Synthesis, Characterization and Properties of Poly(1-hexyl-3,4-dimethyl-2,5-pyrrolylene)

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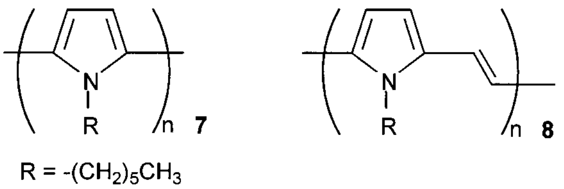
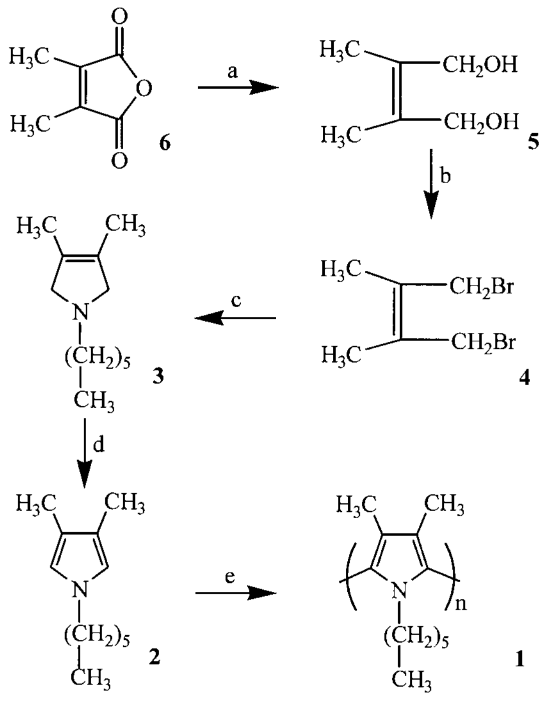
This paper describes a synthetic approach for the preparation of a soluble new conjugated organic conducting polymer, poly(1-hexyl-3,4-dimethyl-2,5-pyrrolylene) obtained by oxidative coupling reaction of 1-alkyl-3,4-dimethylpyrrole derived from *cis*-1,4-dibromo-2,3-dimethyl-2-butene and hexylamine.

An interesting feature of the pyrrole system is the ability to readily prepare a number of functionalized polymers by polymerization of pyrrole monomer. Polypyrroles stand out as an excellent materials having tremendous technological potential such as molecular electronic devices,[1] electrolytic capacitors,[2] actuators,[3] sensors,[4] artificial muscles[5] and light-emitting diodes (LEDs).[6] In particular, an electrochemically prepared polypyrrole shows high conductivity (>100 S cm^{-1}), relative stability to air and moisture in its oxidized form, ability to form strong coherent films, and ease of synthesis.[7] Properties of polypyrrole have also been modified by polymerizing pyrrole derivatives with 1-methyl-3,4-dimethoxy and 3,4-dimethoxy substituents. Conductivities of these polymers are 10^{-2} S cm^{-1} and 6 S cm^{-1}, respectively.[8] However, the room temperature conductivities of poly(1-alkyl-2,5-pyrrolylene) (alkyl = methyl, hexyl, dodecyl) prepared by chemical oxidation fall in the range 10^{-3} to 10^{-6} S cm^{-1}.[9,10] Recently, we reported the difference in conductivity between poly(1-hexyl-2,5-pyrrolylene) ($\sigma = 1.2\times10^{-6}$ S cm^{-1}) (**7**) and poly(1-hexyl-2,5-pyrrolylene vinylene) (σ = 2.5 S cm^{-1}) (**8**) suggesting that the low conductivities of 1-alkylsubstituted polypyrroles as prepared by oxidative polymerization arise from steric interactions between adjacent rings.[11]



Scheme 1.

We now report the successful synthesis of new soluble conducting poly(1-hexyl-3,4-dimethylpyrrole) (**1**) and a new preparative route to 1-alkyl-3,4-dimethylpyrrole that can be applicable to synthesize the conducting polymer as shown in Scheme 2. The direct metal-hydrogen exchange of the proton on the 3,4-dimethylpyrrole nitrogen is not possible due to the presence of the acidic α-hydrogens of the 3,4-dimethyl pyrrole. Duhamel and co-workers have synthesized 1-alkylsubstituted-3,4-dimethylpyrroles by the reduction of α-halogenated imines as intermediates.[12] However, because of unstable α-halogenated imines, the alkyl groups on nitrogen of 1,3,4-alkylsubstituted pyrrole had tertiary alkyl and limited chain length. *cis*-2,3-Dimethyl-2-butene-1,4-diol (**5**) was formed by the reduction of dimethylmaleic anhydride (**6**) with LiAlH$_4$ at refluxing. The bromination of **5** with PBr$_3$ (Et$_2$O, at 0 °C for 1 h, r.t. for 24 h) generated *cis*-1,4-dibromo-2,3-dimethyl-2-butene (**4**). Bromide **4** was reacted with three equivalents of hexylamine (benzene, at 0 °C for 1 h, r.t. for 7 days) to yield a cyclic product, 1-hexyl-3,4-dimethyl-3-pyrroline (**3**) which was a valuable intermediate for the synthesis of 1-alkylsubstituted-3,4-dimethylpyrroles. An oxidation of cyclic products **3** with 30% hydrogen peroxide for 12 h at room temperature, followed by direct reaction with acetic anhydride at 0 °C for 12 h gave a 57% yield of 1-hexyl-3,4-dimethylpyrrole (**2**).



a) Lithium aluminium hydride, ethyl ether, 12 h, Reflux, 74%; b) Pyridine, PBr$_3$, r.t., 24 h, 75%; c) Hexylamine, benzene, r.t., 7 days, 38%; d) 30% H_2O_2, r.t., 12 h, acetic anhydride, 0 ℃, 12 h, 57%; e) Iron chloride (Ⅲ) hexahydrate, acetonitrile, 0 ℃, 12 h, 30% aqueous ammonium hydroxide, 89%.

Scheme 2.

The reaction illustrated above offers a new and convenient route to prepare 1-alkylsubstituted-3,4-dimethylpyrroles starting with the parent heterocycle and provides a potential monomer for the synthesis of conductive polymers. This monomer **2** was smoothly polymerized by iron chloride (III) hexahydrate and gave poly(1-hexyl-3,4-dimethylpyrrole) (**1**). The resulting oxidized polymer was precipitated in ethanol, reduced in concentrated aqueous ammonium hydroxide, and reprecipitated in ethanol to yield a white powder which was completely soluble in THF, $CHCl_3$, hexane, and CH_2Cl_2. In addition, a 0.1 M solution of monomer **2** was polymerized by the multiscan cyclic voltammogram (CV) between 0.0 and 0.9 V vs Ag/Ag^+ in 0.1 M tetrabutylammonium percholate (TBAP)/CH_3CN using a standard three electrode cell on a Pt button working electrode under inert atmosphere. The electrochemically deposited poly(1-hexyl-3,4-dimethyl-2,5-pyrrolylene) (**1b**) on a Pt electrode was rinsed with CH_3CN and dissolved in hexane. It was soluble in common organic solvents.[13]

Table 1. Properties of polymer

Polymer	λ_{max}/nm THF	Mn	Mw/Mn	Conductivity S cm^{-1} (dopant)
1	300	3850	3.89	1.0×10^{-3} ($FeCl_3$)
1b	463	5388	4.47	1.3×10^{-2} ($FeCl_3$)

Comparison of the ^1H NMR spectra of the monomer **2** and polymer **1b** showed complete disappearance of the singlet at δ 6.25, attributable to α and α′ proton on the ring, indicating a reasonably high molecular weight polymer with no visible end groups. In addition, single peaks at δ 122.21 and 117.90 in the ^{13}C NMR spectrum are assigned to α- and β-carbon on the pyrrole ring of the polymer **1b**. These results suggest that the coupling reaction was involved at the α- and α′- positions of monomer **2**. Molecular weight approximation was carried out using GPC (polystyrene standards) with THF as the mobile phase and a weight-average molecular weight was approximated to be 2.4×10^4 for polymer **1b**. The number-average molecular weight of polymer **1b** was approximated to be 5.3×10^3. The average degree of polymerization (DP), for these approximate molecular weights, was 30. Neutral (undoped) polymer **1b** thin films showed absorption maximum at 463 nm in the UV-vis-NIR spectrum. This absorbance is due to the π to π* interband transitions of the conjugated chain, with the onset used to approximate the electronic band gap (Eg) at 2.72 eV. Thermogravimetric analysis (TGA; N_2; 10 °C/min) of polymer **1b** showed the onset of decomposition at 275 °C and 15% weight loss by 475 °C. The conductivity of a thin film of **1b** doped with $FeCl_3$, measured to be 1.3×10^{-2} S cm^{-1}, is comparable to those of electrochemically or chemically prepared poly(1-methylpyrrole) (1×10^{-3} S cm^{-1}),[9] but superior to that of chemically prepared poly(1-hexyl-2,5-pyrrolylene) (**7**)[11] ($\sigma = 1.2 \times 10^{-6}$ S cm^{-1}). The $FeCl_3$-doped conductivity of **1b** is at least 4 orders of magnitude larger than that of the corresponding polymer **7**. This result is attributed to the combination of steric interactions between adjacent rings and from a mixture of α-α′, α-β′ and β-β′coupled monomers in 1-alkylsubstituted polypyrroles as prepared by oxidative polymerization.

The new synthesis methodology presented in this paper opens a rather convenient route for the preparation of 1-alkyl-3,4-dimethylpyrrole systems. Electrical conductivity of a soluble poly(1-hexyl-3,4-dimethylpyrrole) prepared from **2** by oxidative coupling reaction shows the main reason of low conductivity of polypyrroles with an 1-alkylsubstituent. Some interesting properties of polymer **1** such as photoluminescence and life time of light emitting device will be discussed in subsequent papers.

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13 Polymer **1b**, IR: 2925, 2857, 2731, 1450, 1382, 1341, 1119,1000, 725 cm^{-1}. UV–vis–NIR: neutral films: λ_{max} = 463 nm; E_g (Band edge) = 2.72 eV. ^1H NMR (in $CDCl_3$): δ 3.40 (s, 2H); 1.90 (s, 6H); 1.24–0.78 (m, 11H). ^{13}C NMR (in $CDCl_3$): δ 122.21, 117.90, 45.26, 31.24, 30.45, 26.75, 22.41, 13.95, 10.32. Anal. Calcd for $C_{12}H_{19}N$: C, 81.25; H, 10.73; N, 7.95%. Found: C, 80.95; H, 10.44; N, 7.85%.