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Highly Soluble Poly(1,3,4-trisubstituted-2,5-pyrrolenevinylenes)

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Abstract: Pyrroles having long alkoxy groups on the β-position are prepared and utilized as precursors for polypyrrolenevinylenes. The resulting polymers exhibit high solubility not only in a moderately polar solvent but also in a nonpolar solvent such as hexane. These polymers have deep-blue color in the neutral state, while in the doped state the color is completely faded to transparent.

The chemistry of polypyrroles is a subject of growing interest, as a result of both their electronically conducting property and ready modification. The most important characteristics for polymer technology are precisely controlled conductivity and improved processibility. From the standpoint of conductivity, an important contribution is the preparation of pyrroles fused with poly aromatic hydrocarbons. These pyrroles can work as a good precursor for low band gap polymers,[1] but they are quite insoluble and entail an obvious defect such as low processibility. Some attempts were reported to prepare soluble polypyrroles by the introduction of an alkyl chain on the β-position. However, these methods were practically not so effective because of the tedious steps involved. Another approach to preparation of soluble conducting polymers is insertion of a vinylene moiety as the linkage between the two adjoining thiophene or pyrrole rings.[2] We report here a simple synthesis and some optical properties of highly soluble polymers.

Recently, we have presented the preparation of long alkoxy porphyrins which can be dissolved in both chloroform and hexane.[3] Thus, the pyrroles with long alkoxy substituents are suitable as the monomers for soluble polymers.

3,4-Dihydroxypyrroles **1a,b** were prepared according to the literature procedure[4] and the following alkylation was carried out with 1-bromohexadecane in the presence of potassium carbonate. The ester functions in **2a,b** could be readily removed by heating at 170 °C with KOH in ethylene glycol. Disappointingly, the resulting α-free pyrroles could not be applied to polypyrroles because of the failure of electronic polymerization. Therefore, polypyrrolenevinylenes were the target of choice. First, the ester groups were

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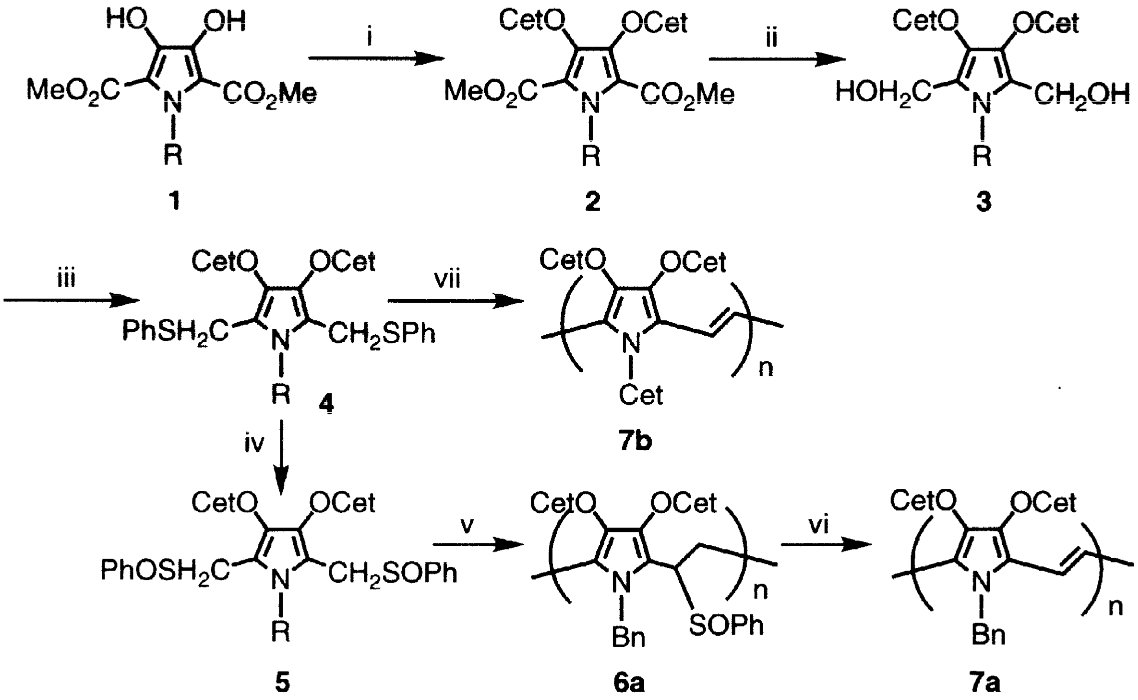
reduced with lithium aluminum hydride and the resulting alcohols **3a,b** were converted into phenylthio groups using thiophenol in the presence of zinc iodide[5] or by the Mitsunobu reaction.[6] After oxidation of sulfide to sulfoxide, the precursor polymer **6a** was obtained by the treatment of the crude mixture of **5a** with potassium *tert*-butoxide. In the case of *N*-benzyl substituted pyrrole, the expected conjugated polymer poly(1-benzyl-3,4-dicetyloxy-2,5-pyrrolenvinylene) **7a** was produced during the removal of the solvent under reduced pressure at 80 °C. In contrast, *N*-cetyl pyrrole **5b** resisted the polymerization. Thus, sulfinylpyrrole **4b** was polymerized using 4 equiv. of potassium *tert*-butoxide[2b] and subsequent thermal elimination to give poly(1,3,4-tricetyloxy-2,5-pyrrolenvinylene) **7b**. (Scheme) These novel long alkoxy substituted polypyrrolenvinylenes **7a,b** were purified by repeated precipitation from chloroform to acetone and obtained as a deep-blue color film with a golden luster. Strikingly, these polymers were soluble not only in moderately polar solvents such as THF, CH_2Cl_2 and $CHCl_3$ but also in nonpolar solvents such as hexane. Polymers substituted with other substituents such as butyloxy, hexyloxy, octyloxy, decyloxy and fused crown ether groups[7] could not be obtained under any conditions.



a R = Bn
b R = Cet (Cet : n-$C_{16}H_{33}$)

	Yield/%			
	2	**3**	**4**	**5**
a	92	97	93	crude
b	60	95	98	31

Scheme *Reagents and conditions*: (i) n-$C_{16}H_{33}Br$, K_2CO_3, DMF, 55 °C, 24h, (ii) $LiAlH_4$, THF, 0 °C, 1h, (iii) PhSH, ZnI_2, $C_2H_4Cl_2$, RT, 3h, under Ar, (iv) *m*-CPBA, $CHCl_3$, RT, 4h, (v) *t*-BuOK, THF, -78 °C then RT, 12h, (vi) vacuum, 80 °C, 30min, (vii) *t*-BuOK (4 eq.), THF, reflux, 5h.

Fig. shows the absorption spectra of neutral polymers **7a** and **7b** compared with I_2 doped polymers. These polymers **7a** and **7b** had a strong absorption band in the visible portion (λ_{max} 618 nm and 580 nm, respectively) which originated from π-π^* transition, and hence they are deep blue colored. Their optical band gaps are determined to be 1.62 and 1.68 eV for **7a** and **7b**, respectively. The second absorption band at about 1100 nm in the spectrum (c) was owing to the polymer partially doped with oxygen. This band could be found only in the spectrum (c) because of the different preparation method and elevated reaction temperature. On the other hand, I_2 doped polymers exhibited no absorption maxima in the visible region. Thus, these doped polymers were extremely transparent. On doping with $FeCl_3$, this fascinating optical property was also observed.

When doping with I_2, this polymer **7a** exhibited conductivities of 3 x 10^{-3} S cm^{-1} and had a number average weight (M_n) of 2.5 x 10^4 and a polydispersity (PD) of 2.78 by GPC using polystyrene standards. Compared with polymer **7a**, **7b** exhibited lower conductivity (σ=1.1 x 10^{-4} S cm^{-1}) on the doped state and smaller number average weight (4.8 x 10^3) because of the steric interactions between long *N*-alkyl substituent and adjacent ring. The value of conductivity of **7b•I$_2$** was equivalent to those of other *N*-alkyl polypyrroles such as *N*-methyl (σ=10^{-3}), *N*-hexyl (4.3 x 10^{-5}) and *N*-dodecyl (1.2 x 10^{-6} S cm^{-1}) polypyrroles.[8] Chemical, optical and electrical properties are summarized in Table.

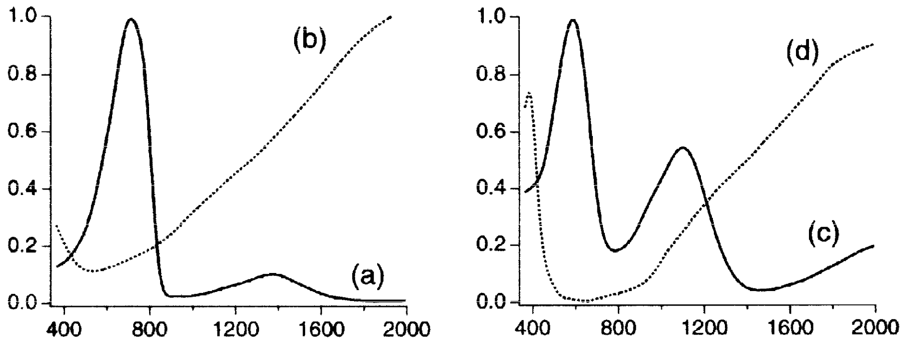


Fig. UV-vis-NIR spectra of undoped **7a** (a), I_2 doped **7a** (b), undoped **7b** (c) and I_2 doped **7b** (d) in chloroform

Table. Properties of polymers **7a,b**

Polymer	λ_{max}/nm[a] Neutral	λ_{max}/nm[a] I_2 doped	Onset optical gap of undoped polymer/eV	Solubility[b]	Doped conductivity[c]/S cm^{-1}
7a	618	over 2000	1.62	Very soluble	2.8 x 10^{-3}
7b	580	over 2000	1.68	Very soluble	1.1 x 10^{-4}

[a] $CHCl_3$ solution. [b] Solubility in $CHCl_3$, CH_2Cl_2, THF, Hexane. [c] Pressed pellet.

We have found highly soluble polypyrroles could be obtained using the pyrroles with long alkoxy groups on the β-position. When an oxidant such as I_2 and $FeCl_3$ was added into the solution of the deep-blue polymers, the color was immediately and completely faded to transparent. Thus, these polymers could act as a sensor for some oxidants. The neutral polymers were not labile under the oxygen-free atmosphere and, moreover, the doped polymers were stable in air for long periods of time (1 year).

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References and Notes

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

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