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New Method for Preparation of Poly(phenylene-vinylene) Film

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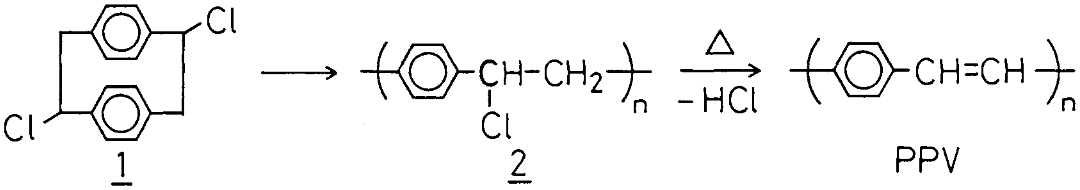
Poly(phenylene-chloroethylene) film was prepared by the vapor deposition polymerization of 1,9-dichloro[2.2]-paracyclophane and was converted into fully extended π-conjugated poly(phenylene-vinylene) by thermal dehydrochlorination at 300 °C under nitrogen for 1 h.

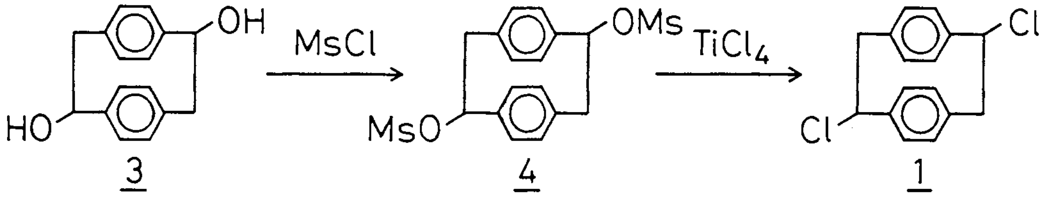
Fully extended π-conjugated systems have attracted special attention because of their practical application potential as electrical conductive and nonlinear optical materials. As one of the most promising conjugated systems poly(phenylene-vinylene) (PPV) was first synthesized as powder by Wittig reaction of p-xylylene bis(triphenylphosphonium chloride) with terephthalaldehyde,1) but it was difficult to process it due to its non-fusibility or insolubility in any solvents. Then, a smart procedure, referred to as a precursor route method, was invented to prepare PPV film. Water-soluble poly(p-xylylene α-diethylsulfonium bromide) was prepared by the reaction of p-xylylene diethylsulfonium bromide with a base in water and then it was cast into a film, which underwent thermal desulfonium reaction to give PPV film.2-4) This procedure was applied to the preparation of poly(2,5-thienylene-vinylene) (PTV) film.5-7) Meanwhile, we contrived another route for preparing PTV film using the vapor deposition process.8) [2.2](2,5)Thiophenophane underwent the vapor deposition process to give poly(2,5-thienylene-ethylene) film which was easily subjected to hydrogen transfer reaction with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to prepare PTV film.

Unsubstituted poly(phenylene-ethylene) (PPE) film obtained by means of the vapor deposition process 9) of [2.2]paracyclophane was hardly converted to PPV because it hardly underwent both thermal oxidation below its melting point (420 °C) and dehydrogenation by DDQ at 100 °C owing to its high thermal and chemical stability. Therefore, some modifications were carried out on [2.2]paracyclophane by introducing a leaving group, which was desirous of being not only stable during the vapor deposition process but also easily removable during the conversion of PPE to PPV.

This letter describes a new preparation of PPV film via the vapor deposition polymerization of 1,9-dichloro[2.2]paracyclophane(1) in which chlorine is used as a leaving group for introducing a carbon-carbon double bond.



Compound 1 was prepared according to the following scheme.



Into 1,9-dihydroxy[2.2]paracyclophane[10] (3)(0.56 g, 2.3 mmol) in 15 cm^3 of pyridine was added methanesulfonyl chloride (0.67 g, 5.7 mmol) at room temperature, and the mixture was stirred at 40 °C for 6 h. Then it was poured into 100 cm^3 of 0.1 mol dm^{-3} hydrochloric acid solution, and the mixture was extracted with three 50-cm^3 portions of ethyl acetate. The combined extracts were dried over anhydrous magnesium sulfate and placed under reduced pressure to remove volatile solvents. The residue was recrystallized from benzene to give 0.75 g (82%) of 1,9-dimesyloxy-[2.2]paracyclophane(4) as white needles, mp 152 °C (decomp); IR(KBr) 1350, 1180 cm^{-1}; ^1H NMR($CDCl_3$) δ 6.66 (m, 8H), 5.9 (m, 2H), 3.8 (m, 4H), 3.02 (s, 6H); Anal. Found: C, 54.65; H, 5.11; S, 16.08%. Calcd for $C_{18}H_{20}O_6S_2$: C, 54.33; H, 5.08; S, 16.17%.

Into the suspension of 4 (0.75 g, 1.9 mmol) in 20 cm^3 of ether was added dropwise titanium tetrachloride (1.44 g, 7.6 mmol) at room temperature. After the mixture was stirred for 3 h, it was washed with three 20-cm^3 portions of water, and the organic layer was dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove solvents. The residue was passed through a short column packed with silica gel with dichloromethane as an eluent to give 0.42 g (77%) of 1 as white powder, mp 185 °C; IR(KBr) 720, 738 cm^{-1}; ^1H NMR($CDCl_3$) δ 6.8 (m, 8H), 5.2 (m, 2H), 3.9 (m, 2H), 3.1 (m, 2H); Anal. Found: C, 69.26; H, 4.89; Cl, 25.90%. Calcd for $C_{16}H_{14}Cl_2$: C, 69.33; H, 5.09; Cl, 25.58%.

Vapor deposition polymerization of 1 was carried out according to the procedure of Gorham.[9] Compound 1 was sublimed under the pressure of

10 Pa at 120 °C to give a gas of 1 which was subjected to vacuum pyrolysis at 580 °C. The pyrolyzed gas condensed on a glass surface at 20 °C to give a tough, transparent, colorless film in quantitative yield. The film obtained was insoluble in acetone, chloroform, THF, DMSO, and m-cresol, but soluble in ethyl benzoate at 150 °C. Its IR spectrum as shown in Fig. 1a exhibited absorption peaks at 720, and 2850 and 2925 cm^{-1}, assigned to C-Cl and CH_2 stretching, respectively. The elemental analysis of the film was in good agreement with the calculated value for 2 (Found: C, 69.51; H, 5.10; Cl, 25.21%. Calcd for C_8H_7Cl: C, 69.33; H, 5.09; Cl, 25.58%). It was concluded on the basis of its solubility in hot ethyl benzoate that the film of 2 was free of cross-linking, suggesting that the pyrolysis of 1 gave exclusively 7-chloro-1,4-quinodimethane which polymerized without unfavorable side reactions when it condensed on the glass surface.

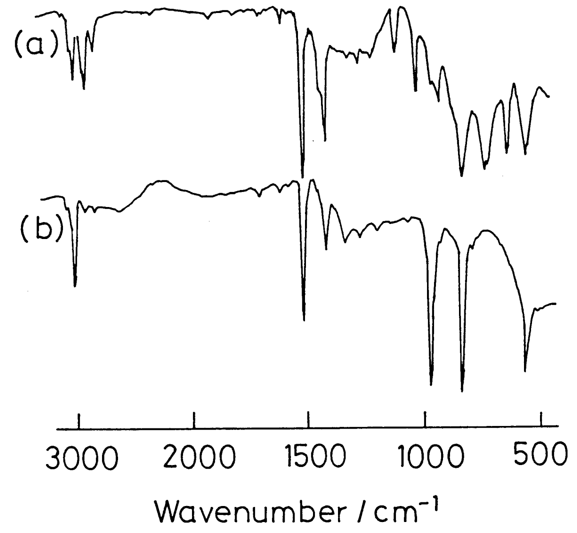


Fig. 1. IR spectra of films of 2: (a) intact and (b) after heat-treated at 300 °C for 1 h.

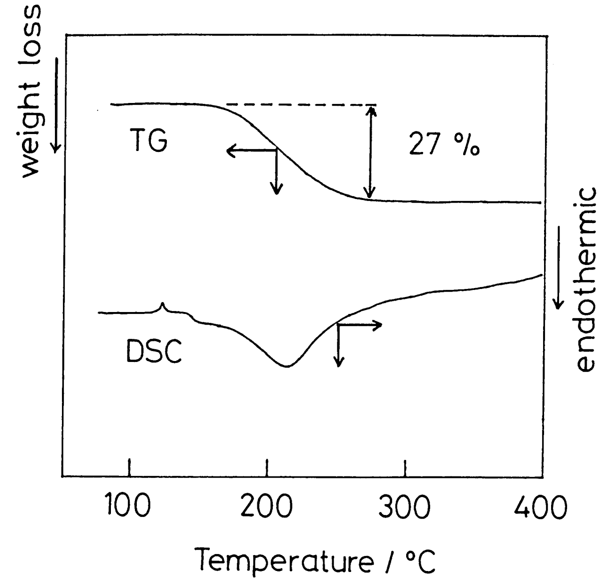


Fig. 2. DSC-TG curves of 2.

DSC-TG curves of 2 are shown in Fig. 2, from which it is obvious that 2 was subjected to an endothermic reaction in a temperature range of 170 to 220 °C with about 27% of weight loss which corresponds well to the theoretical weight loss(26.3%) for the dehydrochlorination of 2, indicating that the thermal dehydrochlorination of 2 took place quantitatively.

A piece of film of 2 was heated at 300 °C under nitrogen for 1 h. The film changed in color from transparent colorless to opaque yellow and it became insoluble even in hot ethyl benzoate. Figure 1b shows IR spectrum of the film after heat treatment. It exhibited no peak at 720, or 2850 or 2925 cm^{-1}, assignable to C-Cl or CH_2 bond, respectively, but a new peak at 966

cm^{-1} assigned to the C-H out-of-plane bending of a trans vinylene group. The elemental analysis of the heat-treated film was in good agreement with the calculated value for PPV(Anal. Found: C, 93.53; H, 5.87; Cl, 0.37%. Calcd for C_8H_6: C, 94.08; H, 5.92%). It was concluded that 2 almost quantitatively underwent dehydrochlorination at 300 °C under nitrogen for 1 h to yield a fully extended π-conjugated PPV film. The dehydrochlorination of 2 took place smoothly under similar thermal conditions to the desulfonium reaction[3] of poly(p-xylylene α-diethylsulfonium bromide). Dunnavant et al. reported that random poly(phenylenevinylene-co-phenylenechloroethylene) obtained from the reaction of p-xylylene chloride with sodium amide in liquid ammonia underwent dehydrochlorination in a temperature range of 150 to 250 °C to yield PPV.[11]

The electroconductivity of the PPV film obtained here was measured to be 0.5 S cm^{-1} upon doping by SO_3(0.3 mol monomer $unit^{-1}$). This value was close to that reported by Murase et al.[3]

In summary, tough, transparent colorless films of poly(phenylenechloroethylene) with various thickness of 0.01 to 0.1 mm were successfully prepared by the vapor deposition polymerization of 1,9-dichloro[2.2]paracyclophane and they were able to to be converted into fully extended π-conjugated PPV film with thermal dehydrochlorination at 300 °C for 1 h. Further studies on some material properties of the PPV film are in progress.

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