

# Synthesis and solid-state polymerization of a diacetylene containing a tetrathiafulvalene group

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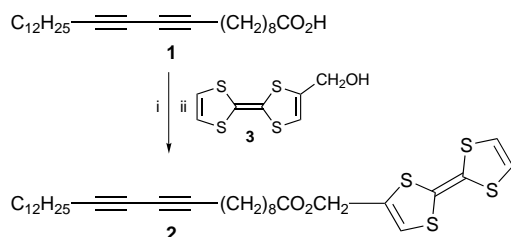
**A diacetylene containing a tetrathiafulvalene substituent has been synthesized and can be readily polymerized in the solid state to yield a novel polydiacetylene.**

Polydiacetylenes (PDAs), which are highly regular conjugated polymers produced by solid-state polymerization, have been attracting much attention because of their electrical transportation and third-order nonlinear optical properties.<sup>1</sup> We have investigated the synthesis of PDAs having aromatic<sup>2</sup> and alkynyl groups,<sup>3</sup> and heteroatoms<sup>4</sup> directly bound to *sp*<sup>2</sup> carbons of the conjugated main chain in order to modulate the electronic structures and thereby modify the electrical and optical properties. Meanwhile, tetrathiafulvalene (TTF) and analogous derivatives are also of interest because they have large electron-donating properties and form highly conductive charge-transfer complexes, which in some cases can be superconducting. Therefore we designed a PDA, obtained by solid-state polymerization, with TTF moieties contained in the side groups. Such a molecular design would have both a conjugated polymer main chain and electron-donating side chains. However, the incorporation of TTF units into the side chains of PDAs has been essentially unexplored so far.<sup>5</sup> Here we report the first example of a PDA derivative containing TTF groups in the substituents.

The monomer **2** of PDA was prepared in two steps as shown in Scheme 1. 4-(Hydroxymethyl)tetrathiafulvalene **3**<sup>6</sup> was used as a building block for TTF. Treatment of pentacos-10,12-diyonic acid **1** with oxalyl chloride in CH<sub>2</sub>Cl<sub>2</sub> quantitatively afforded the corresponding acid chloride. Addition of the acid chloride of **1** to a CH<sub>2</sub>Cl<sub>2</sub> solution of hydroxymethyl-tetrathiafulvalene **3** with triethylamine at room temperature gave the diacetylene derivatives **2**<sup>‡</sup> in poor yield (<10%). However, the condensation reaction proceeded more smoothly to give **2** in 80% yield when 4-dimethylaminopyridine was used as base at 40 °C.<sup>7</sup>

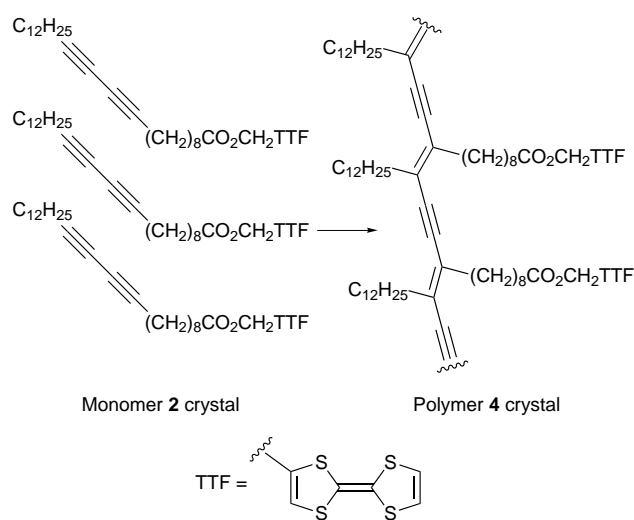
The redox behaviour of monomer **2** was investigated by cyclic voltammetry. (electrolyte Bu<sub>4</sub>NPF<sub>6</sub>, vs. SCE, in MeCN at 25 °C) The monomer **2** exhibits two quasi-reversible redox couples at approximately *E*<sup>1/2</sup><sub>1</sub> +0.30 and *E*<sup>1/2</sup><sub>2</sub> +0.67 V, redox behaviour typical of the TTF system.<sup>7</sup>

The colour of the bulk crystals of monomer **2** changed to dark blue from light yellow after exposure to UV with a low-pressure mercury lamp (4 W) or <sup>60</sup>Co γ-ray irradiation. This indicated



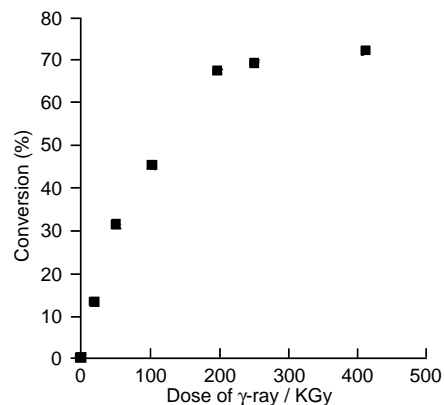
**Scheme 1** Reagents and conditions: i, (COCl)<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, room temp., 3 h; ii, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, reflux, 12 h

clearly that the crystal structures of the monomers were suitable for solid-state polymerization, proceeding via 1,4-addition as shown in Scheme 2.<sup>1</sup>



**Scheme 2**

A detailed study of the solid-state polymerization of monomer **2** stimulated by <sup>60</sup>Co γ-ray irradiation (dose rate *ca.* 9.8 KGy<sup>-1</sup>) was achieved by gravimetry after extraction of the unreacted monomer using benzene, the polymer being insoluble in this solvent, as shown in Fig. 1. The polymer content of the crystals increased with the γ-ray dose up to 250 KGy, to about 72% conversion. However, the rate of polymerization became slow for doses in excess of 250 KGy. This polymerization curve for the monomer **2** is similar to that reported for nonadeca-2,4-diyonic acid<sup>8</sup> and tricos-10,12-diyonic acid.<sup>9</sup>



**Fig. 1** Time-conversion curve for solid-state polymerization of diacetylene **2** induced by <sup>60</sup>Co γ-ray irradiation

The decoupled magic angle cross-polarised solid-state high resolution  $^{13}\text{C}$  NMR spectrum of the reaction product after a 500 KGy radiation dose was measured at 50.2 MHz. The spectrum is consistent with the chemical structure of polymer **4** shown in Scheme 2. In particular, the carbon signals at  $\delta$  102 and 130 correspond to the acetylenic and alkenic carbons of the conjugated backbone of the polymer **4**, respectively, and are comparable to those found in poly(dodeca-5,7-diyne-1,12-diol bis{[(butoxycarbonyl)methyl]urethane}) in the red phase.<sup>10</sup>

By X-ray diffraction techniques it was established that polymer **4** produced by 500 KGy radiation is still similar in crystal structure to monomer **2**.

In conclusion, a novel diacetylene containing a TTF moiety was synthesized and subsequently polymerized in the solid state to yield a novel PDA with TTF groups located in the polymer side chains. Investigations into the physical properties of this PDA are in progress.

#### Footnotes

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‡ Compound **2** gave satisfactory analytical and spectral data. *Selected data* for **2**: light yellow crystals, mp 52 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.81 (t, 3 H,  $J$  6.7 Hz), 1.19–1.29 (m, 32 H), 2.17 (t, 4 H,  $J$  6.7 Hz), 2.27 (t, 2 H,  $J$  7.5 Hz), 4.74 (s, 2 H), 6.24 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  14.11, 19.18, 22.67, 24.78, 28.28, 28.33, 28.73, 28.83, 28.97, 29.03, 29.08, 29.32, 29.46, 29.61, 29.68, 31.89, 33.99, 60.55, 65.19, 65.26, 77.43, 77.59, 111.66, 118.94, 119.06,

131.25, 173.18; Calc. for  $\text{C}_{32}\text{H}_{46}\text{O}_2\text{S}_4$ : C, 65.04; H, 7.85; S, 21.70. Found: C, 65.08; H, 7.97; S, 21.20%.  $m/z$  (EI-MS)  $m/z$  590.2320 (calc. for  $\text{C}_{32}\text{H}_{46}\text{O}_2\text{S}_4$ , 590.2383).

#### References

- 1 H. Bassler, *Polydiacetylenes*, ed. H. J. Cantow, Springer Verlag, Berlin, 1984, p. 1.
- 2 H. Matsuda, H. Nakanishi, T. Hosomi and M. Kato, *Macromolecules*, 1988, **21**, 1238.
- 3 S. Okada, K. Hayamizu, H. Matsuda, A. Masaki, N. Minami and H. Nakanishi, *Macromolecules*, 1994, **27**, 6259 and references cited therein.
- 4 S. Shimada, A. Masaki, S. Okada and H. Nakanishi, *Nonlinear Opt.*, 1995, **13**, 57.
- 5 V. Y. Khodorkovsky, G. V. Tormos, O. Y. Neilands, N. V. Kolotilo and A. Y. Il'chenko, *Tetrahedron Lett.*, 1992, **33**, 973.
- 6 J. Garin, J. Orduna, S. Uriel, A. J. Moore, M. R. Bryce, S. Wegener, D. S. Yufit and J. A. K. Howard, *Synthesis*, 1994, **489**.
- 7 M. R. Bryce, W. Devonport and A. J. Moore, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1761.
- 8 B. Tieke and D. Bloor, *Makromol. Chem.*, 1981, **182**, 133.
- 9 B. Tieke, D. Bloor and R. J. Young, *J. Mater. Sci.*, 1982, **17**, 1156.
- 10 A. D. Nava, M. Thakur and A. E. Tonelli, *Macromolecules*, 1990, **23**, 3055.

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