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Synthesis, Characterization, and Electrical Properties of Poly(1-alkyl-2,5-pyrrylene vinylenes): New Low Band Gap Conducting Polymers

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ABSTRACT: A series of poly(1-alkyl-2,5-pyrrylene vinylenes) (alkyl = methyl (**1a**), hexyl (**1b**), dodecyl (**1c**)) have been synthesized from the monomers, 1-alkyl-2,5-bis(thiophenylmethylene)pyrrole (**2**), by base-induced elimination and polymerization. Characterization of the polymers includes IR, ^{1}H and ^{13}C NMR, and UV−vis spectroscopy as well as TGA and molecular weight studies. Varying the nitrogen substituent on the pyrrole ring among methyl, hexyl, and dodecyl groups strongly affects their electrical properties. The resulting deep purple conjugated polymers (**1b**, **1c**) were soluble in a variety of organic solvents. The highest yield was obtained when the polymers were synthesized by refluxing in THF with a monomer/base mole ratio of 1:4. The band gaps of the undoped polymers were 1.82 eV (**1a**), 1.69 eV (**1b**), and 1.67 eV (**1c**).

Introduction

An interesting feature of the pyrrole system is the ability to readily prepare a number of functionalized polymers by polymerization of the pyrrole monomer.[1] Polypyrroles have been extensively investigated as materials for applications in molecular electronic devices,[2] electrolytic capacitors,[3] actuators,[4] sensors,[5] artificial muscles,[6] and light-emitting diodes (LEDs).[7] In particular, an electrochemically prepared polypyrrole shows high conductivity (>100 S cm^{-1}), good stability to air and moisture in its oxidized form, strong adhesion to the metal surface, and ease of synthesis.[8] Electronic properties have also been modified by polymerizing pyrrole derivatives with 3-alkyl and 3,4-dimethoxy substituents. Conductivites of these polymers are 10^{-2} and 6 S cm^{-1}, respectively.[9]

As the control of conjugated polymer band gap is related to many fundamental and technological problems, the synthesis of narrow band gap conjugated polymers is one of the major focuses in the field of organic conductors.[10] Reduction of band gap (by about 0.4 eV) has been achieved for poly(*p*-phenylene) (PPP) and poly(thienylene) (PT) by the insertion of vinylene linkages between the directly linked aromatic rings to give poly(phenylenevinylene) (PPV) and poly(thienylenevinylene) (PTV), respectively.[11,12] The common backbone of these polymers is made up of aromatic rings bridged by vinylene linkages which not only reduce steric hindrance between backbone rings and groups attached to them but also have a beneficial effect on electronic properties as shown by experimental and theoretical data on both poly(*p*-phenylenevinylenes)[11] and poly(thienylene vinylenes).[13] There currently exists no general synthesis of poly(pyrrylene vinylene) with an alkyl group directly attached to the nitrogen of the pyrrole ring. There has been a report of attempts to prepare poly(pyrrylene vinylene) by the thermal elimination of a precursor polymer,[14] but electrical conductivity of this polymer was 6.9×10^{-7} S cm^{-1}.

We report and characterize for the first time poly(1-alkyl-2,5-pyrrylene vinylene) (**1**) prepared by a new synthetic route from monomers (**2**) having a thiophenyl group as the leaving group using *t*-BuOK as a base for elimination/polymerization.

Experimental Section

The synthesized compounds were identified by ^{1}H and ^{13}C NMR spectra which were obtained using a Bruker MSL 300 spectrometer. FT-IR spectra were recorded on a Digilab FTS-40 FT-IR spectrometer, using powdered samples mixed with KBr in a diffuse reflectance unit and polymer thin films or liquid samples on KBr plates in transmittance.

Melting points were determined with a Fisher-Johns melting point apparatus. UV−vis−NIR spectra were obtained on a Varian Cary 5E UV−vis−NIR spectrophotometer using THF or NMP as solvents and polymer thin films cast onto quartz plates from solutions.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the polymers were performed under nitrogen atmosphere at a heating rate of 10 °C/min with a DuPont 9900 analyzer. Gel permeation chromatography (GPC) was carried out with 10^3, 10^4, and 10^5 Å Ultrastyragel columns in series with a UV detector at 254 nm using polystyrene standards in THF or NMP solutions for relative molecular weight determination. Electrical conductivity measurements were performed using a standard four-in-line probe apparatus.[1] Samples were either pressed pellets of powdered polymers or polymer thin films on quartz by spin casting from THF solution. The thickness of polymer thin films were measured with an Alpha-Step profilometer. Doping experiments were carried out using a iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$)/nitromethane/acetonitrile solution and a gold chloride ($AuCl_3$)/acetonitrile solution in which polymer thin film samples were immersed for 30 s to 6 h. Powdered samples were first submerged in an $FeCl_3$/nitromethane solution for a day and then filtered, followed by repeated washing with clean nitromethane. Samples were dried in a vacuum oven at 40 °C, and then pressed pellets were made for conductivity measurements. Doping by iodine was conducted by placing pressed pellets of the polymer samples into a sealed chamber saturated with iodine vapor for 24 h. Residual iodine vapor was removed under vacuum for 1 h.

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1-Methyl-2,5-bis(dimethylaminomethyl)pyrrole (4a). A literature method[15] was modified and employed here. To a solution of dimethylamine hydrochloride (43.13 g, 0.54 mol) in aqueous formaldehyde (40.20 g, 0.54 mol), 1-methylpyrrole (18.65 g, 0.23 mol) was added dropwise with stirring at 0 °C under nitrogen. The mixture was kept for 1 h at 0 °C, for 2 h at room temperature, and overnight at 0 °C. The mixture was poured into 100 mL of 20% NaOH solution and extracted with 300 mL of ether. The ether extractions were washed with water and dried with $MgSO_4$. A rotary evaporator was used to remove the ether, and 39.01 g (87%) of a liquid product was obtained. ^{1}H NMR (in $CDCl_3$): δ 5.88 (s, 2H), 3.59 (s, 3H), 3.30 (s, 4H), 2.17 (s, 12H). ^{13}C NMR (in $CDCl_3$): δ 129.78, 107.01, 55.39, 44.49, 29.90. Anal. Calcd for $C_{11}H_{21}N_3$: C, 67.59; H, 10.78; N, 21.54. Found: C, 67.35; H, 10.68; N, 21.72. IR: 3056, 2941, 2856, 2811, 2766, 1463, 1356, 1257, 1018, 846, 751 cm^{-1}.

1-Hexyl-2,5-bis(dimethylaminomethyl)pyrrole (4b). Starting with 1-hexylpyrrole (34.73 g, 0.23 mol), the same procedure was followed as for **4a** except the reaction was continued at room temperature for 7 days. The crude product was filtered through 15 cm of Al_2O_3 with hexane as eluent solvent. Evaporation of the solvent gave 51.81 g (85%) of a colorless liquid. ^{1}H NMR (in $CDCl_3$): δ 5.87 (s, 2H), 4.03−3.98 (t, 2H), 3.30 (s, 4H), 2.20−2.17 (s, 12H), 1.72−1.31 (m, 8H), 0.91−0.87 (t, 3H). ^{13}C NMR (in $CDCl_3$): δ 129.79, 107.60, 56.00, 44.98, 43.75, 31.28, 31.18, 26.70, 22.43, 13.92. Anal. Calcd for $C_{16}H_{31}N_3$: C, 73.49; H, 11.99; N, 15.84. Found: C, 73.25; H, 12.32; N, 15.69. IR: 3054, 2935, 2855, 2811, 2765, 1459, 1357, 1019, 846, 751 cm^{-1}.

1-Dodecyl-2,5-bis(dimethylaminomethyl)pyrrole (4c). Starting with 1-dodecylpyrrole (54.05 g, 0.23 mol), the same procedure was followed as for **4b**. The crude product was subjected to column chromatography (silica gel) with acetone as eluent solvent to give 59.39 g (74%) of a colorless liquid. ^{1}H NMR (in $CDCl_3$): δ 5.88 (s, 2H), 4.02−3.97 (t, 2H), 3.30 (s, 4H), 2.17 (s, 18H), 1.68−1.26 (m, 20H), 0.90−086 (t, 3H). ^{13}C NMR (in $CDCl_3$): δ 129.89, 107.67, 56.06, 45.08, 43.84, 31.89, 31.30, 29.68−29.19 (6 peaks), 27.12, 22.66, 14.09. Anal. Calcd for $C_{22}H_{43}N_3$: C, 75.69; H, 12.34; N, 12.02. Found: C, 75.86; H, 12.15; N, 11.87. IR: 3065, 2927, 2854, 2811, 2765, 1460, 1357, 1020, 846, 751 cm^{-1}.

1-Methyl-2,5-bis[(trimethylamino)methyl]pyrrole Diiodide (3a). To a solution of **4a** (9.75 g, 0.05 mol) in 200 mL of dry THF was added 9.0 mL (21.6 g, 0.15 mol) of CH_3I. The mixture was stirred for 4 h at room temperature and filtered to give the bisammonium salt.The pure product **3a** after recrystallization with methanol, was obtained as a colorless solid in 95% (22.75 g) yield. Mp: 165−168 °C dec. ^{1}H NMR (in DMSO): δ 6.54 (s, 2H), 4.66 (4H), 3.74 (s, 3H), 3.07 (s, 18H). ^{13}C NMR (in DMSO): δ 123.77, 115.34, 59.20, 51.35, 32.22. Anal. Calcd for $C_{13}H_{27}N_3I_2$: C, 32.56; H, 5.64; N, 8.76; I, 53.02. Found: C, 32.27; H, 5.34; N, 8.52; I, 53.26. IR: 3436, 3016, 2973, 1622, 1554, 1480, 1393, 1320, 1153, 976 cm^{-1}.

1-Hexyl-2,5-bis[(trimethylammonio)methyl]pyrrole Diiodide (3b). Starting with **4b** (13.25 g, 0.05 mol), the same procedure was followed as for **3a**. The yield was 81%(22.23 g). Mp: 170−173 °C dec. ^{1}H NMR (in DMSO): δ 6.53 (s, 2H), 4.54 (s, 4H), 4.14 (t, 2H), 3.01 (s, 18H), 2.51−1.15 (m, 8H), 0.85−0.81 (t, 3H). ^{13}C NMR (in DMSO): δ 123.54, 115.13, 55.93, 51.23, 43.97, 32.04, 31.02, 25.10, 22.03, 13.82. Anal. Calcd for $C_{18}H_{37}N_3I_2$: C, 39.24; H, 6.73; N, 7.56; I, 46.20. Found: C, 38.94; H, 6.38; N, 7.35; I, 45.94. IR: 3544, 2998, 2926, 2856, 1478, 1449, 1376, 1307, 1238, 971, 872 cm^{-1}.

1-Dodecyl-2,5-bis[(trimethylamino)methyl]pyrrole Diiodide (3c). Starting with **4c** (17.45 g, 0.05 mol), the same procedure was followed as for **3a**. The yield was 74% (23.42 g). Mp: 128−130 °C dec. ^{1}H NMR: (in DMSO): δ 6.55 (s, 2H), 4.65 (s, 4H), 4.22 (t, 2H), 3.17 (s, 18H), 1.32−1.04 (m, 20H), 0.85−0.81 (t, 3H). ^{13}C NMR (in DMSO): δ 123.44, 116.07, 58.70, 54.30, 51.18, 43.99, 32.14, 31.82, 31.13, 30.70, 28.84−28.55 (3 peaks), 25.19, 21.94, 13.83. Anal. Calcd for $C_{24}H_{49}N_3I_2$: C, 45.13; H, 7.74; N, 6.63; I, 40.12. Found: C, 44.85; H, 7.56; N, 6.56; I, 40.42. IR: 3398, 3000, 2924, 2852, 1478, 1376, 1237, 971, 873 cm^{-1}.

1-Methyl-2,5-bis(phenylthiomethyl)pyrrole (2a). A mixture of 5.441 g (11.7 mmol) of **3a** and sodium thiophenoxide (3.2 g, 23.4 mmol) in 200 mL of THF were refluxed for 48 h. The solvent was then removed using a rotary evaporator. A light yellow solid was obtained. Then, 200 mL of ether was added to the light yellow solid in the flask, and the mixture was stirred for 2 h at room temperature. A light yellow solution was obtained after filtration to remove the solid byproduct. The pure product, after column chromatographic purification on silica gel with hexane and dichloromethane (8:2) as eluent solvent, was obtained exhibiting a light yellow color in 78% yield(2.947 g). Mp: 70−71 °C. ^{1}H NMR (in $CDCl_3$): δ 7.27−7.24 (m, 10H), 5.80 (s, 2H), 4.06 (s, 4H), 3.57 (s, 3H). ^{13}C NMR (in $CDCl_3$): δ 135.68, 130.76, 128.72, 128.01, 126.62, 108.28, 31.53, 30.48. Anal. Calcd for $C_{19}H_{19}NS_2$: C, 70.11; H, 5.88; N, 4.30; S, 19.70. Found: C, 70.20; H, 5.97; N, 4.23; S, 19.80. IR: 3093, 3000, 2923, 2852, 1551, 1477, 1407, 1311, 1232, 972, 874 cm^{-1}.

1-Hexyl-2,5-bis(phenylthiomethyl)pyrrole (2b). Starting with **3b** (6.423 g, 11.7 mmol), the same procedure was followed as for **2a**. The pure product, after column chromatographic purification on silica gel with hexane and dichloromethane (8:2) as eluent solvents, was obtained as a light yellow liquid in 57% yield (2.634 g). ^{1}H NMR (in $CDCl_3$): δ 7.32−7.22 (m, 10H), 5.82 (s, 2H), 4.09 (s, 4H), 3.98−3.96 (t, 2H), 1.75−1.30 (m, 8H), 0.98−0.96 (t, 3H). ^{13}C NMR (in $CDCl_3$): δ 135.93, 130.65, 128.75, 127.53, 126.59, 106.74, 43.63, 31.56, 31.54, 31.36, 26.65, 22.51, 13.35. Anal. Calcd for $C_{24}H_{29}NS_2$: C, 72.91; H, 7.34; N, 3.52; S, 16.18. Found: C, 72.72; H, 7.06; N, 3.26. IR: 3057, 2927, 2857, 1582, 1477, 1438, 1311, 1235, 1089, 1025, 740, 692 cm^{-1}.

1-Dodecyl-2,5-bis(phenylthiomethyl)pyrrole (2c). Starting with **3b** (7.406 g, 11.7 mmol), the same procedure was followed as for **2a**. The pure product, after column chromatographic purification on silica gel with hexane and dichloromethane (8:2) as eluent solvents, was obtained as a light yellow liquid in 51% yield (2.858 g). ^{1}H NMR (in $CDCl_3$): δ 7.28−7.21 (m, 10H), 5.83 (s, 2H), 4.08 (s, 4H), 3.97−3.96 (t, 2H), 1.85−1.24 (m, 20H), 1.87−0.85 (t, 3H). ^{13}C NMR (in $CDCl_3$): δ 135.68, 130.41, 128.47, 127.25, 126.32, 108.44, 43.61, 31.59−28.93 (9 peaks), 26.70, 22.36, 13.80. Anal. Calcd for $C_{30}H_{41}NS_2$: C, 75.26; H, 8.57; N, 2.93; S, 13.20. Found: C, 75.56; H, 8.39; N, 3.21. IR: 3058, 2926, 2853, 1583, 1476, 1439, 1371, 1311, 1234, 1089, 1025, 740, 692 cm^{-1}.

Poly(1-methyl-2,5-pyrrylene vinylene) (1a). To a solution of 2.7 g (24.48 mmol) of *t*-BuO$^-$K$^+$ in 30 mL of THF under reflux was added a solution of 2 g (6.12 mmol) of **2a** in 5 mL of THF under nitrogen. Stirring was maintained for 24 h in a round-bottomed flask until the light yellow solution turned purple in color. The reaction mixture was precipitated into 60 mL of water. The polymer was filtered and purified by repeated washing with hot water, methanol and then extracted (Soxhlet) with acetone for 24 h. Drying under vacuum at room temperature gave the deep purple blue polymer **1a**. The overall yield from **2a** to **1a** was 75% (0.45 g). Anal. Calcd for C_7H_7N: C, 79.95; H, 6.71; N, 13.32. Found: C, 74.75; H, 6.51; N, 10.22; S, 4.31. IR: 3040, 3010, 2993, 2851, 1604, 1571, 1442, 1380, 1232, 1093, 1043, 932, 749, 692 cm^{-1}.

Poly(1-hexyl-2,5-pyrrylene vinylene) (1b). Starting with **2b** (2.4 g, 6.12 mmol), the same procedure was followed as for polymer **1a**. The yield was 72% (0.78 g). ^{1}H NMR (in $CDCl_3$): δ 6.8 (s, 2H), 6.5 (s, 2H), 3.9 (t, 2H), 2.3−1.1 (m, 8H), 0.9 (t, 3H). ^{13}C NMR (in $CDCl_3$): δ 134.23, 114.56, 107.73, 43.56, 33.38, 31.29, 27.87, 23.45, 14.62. Anal. Calcd for $C_{12}H_{17}N$: C, 80.23; H, 9.77; N, 7.99. Found: C, 76.74, H, 8.67; N, 7.15; S, 0.99. IR: 3040, 3010, 2990, 2895, 1600. 1650, 1480, 1300, 965, 750 cm^{-1}. T_m: 140 and 150 °C.

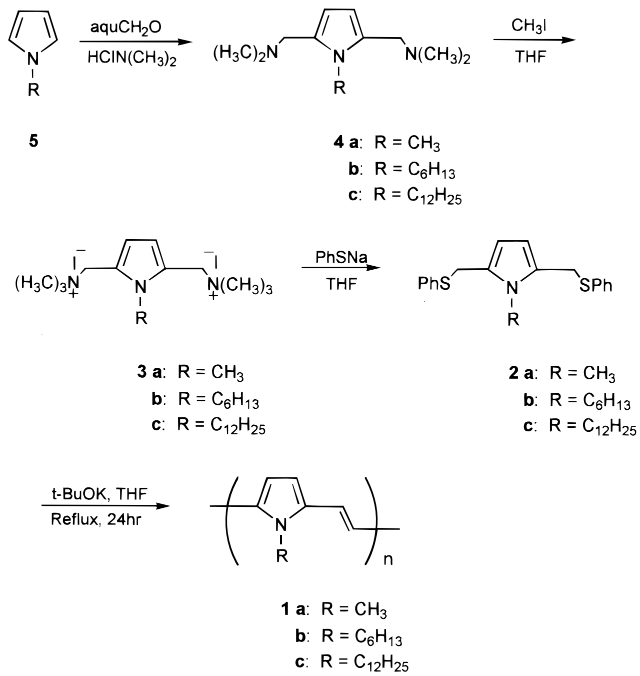
Poly(1-dodecyl-2,5-pyrrylene vinylene) (1c). Starting with **2c** (2.9 g, 6.12 mmol), the same procedure was followed as for polymer **1a**. The yield was 70%(1.10 g). ^{1}H NMR (in $CDCl_3$): δ 6.72 (s, 2H), 6.47 (s, 2H), 3.97 (s, 2H), 2.43−1.25 (m, 20H), 0.84 (t, 3H). ^{13}C NMR (in $CDCl_3$): δ 133.36, 114.49, 106.54, 43.38, 31.93−26.91 (9C), 22.69, 14.13. IR: 3040, 3010, 2924, 2854, 1646, 1539, 1401, 1261, 1092, 1028, 929, 805, 747

Table 1. Properties of Polymers 1a, 1b, and 1c

polymer	λ_{max}/nm THF	λ_{max}/nm film	band gap, eV	M_n	M_w/M_n	doped conductivity, S/cm (dopant)
1a	500[a]		1.82	7 300[b]	1.28	0.02($AuCl_3$), 0.001($FeCl_3$)[c]
1b	550	569	1.69	91 000[d]	1.93	2.5($AuCl_3$), 0.15($FeCl_3$)[e]
1c	548	563	1.67	16 800[b]	1.16	0.48($AuCl_3$), 0.11($FeCl_3$)[e]

[a] In NMP. [b] Gel permeation chromatography in NMP based on PS standards. [c] Pressed powder pellet. [d] In THF based on PS standards. [e] Cast film from THF.

Scheme 1

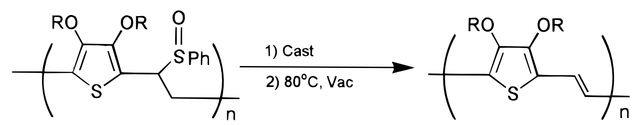


cm^{-1}. Anal. Calcd for $C_{18}H_{29}N$: C, 83.33; H, 11.26; N,5.39. Found: C, 80.50; H, 10.00; N, 5.08; S, 1.15.

Results and Discussion

The synthesis of three poly(pyrrylene vinylenes) containing the alkyl directly attached to nitrogen on the pyrrole, namely poly(1-methyl-2,5-pyrrylene vinylene)-(**1a**), poly(1-hexyl-2,5-pyrrylene vinylene) (**1b**), and poly-(1-dodecyl-2,5-pyrrylene vinylene) (**1c**) is shown in Scheme 1. 1-Methylpyrrole was obtained commercially (Aldrich). 1-Hexyl and 1- dodecylpyrrole (**5**) were prepared as described in the literature.[15] These, in turn, were converted into 1-methyl-, 1-hexyl-, and 1-dodecyl-2,5-bis((dimethylamino)methyl)pyrrole (**4a**, **4b**, and **4c**, respectively) by typical Mannich reactions.[16] The bis-(quaternary ammonium) salts (**3a**, **3b**, and **3c**) were prepared by treatment of **4a**, **4b**, and **4c** with iodomethane. Treatment of **3a**, **3b**, and **3c** with sodium thiophenoxide in refluxing THF for 2 days gave 60−75% yields of 1-methyl-, 1-hexyl-, and 1-dodecyl-2,5-bis-(phenylthiomethylene)pyrrole (**2a**, **2b**, and **2c**) as monomers, respectively. These monomers (**2a**, **2b**, and **2c**) were polymerized on treatment with 4 equiv of *t*-BuOK in THF at 70−75 °C for 1 day and gave poly(1-methylpyrrylene vinylene) (**1a**), poly(1-hexylpyrrylene vinylene) (**1b**), and poly(1-dodecylpyrrylene vinylene) (**1c**), respectively. Conversion from the bis-phenylthio monomers **2** afforded polymers **1** in 70% yield, which is considerably higher than that typically obtained for poly(phenylenevinylene) prepared from bis(sulfonium) salt precursors (20−40%)[17] and for poly(3,4-dialkoxyl-2,5-thienylenevinylenes)[18] synthesized from bis(sulfoxide) precursors (63%). Some properties of these polymers are given in Table 1.

It is well-known that sulfoxides can be thermally eliminated at moderate temperatures to provide alkenes.[19] Recently, Kanga et al. have made conjugated polyacetylene from poly(phenyl vinylsulfoxide) by thermal elimination.[20] Also, poly(phenylenevinylene) has been prepared by the thermal elimination of sulfoxides from precursor polymers.[21] In addition, a new precursor and polymerization route for the preparation of high molecular mass poly(3,4-dialkoxy-2,5-thienylenevinylenes) were prepared using a thermally induced elimination of sulfoxide groups as shown in eq 1.[18]



(**1**)

Attempts to prepare electron rich poly(1-alkyl-2,5-pyrrylene vinylenes) by the precursor polymer route using the bis(sulfoxomethylene) monomers have not been generally successful because of the high difficulty of preparation of these monomers. However, the present account is the first report of the use of the phenylthio moiety as leaving groups in forming conjugated poly-(1-alkyl-2,5-pyrrylene vinylene) (**1a**, **1b**, and **1c**, respectively).

The polymers **1b** and **1c** were soluble in a variety of organic solvents such as THF, $CHCl_3$, CH_2Cl_2, and DMF. Polymer **1a** was not soluble in these solutions, but was soluble in NMP. The spectral properties and changes in the spectra upon going from **2** to **1** were consistent with the expected structure of the polymer as shown in Figures 1 and 2. For example, parts A and B of Figure 1 show that the ^{1}H NMR spectral peak for the CH_2−S hydrogens at δ 4.09 in **2b** and at δ 4.08 in **2c** disappeared with the appearance of new peaks at lower field in the polymers **1b** and **1c** as CH groups (vinyl) (δ 6.42 (A), 6.45 (B)). Parts A and B of Figure 2 show single peaks in the ^{13}C NMR spectra at δ 133.08, 114.13, and 106.19 in **1b** and δ 133.29, 114.43, and 106.48 in **1c** which are assigned to the vinyl carbon (c), α-carbon (b), and β-carbon (a) on the ring, respectively.

IR spectra showed the formation of predominant trans polymers (**1a**, **1b**, **1c**) by the peaks at 950−965 cm^{-1}, corresponding to the *trans*-vinylene C−H out-of-plane bending mode and at 3010−3030 cm^{-1} for the *trans*-vinylene C−H stretching vibration as shown in Figure 3.

Thermogravimetric analysis (TGA; N_2; heating rate = 10 °C/min) of **1a** showed the onset of decomposition at 170 °C, 10% weight loss at about 510 °C, and 50% weight loss by 610 °C. However **1b** showed the onset of decomposition at 225 °C, and 50% weight loss by 430 °C. **1c** showed the onset of decomposition at 180 °C, and

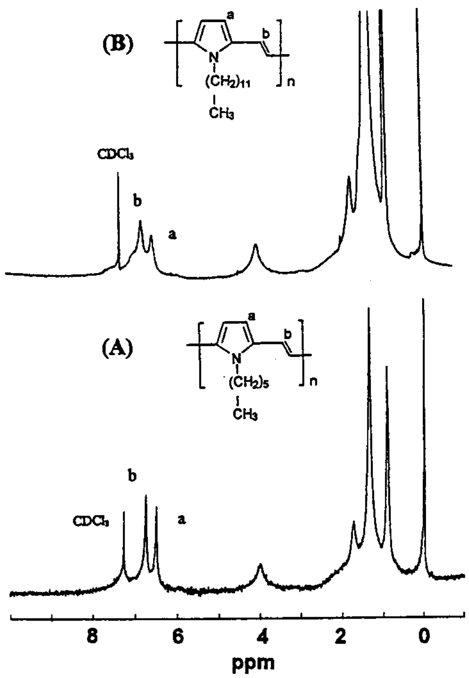


Figure 1. ${}^{1}H$ NMR (300 MHz), $CDCl_3$) spectra of polymer **1b** (A) and polymer **1c** (B).

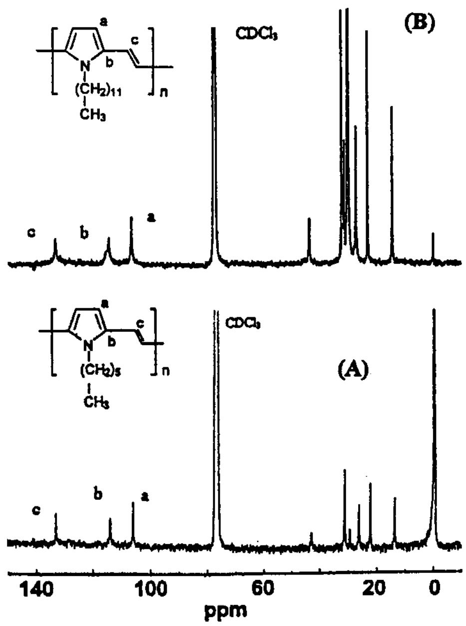


Figure 2. ${}^{13}C$ NMR (300 MHz), $CDCl_3$) spectra of polymer **1b** (A) and polymer **1c** (B).

50% weight loss by 390 °C. Thus, **1b** appears to be a little more thermally stable than **1c**. The weight loss at 170−180 °C in **1a** and **1c** may be due to thermal elimination of residual PhS− groups in these polymers. Both **1a** and **1c** show larger mole ratios of residual sulfur in the polymer than **1b**. Elemental analyses show a N/S ratio of 5.4 for **1a**, 16.5 for **1b**, and 10 for **1c**. Then, on the average, polymer **1a** comprises approximately five to six conjugated pyrrole vinylene repeat units separated by a saturated linkage, whereas polymer**1b** and **1c** comprise 16−17 and 10 conjugated pyrrole vinylene units, respectively (see Figure 4).

DSC (differential scanning calorimetry) analyses of **1b** showed two melting transitions (T_m) at 140 and 150 °C. These repeated several times with no significant

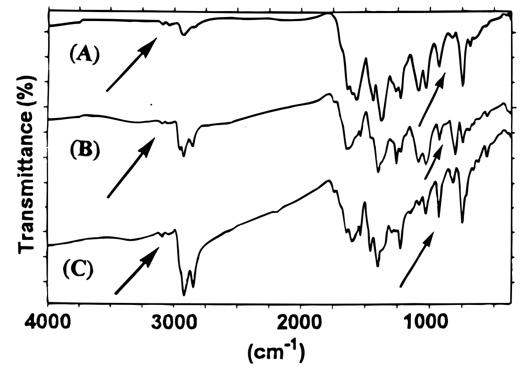


Figure 3. FT−IR spectra of polymer **1a** (A), polymer **1b** (B), and polymer **1c** (C).

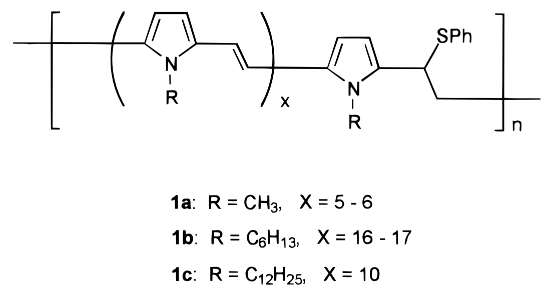


Figure 4. Average conjugation lengths for polymers **1a**, **1b**, **1c**.

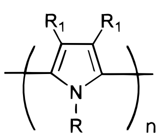
change in the observed thermal transitions, indicating that the thermal responses are inherent to the polymer and do not resulting from a drying process. The observation of two apparent melting transition for **1b** may indicate that this polymer may exist in two polymorphic forms.

The gel permeation chromatography (GPC) of polymers for **1a**, **1b**, and **1c** using polystyrene standards indicated number-average molecular weights (M_n) of around 7.3×10^3−9.1×10^4 (Table 1) with a relatively narrow molecular weight distribution of 1.14−1.92. The average degree of polymerization (DP) for these approximate molecular weights, is 70, 520, and 65 for **1a**, **1b** and **1c**, respectively. It is clear from GPC data that our new polymerization route afforded reasonably high molecular mass polymers with narrow molecular weight distributions.

Polymers showed UV−vis absorption maxima at 500 nm in NMP solutions for **1a** and 550 and 548 nm for **1b** and **1c**, respectively in THF solutions. These UV−vis absorption data suggest that polymers **1b** and **1c** have considerably longer conjugation lengths than polymer **1a**, consistent with the elemental analyses data presented above (Figure 4). The long effective conjugation length and resulting higher electrical conductivity is further evident from the spectra of doped polymer **1b** which exhibits a strong free carrier absorption far into the infrared region without the downturn normally observed for samples with shorter effective conjugation lengths. We obtained band gaps (low energy absorption edge) of 1.82 eV for **1a**, 1.69 eV for **1b**, and 1.67 eV for **1c**.

Electrical conductivities of the polymers **1** were measured using a standard four-probe technique. Table 1 shows the maximum conductivity values with different dopants for polymer films and pressed powder pellets. The higher molecular weight polymer **1b** showed an electrical conductivity of about 2.5 S/cm with $AuCl_3$

as dopant, whereas the corresponding values for **1a** and **1c** were 2×10^{-2} and 4.8×10^{-1} S/cm, respectively. When one takes into account the effective average conjugation lengths available in each of polymers **1a**, **1b**, and **1c** (see Figure 4), these conductivity values suggest that each of these polymers with long effective conjugation lengths would exhibit comparable electrical conductivities (better than 1 S/cm on $AuCl_3$ doping). On long-term (1 month) exposure to air, undoped polymer **1b** apparently became oxygen doped, showing a maximum conductivity of 6.2×10^{-7} S/cm. The $FeCl_3$-doped conductivity of **1b** was at least 4 orders of magnitude larger than that of the $FeCl_3$-doped corresponding polymer **6**, and 2 orders of magnitude larger than $FeCl_3$-doped **7**.[22,23] This result is attributed to the vinylene linkage in **1b**, which not only extends the electronic properties of the polymer chain but also acts as a conjugated spacer to reduce steric interactions of adjacent aromatic rings in **6** and **7**. This provides an increase in the degree of coplanarity in **1b** over that of conjugated polymers **6** and **7**. Therefore, the difference of conductivity between **1b**, **6**, and **7** suggests that the low conductivities of **6** and **7** arise from significant steric interactions between the highly substituted pyrrole rings.[22−23]



6, R_1 = -H, R = -$(CH_2)_5CH_3$

7, R_1 = -CH_3, R = -$(CH_2)_5CH_3$

Conclusion

We have shown that a series of new conducting poly(1-alkyl-2,5-pyrrylene vinylenes)(**1**) were synthesized by bis-phenylthio monomers (**2a**−**c**) using 4 equiv of base in THF. The overall yield from monomers **2** to polymers **1** was at about 70−75%. Polymers **1** prepared by this new polymerization method have shown a relatively narrow molecular distribution and high electrical conductivities. We expect that this new polymerization process will be suitable for the preparation of other electron rich polymers.

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