Poly(3,3′-dibutoxy-2,2′-bithiophene): a New Highly Conjugated Polythiophene Derivative

Renée Cloutier and Mario Leclerc*

Département de Chimie, Université de Montréal, Montréal, Québec H3C 3J7, Canada

Chemical oxidation of 3,3′-dibutoxy-2,2′-bithiophene has led to the synthesis of a nearly transparent conducting (2 S cm^{-1}) polymer which has an oxidation potential at only 0.07 V *vs.* saturated calomel electrode.

Poly(3-alkylthiophenes) have attracted considerable attention because they are soluble in common organic solvents and show interesting electrical and optical properties.[1,2] However, owing to their relatively high oxidation potentials, these polymers are not very stable in the doped state. In order to prepare new processable conducting polymers, we have recently studied some polythiophene derivatives and we found that the presence of an alkoxy group in place of an alkyl substituent decreases both the steric hindrance and the ionization potential of the polymer.[3,4] On the other hand, the polymerization of monosubstituted alkoxythiophenes has given materials with relatively low electrical conductivities.[4,5] These results can be attributed to the strong electron-donating effect of the alkoxy group which increases the reactivity of the monomer and, therefore, decreases the selectivity of the α–α′ couplings during polymerization. Polymerization of alkyl-substituted bithiophenes has also been recently reported[6,7] but the resulting polymers exhibit high oxidation potentials and band gaps. However, these polymers have a more regular structure than that obtained from the polymerization of 3-alkylthiophenes.[7,8] These last results encouraged us to investigate the chemical synthesis of poly(3,3′dialkoxy-2,2′-bithiophenes).

3,3′-Dibutoxy-2,2′-bithiophene was synthesized from 3-butoxythiophene[9] by lithiation with butyllithium followed by oxidative coupling using copper(II) chloride.[6] The crude bithiophene derivative was purified by flash chromatography (light petroleum–chloroform, 80 : 20) on silica gel and, finally, recrystallized from n-hexane. The NMR and IR spectra as well as the elemental analyses were in good agreement with the proposed structure. The polymer was obtained by chemical oxidation of the dimer using iron trichloride according to a procedure similar to that of Sugimoto *et al.*[8,10] Details of the preparation, purification and characterization of this class of polymers will be published elsewhere. Undoped (neutral) polymer was obtained by reduction with an aqueous solution of hydrazine (2% w/w). Doping was performed by soaking the polymer in a nitromethane solution of iron trichloride (0.1 mol dm^{-3}). Four-probe conductivity measurements were carried out on pressed pellets at room temperature in air. Cyclic voltammetry and *in situ* spectroelectrochemistry were performed in dry acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 mol dm^{-3}) as supporting electrolyte.

The undoped poly(3,3′-dibutoxy-2,2′-bithiophene) was found to be soluble in common organic solvents (*e.g.* chloroform, methylene chloride and tetrahydrofuran) and thin films were then cast from these solutions on indium–tin oxide (ITO) coated glass or platinum electrodes.[†] The polymer is electroactive and, as reported in Fig. 1, it shows an oxidation peak at 0.07 V *vs.* saturated calomel electrode (SCE) which is an exceptionally low value for a polythiophene derivative. In contrast to the results reported for alkyl-substituted polythiophenes,[6] the head-to-head structure of poly(3,3′-dibutoxy-2,2′-bithiophene) did not give a material with a high oxidation potential. Indeed, this polymer has a lower oxidation potential than poly(3-butoxythiophene) prepared under similar conditions (0.34 V *vs.* SCE).[4] This particular feature can be explained by the possibility that poly(3,3′-dibutoxy-2,2′-bithiophene) can adopt a coplanar conformation. This assumption is supported by X-ray diffraction measurements that have revealed a coplanar conformation for the dimer.[11] This low oxidation potential can also be related to a low amount of irregular couplings (α–β′ couplings, branchings) along the backbone.

As shown in Fig. 2, neutral poly(3,3′-dibutoxy-2,2′-bithiophene) exhibits an absorption edge near 760 nm (1.63 eV) with a maximum of absorption at 580 nm (2.14 eV). This low band gap is also a direct consequence of the well defined and highly conjugated structure of the polymer. Furthermore, thin films of the blue–violet neutral polymer become nearly transparent in the visible region when chemically or electrochemically oxidized. This behaviour arises when the band gap of the polymer is sufficiently small so that the corresponding band for the oxidized form lies further to the near-IR region with reduced tailing into the visible range.[12–14] Finally, upon doping with iron trichloride in nitromethane, conductivities up to 2 S cm^{-1} were observed for poly(3,3′-dibutoxy-2,2′-bithiophene). This value is about two or three orders of

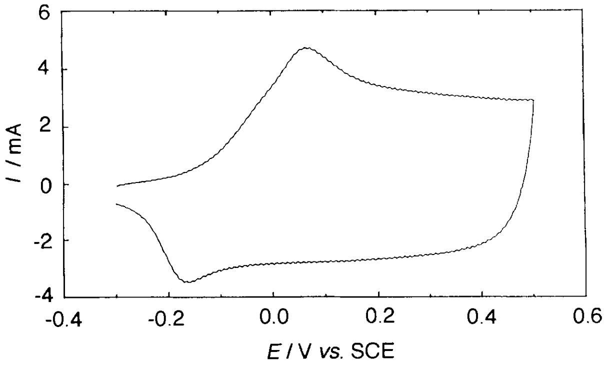

Fig. 1 Cyclic voltammogram of poly(3,3′-dibutoxy-2,2′-bithiophene) cast on a platinum electrode (potentials relative to SCE); sweep rate: 100 mV s^{-1}

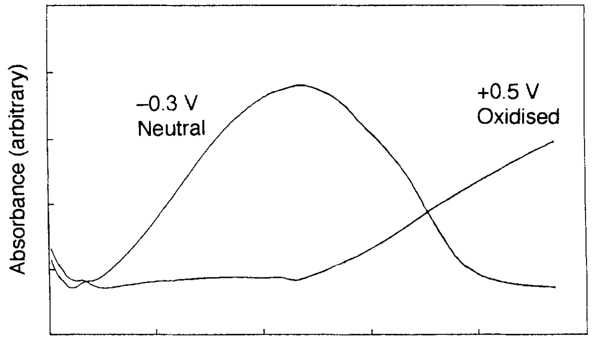

Fig. 2 UV–visible spectra of poly(3,3′-dibutoxy-2,2′-bithiophene) cast on an ITO electrode at different potentials *vs.* SCE

[†] We estimate that the thickness of the films is in the range 500–1000 nm; it has not been possible so far to produce uniform films.

magnitude higher than that obtained with poly(3-alkoxythiophenes).[4,5]

In summary, these results clearly indicate that the polymerization of alkoxy-substituted bithiophenes leads to the synthesis of regular materials with enhanced optical and electrochemical properties. Moreover, the structural parameters developed in this study may be used in preparations of new well defined electroactive polythiophene derivatives.

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