

Synthesis of new conjugated thiophene polymers

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Abstract

Results are presented which explore the synthesis, characterization and photoluminescence of new types of conjugated copolymers which incorporate fused thiophene units. Such materials possess intense purple–red colours and some absorb in the near-infrared. The redox processes showed that the polymers were both p- and n-dopable.

Keywords: Synthesis; Thiophene; Photoluminescence

1. Introduction

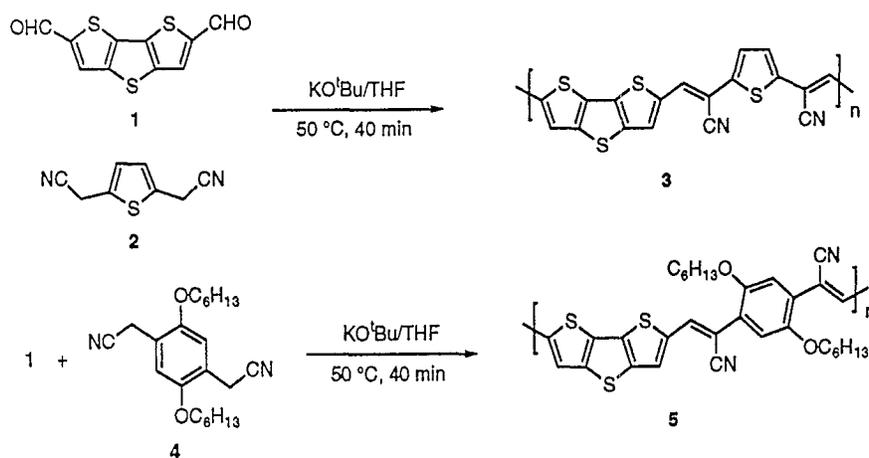
Currently, polythiophene and thiophene oligomers are at the forefront of technological importance [1,2]. Ring-fused systems of linearly condensed thiophenes have rigid planar structures which favour high exciton mobilities, which are considered very important for the future application of electroactive materials.

The HOMO–LUMO energies of organic conjugated systems can be fine-tuned to optimize the energy conversion from sunlight, ideally over the entire visible range, up to 1000 nm. Such materials will have importance for the fabrication of photocells and in the area of xerography where there is a

large market for infrared-sensitive materials for diode laser printers [3].

2. Results and discussion

The preparation of dithieno[3,2-*b*:2,3'-*d*]thiophene-based copolymers was carried out using the Knoevenagel base condensation (Scheme 1). The dialdehyde **1** was selected for condensation with the dinitriles **2** and **4**. Substitution with either long chain alkyl or alkoxy groups is necessary for solution processability of these polymers.



Scheme 1. Polymer synthesis via the Knoevenagel condensation reaction.

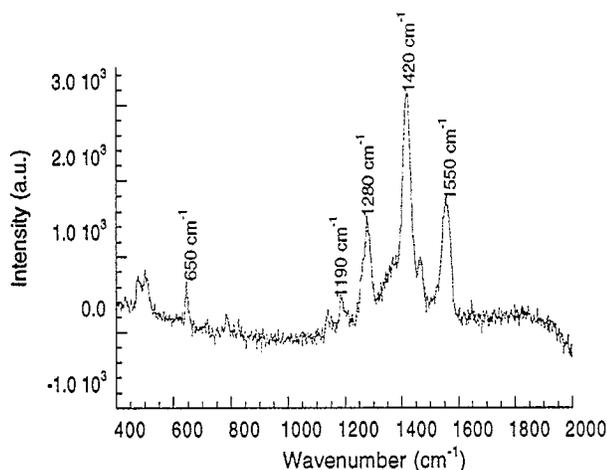


Fig. 1. Raman spectrum of polymer 3.

The polymers **3** and **5** were obtained as purple solids with HOMO–LUMO onsets of around 1.8–2.0 eV, as measured by the UV–Vis absorption spectrum. Gel permeation chromatography (GPC) against polystyrene revealed an M_w of about 20 000 and M_n about 13 000, polydispersity 1.53, corresponding to about 24 subunits of **3**. Polymer **5** had a lower mass, M_w of 13 500 and M_n of 8600, polydispersity 1.57, corresponding to about 18 subunits of **5**. The ^1H NMR spectrum for **3** revealed the vinylene proton as a singlet at δ 8.01 ppm, the two β dithienothiophene protons at δ 7.67 ppm, and the thiophene proton at δ 7.13 ppm.

The infrared spectra displayed the characteristic weak CN stretching frequency at 2284 cm^{-1} . The α -linkage of the thiophenes can be identified by a characteristic strong absorption band at 806 cm^{-1} corresponding to a $\text{C}_\beta\text{--H}$ out-of-plane vibration. The bands at 1425 and 1471 cm^{-1} are assigned to the overlap of the $\text{C}=\text{C}$ antisymmetric and symmetric stretching vibration bands of the thiophene ring. These assignments are based on the reports of Furukama et al. [4] for thiophene oligomers and polythiophenes. The Raman spectrum (Fig. 1) displays three modes at 1550 , 1475 and 1420 cm^{-1} ; the former is assigned to $\text{C}=\text{C}$ vinylene stretching and the latter two assigned to $\text{C}=\text{C}$ ring stretching. The band at 1280 cm^{-1} is associated with a vinylene C--H bending. The weak bands at 1190 and 1140 cm^{-1} are probably due to C--C inter-

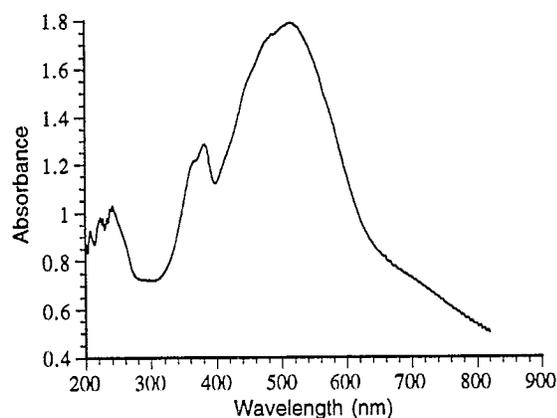


Fig. 2. UV–Vis absorption spectrum of polymer 3.

ring stretching. Further weak bands are seen at 790 and 650 cm^{-1} which are assigned to C--S--C ring deformation modes. The assignments are based on the Raman study of oligothiophenes, reported by Louarn et al. [5].

The UV–Vis absorption spectrum for **3** is shown in Fig. 2; a similar spectrum was obtained for polymer **5**. The peak in the UV region at about 250 nm can be assigned to the $\pi\text{--}\pi^*$ transition of the thiophene rings and is characteristic of all thiophenes. The peak at 382 nm is probably due to the $\pi\text{--}\pi^*$ transition of the dithienothiophene moiety. The peak in the visible region is assigned to the $\pi\text{--}\pi^*$ bandgap transition. The photoluminescence (PL) emission spectrum revealed a shoulder at 470 nm which is due to a localized emission from the fused thiophene rings. A broad peak was also observed between 750 and 900 nm . Although the conductivity of **3** increased by two orders of magnitude when exposed to oxygen, it proved to be neither photoconductive nor photovoltaic.

2.1. Cyclic voltammetry

The advantage of using cyclic voltammetry is that direct information can be gained about the relative position of the LUMO and HOMO energy levels. Such results are important and can determine the choice of cathodic or anodic materials used in diode device manufacture. The electrochemical experiments were performed with a prototype Oxford Instruments potentiostat. A three-electrode cell was used, comprising a Ag/AgNO_3 reference, a platinum mesh counter electrode jacketed in a glass tube and a working platinum disc electrode of effective area 0.38 cm^2 . The acetonitrile solvent was purified by distillation from CaH_2 under an atmosphere of argon and the tetrabutylammonium-perchlorate electrolyte was dried in vacuum at 60°C . A series of thin films about $0.5\text{ }\mu\text{m}$ thick was drop cast from chloroform solution onto the platinum disc. Before each experiment the solution/electrolyte was purged with dry argon for 15 min. The scan rate used was 20 mV s^{-1} .

A semi-reversible oxidation trace with very broad peaks is shown in Fig. 3 for polymer **5**. The two oxidation peaks can be assigned to the p-doping process which represents the

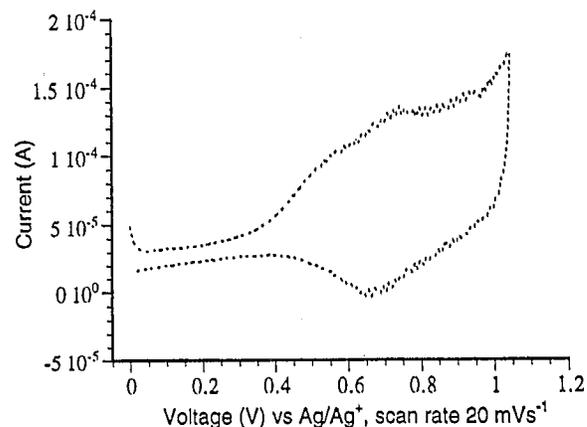


Fig. 3. Cyclic voltammogram of polymer **5** (oxidation cycle) in $\text{MeCN}/(\text{Bu})_4\text{NClO}_4$.

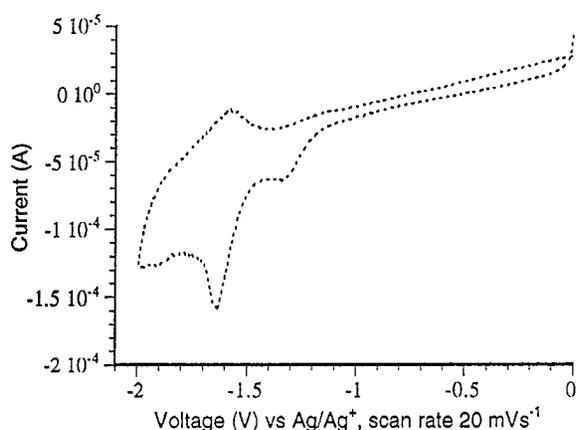


Fig. 4. Cyclic voltammogram of polymer **5** (reduction cycle) in MeCN/ $(\text{Bu})_4\text{NClO}_4$.

successive generation of cation and dications; the process proved reversible for the duration of the experiment (five cycles). The n-doping process of the polymer is shown in Fig. 4 which indicates that the polymer undergoes two subsequent one-electron reductions, which are not fully reversible. The n-doping process is usually found in polythiophenes at $E^0 \approx -2$ V versus Ag/Ag^+ [1]. The first reduction wave is assigned to the reduction of the dithienothiophene moiety, as it occurs roughly in the same position as that for polymer **3**. The electrochemical HOMO–LUMO gap is estimated as 1.66 eV.

3. Experimental

A modified literature procedure was used to prepare dithieno[3,2-*b*:2',3'-*d*]thiophene [6]. Dithieno[3,2-*b*:2',3'-*d*]thiophene-2,6-dicarboxaldehyde [7] was prepared by a literature procedure. The dinitrile monomers (**2** and **4**) have been reported in a previous publication [8,9].

3.1. Preparation of polymer **3**

To a stirred solution of the dialdehyde **1** (44 mg, 0.17 mmol) and 2,5-biscyanomethyl-4-dodecylthiophene **2** (58 mg, 0.17 mmol) in dry THF (2 ml) and *t*-butanol (2 ml) in an inert atmosphere was added KO^tBu (5 mg). The yellow suspension immediately turned dark red–purple and stirring was continued for 40 min. The reaction was cooled to room temperature, and methanol was added. The precipitate was filtered and washed with methanol. The purple solid was collected and re-dissolved in chloroform, filtered to remove insoluble material, and methanol was added to the filtrate to re-precipitate the solid which was dried thoroughly in vacuo (41 mg, 44%). λ_{max} (CHCl_3 , nm): 382, 515, 700 sh. λ_{max}

(thin film, nm): 520 (680 absorption onset). PL emission spectrum, λ_{max} (nm): 470, 800–900, 950 sh. δ_{H} (200 MHz, CDCl_3): 0.8–1.65 (23H, m), 2.47 (2H, m), 7.13 (1H, s), 7.67 (1H, s), 8.01 (1H, s). ν_{max} (cm^{-1} , KBr): 2284, 1651, 3019, 2976. Raman, ν_{max} (cm^{-1}): 1550, 1475, 1420, 1280, 1190, 650. GPC (CHCl_3 , detector wavelength 515 nm, Da): M_n 13 000, M_w 20 000, polydispersity 1.53.

3.2. Preparation of polymer **5**

Polymer **5** was prepared in a similar way to **1** (44 mg, 0.17 mmol) and **4** (56 mg, 0.17 mmol). The solid was dried thoroughly in vacuo (52 mg, 60%). λ_{max} (CHCl_3 , nm): 505, 630 sh. λ_{max} (thin film, nm): 398, 516 (700 absorption onset). δ_{H} (200 MHz, CDCl_3): 0.8–1.85 (23H, m), 3.8 (3H, s), 4.03 (2H, m), 6.91 (1H, s), 6.8 (1H, s), 7.96 (s, 1H), 7.73 (2H, s). GPC (CHCl_3 , detector wavelength 505 nm, Da): M_n 8600, M_w 13 500, polydispersity 1.7.

4. Conclusions

New types of highly coloured polymers have been synthesized via the Knoevenagel polymerization reaction. Weight average masses of some of the materials were in the region of 20 000, and the onset of absorption was in the near-infrared. A device has been fabricated for polymer **3**. However, it was neither photovoltaic nor photoconductive. Redox studies of the polymers showed that they were both p- and n-dopable.

Acknowledgements

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