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Vapor deposition polymerization of 1,9-bis(trimethylsilyloxy)[2.2]paracyclophane

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Summary

Vapor deposition polymerization of 1,9-bis(trimethylsilyloxy)[2.2]paracyclophane (**Me_3SiO-PC**) was carried out to obtain poly(7-trimethylsilyloxy-p-xylylene) (**Me_3SiO-PPX**) as a colorless tough film. The **Me_3SiO-PPX** film was successfully converted to poly(7-hydroxy-p-xylylene) (**HO-PPX**) film by the hydrolysis reaction in THF in the presence of hydrochloric acid.

Introduction

In 1966 Gorham found that [2.2]paracyclophane was subject to vapor-phase pyrolysis under reduced pressure at 600 °C to give p-xylylene in gas state which condensed and simultaneously polymerized to give linear poly(p-xylylene) as a colorless transparent film (1). This polymerization technique is called the vapor deposition polymerization method. A limited range of highly strained compounds including [2.2]paracyclophane (1), its ring-substituted derivatives (1), [2.2](2,5)thiophenophane (2), dispiro[2.2.2.2]deca-4,9-diene (3), and nitrogen-containing heterophanes such as [2.2](2,5)pyridinophane, [2.2](2,5)-pyradinophane and *N,N'*-dimethyl[2.2](2,5) pyrolophane (4) were found to undergo vapor deposition polymerization. Vapor deposition polymerization offers some advantages such as (a) easy isolation of the product, which coats the surface of the deposition chamber and can be peeled off as a thin, free-standing film and (b) easy control of film thickness (1). However, vapor deposition polymerization has not been applied to functional polymer film due to the instability of the functional group in the pyrolysis process.

In this work was studied the vapor deposition polymerization of a compound carrying hydroxyl group to extend the vapor deposition polymerization to the preparation of a functional polymer film. The vapor deposition polymerization of **Me_3SiO-PC** with a trimethylsilyloxy group as a protecting group for hydroxyl functionality and the deprotection reaction of **Me_3SiO-PPX** were carried out.

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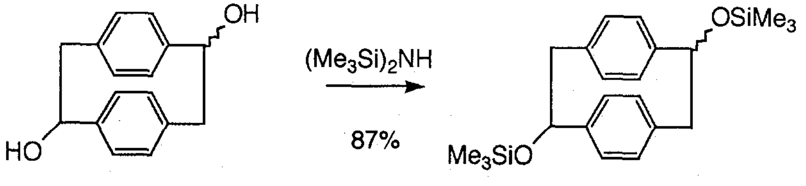
Experimental

1,9-Dihydroxy[2.2]paracyclophane (HO-PC)

The cyclophane compound **HO-PC** was prepared in 20 % yield via three steps from [2.2]paracyclophane according to the method reported by Dewhirst and Cram (5). mp 200-202 °C (lit. 200-203 °C).

Me_3SiO-PC

To a stirred suspension of **HO-PC** (0.24 g, 1.0 mmol) and bis(trimethylsilyl)amine (0.65 g, 5.0 mmol) in chloroform (10 ml) was added a drop of chlorotrimethylsilane and the mixture was heated under reflux for 10 h. The reaction mixture was placed under reduced pressure to remove the volatile materials and the residue was recrystallized from hexane to give 0.33 g (87%) of **Me_3SiO-PC** as colorless plates. mp 100 °C; ^1H NMR ($CDCl_3$) δ 6.9-6.3 (m, 8H), 5.3-5.1 (m, 2H), 3.6-3.4 (m, 2H), 3.0-2.8 (m, 2H), 0.20 (s, 18H); IR (KBr) 1230, 1060, 835, 740 cm^{-1}; Anal. Found: C, 68.89; H, 8.27%. Calcd for $C_{22}H_{32}Si_2O_2$: C, 68.69; H, 8.39%.



HO-PC **Me_3SiO-PC**

Vapor deposition polymerization of Me_3SiO-PC

Vapor deposition polymerization of **Me_3SiO-PC** was carried out according to the method of Gorham (1). The outline of the apparatus is shown in Figure 1. A glass tube with a diameter of 1 cm and a length of 50 cm was employed with one end connected to a mechanical vacuum pump through a liquid-nitrogen trap. A given amount of cyclophane compound (50 mg~150 mg) was set in the other end and the system was evacuated to 0.1 mmHg. The cyclophane **Me_3SiO-PC** was sublimed by heating the vaporization zone at 130 °C. The sublimed vapor was introduced into the pyrolysis part kept between 400 and 450 °C. The pyrolyzed gas was led to a deposition chamber held at 0 °C, where polymerization took place on the gas-solid interface. After completion of this pyrolytic conversion, the system was equilibrated to atmospheric pressure and the polymeric film formed at the deposition chamber was peeled from the wall to give a colorless tough film in a quantitative yield.

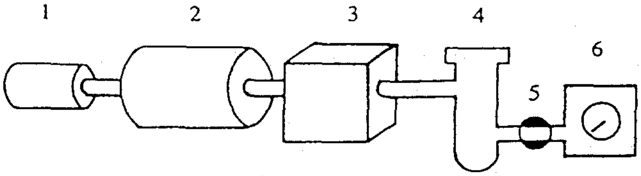


Figure 1. Apparatus for the vapor deposition polymerization: 1, vaporizer; 2, 800-W furnace; 3, deposition chamber; 4, liquid nitrogen trap; 5, stopcock; 6, vacuum pump.

Hydrolysis reaction

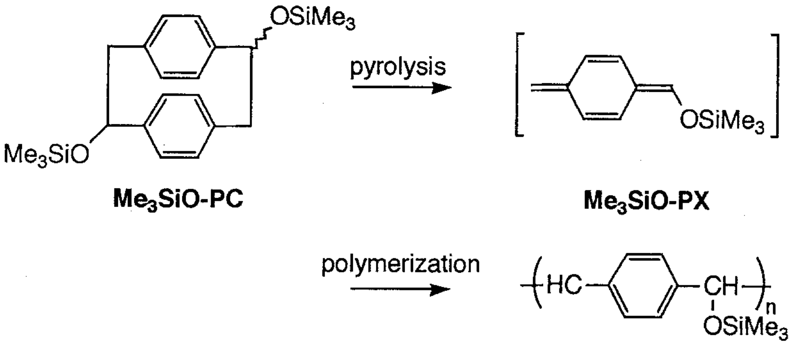
Into 10 ml of methanol or THF containing two drops of hydrochloric acid was added a piece of film of **Me_3SiO-PPX** (~20 mg) and the mixture was refluxed for 10 h. Then the reacted film was picked up from the reaction mixture and washed well with methanol.

Results and Discussion

Vapor deposition polymerization of Me_3SiO-PC

Preliminary experiments in our laboratory showed that the vapor deposition polymerization of **HO-PC** was unsuccessful. Only tar material was obtained in the tube at the pyrolysis zone, suggesting the existence of undesired side reactions. Our idea was to protect the hydroxy group in order to prevent undesired side reactions. Several protecting groups for the hydroxy group have been reported such as ethers, esters, and sulfonate (6-8). Among them trimethylsilyl ether can be easily hydrolyzed by acid treatment. Further, trimethylsilyl ether function is expected to be stable in the pyrolysis condition since trimethylsilyl ethers are widely used for gas chromatography analysis of alcoholic compounds. Therefore, we prepared cyclophane **Me_3SiO-PC** with a trimethylsilyloxy group.

In contrast to **HO-PC**, **Me_3SiO-PC** was found to be subject to the vapor deposition method to give a colorless tough film in a quantitative yield. The polymeric film obtained was not soluble in acetone, methanol, chloroform, or THF but soluble in m-cresol and ethyl benzoate at 100 °C, suggesting that this film was free of cross-linking. Its IR spectrum exhibited characteristic absorption peaks at 1230 (δ_{CH_3} in Si-CH_3), 1080 ($\nu_{Si\text{-}O}$), and 835 and 742 cm^{-1} ($\delta_{C\text{-}H}$ and $\delta_{Si\text{-}C}$ in Si-CH_3) as shown in Figure 2a. The elemental analysis of the film was in good agreement with the calculated value for **Me_3SiO-PPX** (Found: C, 68.77; H, 8.29%. Calcd for $C_{11}H_{16}SiO$: C, 68.69; H, 8.39%). It was concluded therefore that the pyrolysis of **Me_3SiO-PC** gave exclusively 7-trimethylsilyloxy-p-xylylene (**Me_3SiO-PX**) which polymerized without unfavorable side reaction when it condensed on the glass surface at 0 °C.



Me_3SiO-PC

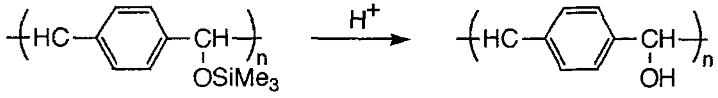
Me_3SiO-PX

Me_3SiO-PPX

Hydrolysis reaction

The results of the hydrolysis reaction were summarized in Table 1. When THF was used as a solvent, the conversion increased to 95% (run 4). Figure 2b showed the IR spectrum of the film obtained from run 4. It exhibited no peak at 1230, 1080, 835, or 742 cm^{-1}, assignable to trimethylsilyloxy group. New peaks appeared at 3450 ($\nu_{O\text{-}H}$) and

1030 cm^{-1} (ν_{C-O}), indicating the transformation of **Me$_3$SiO-PPX** to **HO-PPX**. The hydrolyzed film became insoluble even in hot m-cresol or ethyl benzoate.



Me$_3$SiO-PPX **HO-PPX**

Table 1. Hydrolysis reaction of **Me$_3$SiO-PPX**

run	solvent	temp.,°C	time, h	anal. %C	anal. %H	conv.,%
1	MeOH	60	12	72.41	7.80	44
2	MeOH	60	24	74.51	7.35	63
3	THF	65	12	77.08	6.98	82
4	THF	65	24	79.10	6.89	95

Determined from %C.

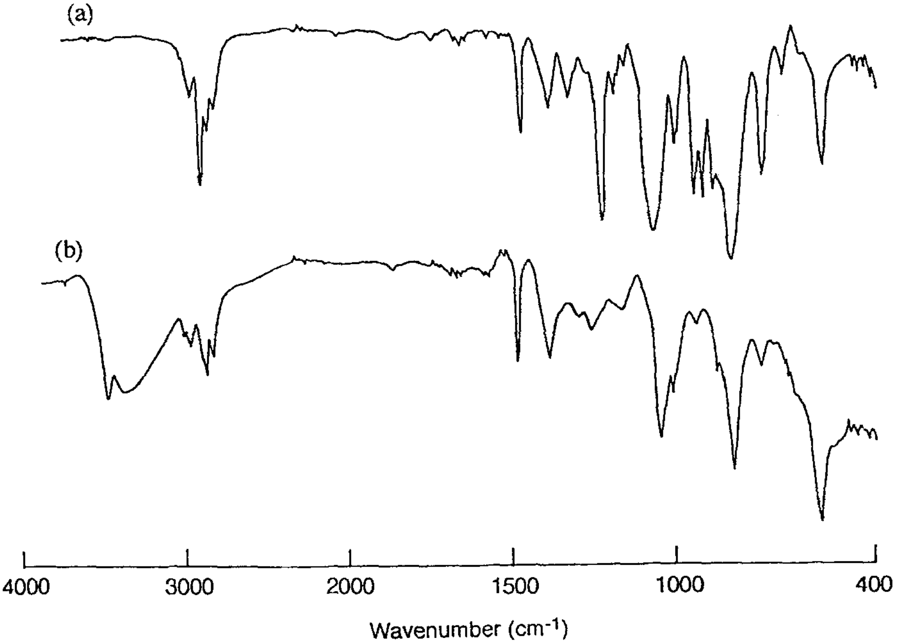


Figure 2. IR spectrum of (a) **Me$_3$SiO-PPX** and (b) **HO-PPX**.

The TG-DTA measurements of **Me$_3$SiO-PPX** and **HO-PPX** were performed under nitrogen at a heating rate of 10 °C/min as shown in Figure 3. In the case of **Me$_3$SiO-PPX** the weight loss started at 200 °C and the 50% weight loss occured at 430 °C. Polymer **HO-PPX** showed better thermal stability than **Me$_3$SiO-PPX**.

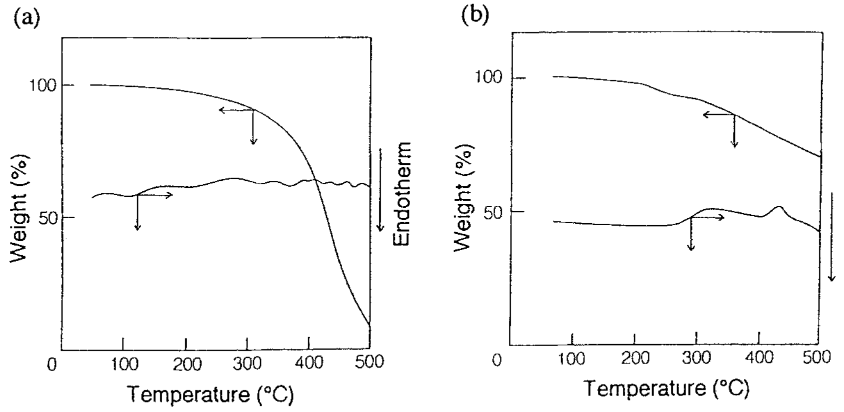


Figure 3. TG-DTA curves of (a) **Me$_3$SiO-PPX** and (b) **HO-PPX**.

In conclusion, trimethylsilyloxy group was found to be a suitable protecting group for the hydroxy group of **HO-PC**. Functional polymer film was successfully prepared by the vapor deposition polymerization.

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