# Design of New Conducting 3,4-Disubstituted Polythiophenes

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Chemical oxidation of 3,4-dialkylthiophenes gave non-planar polymers exhibiting reduced conductivities; however, decreasing the steric hindrance, by using alkoxy derivatives, led to the synthesis of soluble and highly conducting disubstituted polythiophenes.

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During the last few years, many studies have been devoted to the development of processable conducting polymers. It has been shown recently that polymerization of long-chain 3-substituted thiophenes gives soluble conducting polymers.[1—5] This substitution in the 3-position also improves the regularity of the thiophene backbone but structural defects (irregular couplings, branchings, cross-linking) are still present in these polymers.[6] Polymerization of 3,4-disubstituted thiophenes should be a convenient way for preparing regular conducting polymers but, as found with substituted polyacetylenes[7] and *N*-substituted polypyrroles,[8] steric interactions between the substituents and the polymer backbone have to be avoided in order to keep the planar conformation which is an important criterion for high electrical conductivities. Recent studies on poly(3,4-dimethylthiophene) and poly(3,4-cycloalkylthiophenes)[9,10] have shown that slight modifications in the position and/or the bulkiness of the substituents may have a strong influence on both conjugation and conductivity of the resulting materials. In order to obtain more information concerning the steric hindrance occurring in 3,4-disubstituted polythiophenes and its influence on the electrical properties, we report here the synthesis and characterization of new alkyl and alkoxy disubstituted polythiophenes. Some alkoxy derivatives have been found particularly interesting since they are the first examples of soluble and highly conducting disubstituted polythiophenes.

3-Butoxy-4-methylthiophene and 3,4-dibutoxythiophene were prepared from 3-bromo-4-methylthiophene and 3,4-dibromothiophene respectively.[11] Alkylation of these bromo derivatives by Grignard reagents[12] gave the corresponding 3-octyl-4-methylthiophene and 3,4-dihexylthiophene. All monomers were purified by fractional distillation under reduced pressure or by chromatography on silica gel. They were subsequently characterized by NMR and IR spectroscopies and mass spectrometry. Polymers were obtained by chemical oxidation of the monomers using iron trichloride according to a procedure similar to that of Sugimoto *et al.*[3] Details of the preparation, purification, and characterization of these polythiophene derivatives will be published elsewhere. Undoped polymers were obtained by reduction with an aqueous solution of hydrazine. Doping was performed by soaking the polymers in a nitromethane solution of iron trichloride (0.1 M). Four-probe conductivity measurements were carried out on pressed pellets at room temperature in air.

**Table 1.** Physical properties of alkyl and alkoxy disubstituted polythiophenes.

| Polymer | $\lambda_{max.}$[a] /nm | $\lambda_{max.}$[b] /nm | Conductivity /ohm$^{-1}$ cm$^{-1}$ |
|---|---|---|---|
| Poly(3-octyl-4-methylthiophene) | 325 | 325 | $10^{-5}$ |
| Poly(3,4-dihexylthiophene) | 315 | 315 | $<10^{-5}$ |
| Poly(3-butoxy-4-methylthiophene) | 545 | 420 | 2 |
| Poly(3,4-dibutoxythiophene) | 460 | 480 | $10^{-5}$ |

[a] Taken from neutral polymer films cast on quartz plates. [b] Taken from neutral polymers dissolved in chloroform.

Chemical polymerization of the 3,4-dialkylthiophenes gave pale blue–green products whereas poly(3-butoxy-4-methylthiophene) and poly(3,4-dibutoxythiophene) were found as blue–black powders. After treatment with an aqueous solution of hydrazine, all polymers were soluble in chloroform. As reported in Table 1, the UV-VIS spectra of neutral poly(3-octyl-4-methylthiophene) and poly(3,4-dihexylthiophene) show absorption maxima at relatively short wavelengths for conjugated polymers. For instance, the poly(3-alkylthiophenes) exhibit an absorption maximum around 500 nm.[1—4] This behaviour of the poly(3,4-dialkylthiophenes) can be easily explained by a non-planar conformation of the polymer backbone resulting from steric interactions between the substituents and the thiophene rings. This non-planar conformation reduces the effective conjugation length, which leads to a blue shift of the UV-VIS absorption. Moreover, still in contrast to poly(3-alkylthiophenes),[4] the poly(3,4-dialkylthiophenes) did not show any solvatochromic properties and exhibited similar non-planar conformations in solution and in the solid state.

On the other hand, poly(3-butoxy-4-methylthiophene) shows a maximum of absorption in the visible region which can be related to a highly conjugated backbone. It has been reported recently that some poly(3-alkoxy-4-methylthiophenes) can also be prepared by electropolymerization.[13] Incorporation of alkoxy substituents is expected to have only a small influence on the band gap of the resulting polymers[14] and we therefore consider that this major difference in the maxima of absorption between the alkyl and alkoxy derivatives is mainly due to the presence of two completely different conformational structures. From the results of the optical absorption spectra taken in the solid state, we think that a co-planar conformation (a rod-like structure) is possible for poly(3-alkoxy-4-methylthiophenes), which can be attributed to the fact that steric hindrance in the vicinity of the backbone is minimized. However, poly(3,4-dibutoxythiophene) exhibits a maximum of absorption at a shorter wavelength than poly(3-butoxy-4-methylthiophene), which indicates that steric interactions between the two long substituents induce a twisted conformation of the backbone. It is also noteworthy that, like poly(3-alkylthiophenes),[4] the conformation of poly(3-butoxy-4-methylthiophene) in solution is that of a coil with a smaller effective conjugation length.

As shown in Table 1, the conformational structures in the solid state also have a strong influence on the conductivity of the doped polymers. Indeed, the electrical conductivity of poly(3-butoxy-4-methylthiophene) is at least five orders of magnitude higher than those obtained with the dialkyl or dialkoxy derivatives. Nonplanar conformations and bulky substituents lead to poor inter-chain contacts by keeping the chains away from one another, thereby reducing the probability of charge carrier hopping.[7] Moreover, the doped state of the poly(3-butoxy-4-methylthiophene) is more stable than the alkyl derivatives, which is consistent with the results reported for poly(3-methoxythiophene).[15] This property should result from a decrease of the ionization potential due to the presence of the electron-donating alkoxy group. In summary, the high level of conductivity obtained with poly(3-butoxy-4-methylthiophene) clearly shows that by designing molecules with reduced steric hindrance, it is possible to prepare regular, soluble, and highly conducting polymers.

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