

Poly(2,5-thienylene-1,2-dimethoxy-ethenylene): synthesis and characterization

L. Peeters, W. Eevers, M. Van Der Borgh, S. Jacobs and H. J. Geise*

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium
(Received 11 June 1993)

The synthesis of poly(2,5-thienylene-1,2-dimethoxy-ethenylene) is reported. It involves a benzoin condensation of thiophene-2,5-dicarboxaldehyde, followed by deprotonation by a Schlösser base and oxymethylation by dimethyl sulfate. The new polymer, soluble in organic solvents, has a molecular weight, M_w , of 5500 dalton, an optical band gap of 2.13 eV and a conductivity of 0.4 S cm^{-1} upon iodine doping.

(Keywords: poly(thienylene vinylene); synthesis; conducting polymer)

Polymers that combine a high degree of conjugation with a high degree of substitution are of interest, because they may combine semiconductivity with solubility. Several alkyl-substituted poly(thiophene)s have been reported to be soluble, highly conducting and environmentally stable on acceptor doping¹. This stabilizing effect can be increased by incorporating alkoxy substituents on the conjugated system. At the same time, these electron-donating substituents can reduce the band gap and the ionization potential such that it becomes possible to dope the polymers with milder oxidizing reagents².

The objective of the research communicated here is the synthesis of a soluble, stable and well-characterized poly(thienylene vinylene) (PTV), dimethoxy-substituted on the vinylene linkages. The synthetic route chosen is shown in Scheme 1. This communication gives the initial results of this project.

Thiophene-2,5-dicarboxaldehyde (I) was prepared according to the procedure of Feringa *et al.*³. Using benzoin condensation, the monomer (I) was polymerized to the precursor polymer poly(2,5-thienylene-1-oxo-2-hydroxy-ethylene) (II)⁴. In order to prevent the Cannizzaro side reaction, the polymerization time was limited⁵ to 3 h. Then a solution of the polyacyloin precursor (II) in dimethylsulfoxide was added at 0°C to a Schlösser base^{6,7} to obtain the polydianion (III). The temperature of this black suspension was raised from 0°C to room temperature before freshly distilled dimethyl sulfate was added dropwise. The mixture was stirred for 15 h at room temperature and then concentrated on a rotary evaporator to a syrup, which was poured into water under stirring to give an oily precipitate. After purification by dropwise addition to a stirring hexane solution, the pure polymer could be dissolved in chloroform from which films of IV could be cast.

The dark brownish colour of IV before doping (optical band gap, $E_g = 2.13 \text{ eV}$), and its conductivity of 0.4 S cm^{-1} after doping with iodine, clearly indicate that in spite of the large substituents, the polymer is conjugated. However, comparison of the band gap energy to those of unsubstituted PTV (Wittig PTV, 2 eV (ref. 8); soluble precursor PTV, 1.7 eV (ref. 2)) indicates that

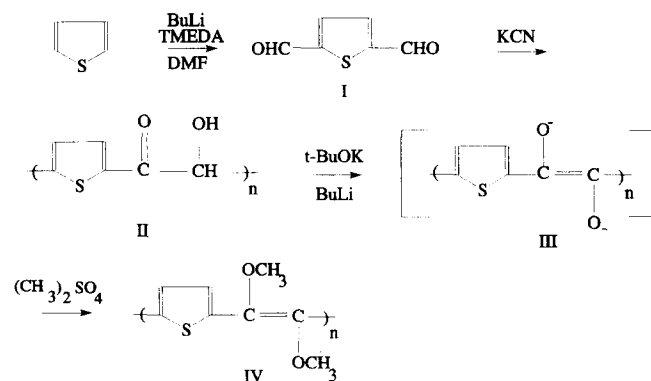
dimethoxylation allows less extensive conjugation than in unsubstituted PTV, presumably due to increased steric interactions. Despite its lower effective conjugation, the conductivity ($\sigma = 0.4 \text{ S cm}^{-1}$) of iodine-doped IV is high compared to that of iodine-doped Wittig-synthesized PTV⁹ ($\sigma = 9 \times 10^{-5} \text{ S cm}^{-1}$), probably due to the fact that IV was doped as a film and the Wittig PTV as a pressed pellet. On the other hand, the conductivity of iodine-doped IV is low compared to that of an iodine-doped PTV film synthesized via the soluble precursor route¹⁰ ($\sigma = 230 \text{ S cm}^{-1}$).

Polymer IV is soluble in chloroform, dimethylformamide, acetone, methanol, diethylether and nitromethane, but not in apolar solvents, e.g. hydrocarbons.

Thermogravimetric FTi.r. experiments showed IV to be stable up to 150°C, after which methanol splits off.

Gel permeation chromatographic measurements on solutions of IV in tetrahydrofuran, using low-molecular-weight polystyrene standards for calibration, show that the degree of polymerization varies between 6 and 37 ($M_n = 1010$; $M_w = 5548$; degree of polydispersion, $P_d = 5.4$) which is comparable to values found for poly(1,4-phenylene-1,2-dimethoxy-ethylene)⁴, synthesized via the same route.

The polymeric product was examined by diffuse reflection Fourier transform (DRIFT) i.r. spectroscopy, showing bands at 3093, 1520 and 1447 cm^{-1} caused by the thiophene ring and signals at 1070, 1100 and



Scheme 1

* To whom correspondence should be addressed

1279 cm^{-1} originating from the presence of the O-CH₃ ether bonds.

In spite of certain limitations, this class of conducting polymers promises to combine convenient processing and environmental stability with the mechanical properties needed for applications.

References

- 1 Jen, K.-Y., Miller, G. G. and Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* 1986, 1346
- 2 Eckhardt, H., Shaklette, L. W., Jen, K.-Y. and Elsenbaumer, R. L. *J. Chem. Phys.* 1989, **91**, 1303
- 3 Feringa, B. L., Hulst, R., Rikers, R. and Brandsma, L. *Synthesis* 1988, 316
- 4 Kaul, S. N. and Fernandez, J. E. *Macromolecules* 1990, **23**, 2875
- 5 Eevers, W., Peeters, L. and Geise, H. J. *Bull. Soc. Chim. Belg.* 1993, **102**, 141
- 6 Schlösser, M. and Strunk, S. *Tetrahedron Lett.* 1984, **25**, 741
- 7 Hartmann, J., Muthukrisnan, R. and Schlösser, M. *Helv. Chim. Acta* 1974, **57**, 2261
- 8 Geens, R. PhD thesis, University of Antwerp, UIA, Belgium, 1988 (in Dutch)
- 9 Wouters, F. PhD thesis, University of Antwerp, UIA, Belgium, 1988 (in Dutch)
- 10 Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Polym. Commun.* 1987, **28**, 229