Preparation of a new poly(arylacetylene) with a tetrathiafulvalene (TTF) unit in the side chain

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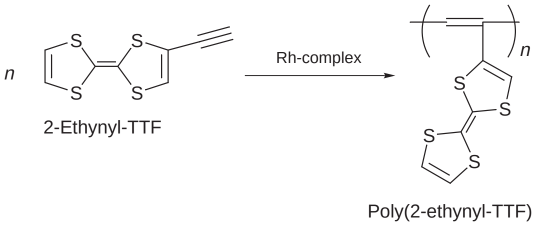
A new poly(arylacetylene) having a strongly electron donating unit, a tetrathiafulvalene (TTF) unit, in the side chain has been prepared by Rh-catalyzed polymerization, and optical, electrochemical and electric properties of the polymer have been revealed.

Tetrathiafulvalene (TTF) and its analogues have long attracted the attention of chemists because of their ability to form highly electrically conducting charge transfer (CT) complexes with electron acceptors.[1] Many efforts have been made to prepare polymeric materials of TTF in order to obtain mechanically tough CT adducts with a larger π-conjugation system, and preparation of π-conjugated polymers containing the TTF unit has been reported.[2] However, preparation of a poly(arylacetylene) containing the TTF unit in its side chain has not been reported. Recent synthesis of an acetylenic derivative of TTF, 2-ethynyl-TTF, by Otsubo *et al.*[3] has prompted us to carry out the polymerization of 2-ethynyl-TTF, and here we report the results of the polymerization and redox properties of the obtained polymer.

Polymerization of 2-ethynyl-TTF was carried out by using $[Rh(\mu\text{-}Cl)(\eta^4\text{-}nbd)]_2$ (nbd = norbornadiene), which is known as an active catalyst for polymerization of arylacetylenes, and NEt_3 as the cocatalyst [eqn. (1)].[4] Addition of PPh_3, for modification of the catalyst, was also carried out.



(1)

The polymerization of 2-ethynyl-TTF proceeds smoothly at room temperature and a dark-brown powder of poly(2-ethynyl-TTF) was obtained.† When the polymerization was carried out in neat NEt_3 without THF, insoluble polymer was obtained (Table 1, entry 1), although the IR spectrum of the polymer was essentially identical to those of polymers obtained in other runs. The insolubility of the polymer obtained in neat NEt_3 seems to arise from its very high molecular weight. It is reported that use of neat NEt_3, instead of other solvents, in the polymerization of phenylacetylene with the Rh catalyst leads to the formation of a polymer with a much higher molecular weight.[4c] On the other hand, carrying out the polymerization in THF (Table 1, entry 2) gave a soluble polymer having a number average molecular weight (M_n) of 11 700 in 47% yield at a high catalyst concentration of 41 mM. Lower concentration of the catalyst and shorter reaction time (entry 3) as well as addition of PPh_3 (entry 4) gave polymers with lower molecular weight. Since the Rh complex catalyst was inert over several days towards usual low molecular weight TTFs, occurrence of side reactions such as cleavage of the C–S bond of the monomer or the polymer by the catalyst was unlikely.

Table 1 Results of the polymerization of 2-ethynyl-TTF[a]

Entry	Solvent	Ligand added	Catalyst/ mM	*t*/h	Yield (%)	M_n[b]	M_w/M_n[b]
1	None	—	5	18	26	[c]	[c]
2	THF	—	41	2	47	11 700	1.23
3	THF	—	5	3	52	10 000	1.49
4	THF	PPh_3 (0.1 mM)	5	48	52	6 000	1.85

[a] Carried out in THF in the presence of NEt_3 (2.4 M) at room temperature except for entry 1 (in NEt_3). Concentration of 2-ethynyl-TTF = 0.21 M. Catalyst = $[Rh(\mu\text{-}Cl)(\eta^4\text{-}nbd)]_2$. [b] Determined by GPC (polystyrene standards; eluent = DMF containing 0.006 M LiBr). [c] Insoluble.

The obtained polymers in entries 2–4 of Table 1 were soluble in some polar solvents including Me_2SO and DMF. Fig. 1 compares IR spectra of 2-ethynyl-TTF and poly(2-ethynyl-TTF). The IR spectrum of the polymer exhibits absorption bands characteristic of the TTF unit (*e.g.* 775, 793 and 1432 cm^{-1}). However, the $\nu(C\equiv C)$ peak (at *ca.* 2100 cm^{-1}) and the $\nu(C\text{–}H)$ peak of terminal acetylene (at *ca.* 3250 cm^{-1}) observed with 2-ethynyl-TTF completely disappear after polymerization. Poly(2-ethynyl-TTF) is stable under N_2, however, it is gradually degraded under air. Fig. 1(c) shows the IR spectrum of the polymer after exposure to air for one month. The IR spectrum exhibits new absorption peaks, which are considered to originate from OH, OOH, epoxide, and/or ether groups formed by air-oxidation. Similar air-sensitive properties and IR changes have been reported for polyacetylene[5a,b] and an analogous polymer.[5c] No apparent change in colour of the polymer, however, was observed after one month.

The ^1H NMR spectrum of poly(2-ethynyl-TTF) in $(CD_3)_2SO$ showed only broad peaks in the range δ 6.2–6.9, similar to those of reported poly(arylacetylene)s such as poly(phenylacetylene).[6] The TTF and vinyl protons are considered to overlap

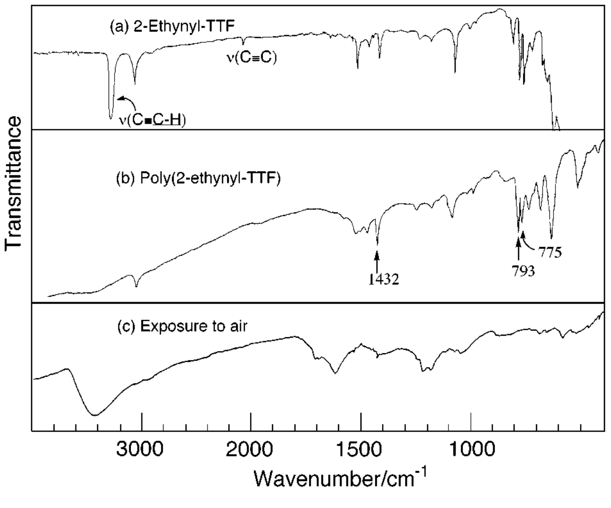


Fig. 1 IR spectra of (a) 2-ethynyl-TTF, (b) poly(2-ethynyl-TTF) (Table 1, entry 2) and (c) poly(2-ethynyl-TTF) after exposure to air for a month; (a) between NaCl crystal plates, (b) and (c) as KBr disks.

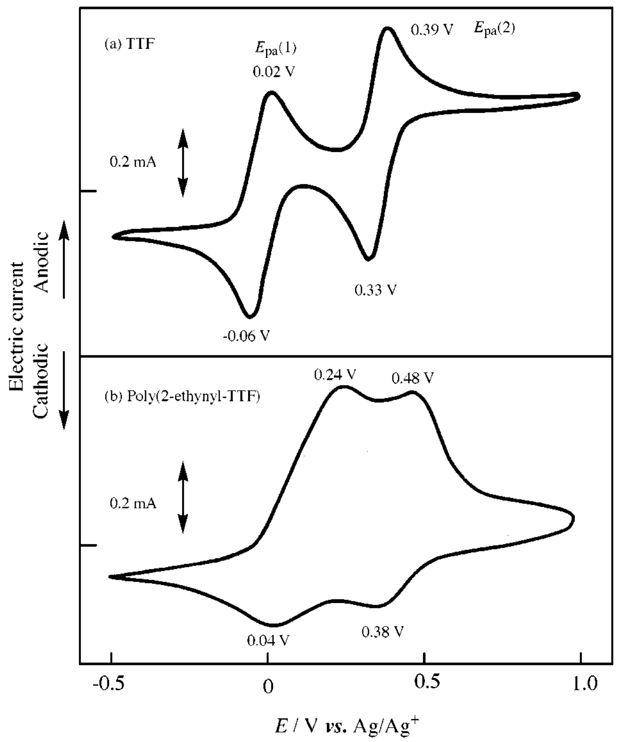


Fig. 2 Cyclic voltammograms of (a) TTF (0.10 M) and (b) poly(2-ethynyl-TTF) cast on a Pt plate (1× 1 cm) in an acetonitrile solution of $[NEt_4]BF_4$ (0.10 M). Scanning rate = 50 mV s^{-1}.

with each other to give the broad signal. The π–π* absorption band of the monomer at 395 nm disappeared after the polymerization, and poly(2-ethynyl-TTF) gives rise to a new broad absorption band at *ca*. 490 nm due to the expansion of the π-system.

Poly(2-ethynyl-TTF) is electrochemically active, and its redox behaviour has been followed by cyclic voltammetry with a film cast from a Me_2SO solution. As shown in Fig. 2(b), the cyclic voltammogram of the insoluble poly(2-ethynyl-TTF) film shows first and second E_{pa} values at 0.24 and 0.48 V *vs.* Ag/Ag$^+$ in MeCN solution containing 0.1 M $[NEt_4]BF_4$.

For TTF in solution, the two oxidation peaks, $E_{pa}(1)$ and $E_{pa}(2)$, are clearly separated with a potential difference, $E_{pa}(2) - E_{pa}(1)$, of 0.37 V [*cf.* Fig. 2(a)]. However, for the film of poly(2-ethynyl-TTF), the separation is not clear and the two peaks overlap with a smaller $E_{pa}(2) - E_{pa}(1)$ of 0.24 V. Similar differences between monomeric and π-conjugated polymeric compounds in their electrochemical redox processes have been reported for a two-step reduction of anthraquinone in a solution and π-conjugated poly(anthraquinone) in a film.[7] In Me_2SO containing 0.1 M $[NEt_4]BF_4$, both solutions of TTF and poly(2-ethynyl-TTF) give rise to $E_{pa}(1)$ and $E_{pa}(2)$ peaks at almost the same positions (0.11, 0.32 V and 0.14, 0.35 V, respectively, *vs.* Ag/Ag$^+$) although the anodic peaks of the polymer are also considerably broadened.

Poly(2-ethynyl-TTF) shows a low electrical conductivity of $< 1 \times 10^{-9}$ S cm^{-1}. The polymer reacts to give CT adducts with electron acceptors such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), tetrafluorotetracyanoquinodimethane ($TCNQF_4$), dichlorodicyanoquinone (DDQ), and iodine. The ν(C≡N) band of the electron acceptors is shifted to a lower frequency by 10–50 cm^{-1} upon adduct formation, similar shifts having been reported for the CT complexes of TTF with electron acceptors.[8] Among these adducts, the CT complex with TCNQ [poly(2-ethynyl-TTF) : TCNQ = 5 : 1 molar ratio] shows the highest electrical conductivity of 2.1×10^{-3} S cm^{-1} as measured on a compressed pellet of the adduct.

Notes and references

† Analytical data of poly(2-ethynyl-TTF). Calc. for $(C_8H_4S_4)_n$: C, 42.07; H, 1.77. Found: C, 42.28; H, 1.78%.

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