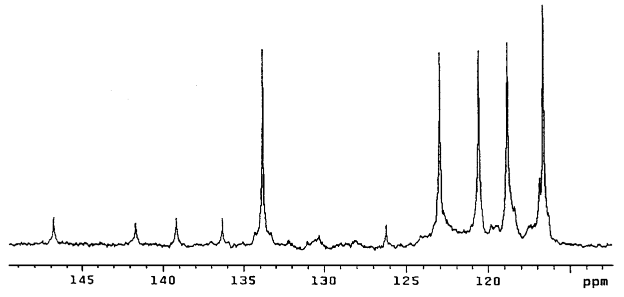


Fig. 5 ^{13}C NMR spectrum of PPSTEA (**5**).

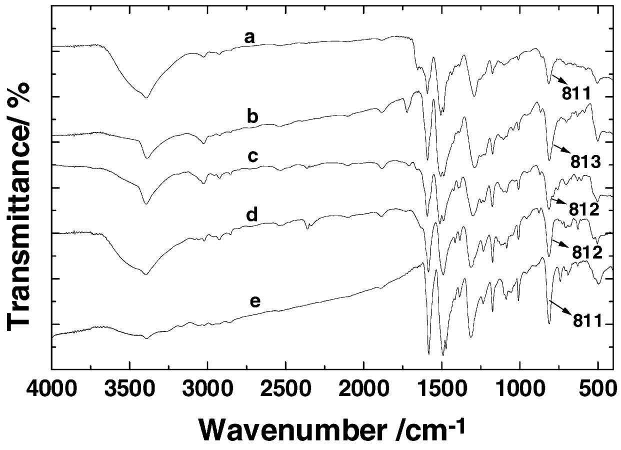


Fig. 6 FTIR spectra of synthesized polymers: (a) **5**, (b) **4**, (c) **3**, (d) **2** and (e) **7**.

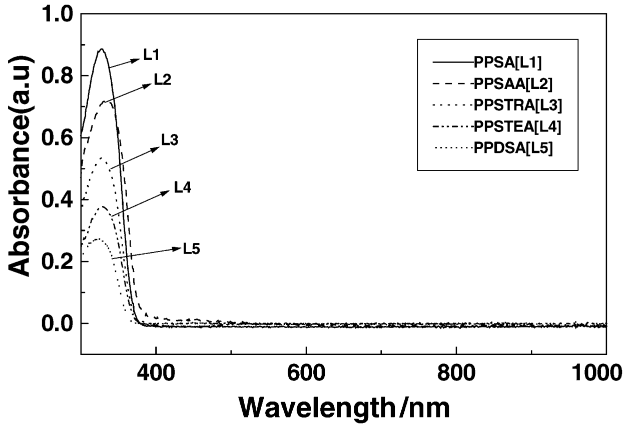


Fig. 7 UV–vis spectra of the fully reduced state of synthesized polymers (20 °C, film coated onto Vycor): **2** (L1), **3** (L2), **4** (L3), **5** (L4) and **7** (L5).

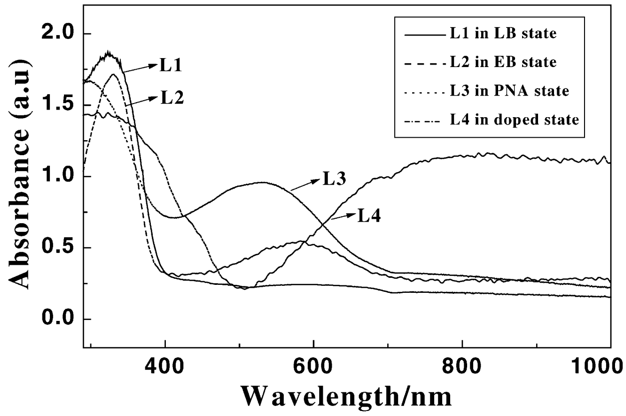


Fig. 8 UV–vis spectra of PPSTEA (**5**) at different oxidation states (20 °C, film coated onto Vycor): L1, in fully reduced state; L2, in partially oxidized state; L3, in fully oxidized state; L4, doped with HCl.

THF, DMF, DMSO and NMP, analogous to PPSA and PPSAA. Molecular weights, reported in Table 1, were determined by gel-permeation chromatography (GPC) with uniform polystyrene standards. From Table 1 we can see that PPSA has the highest molecular weight of all the polymers. The greater the number of aminophenyl groups, the lower the molecular weight of the polymer. We explain this by the more sensitive oxidative character of these monomers, but further investigations are under way.

Thermogravimetric analyses (TGA) of different nitrogen- and sulfur-containing polymers show that polymers **4**, **5** and **7** are stable up to 370 °C, 395 °C, and 320 °C in nitrogen respectively. Differential scanning calorimetry (DSC) suggests that **4**, **5**, and **7** possess glass transitions (T_g) of 114 °C, 112 °C, and 90 °C, respectively, and no melting transition can be detected. X-Ray diffraction patterns are all composed of a diffuse peak at $2\theta = 18°$, which along with the results of DSC, indicates the amorphous nature of the synthesized polymers.

3 Electronic properties of polymers

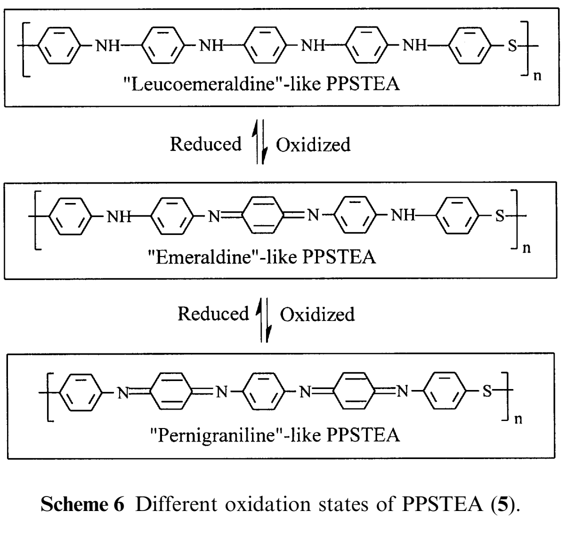
By UV–vis spectroscopic analysis, there were strong absorptions at about 320 nm, assignable to the π–π* transition of the aniline rings in neutral forms of **4**, **5**, and **7** (see Fig. 7). When the fully reduced PPSTEA film was oxidized with iodine, its color changed gradually from colorless to 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 Fig. 8) and it moved to 530 nm for fully oxidized PPSTEA (L3 in Fig. 8). It was interesting that when partially oxidized PPSTEA film was doped with hydrochloric acid, its color changed from purple to green. As shown in Fig. 8 (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 polymer 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 a conductive state by protonic acids.[14,15] (Scheme 6)

Table 1 Molecular weights of the synthesised polymers

Polymer	M_n[a,b]/Da	M_w[a,c]/Da	M_w/M_n	N_n[d]
2	56600	97800	1.73	285
3	19000	42800	2.25	65
4	9000	19700	2.80	23
5	10600	20900	1.97	22
7	6100	8300	1.36	20

[a] Determined by gel-permeation chromatography (GPC) with uniform polystyrene standards and THF as solvent. [b] Number-averaged molecular weight. [c] Weight-averaged molecular weight. [d] Number-averaged degree of polymerization.

Cyclic voltammetry (CV) measurements were carried out in acetonitrile solution at room temperature with 0.1 M tetra-*n*-butylammonium perchlorate as supporting electrolyte. A



Scheme 6 Different oxidation states of PPSTEA (**5**).

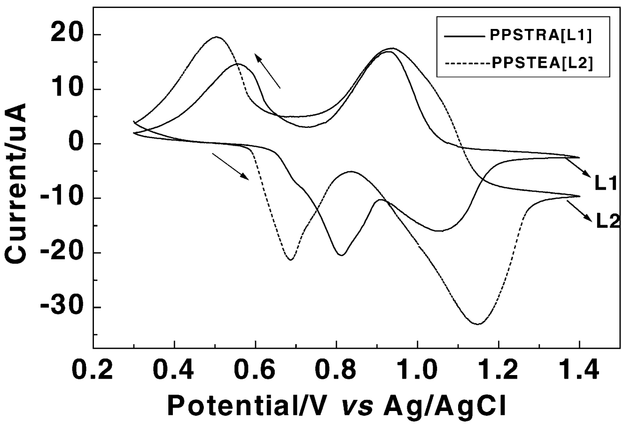


Fig. 9 Cyclic voltammogram of PPSTRA (L1) and PPSTEA film (L2): 20 °C, 0.1 M Bu_4NClO_4 in acetonitrile, voltage *vs.* Ag/AgCl, scan rates 50 mV s^{-1}.

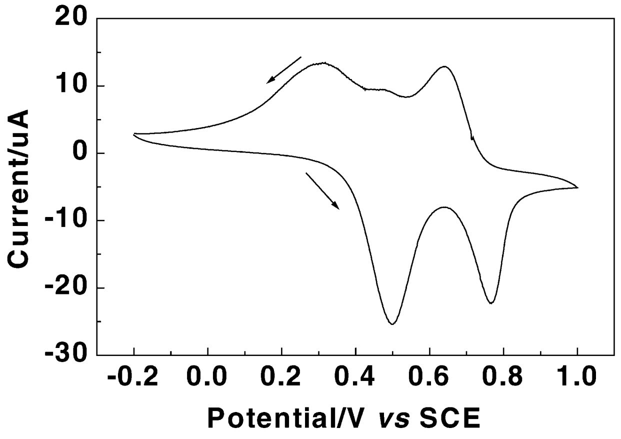


Fig. 10 Cyclic voltammogram of PPSTEA–film: 20 °C, 1 M HCl, voltage *vs.* SCE, scan rates 50 mV s^{-1}

three-electrode system was used; polymer film coated with Pt as working electrode (id 0.8 mm); a Pt wire as a counter electrode and Ag/AgCl as reference electrode. The CV curves of PPSTEA and PPSTRA (Fig. 9) showed two main redox peaks at 0.46 and 0.92 V, 0.59 and 0.84 V, respectively. After over 50 cyclic scans, the redox peaks remained unchanged, implying electrochemical reversibility and stability. Moreover, the CV of PPSTEA film obtained by sweeping the potential between −0.2 and 1.0 V in a blank (1 M HCl) medium is shown in Fig. 10. It displayed two main redox peaks at 0.45 and 0.78 V *vs.* SCE reference electrode.

Preliminary doping tests were carried out on free-standing films or compressed powder pellets. The free-standing films were cast from 0.5–1% w/w solutions of synthesized polymers in chloroform. The conductivity was determined by the four-probe technique. All these undoped synthesized polymers are insulating with conductivity lower than 10^{-9} S cm^{-1}. The film of the fully reduced PPSTEA doped with iodine had a conductivity of 10^{-2} S cm^{-1}. When the partially oxidized PPSTEA was doped with hydrochloric acid (HCl), its conductivity is estimated to be 10^{-1} S cm^{-1}. In the same way, doped tetraaniline (**16**) had a conductivity of 10^{-3} S cm^{-1}. However, the effects on the electrical conductivity of protonic doping of other polymers such as PPSAA and PPSTRA have turned out to be disappointing. It has not been possible to obtain any conducting films through this type of doping method. Furthermore, the same results were obtained from the oxidatively doped films of these leucoemeraldine-like samples, by treating them with iodine or bromine. It is well known that highly conducting doped forms of polyaniline could be reached by two completely different processes—protonic acid doping and oxidative doping.[16] The emeraldine base state is protonically acid doped to the metallic regime by a process involving no change in the number of electrons on the polymer chain; the leucoemeraldine state, on the other hand, is oxidatively doped, either chemically or electrochemically, by conventional redox doping of the type found in other conducting polymers.[17] As we can obtain the conductive form of PPSTEA *via* a protonic acid doping without changing the number of electrons of the backbone in the sample, it is deduced that at least four iminophenylene units are required for completing the insulator–conductor transition of common polyaniline by doping with protonic acid.

The sulfur atom has been regarding as inhibiting the extensive conjugation along the polymer chain for PPSA and PPSAA, and the charge transport has to proceed *via* a 'hopping' mechanism along several chains.[8*b*,9] However, this is not true for PPSTEA. This is because PPSTEA can complete the protonic acid doping without changing the number of polymer backbone, and the conductivity of a protonic acid or iodine oxidative doping test is 2 orders higher than that of tetraaniline. So we can envisage that the sulfur atom in the polymer chain is not an inhibitor for furthering the conjugation interaction. On the contrary, it may participate in the charge transport to some extent. The actual reason for the lower conductivity of PPSA, PPSAA, and PPSTRA should not be ascribed to the interruption of the conjugation by sulfur, but to the too short length of the phenylamine segments in the repeated units. Further experiments on the confirming the doping site (the actual site of quinone diimine in the repeat unit), the charge transport, and the optimization of the doping process in PPSTEA is in progress.

Conclusion

In conclusion, we have successfully synthesized a series of novel nitrogen- and sulfur-containing conjugated polymers poly(phenylene sulfide–trianiline) (PPSTRA) and poly(phenylene sulfide–tetraaniline) (PPSTEA) whose repeat units are the combination of one phenylene sulfide and tris(aniline) or tetrakis(aniline) segments by using acid-induced polycondensation of 4-methylsulfinylphenyl capped trianiline and 4-methylsulfinylphenyl-capped tetraaniline. With the increase in the number of aminophenyl groups, these polymers have shown similar electrical properties to polyaniline (PAn). The new conducting polymer PPSTEA, which represents the first soluble conducting polyaniline analogue with a well-defined structure, has high molecular weight, good solubility in common organic solvents and good film-forming properties. From the results on its protonic-doping reaction and conductivity study, it is deduced that at least four iminophenylene units (one benzenoid diamine and one quinone 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 analogues containing much longer fixed conjugation lengths. Further studies in this regard are currently under way in our laboratory.

Experimental

General

Commercial reagents were used without further purification unless specially noted. Solvents were purified, dried, and degassed according to standard procedures. All synthesis was carried out under argon. ^1H NMR and ^{13}C NMR data were obtained on Varian Unity Inova 400 MHz and Bruker AC-F 80 MHz spectrometers. The chemical shifts were calibrated from tetramethylsilane (TMS). FT-IR spectra were recorded on a Bio-Rad FTS-135 (USA) using KBr pellets. UV–Vis spectra were recorded using a Varian Cray 50 type spectrometer. Gel permeation chromatograms (GPC) were obtained on a Waters 510, polystyrene as standard and THF as eluent at a 1.0 mL min^{-1} flow rate. Cyclic voltammetry (CV) measurements were done in a three electrode system using a platinum microelectrode as working electrode, Pt wire as counter electrode and Ag/AgCl or saturated calomel electrode (SCE) as reference, and potentiostat configuration from EG&G 283 Princeton Applied Research. C, H, N and S elemental analysis were recorded on Bio-Rad Co's elemental analytical instrument. Differential scanning calorimetric (DSC) and thermal gravimetric analysis (TGA) were recorded on Perkin-Elmer DSC-7 and Perkin-Elmer TGA-7, temperature increase rate: 10 °C min^{-1} under N_2 or air.

Synthesis

4-Bromo(methylsulfinyl)benzene (9). Dry silica gel (60 g) was placed in a 250 mL round bottomed flask containing a magnetic stirring bar and a loosely fitted rubber septum. Water (30 g) was added to the vigorously stirred silica gel. After complete addition of the water, stirring continued until a free flowing powder was obtained. CH_2Cl_2 (100 mL) was added to the flask. A solution of 4-bromothioanisole (50 mmol, 10.1 g) in CH_2Cl_2 was added to the stirred heterogeneous mixture. A solution of Br_2 (2.70 mL, 52 mmol) in CH_2Cl_2 (5 mL) was added dropwise from a syringe to the mixture. The color of the Br_2 disappeared instantly. The mixture was stirred at RT for 10 min. During this period complete disappearance of 4-bromothioanisole was confirmed by TLC (SiO_2, EtOAc–hexane = 4 : 1, R_f = 0.45). The mixture was then filtered through a sintered glass funnel, the solid residue was washed with CH_2Cl_2 (100 mL) and the washings were added to the filtrate. Removal of the solvent from the CH_2Cl_2 solution under vacuum gave pure sulfoxide (**9**) 10.9 g (99% yield) as a colorless solid (mp 86 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 2.73(s, 3H, $SOCH_3$), 7.52(d, 2H, aromatic H), 7.64(d, 2H, aromatic H). Anal. Calcd for C_7H_7SOBr: C, 38.37; H, 3.20; S, 14.62. Found: C, 38.21; H, 3.27; S, 14.56%.

Preparation of uncapped tetraaniline (16). The uncapped tetraaniline (TEA) was prepared from 4-aminophenyl(phenyl)-amine (**13**) by means of a modified MacDiarmid method, *i.e.*, oxidative coupling by ammonium persulfate (APS) in an acetone–HCl solution. 4-Aminophenyl(phenyl)amine (5.5 g, 30 mmol) was dissolved in a mixture of acetone (250 mL) and aqueous HCl (200 mL, 2.0 M). The solution was cooled in an ice–salt bath. $(NH_4)_2S_2O_8$ (APS) (5.5 g, 24 mmol) dissolved in 50 mL H_2O–acetone (1 : 1 = v/v) mixture solution was added dropwise into the solution. After about 15 min, the color of the solution changed to blue. The reaction solution was stirred vigorously for an additional 4–5 h. The solid product was collected by filtration through a G4 sintered glass funnel under a reduced pressure, and was washed with 1.0 M HCl and acetone. The product was treated with 1.0 M aqueous NH_3, and filtered. The remaining solid was washed with distilled water until the filtrate became neutral. Upon drying at 40 °C overnight under vacuum, a brown powder was obtained. It was reduced by phenylhydrazine in ethanol solution. 9.8 g (90% yield) light blue powder (fully reduced state **16**) was obtained. *m*/*z* (MALDI-TOF MS): 367 (M^+). Anal. Calcd for $C_{24}H_{18}N_4$: C, 79.56; H, 4.97; N, 15.47. Found: C, 79.44; H, 5.07 N, 15.45%.

General procedure for the acetylation of uncapped oligoaniline

The synthesis of **17** was used as an example for the acetylation of uncapped oligoaniline. Acetic anhydride (7.3 g, 70 mmol) in glacial acetic acid (10 mL) was added dropwise to a solution of fully reduced uncapped tetraaniline (**16**) (5.8 g, 16 mmol) in glacial acetic acid (70 mL) under argon. After the addition was complete, the mixture was heated to 70 °C and stirred for an additional 6 h. The glacial acetic acid was removed by distillation under reduced pressure. By column chromatography (SiO_2, acetone–EtOAc = 1 : 4 as eluent, R_f = 0.35) **17** was obtained as a colorless solid.

***N*,*N*′,*N*″,*N*‴-Tetraacetyl-uncapped tetraaniline (17).** Yield 6.1 g (70%); mp 155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 2.05(s, 12H, H_3CCO), 7.20–7.26(m, 17H, aromatic H). Anal. Calcd for $C_{32}H_{30}N_4O_4$: C, 71.91; H, 5.62; N, 10.45. Found: C, 71.79; H, 5.78; N, 10.37%.

***N*-Phenyl-*N*,*N*′-(1,4-phenylene)diacetamide (14).** Yield 4.3 g (75%); mp 135 °C. ^{1}H NMR (80 MHz, $CDCl_3$) δ(ppm) 2.00(s, 6H, $COCH_3$), 7.20–7.26(m, 9H, aromatic H). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.64; H, 5.97; N, 10.45. Found: C, 71.59; H, 6.05; N, 10.37%.

General procedure for the coupling reaction of amides and 4-bromo(methylsulfinyl)benzene (modified Goldberg reaction)

The synthesis of 4-(methylsulfinyl)phenyl capped tetraaniline **18** was used as an example. Monomer **18** was prepared in the following procedure: a 50 mL round bottomed flask was charged with a Teflon-covered magnetic bar and a thoroughly ground mixture of **17** (5.0 g, 9.3 mmol), 4-bromo(methylsulfinyl)benzene (**9**) (2.1 g, 9.3 mmol), K_2CO_3 (1.6 g) and CuI (0.6 g), 18-crown-6 (0.2 g). The reaction was allowed to proceed at 180 °C under argon for 24 h. The resulting highly viscous mixture was taken up in CH_2Cl_2 and continuously washed with 1 M HCl, NH_4OH and brine then dried with anhydrous Na_2SO_4. The combined solvent was removed by distillation under reduced pressure and the residue was chromatographed over silica (EtOAc–MeOH = 4:1 as eluent, R_f = 0.4). After the combined solvent was distilled under reduced pressure, the residue was dissolved in ethanol (100 mL) containing KOH (4.5 g) and heated to reflux for 6 h. The purple solution was cooled and poured into 500 mL of water. The precipitate was filtered off over a G4 sintered glass funnel and reduced with phenylhydrazine and recrystallized from toluene. **18** was obtained as a light blue crystalline solid.

4-(Methylsulfinyl)phenyl-capped tetraaniline (18). Yield 2.3 g (50%); mp 197 °C. ^{1}H NMR (400 MHz, 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, DMSO-d_6) δ(ppm) 43.17, 113.73, 114.67, 115.30, 116.46, 117.98, 118.87, 119.43, 120.74, 122.65, 125.66, 129.14, 129.45, 132.70, 134.82, 136.26, 137.14, 138.55, 140.45, 145.57, 148.70. 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, 5.66; N, 11.08; S, 6.32%. *m*/*z* (MALDI-TOF MS): 505 (M^+).

4-Methylsulfinylphenyl(phenyl)amine (11). Yield 3.43 g (75%); mp 135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 2.71(s, 3H, $SOCH_3$), 6. 80(s, 1H, NH), 7.05–7.07(t, 1H), 7.10–7.12(d, 2H), 7.14–7.16(d, 2H), 7.31–7.35(t, 2H), 7.51–7.53(d, 2H); ^{13}C NMR (400 MHz, DMSO-d_6) δ(ppm) 43.28, 115.91, 118.94, 121.72, 125.94, 129.85, 135.57, 142.84, 147.23. Anal. Calcd for $C_{13}H_{13}NSO$: C, 67.50; H, 5.66; N, 6.06; S, 13.86. Found: C, 67.59; H, 5.70; N, 6.00; S, 13.93%.

Preparation of (4-iodophenyl)(4-methylsulfinylphenyl)amine (12). To a solution of 4-methylsulfinylphenyl(phenyl)amine (2.3 g, 10 mmol) in dichloromethane–methanol (50 mL–20 mL), benzyltrimethylammonium dichloroiodate (BTMA.ICl_2) (3.8 g, 10.5 mmol) and calcium carbonate (1.1 g) were added in one portion. The mixture was stirred for 16 h at room temperature, during which the color of the solution gradually changed from yellow to light brown. Excess calcium carbonate was filtered and the filtrate was concentrated; then, the obtained residue was extracted with ether. The ether layer was continual washed with 10% $NaHSO_3$ and brine, then dried with anhydrous Na_2SO_4 and evaporated under vacuum to give light gray crystals (from 1 : 3 methanol–water). Yield 3.4 g (95%); mp 153 °C. ^1H NMR (80 MHz, $CDCl_3$) δ(ppm) 2.70(s, 3H, $SOCH_3$), 5.82(s, 1H, NH), 6.83(d, 2H), 7.03(d, 2H), 7.55(d, 2H), 7.61(d, 2H). Anal. Calcd for $C_{13}H_{12}NSOI$: C, 43.70; H, 3.36; N, 3.92; S, 8.96. Found: C, 43.21; H, 3.50; N, 3.86; S, 8.85%.

4-Methylsulfinylphenyl-capped trianiline (15). With the same procedure used for **18**, **15** was obtained by the condensation of compounds **12** and **14**. Yield 1.2 g (30%); mp 150 °C. ^1H NMR (400 MHz, DMSO-d_6) δ(ppm) 2.78(s, 3H, $SOCH_3$), 6.82(t, 1H), 7.04–7.17(m, 12H), 7.26–7.30(t, 4H), 7.40–7.43(t, 2H), 7.56–7.65(m, 2H), 7.92–7.95(d, 1H), 8.37(s, 2H, NH), 8.70(s, 1H, NH). Anal. Calcd for $C_{25}H_{23}N_3SO$: C, 72.64; H, 5.57; N, 10.17; S, 7.75. Found: C, 72.38; H, 5.70; N, 10.11; S, 7.71%.

(4-Methylsulfinylphenyl)(4-phenylthiophenyl)amine (19). A 50 mL round bottomed flask was charged with a Teflon-covered magnetic bar and a thoroughly ground mixture of **12** (2.1 g, 6 mmol), thiophenol (1.0 g, 9 mmol), K_2CO_3 (1.5 g), and DMF (10 mL). The reaction was allowed to proceed at 135 °C under argon for 16 h. After cooling to room temperature, the resulting mixture was poured into water (200 mL), extracted with CH_2Cl_2 and continuously washed with dilute KOH solution and brine, then dried with anhydrous Na_2SO_4. The combined solvent was removed by distillation under reduced pressure and the residue was purified by chromatography over silica (EtOAc–acetone = 4 : 1 as eluent, $R_f = 0.4$). **19** was obtained as colorless crystals. Yield 1.8 g (90%); mp 157 °C. ^1H NMR (400 MHz, $CDCl_3$) δ(ppm) 2.77(s, 3H, $SOCH_3$), 6.12(s, 1H, NH), 7.09(d, 2H,), 7.14(d, 2H), 7.27(m, 5H), 7.37(d, 2H), 7.54(d, 2H). Anal. Calcd for $C_{19}H_{17}NS_2O$: C, 67.27; H, 5.01; N, 4.13; S, 18.88. Found: C, 67.01; H, 5.40; N, 4.11; S, 18.80%.

General procedure for the preparation of polymers 2, 4, 5, and 7 by the acid-induced self-condensation of corresponding monomers with methylsulfinyl as functional groups

The polymerization of the tetraaniline-containing monomer **18** was used as an example. A 25 mL round bottomed flask was charged with a Teflon-covered magnetic bar and 8 mL of methanesulfonic acid was added. Monomer **18** (0.5 g, 1 mmol) was added at RT and stirred for 24 h under argon. The resulting highly viscous mixture was precipitated into an ice–water mixture and filtered off, washed with water, and dried under reduced pressure to obtain the precursor.

A 100 mL, round bottomed flask was charged with a Teflon-covered magnetic bar, the above precursor and pyridine (25 mL) were added. The mixture was refluxed for 6 h under argon. After cooling, the clear solution was poured into cold methanol (300 mL) and stirred for 2 h. The polymer was filtered off, washed with water and methanol, reduced with phenylhydrazine in THF, then reprecipitated in methanol and dried under reduced pressure to obtain the fully reduced structure **5**.

Poly[phenylene sulfide-*alt*-tetrakis(aniline)] (PPSTEA) (5). Yield 0.42 g (90%). ^1H NMR (400 MHz, DMSO-d_6) δ(ppm) 6.97–7.25(m, 20H, aromatic H), 7.76(s, 2H, NH), 8.04(s, 2H, NH); ^{13}C NMR (400 MHz, 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. 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%.

Poly[phenylene sulfide-*alt*-tris(aniline)] (PPSTRA) (4). Yield 0.35 g (89%). ^1H NMR (400 MHz, DMSO-d_6) δ(ppm) 6.97–6.99(d, 4H), 7.06–7.11(m, 8H), 7.29–7.26(d, 4H), 7.87(s, 1H, NH), 8.08(s, 2H, NH); ^{13}C NMR (400 MHz, DMSO-d_6) δ(ppm) 115.23, 117.79, 121.01, 123.31, 132.56, 134.50, 138.58, 144.89. Anal. Calcd for $C_{24}H_{19}N_3S$: C, 75.59; H, 4.99; N, 11.02; S, 8.40. Found: C, 74.80; H, 5.18; N, 10.96; S, 8.32%.

Poly(phenylene sulfide-*alt*-aniline) (PPSA) (2). Yield 0.19 g (91%). ^1H NMR (400 MHz, DMSO-d_6) δ(ppm) 7.13–7.15(d, 4H), 7.29–7.31(d, 4H), 8.55(s, 1H, NH); ^{13}C NMR (400 MHz, DMSO-d_6) δ(ppm) 118.12, 125.81, 132.71, 142.83. Anal. Calcd for $C_{12}H_9NS$: C, 72.35; H, 4.65; N, 7.04; S, 16.06; Found: C, 74.41; H, 4.71; N, 6.92; S, 16.26%.

Poly[bis(phenylene sulfide)-*alt*-aniline] (PPDSA) (7). Yield 0.28 g (89%). ^1H NMR (400 MHz, DMSO-d_6) δ(ppm) 7.17–7.42(12H, aromatic H), 8.71(s, 1H, NH); ^{13}C NMR (400 MHz, DMSO-d_6) δ(ppm) 117.43, 119.80, 125.11, 132.50, 134.58, 142.41. Anal. Calcd for $C_{18}H_{13}NS_2$: C, 70.36; H, 4.23; N, 4.56; S, 20.85. Found: C, 70.08; H, 4.52; N, 4.50; S, 20.65%.

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