Conducting Polymers from Dimethyl-2,2′-bithiophenes

Bernd Krische,* Jonas Hellberg, and Christina Lilja

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Electrochemical oxidation of symmetrical dimethylbithiophenes with free α-positions yields electroactive polymers with excellent cycling ability.

The literature offers differing views[1,2] as to whether organic conducting polymers derived from thiophene itself and its oligomers are identical. Polymerization conditions for the oligomers differ because of differences in oxidation potentials (thiophene +2.0, bithiophene +1.3, terthiophene +1.0 V). This might influence the outcome of polymerization[3] and complicates the interpretation.

To study the importance of β-coupling in bithiophene polymerization, which was claimed to be responsible for the relatively poor conductivity of polybithiophene,[1] we have synthesized and polymerized the symmetrical dimethyl derivatives (**2**)—(**4**) of bithiophene (**1**).† We have assumed that the configuration (conformation) of the central bond of the bithiophenes is *E* as drawn for (**4**) and as demonstrated for the 5,5′-dinitro derivative.[4]

For iodination we used the method of Suzuki *et al.*,[5] which is superior to almost all other iodination methods for aromatic compounds with respect to yield, selectivity, ease of performance, work-up, and environmental problems. Reductive dimerization[6] of the iodo(methyl)thiophenes (**6**) and (**8**) gave the bithiophenes (**2**) and (**4**), whereas oxidative coupling of the lithiated methylthiophene (**9**)[7] yielded 4,4′-dimethylbithiophene (**3**).

Cyclic voltammetry of the dimethylbithiophenes showed that they have rather similar oxidation potentials, around 1.2 V *vs.* Ag/AgCl (see Table 1). The 3,3′- and 4,4′-dimethyl derivatives (**3**) and (**4**) polymerized even in the rather dilute (0.001 M) solutions used here. Films for cyclic voltammetry were grown under galvanostatic conditions‡ on platinum gauze electrodes. The derivative (**2**) did not polymerize under those conditions; the anode solution turned greenish brown and no film was formed. At high potentials (>1.8 V), however, (**2**) yielded a thin, yellow, insulating film. The bithiophenes with free α-positions (**3**) and (**4**) gave rise to black powdery deposits which adhere much better to a gauze than to a plate during the washing and drying procedures.§ The smooth deposits on Pt plates were impossible to peel off as free-standing films because of their powdery nature. By stripping off the outer layer with adhesive tape it was possible to demonstrate that the polymers are conducting.¶ Electron

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† δ_H ($CDCl_3$; Me_4Si): (**2**) 6.86 (d, 2H), 6.62 (d, 2H) (*J* 3.3 Hz), and 2.46 (s, 6H); m.p. 63.5 °C (lit.,[8] 67 °C); (**3**) 6.94 (d, 2H, *J* 1.4 Hz), 6.75 (m, 2H) and 2.24 (d, 6H, *J* 1.1 Hz), m.p. 67 °C; (**4**) 7.23 (d, 2H), 6.89 (d, 2H, *J* 5.2 Hz), and 2.16 (s, 6H); b.p. 135 °C at 16 Torr) (lit.,[9] 131 °C at 11 Torr).

‡ Acetonitrile solution, 0.1 M-NBu_4ClO_4, 0.05 M in monomer, 1.5 mA cm^{-2}, 0.15 C cm^{-2}.

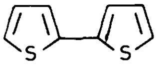
§ Extracting with acetonitrile (Soxhlet) for 1 h, and pumping for 1 h under dynamic vacuum.

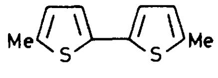
¶ The very thin and not particularly dense layer had a resistivity of a few kΩ. From this one can estimate a specific conductivity of about 0.1 S cm^{-1}.

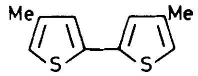
Table 1. Peak oxidation/reduction potentials for bithiophene monomers and polymers. See also ref. 1.

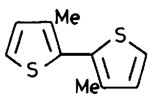
Electrolyte (0.1 M) (+ MeCN)	Monomers E_{pa}/V	Polymers E_{pa}/V	Polymers E_{pc}/V of oxidized polymer
(**1**) NBu_4ClO_4	1.27	0.97—0.91[a]	0.81—0.76[a]
NBu_4PF_6	—	1.00	0.97
(**2**) NBu_4ClO_4	1.21	—	—
(**3**) NBu_4ClO_4	1.15	(0.40), 0.73	0.22, 0.62
NBu_4PF_6	—	(0.45), 0.82	0.25, 0.73
(**4**) NBu_4ClO_4	1.19	(0.42), 0.70	0.33, 0.69
NBu_4PF_6	—	(0.43), 0.73	0.31, 0.74

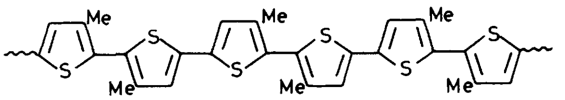
[a] Shifted on cycling.


(**1**)


(**2**)

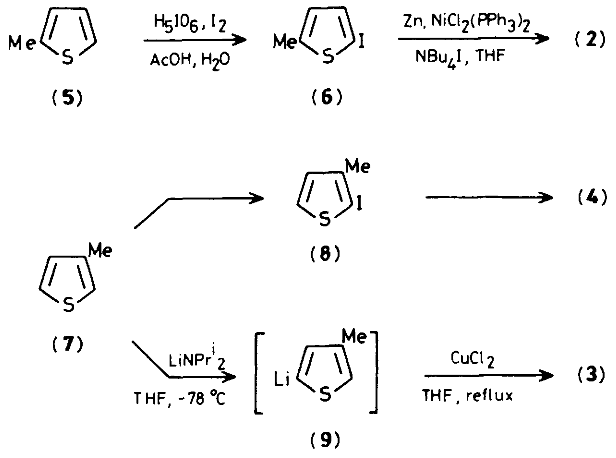

(**3**)


(**4**)


(**10**)

micrographs of 'films' grown on Kanthal 05D heating band** show a very porous morphology made up of agglomerates of small spherical units about 0.3 μm in diameter.

The monomers (**3**) and (**4**) should on polymerization yield the same polymer (**10**) (except at the chain ends) if coupling proceeds exclusively in the α-positions (5,5′-). The resulting polymers looked very similar both to the eye and in an electron microscope, but cyclic voltammetry showed some differences, especially for thick films (see Figure 1). Films of poly-(**4**) released on cycling some soluble products which gave a greenish colour to the anode solution; poly-(**3**) did not. The reduced (*i.e.* neutral) polymers are yellow-brown in both cases [$\lambda_{max.}$ (tetramethylene sulphone) 417 nm]. The oxidation peak for rather thick films (1.0 C on a 1.5 cm^2 gauze) of poly-(**3**) is wider than that of poly-(**4**). Most revealing is the effect of change of anion: oxidizing a neutral film (synthesized with ClO_4^-) in acetonitrile/NBu_4PF_6 leads to changes in peak potentials as compared with NBu_4ClO_4. The shifts for poly-(**3**) and poly-(**4**) are not identical (see Table 1), indicating the presence of a different polymer. The difference may be chemical (*e.g.* molecular structure) or merely physical (*e.g.* other morphology) in nature. For both polymers the peak current increases linearly with sweep rate (in the measured range 5—100 mV s^{-1}) with a slightly steeper slope for poly-(**4**).



Scheme 1

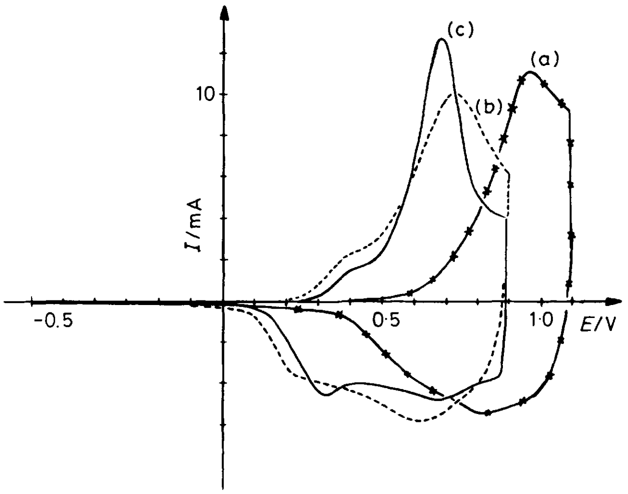


Figure 1. Cyclic voltammograms for thick films (1.0 C on 1.5 cm^{-2} Pt gauze electrode) of polydimethylbithiophenes; sweep rate 20 mV s^{-1}, 0.1 M NBu_4ClO_4 in acetonitrile, voltage *versus* Ag/AgCl reference: (a) poly-(**1**), (b) poly-(**3**), (c) poly-(**4**).

The form of the reduction wave in these polymers is intriguing; double peaks are found in other systems too.[1] The origin is not established yet, but since the shape of the reduction wave changes with time, *e.g.* on waiting after oxidation or with slower scan rates the more negative peak becomes more pronounced, it is probably connected with anion-diffusion processes in the polymer or changes in the crystalline/amorphous ratio.

A 1.00 C film of poly-(**3**) had on cycling a higher usable charge [1.88 *vs.* 1.62 10^{-1} C for poly-(**4**)], which indicates that (**3**) provides more active material. The reason for this could be that (**4**) yields on polymerization more short oligomers (indicated by the coloration) which are washed out during work-up. However, the cyclable charge (on sweeping between −0.6 and + 0.9 V *vs.* Ag/AgCl) indicates that the electrochemical yield for polymerization is very high.†† The poly-

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[**] We did not like to cut our platina electrodes, and this material is stable in the electrolyte to 1.3 V, *i.e.* sufficient for polymerization conditions.

[††] Assuming 2 electrons for polymerization this means that the polymer with 0.19 as in the charged state is doped to 38% per monomer unit, *i.e.* one unit charge for every five rings.

mers are reversible in their charge/discharge behaviour: *e.g.* for poly-(**3**) 0.1906 C in and 0.1882 C out (98.7%); for poly-(**4**) 0.1629 C in and 0.1615 C out (99.1%) at 20 mV s^{-1} sweep rate and with peak currents of about 15 mA. Furthermore, although Q_{out} is only about 99% of Q_{in}, the charge of the following cycles is not much smaller: in one sample of poly-(**3**) Q_{in} had dropped after 12 cycles to 96% and that for another sample remained constant over 10 cycles. The largest changes occur in the first first five cycles, probably owing to some loss of material.

From the failure to polymerize (**2**), it appears that β,β-coupling does not play a major role in polymerization of bithiophenes. Free α-positions seem to be necessary. α,β-Coupling is rather unlikely in (**3**) from sterical considerations, whereas no such constraints are obvious for (**4**). Thus α,β-coupling might be the reason for the formation of soluble products. We do not believe this explanation but we cannot exclude it yet from experimental evidence. In any case, the polymers derived from (**3**) or (**4**) are different in some way, perhaps owing to a larger fraction of short-chain polymers in poly-(**4**) or a different structure/morphology.

The porous nature of the polymers derived from 3,3′- and 4,4′-dimethyl-2,2′-bithiophene together with their good cyclability makes them promising materials for polymer battery applications.

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