

## New Synthetic Routes to Electroconductive Polymers containing Thiophene Units

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A novel entry to polymers containing thiophene units is presented, based on coupling of monomers bis-lithiated at the thiophene termini; iodine and  $\text{AsF}_5$ -doping of the polymers to give electroconductive materials is described.

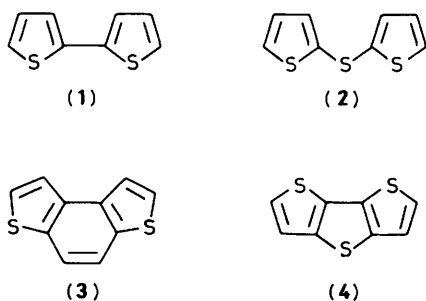
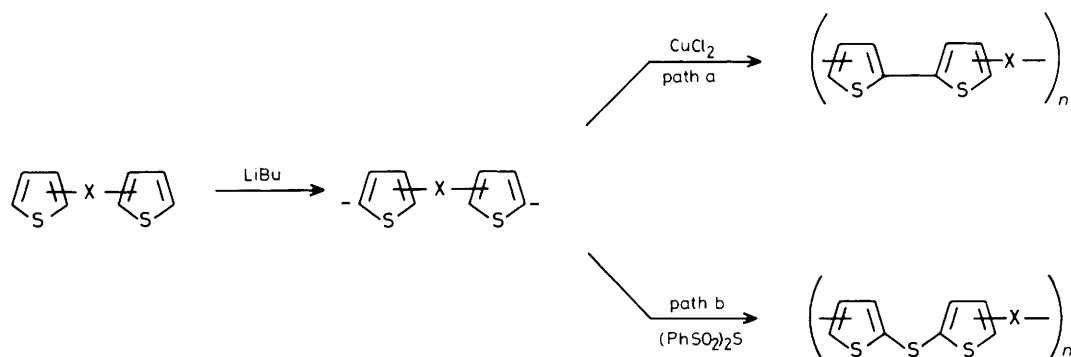
Polymers containing thiophene units constitute an important class of organic electroconductive materials, poly(thiophene) (PT)<sup>1</sup> and poly(2,5-thienylene sulphide) (PTS)<sup>2</sup> being the best known examples. We present herein a new method of wide synthetic scope for the simple production of these materials.

The general synthetic scheme involves a monomer carrying thiophene units at its termini: the exhaustive lithiation with

*n*-butyl-lithium at position  $\alpha$  of both the thiophene rings afforded a localized bis anion<sup>†</sup> which could be either

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<sup>†</sup> Treatment of 2,2'-dithienyl with *n*-butyl-lithium in diethyl ether followed by quenching with  $\text{D}_2\text{O}$  showed<sup>3</sup> that the deuterium entered exclusively at the 5 and 5' positions with a 92% yield.



oxidatively coupled with copper chloride or bridged with sulphur by reaction with bis(benzenesulphonyl) sulphide.

A fortunate peculiarity of this polymerization method is that no functional groups are present in the starting monomer; this eliminates the general detrimental effect exerted<sup>1</sup> by the terminal groups on the conductivity of the final polymer.

The monomers (1)–(4) have been polymerized in this way and give evidence for the wide scope of the method ranging from the synthesis of PT [substrate (1), path a in Scheme 1] and PTS [substrate (2), path b in Scheme 1], to more sophisticated structures.‡ High level doping of the pristine polymers was carried out with arsenic pentafluoride (1 atm) or with iodine vapours.

‡ The experimental conditions for the lithiation of the substrates and their coupling were similar to those described for the synthesis of a few anellated thiophene derivatives.<sup>4</sup> The lithiation was carried out with BuLi (1.6 M solution in hexane, 2 equiv. per mole of the starting material) in dry Et<sub>2</sub>O solution under N<sub>2</sub> at –10 °C; the bis-lithium derivatives separated in a few cases as a solid precipitate. A slurry of anhydrous CuCl<sub>2</sub> in dry anisole was then added and the temperature was gradually raised to 100 °C in order to increase the polymer length; in the meantime the Et<sub>2</sub>O was distilled off. The reaction mixture was quenched with water and the brown precipitate was filtered off, thoroughly ground with conc. HCl solution, then washed with a 20% NH<sub>3</sub> solution, and finally rinsed to neutral with water. The recovered material was submitted to Kumagawa extraction, first with MeOH, and then with CHCl<sub>3</sub> (48 h each) in order to remove the oligomers. Final yields ranged from 25 to 50%. Elemental analytical data of the neutral polymers and the <sup>1</sup>H n.m.r. spectra for some of them recorded in Me<sub>2</sub>SO at 175 °C provide evidence for a good level of purity of the products.

AsF<sub>5</sub> doped PT and PTS prepared according to this method showed conductivities of 4.8 S cm<sup>-1</sup>§ and 7.5 × 10<sup>-5</sup> S cm<sup>-1</sup>¶ respectively, close to the best literature values for these materials (PT: σ = 14 S cm<sup>-1</sup>;§<sup>1</sup> PTS: σ = 2.6 × 10<sup>-5</sup> S cm<sup>-1</sup><sup>2</sup>). A further rewarding result was obtained in the case of the AsF<sub>5</sub> doped poly(2,5-benzo[1,2-*b*:4,3-*b'*]dithiophene) [substrate (3),<sup>5</sup> path a in Scheme 1] which showed a conductivity of 8.3 × 10<sup>-7</sup> S cm<sup>-1</sup>,¶ better than that exhibited by the electrochemically prepared product (σ = 10<sup>-11</sup> S cm<sup>-1</sup><sup>6</sup>); the lithiation is probably much more selective than the electro-oxidation in discriminating the α and β-thiophene positions, affording therefore a less disordered material.

For the poly(2,6-dithieno[3,2-*b*:2',3'-*d*]thiophene) (PDTT) [substrate (4), path a in Scheme 1] data are available only for a material doped with iodine whose conductivity was found to be 3.1 × 10<sup>-5</sup> S cm<sup>-1</sup>;§ this result allows us to predict a value at least three orders of magnitude higher for the conductivity of the polymer doped with AsF<sub>5</sub>, a figure not too far from that reported for the electrochemically produced PDTT.<sup>7</sup>

The new poly[5,5'-(2,2'-bisthiénylene) sulphide] [substrate (2), path a in Scheme 1] doped with AsF<sub>5</sub> showed a conductivity of 4.2 × 10<sup>-5</sup> S cm<sup>-1</sup>,§ very similar to that shown by PTS, indicating that a 50% decrease in the sulphur bridges of the chain does not promote a substantial increase in conductivity. Preliminary experiments of electro-oxidation of (2) afforded a material whose conductivity<sup>8</sup> was close to that of the aforementioned AsF<sub>5</sub> doped product.

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## References

- 1 M. Kobayashi, J. Chen, T.-C. Chung, F. Moraes, A. J. Heeger, and F. Wudl, *Synth. Metals*, 1984, **9**, 77, and references therein.
- 2 K.-Y. Jen, N. Benfaremo, M. P. Cava, W.-S. Huang, and A. G. MacDiarmid, *J. Chem. Soc., Chem. Commun.*, 1983, 633, and references therein.
- 3 R. M. Kellogg, A. P. Schaap, and H. Wynberg, *J. Org. Chem.*, 1969, **34**, 343.
- 4 P. de Long and M. Jansen, *J. Org. Chem.*, 1971, **36**, 1645.
- 5 R. M. Kellogg, M. B. Groen, and H. Wynberg, *J. Org. Chem.*, 1967, **32**, 3093.
- 6 R. Danieli, F. Sannicolò, C. Taliani, and R. Zamboni, submitted for publication to *Synth. Metals*.
- 7 P. Di Marco, M. Mastragostino, and C. Taliani, *Mol. Cryst. Liq. Cryst.*, 1985, **118**, 241.
- 8 M. Bragadin, personal communication.

§ Pressed pellets, four probe apparatus, room temperature.

¶ Pressed pellets, two probe apparatus, room temperature.