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Notes

Synthesis of Novel Ladder Polymer Electrolytes Bridged by Sulfonio and Imino Groups

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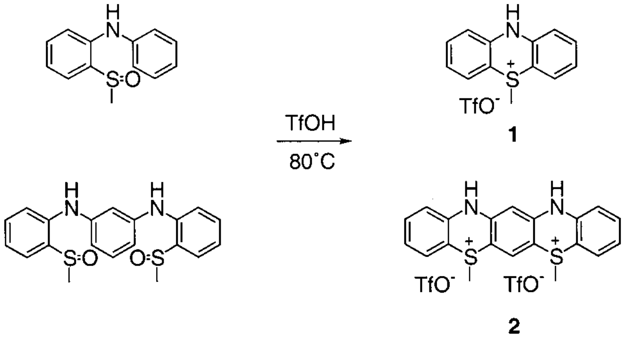
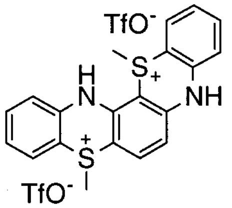
Ladder or double-stranded polymers have been extensively studied since the early 1960s, originally as structural (high-performance) materials and recently as electronic and optical materials as well.[1] Since the irreversible near-planar conformation of a laddered structure renders excellent thermal and mechanical strength, and optimum π-orbital overlap to lower the band gap, they are potentially useful for electron-conducting, photoluminescent, or third-order nonlinear-optical applications. Among them are, for example, polyacenes (PA),[2] polyquinoxalines (PQL),[3] poly(*p*-phenylene) ladders (LPPP),[4] phenothiazine ladders (PTL),[5] and others.[6]

Ladder polymers are usually synthesized either by cyclization of a functionalized single-stranded precursor polymer or by ring-forming condensation (or cycloaddition) reaction of multifunctionalized monomers. The rigid skeleton of such polymers requires substituents (e.g., flexible alkyl groups) for solubility and processability, sacrificing the crystallinity and therefore the important intermolecular interactions. Incorporating ionic groups into polymers often makes them soluble in polar solvents. In the previous paper, we reported oligo(*p*-phenylene) ladders containing sulfide and sulfonio linkages.[7] The oligomers with a planar π-conjugated structure do not have bulky substituents, and yet they are soluble in protonic acids. We report herein novel ladder polymers bridged by imino and sulfonio groups. The polymers with moderately high molecular weights have been synthesized by taking advantage of a Pd-catalyzed arylamination reaction followed by the acid-induced ring-closing reaction. The products are soluble in organic solvents. The characterization, thermal, and electronic properties are described.

We first carried out two model reactions in order to confirm the formation of ladder oligomers by the Swern reaction of aryl sulfoxides[8] (Scheme 1). The reaction does not take place at 20 °C and requires heating at 80 °C. The ring-closed compounds **1** (10-hydro-5-methylphenothiazinium triflate) and **2** (12,14-dihydro-5,7-bis(methylsulfonio)-12,14-diazapentacene bis(triflate)) could be isolated in >95% yield. The products were characterized by elemental analyses and ^{1}H, ^{13}C NMR, and IR spectroscopies. Triflic acid, as the strongest monobasic acid, is found to be most effective to give quantitative reactions. The bent isomer **2′** was not formed. The large steric hindrance between the sulfonium cation and the neighboring imino groups could prevent the formation of **2′** under the given conditions.

Scheme 1. Synthesis of Model Compounds 1 and 2 by Swern Reaction





2'

The title polymer **9** was synthesized as outlined in Scheme 2. 1,3-Dibromo-4,6-bis(methylthio)benzene (**3**), prepared from 1,3-benzenedithiol in two steps, was polymerized with *m*-phenylenediamine by Pd-catalyzed amination.[9] The polycondensation proceeds in toluene at 90 °C under an argon atmosphere. The sterically hindered phosphine compound, BINAP (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl),[9d] serves as a good ligand for the polymerization to give polymer **5** as a pale brown powder in 97% yield (Table 1). The molecular weight of the polymer was determined by GPC to be $M_w = 12\ 200$ and $M_n = 6000$. In the FAB-MS spectrum, the peaks corresponding up to the nonamer with bromine and amino end groups could be observed. Utilizing other solvents for higher reaction temperatures (at 140 °C in *o*-xylene and at 160 °C in anisole) resulted in lower molecular weight polymers. The polymerization of **4** with *m*-phenylenediamine gave a polymer **6** ($M_w = 7100$ and $M_n = 3000$) in 96% yield. The polymers were characterized by spectroscopies. In the ^{1}H NMR spectrum of **5** (Figure 1, top), a singlet peak of methyl groups appears at 2.22 ppm. The peaks from 6.68 to 7.60 ppm are well-assigned to the aromatic and imine protons. The integration ratio of those peaks also supports the

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Scheme 2. Synthetic Route to Ladder Polymer Electrolytes 9 and 10

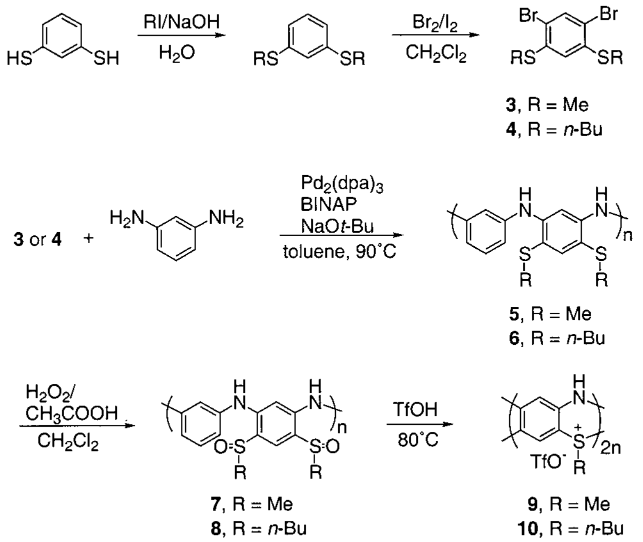

Table 1. Pd-Catalyzed Polymerization of *m*-Phenylenediamine with 3 or 4

monomer	solvent	ligand	yield (%)	M_w[c]	M_n[c]
3	toluene	P(*o*-tolyl)$_3$	0		
3	toluene	BINAP	97	12200	6000
3	*o*-xylene[a]	BINAP	94	11500	2200
3	anisole[b]	BINAP	56	4800	2000
4	toluene	BINAP	96	7100	3000

[a] Polymerization run at 140 °C. [b] Polymerization run at 160 °C. [c] Determined by gel permeation chromatography vs polystyrene standards.

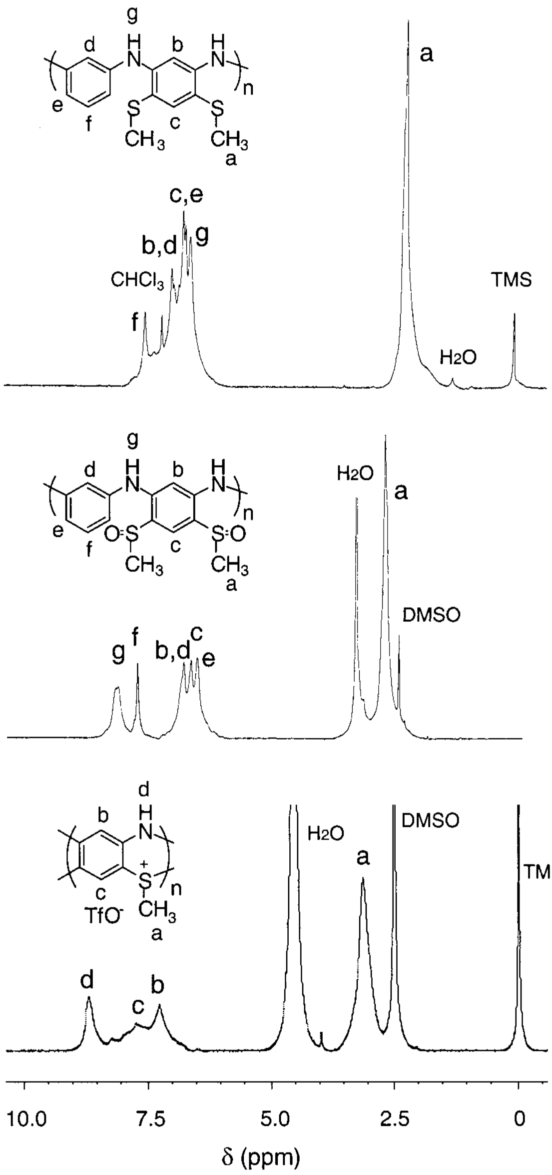

Figure 1. ^{1}H NMR spectra of **5** (top), **7** (middle), and **9** (bottom).

structure. The ^{13}C NMR spectrum shows a methyl carbon at 19.6 ppm and eight aromatic carbons from 100.3 to 145.5 ppm as expected.[10]

The alkylthio substituents on polymers **5** and **6** were quantitatively oxidized to the corresponding sulfoxide with hydrogen peroxide in acetic acid. The peaks of methyl groups of the oxidized product (polymer **7**) appear at lower magnetic field in the NMR (2.76 ppm for ^{1}H: Figure 1, middle, and 41.6 ppm for ^{13}C)[10] spectra than those of the parent polymer **5**, due to the electron-withdrawing nature of sulfoxide group. A strong absorption band of the S=O stretching vibration of sulfoxide is observed at 1020 cm^{-1} for **7** and 1014 cm^{-1} for **9** in the IR spectra. Further oxidation to sulfones or decomposition of the main chain could not be confirmed when the reaction was done below 30 °C. The sulfinylation makes the polymers less soluble in nonpolar solvents (e.g., $CHCl_3$) and more soluble in polar solvents (e.g., DMSO).

Polymers **7** and **8** were dissolved in triflic acid and heated to 80 °C for 20 h to give ladder polymers **9** and **10**, respectively. The reaction mixture is a dark brown homogeneous solution. After treating the mixture with diethyl ether, brown polymers were obtained in quantitative yields. The products were soluble in polar organic solvents (DMSO, DMF, and pyridine) as well as in protonic acids (formic acid, sulfuric acid, and triflic acid) at room temperature. The elemental analyses support the formation of the laddered structure. In the ^{1}H NMR spectrum of polymer **9** (Figure 1, bottom), the peak of methylsulfonio groups is observed at 3.14 ppm, which is at further lower magnetic field than the peak of methyl sulfoxide groups of **7**. The two peaks of aromatic protons at 7.27 and 7.75 ppm and the peak of imino protons at 8.69 ppm correspond to the proposed structure. The absorption bands at 1172, 1031, and 640 cm^{-1} in the IR spectrum are attributed to the triflate anion. From the analytical data, no residual sulfoxide moieties could be detected in the polymers. The ^{13}C NMR analyses, however, were not successful, and a spectrum with a good S/N ratio was not obtained even after more than 50 000 times of accumulation. Unlike the common alkyl diarylsulfonium compounds,[11] the sulfonio groups of the ladder polymers are inactive to nucleophiles; the dealkylation reaction does not take place by the treatment with triethylamine or aqueous NaOH. Polymers **9** and **10** begin to decompose at 165 °C under nitrogen as measured by thermogravimetric analyses. Glass transition and melting temperatures were not observed below the decomposition temperature.

The UV−vis spectrum of polymer **9** was compared to the model compounds (Figure 2). Compound **1** has an absorption maximum at 349 nm, more bathochromically shifted than its thioether analogue (phenothiazine, λ_{max} = 317 nm), suggesting a weak d−π conjugative interaction on the arylsulfonium group.[12] The further batho-

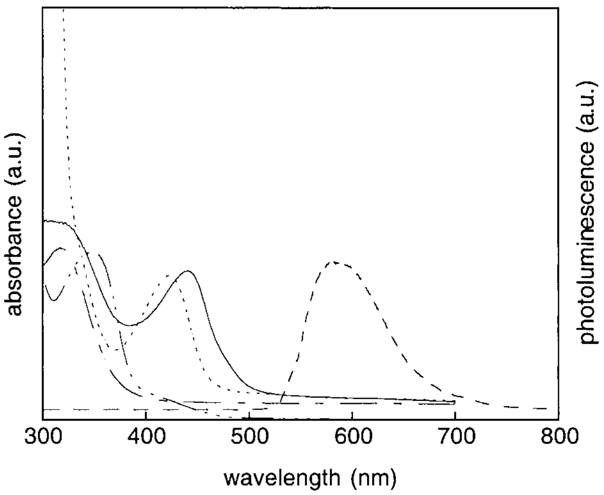

Figure 2. UV−vis spectra of phenothiazine (EnDash− ·), **1** (− ···), **2** (···), and **9** (−) and emission spectrum of **9** (- - -) excited at 340 nm.

chromical shifts were observed in the higher homologue **2** ($\lambda_{\max} = 426$ nm) and polymer **9** ($\lambda_{\max} = 440$ nm). The small 14 nm shift and the rather broad absorption band of **9**, which are not typical for a π-conjugated ladder polymer,[1a] indicate that the d−π interaction based on sulfonium does not extend throughout the polymer chain. The optical band gap, E_g, estimated from the onset wavelength (520 nm) is 2.4 eV, comparable to those of ladder polymers with a hetero acene skeleton.[1b] Polymer **10** shows a similar absorption spectrum ($\lambda_{\max} = 438$ nm) to that of **9**. The ladder polymers are fluorescent. The photoluminescent spectra from DMSO solution show a maximum at 584 nm (**9**) and 549 nm (**10**) when excited at 340 nm. Polymer **9** can form a flexible film by casting from solution. The electric conductivity measurements were carried out on the film by the four-point method with direct current. Polymer **9** shows relatively high conductivity of 8×10^{-6} S cm^{-1} without doping. The polymer retains almost the same value of conductivity up to 150 °C under air.

In conclusion, novel aromatic ladder polymers containing imino and sulfonio bridging groups have been synthesized by Pd-catalyzed polymerization of arylene diamine and dibromides followed by an acid-induced ring-closing reaction. The polymers are soluble in polar organic solvents and protonic acids despite their robust double-stranded structure. Fluorescence emission and semiconductivity were observed for the polymers.

Experimental Section

Synthesis of 10-Hydro-5-methylphenothiazinium Triflate (1). 2-(Methylsulfinyl)diphenylamine (0.21 mmol) was dissolved in 1 mL of dichloromethane and added dropwise to 4.2 mL of triflic acid at 20 °C. The solution was heated to 80 °C with stirring for 20 h. The mixture was then poured dropwise into 100 mL of diethyl ether to precipitate a dark green powder. The product was washed with diethyl ether and dried in a vacuum for 10 h to give 10-hydro-5-methylphenothiazinium triflate (**1**). Yield 95%. ^{1}H NMR (DMSO-d_6): δ 11.10 (s, 1H), 8.15 (d, 2H, $J = 1.5$ Hz), 7.87 (dd, 2H, $J = 8.5$, 1.8 Hz), 7.34 (s, 2H), 7.32 (s, 2H), 2.95 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 143.1, 139.4, 131.9, 127.9, 126.3, 121.8, 119.3, 116.9, 114.8, 100.7, 33.7. IR (KBr): 2955, 1584, 1475, 1225, 1129, 1033, 764, 679, 638 cm^{-1}. Anal. Calcd for $C_{14}H_{12}F_3NO_3S_2$: C, 46.27; H, 3.33; N, 3.85; S, 8.82. Found: C, 46.33; H, 3.60; N, 3.87; S, 8.51.

Synthesis of 12,14-Dihydro-5,7-bis(methylsulfonio)-12,14-diazapentacene Bis(triflate) (2). Compound **2** was similarly synthesized from *N,N'*-bis(2-methylsulfinylphenyl)-*m*-phenylenediamine and triflic acid. Yield 98%. ^{1}H NMR (DMSO-d_6): δ 11.44 (s, 1H), 8.61 (s, 1H), 8.58 (s, 1H), 8.29 (d, 1H, $J = 1.8$ Hz), 8.28 (d, 1H, $J = 1.8$ Hz), 7.90−7.93 (m, 2H), 7.38 (d, 1H, $J = 5.5$ Hz), 7.36 (d, 1H, $J = 5.5$ Hz), 7.15 (s, 1H), 7.13 (s, 1H), 3.05 (s, 3H), 3.02 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 144.1, 143.5, 142.8, 138.3, 138.1, 136.5, 132.3, 132.2, 128.0, 126.3, 121.8, 119.3, 117.4, 117.3, 114.8, 101.9, 101.8, 96.2, 95.1, 35.1, 35.0. IR (KBr): 2956, 1597, 1468, 1257, 1130, 1032, 839, 761, 673, 640 cm^{-1}. Anal. Calcd for $C_{22}H_{18}F_6N_2O_6S_4$: C, 40.74; H, 2.80; N, 4.32; S, 19.77. Found: C, 40.49; H, 3.09; N, 4.44; S, 20.05.

Polymerization. Compound **3** (3.05 mmol) and *m*-phenylenediamine (3.05 mmol) were dissolved in 23 mL of freshly distilled toluene. To the solution were added $Pd_2(dba)_3$ (0.076 mmol), BINAP (0.23 mmol), and sodium *tert*-butoxide (9.15 mmol) under argon. The mixture was heated to 90 °C with stirring for 20 h. The solution was then allowed to cool to 20 °C and poured into 500 mL of methanol to precipitate a pale brown powder. The product was washed with methanol and aqueous ammonia and dried under vacuum for 20 h. Yield 97%.

Poly(imino-1,3-phenyleneimino-4,6-bis(methylthio)-1,3-phenylene) (5). ^{1}H NMR ($CDCl_3$): δ 7.61 (s, 1H), 7.05 (s, 1H), 7.02 (s, 1H), 6.82 (s, 2H), 6.78 (s, 1H), 6.68 (s, 2H), 2.22 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): $\delta = 145.5$, 142.9, 142.2, 130.1, 113.6, 112.8, 111.1, 100.3, 19.6. IR (KBr): 2979, 2914, 1560, 1491, 1411, 1252, 841, 761, 689 cm^{-1}. Anal. Calcd for $C_{14}H_{14}N_2S_2$: C, 61.28; H, 5.14; N, 10.21; S, 23.37. Found: C, 61.14; H, 5.50; N, 10.47; S, 23.49.

Oxidation of Polymer 5. Polymer **5** (1.2 mmol) was dissolved in 3.7 mL of dichloromethane, and 0.63 mL of 30 wt % aqueous hydrogen peroxide was added. To the solution was added dropwise 1.6 mL of acetic acid at 0 °C. The solution was allowed to warm to 20 °C with stirring over 1 h. After 24 h, the mixture was poured dropwise into 100 mL of methanol to precipitate a pale brown powder. The product was washed with methanol and water and dried in a vacuum for 20 h. Yield 100%.

Poly(imino-1,3-phenyleneimino-4,6-bis(methylsulfinyl)-1,3-phenylene) (7). ^{1}H NMR (DMSO-d_6): δ 8.28 (br, 2H), 7.85 (s, 1H), 6.89 (br, 2H), 6.75 (s, 1H), 6.62 (s, 2H), 2.76 (s, 6H). ^{13}C NMR (DMSO-d_6): δ 145.9, 145.5, 143.3, 130.5, 124.3, 113.6, 111.1, 106.3, 41.6. IR (KBr): 2997, 1575, 1488, 1415, 1255, 1020, 849, 759, 690 cm^{-1}. Anal. Calcd for $C_{14}H_{14}N_2O_2S_2$: C, 54.88; H, 4.61; N, 9.14; S, 20.93. Found: C, 54.46; H, 4.38; N, 9.53; S, 21.22.

Ring-Closing Reaction of Polymer 7. Polymer **7** (0.21 mmol) was dissolved in 2 mL of dichloromethane and added dropwise to 8.4 mL of triflic acid at 20 °C. The solution was heated to 80 °C with stirring for 20 h. The mixture was then poured dropwise into 200 mL of diethyl ether to precipitate a brown powder of **9**. The product was washed with diethyl ether and dried in a vacuum for 20 h. Yield 100%.

Ladder Polymer 9. ^{1}H NMR (DMSO-d_6): δ 8.69 (s, 1H), 7.75 (s, 1H), 7.27 (s, 1H), 3.14 (s, 3H). IR (KBr): 2927, 1595, 1451, 1254, 1172, 1031, 856, 640 cm^{-1}. Anal. Calcd for $C_8H_6F_3NO_3S_2$: C, 33.68; H, 2.12; N, 4.91; S, 22.48. Found: C, 33.26; H, 2.50; N, 4.59; S, 22.81.

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Supporting Information Available: Synthetic and characterization details for compounds **1**−**10** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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