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Synthesis of Poly(2,5-dimethoxy-p-phenylenevinylene) Film through a New Precursor Polymer

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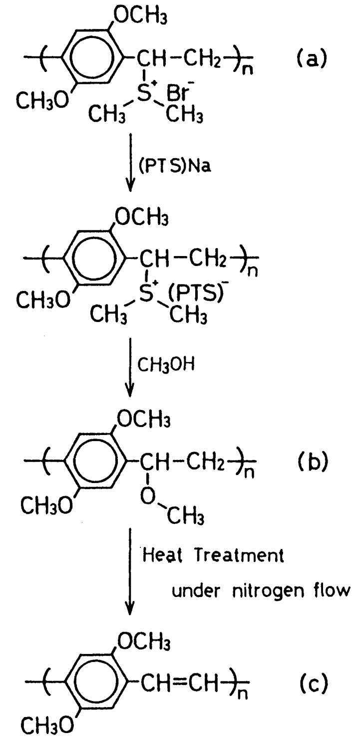
Poly(2,5-dimethoxy-p-phenylenevinylene) was synthesized through a new precursor polymer. The new precursor polymer was soluble in organic solvents and chemically stable at room temperature.

Poly(arylenevinylene) films have been synthesized by the sulfonium salt process;[1-3] thermal elimination reaction of precursor polymer films which were prepared by casting aqueous solutions of precursor sulfonium polyelectrolytes. Murase et al. reported the preparation of poly(2,5-dimethoxy-p-phenylenevinylene) (CH_3O-PPV) film via the sulfonium salt process and showed the films exhibited high conductivity of over 100 S/cm by iodine doping.[4] The aqueous solution of the precursor polymer of CH_3O-PPV, however, possesses the tendency to form gels, and the gradual elimination of sulfonium groups in the solid precursor polymer can not be avoided even at room temperature. The gel formation in the aqueous solutions and the lack of stability of the precursor polymer films greatly diminish the virtue of the precursor-route preparation of π-conjugated polymers.

Recently, we and Murase et al. have reported the synthesis of poly(2,5-thienylenevinylene)(PTV) film via a similar route to the sulfonium salt process.[5,6] In those cases, the leaving pendant group in the precursor polymer was not the sulfonium salt group but a methoxy group. The precursor polymer was soluble in organic solvents and highly processible. Moreover, no elimination of the methoxy group from solid precursor films occurred below 100 °C. Then, we started investigating the possibility of obtaining a new stable precursor polymer of CH_3O-PPV which had the methoxy leaving group.

In this letter, we report the new route for the synthesis of CH_3O-PPV films through a new-type of the precursor polymer which is soluble in organic solvents. Both the processibility and the stability of the precursor polymer of CH_3O-PPV have been markedly improved.

The sulfonium polyelectrolyte precursor of CH_3O-PPV was synthesized according to the sulfonium salt process. The monomer, 2,5-dimethoxy-p-xylylene bis(dimethyl sulfonium bromide) was caused to polymerize by mixing equal volumes of 0.05 M aqueous monomer solution and 0.05 M NaOH at 0 °C under nitrogen flow. After the reaction of 6 h, a pale yellow solution containing resulted sulfonium salt polymer was obtained. The reaction was quenched by the addition of hydrobromic acid. To the solution, the excess amount of p-toluene sulfonic acid sodium salt ((PTS)Na) was added giving a precipitate of the sulfonium salt polymer with the p-toluene sulfonic acid counter anion (See Scheme 1). The precipitate was dissolved in methanol and allowed to react with methanol at 20 °C. After 12 h stirring, a powdery precipitate was obtained. The precipitate was not soluble in water but soluble in organic solvents such as chloroform, tetrahydrofuran and dimethylformamide. It was purified by reprecipitation from chloroform solution into diethylether.



Scheme 1. New precursor route in CH_3O-PPV synthesis.

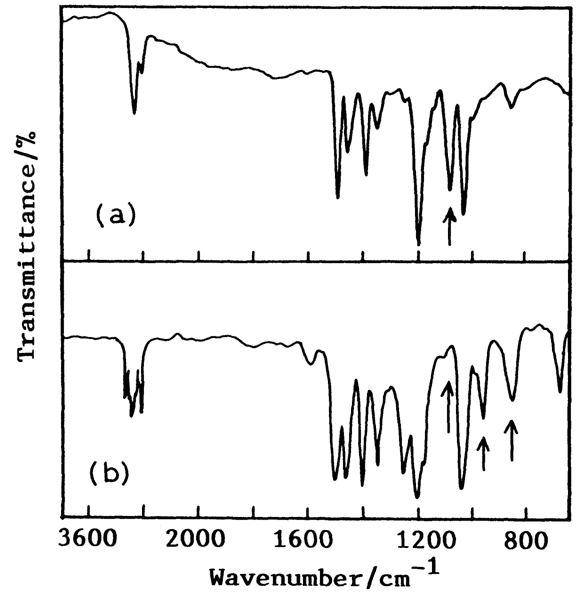


Fig. 1. Infrared spectra of (a) new precursor polymer film and (b) CH_3O-PPV film prepared at 200 °C.

The IR spectrum of the product indicated the presence of a methoxy group (O-C stretching at 1100 cm^{-1}) as shown in Fig.1(a). The ^1H-NMR ($CDCl_3$) spectrum showed signals at 3.2 ppm (methylene protons), 3.6 ppm (methyl protons of methoxy group) and 4.9 ppm (

methine proton). The IR spectrum, the ^{1}H-NMR spectrum and the elemental analysis (Found : H, 7.25% ; C, 67.61%. Calcd for ($C_9H_{14}O_3$) : H, 7.27% ; C, 68.02%) proved the structure of the precursor ((b) in Scheme 1).

The new methoxy-pendant precursor polymer was chemically much stable than the sulfonium salt precursor polymer. Improvement of solubility to organic solvents brought about excellent processibility of the precursor polymer; one can easily obtain free-standing dense polymer films by the conventional casting method and polymer thin films on appropriate substrates by the spin coating method from chloroform solutions.

A large endotherm peak associated with the elimination of methoxy groups from the precursor polymer was observed at around 170-210 °C in differential scanning calorimetry. Then, the elimination of methoxy groups was carried out by heating between 100 and 300 °C for 1 h under nitrogen flow. As we found that the acid catalysts such as hydrochloric acid were indispensable for the perfect elimination of methoxy groups and the formation of vinylene double bonds, the precursor polymer films were soaked in conc. hydrochloric acid for 2 h before heat treatments. As is shown in Fig. 1(b), the IR spectrum of the film treated at 200 °C gave the absorptions at 960 cm^{-1} and 700 cm^{-1} associated with trans and cis C=C linkages, respectively, and the absorption at 1100 cm^{-1} perfectly disappeared. The elemental analysis also gave the evidence that the precursor polymer was completely converted to CH_3O-PPV ; Found : H, 6.20%; C, 73.10%. Calcd for ($C_{10}H_{10}O_2$) : H, 6.21%, C, 74.06%. Wide angle X-ray diffraction pattern indicated that the CH_3O-PPV films have low crystallinity.

The UV absorption spectra of the precursor polymer film spin coated on silica glass substrates and those followed by heat treatments at various temperatures are shown in Fig. 2. The precursor polymer showed a small absorption at around 360 nm (3.4 eV),

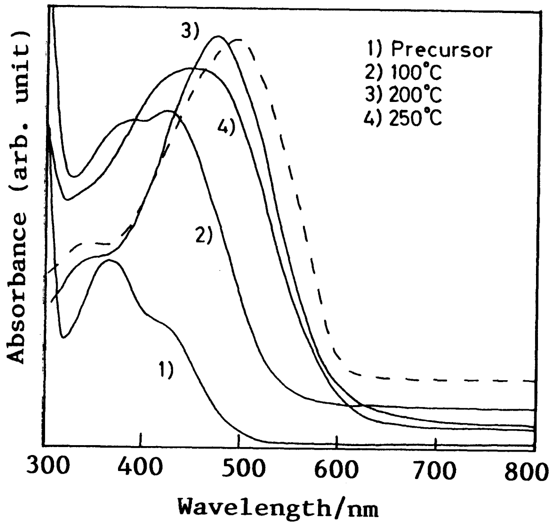


Fig. 2. Optical absorption spectra of (—) the thin films prepared via new precursor route and (---) CH_3O-PPV thin film prepared via conventional route.

while the films treated at above 100 °C exhibited large absorptions in the longer wavelength region. The longest peak wavelength, 470 nm (2.6 eV), which is attributable to $\pi - \pi^*$ transition was obtained in the CH_3O-PPV thin film prepared at 200 °C. This result was consistent with the results of the IR spectrum and the elemental analysis. The peak position of $\pi - \pi^*$ transition of the CH_3O-PPV prepared by the 200 °C treatment was close to that of the CH_3O-PPV film prepared via the sulfonium salt process as shown in Fig. 2.[7)]

The electrical conductivity of the CH_3O-PPV film at room temperature in a vacuum was 10^{-13} S/cm. By iodine doping, the conductivity increased up to ca. 50 S/cm that was little smaller than that in the CH_3O-PPV film prepared via the sulfonium salt process.

We are now performing more detailed characterization on aggregated structure and morphology of new CH_3O-PPV films in comparison with the films from the conventional sulfonium salt process.

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