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Preparation of Poly(2,5-thienylene-vinylene) Film by Hydrogen Transfer Reaction

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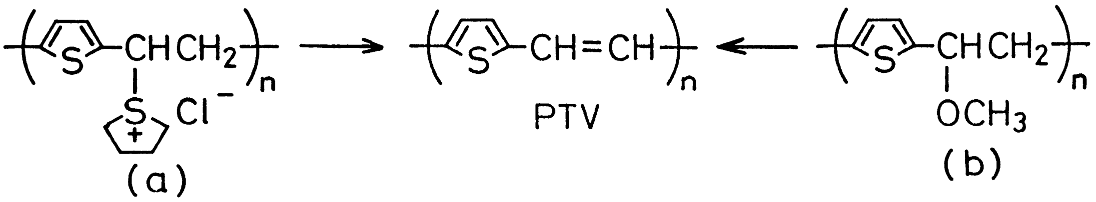
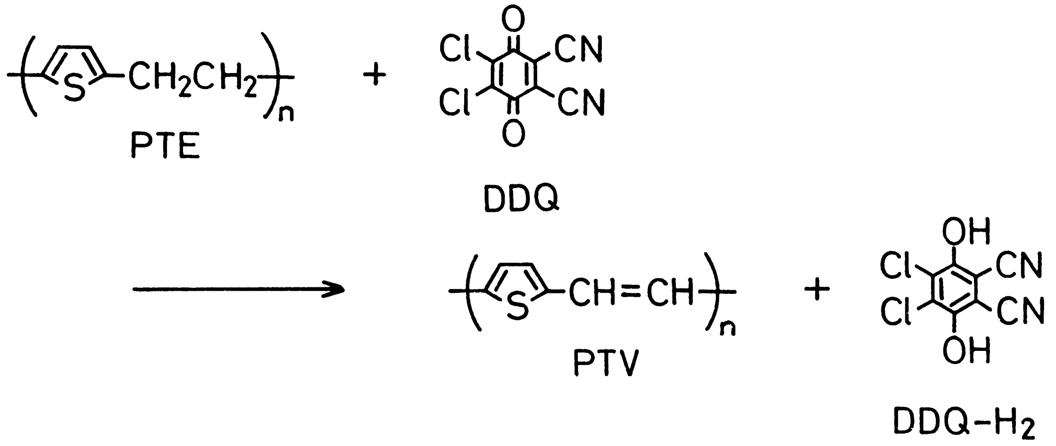
A tough film of fully conjugated poly(2,5-thienylene-vinylene) was successfully prepared by hydrogen transfer reaction in dioxane from poly(2,5-thienylene-ethylene) film obtained in the vapor deposition process with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as an oxidizing reagent.

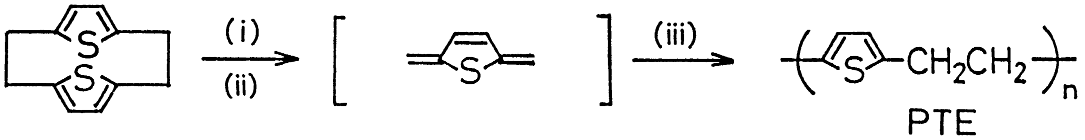
Poly(2,5-thienylene-vinylene) (PTV) with a fully conjugated structure has attracted great attention for its high electric conductivity. In 1970 Kossmehl et al.[1,2] first synthesized powder of PTV by the Wittig reaction of thiophene-2,5-dicarbaldehyde with (2,5-thiophenediyldimethylene)bis(triphenylphosphonium chloride). Fully conjugated polymers such as PTV[3-6] and polyacetylene[7] are intractable due to their nonfusibility and insolubility. Therefore a precursor route synthesis has been designed to provide a processibility for them. The precursor polymer is designed with somewhat modified structure which is tractable to shape a desired article and can be converted by thermal or simple chemical reaction into the conjugated structure. Jen et al.[4] synthesized PTV film according to this technique. The precursor of polyelectrolyte (a) was prepared in the reaction of 2,5-bis(tetrahydrothiophenium methyl)thiophene dichloride with base in water and cast from its aqueous solution into the film, which was then subjected to thermal degradation to give PTV. Murase et al.[5] and Yamada et al.[6] independently prepared PTV film using the precursor (b).



In this letter we report a new method for the preparation of PTV film by hydrogen tranfer reaction of poly(2,5-thienylene-ethylene) (PTE) with DDQ.



Recently we reported the preparation of PTE film in the vapor deposition process with [2.2](2,5)thiophenophane as a starting material.8) The film



(i) vaporizing : 100 °C
(ii) pyrolysis : 580 °C
(iii) deposition : 0 °C

obtained is tough and insoluble in conventional organic solvents such as acetone, chloroform, and tetrahydrofuran at room temperature but soluble in m-cresole at an elevated temperature of 180 °C, suggesting that it is a linear polymer.

DDQ (0.411 g, 1.8 mmol) as an oxidizing reagent was dissolved in dioxane (50 ml) and a piece of PTE film (0.165 g, 1.5 mmol) was added. The mixture was refluxed under nitrogen for 4 h. This reaction was carried out in liquid-solid phase. The film changed in color with reaction time from transparent to reddish black with golden lustre. Figure 1 shows the IR spectra of the films with various reaction times. It was found that two peaks at 2925 cm^{-1} and 2850 cm^{-1}, assigned to the CH_2 stretching, decrease in the reaction time of 10 min and disappear completely in 4 h. On the other hand, a new strong peak emerges at 935 cm^{-1}, assigned to the C-H out-of-plane bending of the trans vinylene. The IR spectrum of the film reacted for 4 h (Figure 1c) was the same to that of PTV reported by Murase et al.[5] (3060, 3010, 1760, 1590, 1430, 1260, 1240, 1120, 1030, 930, 800 cm^{-1}).

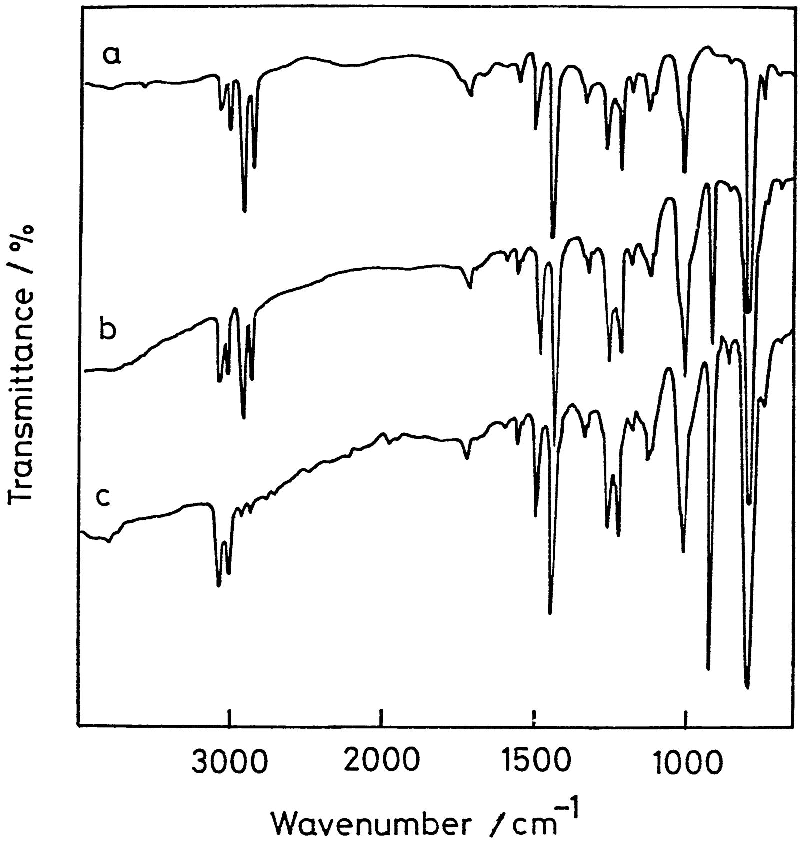


Fig. 1. IR spectra of the films with various reaction times.
(a) PTE
(b) 10 min
(c) 4 h

Then the reacted film was picked up from the reaction mixture and extracted for purification in a Soxhlet apparatus with dioxane for 3 h to give 0.177 g of the colored film. Its elemental analysis (Found: C, 63.1; H, 3.34; N, 1.03; S, 26.3%) corresponds with that of PTV containing 0.05 mol DDQ per monomer unit (Calcd for $[C_6H_4S]_{1.00}[C_8Cl_2N_2O_2]_{0.05}$: C, 64.3; H, 3.37; N, 1.17; S, 26.8%). It is conceivable that this amount of DDQ should be so strongly absorbed on PTV to combine chemically with it.

The residual reaction solution was kept at room temperature for 12 h to deposit 0.190 g of pale purple crystals (mp 262 °C (dec)[lit[9] 264 °C (dec) of

DDQ-H_2] ; Anal. Found: C, 41.8; H, 0.75; N, 12.3%. Calcd for $C_8H_2Cl_2N_2O_2$: C, 42.0; H, 0.88; N, 12.2%). Thus, it was concluded to be 2,3-dichloro-5,6-dicyano-hydroquinone (DDQ-H_2).

From the results of IR spectra, elemental analysis, and formation of DDQ-H_2, it is evidenced that fully conjugated PTV can be obtained by hydrogen transfer reaction of PTE film with DDQ in liquid-solid system.

The electric conductivity of the PTV film obtained was measured by a conventional four-probe d.c. technique with conducting carbon paste to be 0.2 S cm^{-1}. Yamada et al.$^{6)}$ reported that the conductivity of PTV without any dopant is below 10^{-13} S cm^{-1}. Thus, the DDQ contained in the film can be regarded to be effective as a dopant. This value of the conductivity was kept as constant for more than a month. On exposure to iodine vapor at room temperature (the film being containing 0.14 mol I_2 per monomer unit), the conductivity of the film increased up to 160 S cm^{-1}.

This process to obtain a tough PTE film in the vapor deposition method and to convert it into the highly conjugated PTV is believed to be a new advantageous method of preparing a tough PTV film.

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