Solution processible poly(1-alkyl-2,5-pyrrolenevinylenes): new low band gap conductive polymers

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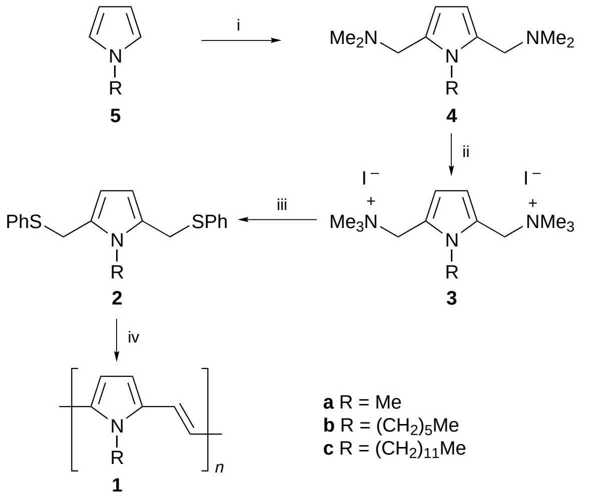
Bis(phenylthiomethylene) derivatives of 1-alkylpyrroles afford conjugated polymers by base induced elimination of thiophenyl groups.

Electrochemically prepared polypyrrole is employed as an electrode in capacitors and batteries owing to its 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.[1] Conductive properties are related to the nature of the counter anions in polypyrrole films.[2] Properties have also been modified by polymerizing pyrrole derivatives with 3-methyl and 3,4-dimethyl substituents. Conductivities of these polymers are 4 and 10 S cm^{-1}, respectively.[3,4] 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}.[5,6] The large decrease in conductivity of doped poly(pyrrolylenes) with an *N*-alkyl substitutent and an increase in size of the alkyl substituent has been rationalized on a steric basis.[7]

Reduction of band gaps in conjugated polymers such as poly(*p*-phenylene) and poly(thienylene) has been achieved by the insertion of vinylene linkages between the aromatic rings in the polymer chain to give poly(phenylenevinylene) and poly(thienylenevinylene),[8–10] respectively. The backbone of these polymers is made of aromatic rings bridged by vinylene linkages wherein the vinylene linkage not only reduces steric hindrance between backbone rings attached to them, but also has a beneficial effect on electronic properties as evidenced by experimental and theoretical data on both poly(*p*-phenylenevinylene)[4] and poly(thienylenevinylene).[11]

Recently, we reported a new precursor and polymerization route for the preparation of high molecular mass poly(3,4-dialkoxy-2,5-thienylenevinylene)s as low band gap conductive polymers made by base/acid and thermally induced elimination of sulfoxide groups.[12] We now report a convenient synthesis of 1-alkyl-2,5-bis(phenylthiomethylene)pyrroles (**2a**–**c**) using the Mannich reaction.[13] These can be readily polymerized using 4 equiv. of Bu^{t}OK (Scheme 1). The present account is the first report of the use of phenylthio as a leaving group in forming poly(1-alkyl-2,5-pyrrolenevinylene)s (**1a**–**c**).

1-Alkylpyrroles (**5a**–**b**) were prepared as described in the literature.[14] Treatment of **5a**–**c** with aq. HCHO and $Me_2NH{\cdot}HCl$ at room temperature for 7 d, the Mannich reaction, gave 70–85% yields of 1-alkyl-2,5-bis[(dimethylamino)methyl]pyrroles (**4a**–**c**) and these, in turn, were converted into bisquaternary ammonium salts (**3a**–**c**) (yield: 75–92%) after reaction with MeI in THF at room temperature. We chose 1-alkyl-2,5-bis[(trimethylammonio)methyl]pyrrole diiodide (**3a**–**c**) as initial target monomers because of their crystallinity and good stability. However, attempts to polymerize these monomers (**3a**–**c**) with 5–10% aq. NaOH in a temperature range from 0 °C to reflux have not been successful. Manipulation of the bisquaternary ammonium salt functional groups in **3a**–**c** into a phenylthio leaving group **2a**–**c** (yield: 55–70%) provided a facile approach to a new class of polymerizable monomers (Scheme 1).†



Scheme 1 *Reagents and conditions*: i, aq. CH_2O, $HClHN(CH_3)_2$, 0–25 °C; ii, MeI, THF, room temp.; iii, PhSNa, THF, reflux; iv, Bu^{t}OK, THF, reflux

The bis(phenylthiomethylene) derivative **2b** of 1-alkylpyrrole was treated with Bu^{t}OK (4 mol) in THF at room temperature and then gradually warmed to reflux. This monomer polymerized to give poly(1-hexyl-2,5-pyrrolylenevinylene) (PHxPyV), **1b**. This polymer was purified by four reprecipitations from THF into MeOH and acetone and had a deep blue color with a gold luster. On exposure to air, the polymer became slightly doped reaching a limiting conductivity of 10^{-6} S cm^{-1}. On doping with $AuCl_3$, PHxPyV films (cast on quartz) exhibited conductivities of 2.5 S cm^{-1} (four-in-line probe) in air. The undoped conjugated polymer **1b** was soluble in many common organic solvents. Conversion from the bisphenylthio monomer **2b** afforded PHxPyV in 72% yield, which is considerably higher than that typically obtained for poly(phenylenevinylene) prepared from bis-sulfonium salt precursors (20–40%).[15] As indicated by the UV–VIS–NIR spectrum shown in Fig. 1(*a*) on an undoped film of cast polymer **1b**,

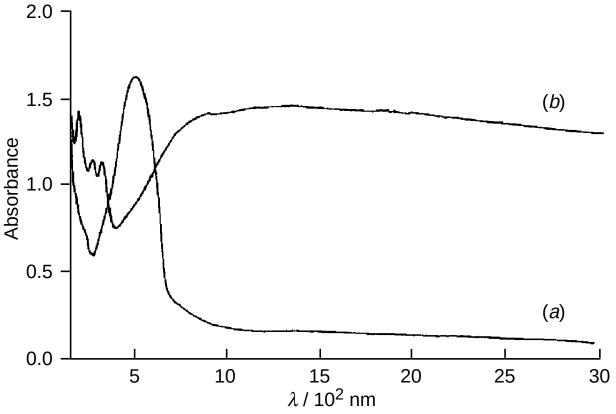


Fig. 1 UV–VIS–NIR absorption spectra of (*a*) undoped and (*b*) $FeCl_3$ doped PHxPyV (**1b**) (cast film on quartz)

Table 1 Properties of polymers **1a–c**

Polymer	λ_{max}/nm THF	λ_{max}/nm Film	Onset optical gap/eV	Solubility[a]	Doped conductivity/S cm^{-1} (dopant)
1a	500[b]	—	1.89	Insoluble	0.02 ($AuCl_3$), 0.001 ($FeCl_3$)[c]
1b	550	569	1.69	Very soluble	2.5 ($AuCl_3$), 0.15 ($FeCl_3$)[d]
1c	548	563	1.65	Very soluble	0.48 ($AuCl_3$), 0.11 ($FeCl_3$)[d]

[a] Solubility in moderately polar solvent such as $CHCl_3$, THF, CH_2Cl_2. [b] NMP. [c] Pressed powder pellet. [d] Cast film.

the onset band gap (low energy absorption edge) was determined to be 1.69 eV for PHxPyV. Poly(1-dodecyl-2,5-pyrrolylenevinylene) (PDoPyV), **1c**, was prepared from bis-phenylthio monomer **2c** as indicated in Scheme 1. This polymer had an onset band gap of 1.65 eV and had, by GPC using polystyrene standards, a number average weight (M_n) of 1.6 × 10^4 and a polydispersity (PD) of 1.16. This band gap is similar to that observed with PHxPyV. A comparison of the properties of **1a–c** made by the same route are summarized in Table 1.

The difference in conductivity between poly(1-alkyl-2,5-pyrrolylene) [$\sigma = 10^{-3}$ (methyl), 4.3×10^{-5} (hexyl) and 1.2×10^{-6} S cm^{-1} (dodecyl)] and **1a–c** suggests that the low conductivities of *N*-substituted polypyrroles as prepared by oxidative polymerization arise from a combination of steric interactions between adjacent rings[7] and from a mixture of α–α', α–β', and β–β' coupled monomer.[16]

We have found the polymerization of bis-phenylthio monomers (**2a**–**c**) to be general for the electron rich 1-alkylpyrroles. Also, we fully expect that this polymerization process will be suitable for the preparation of other electron rich polymers, and we are presently in the process of attempting to prepare representative examples.

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Notes and References

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† Satisfactory spectroscopic and analytical data have been obtained for all new compounds.

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