MATERIALS CHEMISTRY COMMUNICATION

New π-conjugated polymers containing tetrathiafulvalene as the monomeric unit

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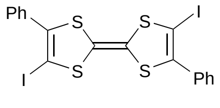
Four kinds of poly(arylene)- and poly(aryleneethynylene)-type polymers containing TTF units in the π-conjugated main chain, which are susceptible to chemical and electrochemical oxidation, have been prepared by organometallic polycondensation.

Tetrathiafulvalene (TTF) and its analogues have been the subject of many recent papers.[1] Molecular design of polymers containing TTF units has also been carried out,[1a,2] however, examples of polymers containing TTF units in the π-conjugated main chain have been limited. Here we report the preparation of new π-conjugated polymers containing TTF units in the π-conjugated main chain and the redox behavior of the polymers.

The Ni-[3] [eqn. (1)] and Pd-promoted[3a,4] [eqn. (2)] polycondensations and copolymerizations of monomers **1** and **2** with **3** give π-conjugated polymers **4**–**7** in high yields.



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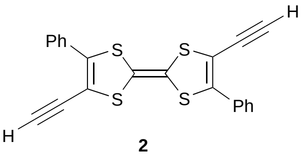

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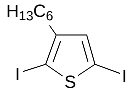

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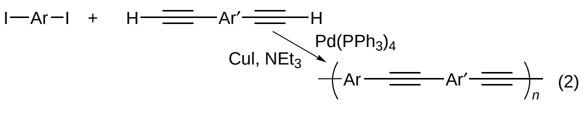
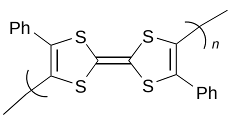
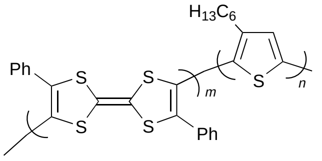
$$\mathrm{I{-}Ar{-}I} \xrightarrow{\mathrm{Ni(cod)_2}} \left(\mathrm{Ar}\right)_n \qquad (1)$$



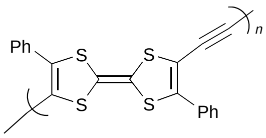
$$\mathrm{I{-}Ar{-}I} + \mathrm{H{-}C{\equiv}C{-}Ar'{-}C{\equiv}C{-}H} \xrightarrow[\mathrm{CuI,\ NEt_3}]{\mathrm{Pd(PPh_3)_4}} \left(\mathrm{Ar{-}C{\equiv}C{-}Ar'{-}C{\equiv}C}\right)_n \qquad (2)$$



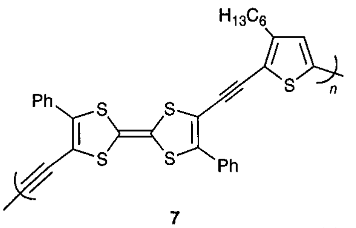
4 (λ_{max} = 430 nm)
hompolymer from **1** [eqn.(1)]



5
copolymer from **1** and **3** [eqn.(1)]



6 (λ_{max} = 502 nm)
polycondensation between **1** and **2** [eqn.(2)]



7
polycondensation between **2** and **3** [eqn.(2)]

The monomer **1** was prepared by lithiation of commercially available (Aldrich) diphenyl-TTF followed by treatment with perfluorohexyl iodide (62%). The precursor [*trans*-diphenylbis(trimethylsilylethynyl)-TTF] of **2** was prepared *via* reaction of **1** with trimethylsilylacetylene in the presence of $Pd(PPh_3)_4$ and CuI in THF–NEt_3 (1 : 1), and **2** was obtained by hydrolysis of the precursor with aqueous KOH. The *trans* structures of **1** and the precursor of **2** were confirmed by X-ray crystallography; details of the preparation of **1** and **2** will be reported elsewhere. The monomer **3** was prepared as previously reported.[3,4] IR spectra of the polymers are consistent with their assigned structures and peaks due to the C–I bond and terminal acetylenic unit of the monomers are not observed.

The nickel-promoted polycondensation proceeds smoothly using a mixture of bis(cycloocta-1,5-diene)nickel(0) [$Ni(cod)_2$] and 2,2′-bipyridyl (bpy) in DMF at 50 °C to yield **4** and **5** in 100 and 85% yields, respectively; the polymerization times were 48 and 24 h for **4** and **5**, respectively. The π–π* absorption peak of **4** in THF appears at 430 nm, which is at a longer wavelength by 40 nm compared with the absorption peak of monomer **1**. Elemental analysis data for **4** are consistent with the assigned structure. The copolymer **5**, obtained from a 1 : 1 mixture of **1** and **3**, exhibits a π–π* absorption peak at 410 nm in THF. The GPC trace for **5** gives M_n (number average molecular weight) and M_w (weight average molecular weight) of 4700 and 5800 (eluent, DMF; polystyrene standard), respectively, and **5** has an $[\eta]$ value of 0.17 dl g^{-1} in THF at 30 °C. The ^1H NMR spectrum of **5** in $CDCl_3$ is consistent with a 1 : 1 composition (m:n) of the copolymer: δ_H 0.86 (CH_3, s, 3H), 1.0–1.8 (CH_2, m, 8H), 2.53 and 2.78 (0.73 : 0.27) (α-CH_2, 2H) (the splitting of the α-CH_2 peak is considered to be due to the presence of both head-to-tail and head-to-head sequences), 6.8–7.6 (11H, aromatic H).

The palladium-promoted polycondensation also proceeds smoothly in a mixture of NEt_3 and THF at 60 °C to yield **6** and **7** in 93 and 100% yield, respectively, after 24 h. The homopolymer **6** is partly (about 60 wt%) soluble in THF, and the THF soluble part gives rise to an absorption peak at 502 nm, which is located at a longer wavelength by about 110 and 60 nm from the peak positions of monomers **1** and **2**, respectively. The larger bathochromic shift of **6** from the peak position of the monomer, compared with the bathochromic shift observed with **4**, is ascribed to effective expansion of the π-conjugation system in **6** due to the presence of the spacing C≡C group, which will ease the steric repulsion between the

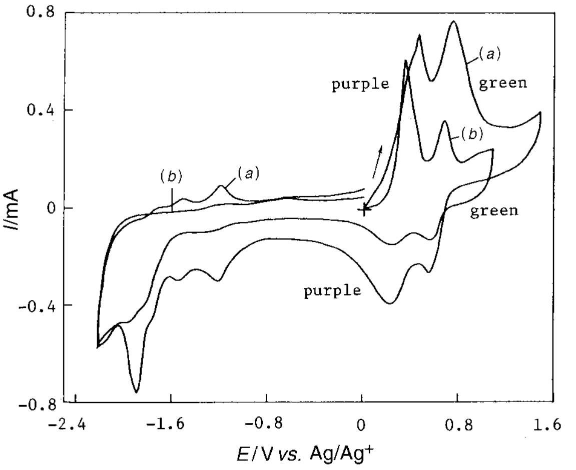


Fig. 1 Cyclic voltammograms of cast films of (*a*) polymer **6** and (*b*) polymer **7** (in an MeCN solution of 0.10 M $[NEt_4]BF_4$ at 200 mV s^{-1}). Both the polymer films exhibit essentially the same colour changes, shown in this figure.

TTF monomeric units. The THF soluble part of **6** shows M_n and M_w of 2320 and 4700, respectively, as determined by GPC (eluent, THF; polystyrene standard). The THF insoluble part of **6** exhibits an IR spectrum identical to that of the THF soluble part and is considered to have a higher molecular weight. The powder X-ray diffraction chart of **6** shows clear peaks at 2θ (Cu-Kα) = 23.95, 27.09 and 31.90 °, supporting the suggested formation of a crystalline polymer with a regular repeating unit.

The copolymer **7** obtained from a 1 : 1 mixture of **2** and **3** is also partly (about 60–80 wt%) soluble in THF, and the THF soluble part gives an absorption peak at 495 nm in THF. The THF soluble part shows an $[\eta]$ value of 0.39 dl g^{-1} in THF at 30 °C, and its light scattering analysis in 1,1,2,2-tetrachloroethane using an He-Ne laser at 632.8 nm gives an M_w value of 610 000. The ^1H NMR data for **7** are consistent with a 1 : 1 composition between the monomeric units: δ_H (CD_2Cl_2) 0.82 (CH_3, 3H), 1.08 (CH_2, 6H), 1.50 (β-CH_2 2H), 2.48 (α-CH_2, 2H), 6.82 (thiophene ring-H, 1H), 7.14 (*m*- and *p*-H of Ph, 6H), 7.67 (*o*-H of Ph, 4H).

All of the polymers are electrochemically active and their cast films give two-step oxidation peaks† at about 0.4 and 0.7 V *vs.* Ag/Ag$^+$, respectively, which are characteristic of TTF and its analogues,[1,2,5] although the oxidation peaks locate at fairly high potentials compared with those of other TTF derivatives. Poly(aryleneethynylene) type polymers $-Ar-C{\equiv}C-_n$ usually have electron-accepting properties due to the electron-withdrawing C≡C group,[4a] and the high oxidation potential reflects the electron-withdrawing effect of the C≡C group. Poly(aryleneethynylene) type polymers are ordinarily inert to electrochemical oxidation, even when they contain an electron-donating thiophene ring as the Ar unit.[4] However, due to the strong electron-donating ability of the TTF unit, polymers **6** and **7** are electrochemically active in the oxidation region, as depicted in Fig. 1. This is the first example of a poly(aryleneethynylene) type polymer which is active for electrochemical oxidation. The oxidation is also accompanied by a colour change, as depicted in Fig. 1. Neutral **6** and **7** are purple, and the colour of the films changes to green during the oxidation. The polymers **6** and **7** are also active in the reduction region, similar to other poly(aryleneethynylene) type polymers, and give several redox cycles in the reduction region.

Polymers **6** and **7** have electrical conductivities of 2.1×10^{-7} and 8.5×10^{-8} S cm^{-1}, respectively, as measured on compressed powders. Oxidation with iodine raises the electrical conductivities of 4.7×10^{-3} and 2.7×10^{-4} S cm^{-1}, respectively, at 300 K. The electrical conductivity (σ) of 4.7×10^{-3} S cm^{-1} for the iodine adduct of **6** (I/monomer unit = 1.67) at 300 K varies with changes of temperature following eqn. (3)

$$\sigma = 3\times10^{-3}\exp(-95T^{-0.25}) \qquad (3)$$

over a temperature range of 100–300 K. In contrast to polymers **6** and **7**, poly(aryleneethynylene) type polymers do not usually undergo chemical oxidation with iodine.[4]

Polymer **6** seems to be partly oxidized in air and gives an EPR signal at $g = 2.0081$ with a peak-to-peak line width ΔH_{pp} of 1.44 mT and a spin concentration of 3.2×10^{18} g^{-1} in air. Oxidation with iodine leads to an increase in the spin concentration and causes broadening of the EPR signal. For example, the iodine adduct of **6** (I/monomer unit = 0.85) gives rise to a symmetrical and very broad EPR signal at $g = 2.014$ with a ΔH_{pp} value of 14.2 mT and a spin concentration of 9.6×10^{18} g^{-1}. The marked broadening of the signal suggests coupling of the radical species with many H nuclei due to moving of the radical species over a wide range. Polymer **5** also shows a very broad EPR signal upon oxidation with iodine. As described above, **6** is crystalline, however, the iodine doped sample of **6** is not crystalline as proved by powder X-ray crystallography, and the adduct may contain *cis*-TTF units in addition to the *trans*-TTF units since *trans–cis* isomerization of a TTF derivative *via* a cationic species of the TTF derivative has been reported.[6]

As described above, new π-conjugated polymers containing the highly electron-donating TTF unit can be prepared *via* organometallic polycondensation. Among the polymers, the poly(aryleneethynylene) type polymers **6** and **7** have well-expanded π-conjugation systems due to C≡C spacer groups, and they are active for both chemical and electrochemical oxidation even when containing strongly electron-withdrawing C≡C groups.

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References

1 *E.g.* (*a*) G. Schukat, A. M. Richter and E. Fanghänel, *Sulfur Rep.*, 1987, **7**, 155; (*b*) T. Otsubo, Y. Aso and K. Takimiya, *Adv. Mater.*, 1996, **8**, 203; (*c*) N. L. Narvor, N. Robertson, T. Weyland, J. D. Killurn, A. E. Underhill, M. Webster, N. Svenstrup and J. Becher, *Chem. Commun.*, 1996, 1363.

2 (*a*) L. van Hink, G. Schukat and E. Fanghänel, *J. Prakt. Chem.*, 1979, **321**, 299; (*b*) M. R. Bryce, A. C. Chissel, J. Gopal, P. Kathirgamanathan and D. Parker, *Synth. Met.*, 1991, **39**, 397; (*c*) C. Thobie-Gautier, A. Gorgues, M. Jubault and J. Roncali, *Macromolecules*, 1993, **26**, 4094; (*d*) M. Fourmigue, I. Johannsen, K. Boubekeur, C. Nalson and P. Batail, *J. Am. Chem. Soc.*, 1993, **115**, 3752; (*e*) S. Frenzel, S. Arndt, R. M. Gregorious and K. Müllen, *J. Mater. Chem.*, 1995, **5**, 1529; (*f*) A. Charlton, A. E. Underhill, G. Williams, M. Kalaji, P. J. Marphy, D. E. Hibbs, M. B. Hursthous and K. M. A. Malik, *Chem. Commun.*, 1996, 2423.

3 (*a*) T. Yamamoto, *Prog. Polym. Sci.*, 1992, **17**, 1153; (*b*) T. Yamamoto, K. Sugiyama, T. Kushida, T. Inoue and T. Kanbara, *J. Am. Chem. Soc.*, 1996, **118**, 3930.

4 (*a*) T. Yamamoto, W. Yamada, M. Takagi, K. Kizu, T. Maruyama, N. Ooba, S. Tomaru, T. Kurihara, T. Kaino and K. Kubota, *Macromolecules*, 1994, **27**, 6620; (*b*) K. Sanechika, T. Yamamoto and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 752; *Polym. Prepr. Jpn.*, 1981, **30**, 160.

5 (*a*) V. Khodorkovsky, A. Edzifna and O. Neiland, *J. Mol. Electron.*, 1989, **5**, 33; (*b*) Y. N. Kreitsberga, A. S. Edzhinya, R. B. Kampare and O. Y. Neiland, *J. Org. Chem. USSR* (*Engl. Transl.*), 1989, **25**, 1312.

6 A. Souizi, A. Robert, P. Batail and L. Ouahab, *J. Org. Chem.*, 1987, **52**, 1610.

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† E_{pa} (1), E_{pc} (1), E_{pa} (2) and E_{pc} (2) *vs.* Ag/Ag$^+$ (in V) are: **4**: 0.27, 0.07 [E^0 (1) = (0.27 + 0.07)/2 = 0.17], 0.58 and 0.43 [E^0 (2) = 0.51]; **5**: 0.29, 0.15 [E^0 (1) = 0.22], 0.62 and 0.46 [E^0 (2) = 0.54] in an MeCN solution of 0.10 M $[NEt_4]BF_4$; for **6** and **7**, see Fig. 1.