

Towards Chiral Metals. Synthesis of Chiral Conducting Polymers from Optically Active Thiophene and Pyrrole Derivatives

Dilip Kotkar, Vishwas Joshi, and Pushpito K. Ghosh*

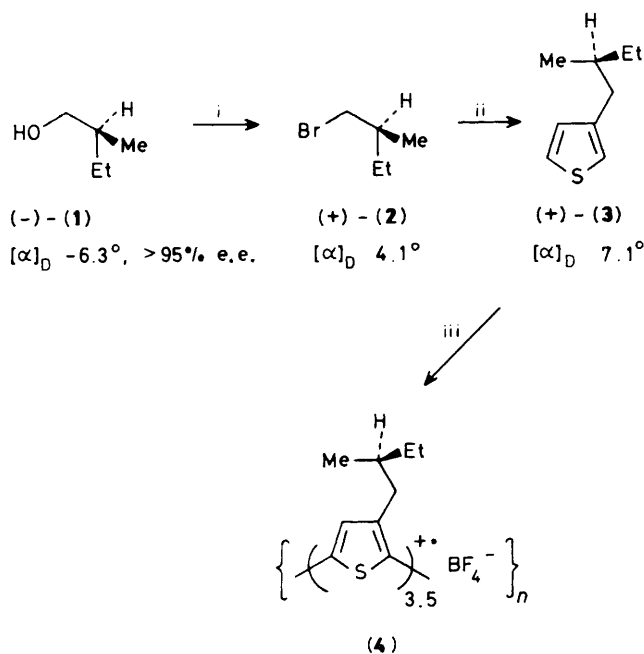
Alchemie Research Centre, P.O. Box 155, Thane-Belapur Road, Thane-400 601, Maharashtra, India

The synthesis of free standing and clay-supported chiral conducting polymer films is described.

We report here our preliminary results on the preparation and characterisation of free standing and clay-supported chiral conducting polymer films based on (*S*)-(+)-3-(2-methylbutyl)thiophene (**3**) and (*S*)-(+)-3-(2-methylbutyl)pyrrole.

There is growing interest in the design of conducting polymers with improved conductivity, thermal and environmental stability, and greater ease of processability.¹ This research has concentrated on modifications of the basic monomeric units, although not all such modifications are useful owing to their adverse effect on the conductivity of the polymer.² 3-Alkyl substituted thiophenes and pyrroles, however, have been found to yield polymers with acceptable conductivity.²⁻⁶ In view of the concept of 'chiral metals', we sought to introduce an optically active alkyl moiety at the 3-position of thiophene and pyrrole, for further conversion to chiral conducting polymers. Such materials could conceivably exhibit exotic properties and serve as asymmetric electrodes for chiral electrosynthesis. We note previous work in this direction by Komori and Nonaka,⁷ Salmon and Bidan,⁸ and Lemaire *et al.*⁹

We have synthesised (+)-(**3**) $\{[\alpha]_D^{25} 7.1^\circ (c 1, \text{CHCl}_3), >95\%$ enantiomeric excess (e.e.) $\}^\dagger$ in ca. 70% yield by the $\text{Ni}[\text{Cl}_2(\text{dppp})]$ ($\text{dppp} = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$)-catalysed coupling reaction between 3-bromothiophene and (*S*)-2-methylbutyl magnesium bromide,¹⁰ the latter having been derived from (+)-(**2**) $\{[\alpha]_D^{25} 4.1^\circ (c 6, \text{CHCl}_3)\}$ (Scheme 1). Compound (**2**),



Scheme 1. Reagents and conditions: i, PBr_3 , pyridine, 0°C ; ii, Mg, Et_2O , 0°C , then 3-thienyl bromide, $\text{NiCl}_2(\text{dppp})$; iii, 5 V, Et_4NBF_4 , MeCN.

† It is assumed that the reactions shown in Scheme 1 do not affect the chiral carbon centre.

in turn, could be readily prepared in large quantities from the inexpensive (*S*)-(**1**) $\{[\alpha]_D^{25} -6.3^\circ (c 10, \text{EtOH}), >95\%$ e.e. $\}^{11}$. We note that the chiral 2-methylbutyl group has been employed in the design of chiral nematic liquid crystals for special optical effects.¹²

With an applied potential of 5 V,¹³ (**3**) (0.25 M) could be oxidatively electropolymerised in a single-compartment, two-electrode cell, consisting of a glassy-carbon working electrode (0.26 cm^2), a platinum wire counter electrode, and dry MeCN and Et_4NBF_4 (0.25 M) as solvent and supporting electrolyte, respectively. The cell was maintained under nitrogen and immersed in an ice-water bath during electrolysis. The cell current was fairly constant (3.8–4.2 mA) throughout the polymerisation process, and in most cases polymerisation was discontinued after 4 C had passed. The working electrode was then rinsed with MeCN and air dried, and the blue-black film peeled from the electrode surface. This film (1.8 mg) was tough, shiny, smooth, and flexible, and showed a minimum specific conductivity of 0.2 S/cm , ‡ as determined by a two-probe measurement. From its appearance the film was of superior quality than that of films obtained from *n*-butylthiophene, under similar conditions. Elemental analyses (C, H, N, S) indicated that our films were not contaminated with the solvent and the supporting electrolyte salt (inferred from the absence of nitrogen), and were consistent with the molecular formula (**4**) (Scheme 1). § The value of *n* was not estimated, however. Differential scanning calorimetric studies indicated a somewhat heterogeneous polymer matrix, but with a moderately sharp endothermic transition at ca. 215°C . Further visual examination of the polymer revealed complete retention of shape and form, even after heating to 300°C . The concentration of the supporting electrolyte critically affected film conductivity, and films grown from solutions containing lower concentrations (0.05 M) of Et_4NBF_4 were resistive, although otherwise similar in texture. Elemental analysis of such films suggested that the polymer contained one BF_4^- ion for every nine units of the monomer; hence their higher resistivity may be ascribed to a lower concentration of the free electron carriers.¹⁴ Microscopic examination showed that conducting films are fairly non-porous, and this was confirmed by the lack of any voltammetric response of the film-containing electrode towards solution redox couples which are otherwise electroactive on the exposed glassy-carbon surface.

Soma *et al.* have recently shown that adsorption of thiophene on Fe^{3+} -montmorillonite clay leads to formation of a blue-black polymer whose Raman spectrum is similar to that of the corresponding free-standing conducting polymer prepared *via* electrosynthesis.¹⁵ We have found a similar colouration of Fe^{3+} -montmorillonite films upon adsorption of (**3**), but characterisation of the clay-polymer composite remains incomplete.

‡ The film thickness value required for calculation of specific conductivity was not measured as such, but estimated by assuming a polymer bulk density of 0.95 g cm^{-3} . Thus, the thickness was $67 \mu\text{m}$ for the film weighing 1.8 mg.

§ Found: C 60.5, H 6.9, S 18.6; calc. for (**4**): C 61.1, H 6.8, S 18.1%.

Finally, our attempts to synthesise the pyrrole analogue of (3) yielded a mixture of the 3- and 2-alkyl substituted chiral pyrroles.¹⁶ Electrochemical polymerisation from a solution containing pyrrole and the above mixture of alkyl-pyrroles yielded a polymer whose elemental analysis suggested formation of a copolymer of pyrrole and alkyl-pyrrole. This copolymer was found to be modestly conducting (<0.01 S/cm) and brittle.

In conclusion, free standing chiral conducting polymer films, based on optically active 3-alkyl derivatives of thiophene and pyrrole, have been prepared *via* electropolymerisation, and such polymerisation could also be effected on Fe³⁺-montmorillonite to yield a clay-chiral polymer matrix. The free-standing chiral poly(thiophene) films are mechanically strong but their conductivity is substantially lower than literature values for poly(alkyl-thiophene).² Our polymerisation process has not been optimised and improvements in conductivity are therefore likely.

We acknowledge stimulating discussions with Dr. Peter Day, University of Oxford, on the concept of chiral metals and thank Dr. A. K. Mandal for his helpful comments. This work was supported by IEL Ltd.

Received, 19th February 1988; Com. 8/0675J

References

- 1 'Conducting Polymers: Special Applications,' ed. L. Alcacer, Reidel, Holland, 1987.
- 2 J. Roncali, R. Garreau, A. Yassar, P. Marque, F. Garnier, and M. Lemaire, *J. Phys. Chem.*, 1987, **91**, 6706, and references cited therein.
- 3 G. B. Street, T. C. Clarke, R. H. Geiss, V. Y. Lee, A. Nazzari, P. Pfluger, and J. C. Scott, *J. Phys. Chem.*, 1983, **3**, 599.
- 4 K. Y. Jeh, G. G. Miller, and R. L. Elsenbaumer, *J. Chem. Soc., Chem. Commun.*, 1986, 1346; R. L. Elsenbaumer, K. Y. Jen, and R. Oboodi, *Synth. Met.*, 1986, **15**, 169.
- 5 M. R. Bryce, A. Chissel, P. Kathirgamanathan, D. Parker, and N. R. M. Smith, *J. Chem. Soc., Chem. Commun.*, 1987, 466.
- 6 M. Sato, S. Tanaka, and K. Kaeriyama, *J. Chem. Soc., Chem. Commun.*, 1986, 873.
- 7 T. Komori and T. Nonaka, *J. Am. Chem. Soc.*, 1983, **105**, 5691; 1984, **106**, 2656.
- 8 M. Salmon and G. Bidan, *J. Electrochem. Soc.*, 1985, **132**, 1987.
- 9 M. Lemaire, D. Delabouglise, R. Garreau, and J. Roncali, in Proceedings of ISEOS, Kurashi, Japan, Oct. 31—Nov. 3, 1986.
- 10 K. Tamao, S. Kodama, I. Nakajima, M. Kumada, A. Minato, and K. Suzuki, *Tetrahedron*, 1982, **38**, 3347.
- 11 F. C. Whitmore and J. H. Olewine, *J. Am. Chem. Soc.*, 1938, **60**, 2569.
- 12 G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst.*, 1978, **48**, 37.
- 13 Such potentials have been previously employed in the synthesis of pyrrole-based polymer gas sensors: J. J. Miasik, A. Hooper, P. T. Moseley, and B. C. Tofield in ref. 1, p. 189.
- 14 J. C. W. Chien, 'Polyacetylene: Chemistry, Physics, and Material Science,' Academic Press, 1984.
- 15 Y. Soma, M. Soma, Y. Furukawa, and I. Harada, *Clays Clay Miner.*, 1987, **35**, 53.
- 16 The mixture of alkyl substituted pyrroles was prepared from the reaction of pyrrolylmagnesium iodide and (2): P. S. Skell and G. P. Bean, *J. Am. Chem. Soc.*, 1962, **84**, 4660.