

Synthesis of Poly(*p*-xylylene) from α,α' -Bis(alkoxy or aryloxy)-*p*-xylenes by Chemical Vapor Deposition Polymerization

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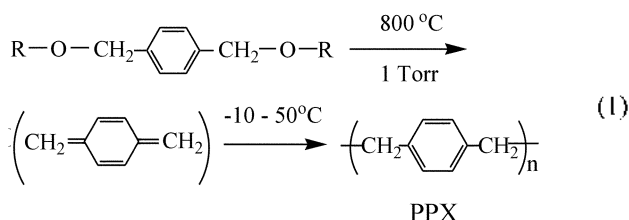
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Poly(*p*-xylylene) (PPX) has been attracting a great deal of interest because of its high thermal and chemical stability, excellent mechanical properties and low dielectric constant.¹ The polymer was discovered by Szwarc² in 1947 and then later commercialized by the Union Carbide Corporation based on the so-called Gorham process.^{3,4}

Greiner⁵ *et al.* recently published an excellent review on the synthesis and properties of poly(*p*-xylylene)s. PPX is usually synthesized by chemical vapor deposition polymerization (CVD) of paracyclophane, pxylylene⁶⁻⁸ or esters of α,α' -bis(hydroxymethyl)-*p*-xylene.⁹ The advantage of the CVD method, due to its unique synthetic approach, exhibits a good gap-fill properties and chemical purity with no contamination by solvent molecules. The CVD method also allows us to prepare insoluble polymers in various shapes in nano dimensions by using various substrates.¹⁰

In this investigation, we attempted CVD of the following four different diether derivatives of *p*-xylene.



R = CH₃ (1), C₂H₅ (2), C₆H₅ (3) and C₆H₅CH₂ (4)

Surprising enough, all of the four compounds produced only PPX when they were subjected to CVD. None of them produced either poly(*p*-phenylenevinylene) (PPV) or copolymers consisting of the *p*-phenylenevinylene and *p*-xylylene units.

This report briefly summarizes our experimental observations made in the course of our research on CVD of various compounds.¹¹

The monomer **1** and **2** are liquid at room temperature and are available from TCI (Tokyo, Japan) and Aldrich Chemicals (Milwaukee, U.S.A.), whereas the monomer **3** and **4** were synthesized by us from α,α' -dibromo-*p*-xylene and phenol, and α,α' -dibromo-*p*-xylene and benzyl alcohol, respectively. The monomer **3** and **4** are solids, whose melting temperatures are 144 °C and 65 °C, respectively. The polymerization procedure utilized in this investigation is as described earlier

by us.¹⁰ The monomer (up to 0.5 mL for monomer **1** and **2** and 80 mg for monomer **3** and **4**) placed in the tungsten boat was vaporized at 90-95 °C for monomer **1**, **2** and **4** or at 120-125 °C for monomer **3**. The vaporized monomer was allowed to pass through the pyrolysis zone at 800 °C. The temperature of the deposition zone, where the substrate (KBr pellet) was placed, was maintained at -10 to 50 °C.

After CVD process, side products in the form of liquid are seen in the deposition zone. The side products will be discussed later. The polymeric material formed was purified by soxhlet extraction with THF for several days. The IR-spectra of monomer **1**, the CVD material deposited on a KBr pellet surface at 50 °C, before and after soxhlet extraction, and PPX separately prepared from paracyclophane are compared in Figure 1. Figure 1b shows many absorption peaks in addition to those observed for the monomer and the final polymer PPX. Especially, two new strong peaks are discernible at 1701 cm⁻¹ and 1609 cm⁻¹. The peak at 1701 cm⁻¹ is from the carbonyl C=O stretching vibration and the one at 1609 cm⁻¹ from the C=C stretching vibrational mode, that must be originated from the side products. Although we do not yet clearly understand by what mechanism the side products are formed, it is clear that they are easily removed by soxhlet extraction. This conclusion was derived from the fact that the IR-spectrum (Figure 1c) of the purified sample was completely identical to that (see top IR spectrum in Figure 1) of authentic PPX and was free from all the peaks of the side products. The strong ether peak from the starting monomer at 1103 cm⁻¹ (Figure 1a) was not

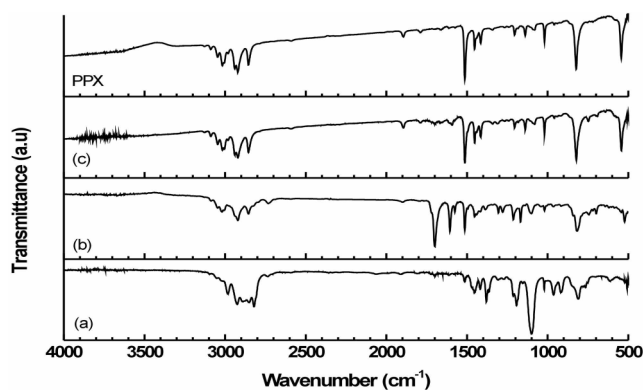


Figure 1. Comparison of the IR-spectra of the CVD polymer prepared from monomer **1** and PPX (a): Monomer, (b): Before soxhlet extraction and (c): After soxhlet extraction.

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observed at the final polymer. The final polymer obtained from the monomer **1** and PPX exhibited IR absorption peaks characteristic of sp^2 C-H stretching (3025 cm^{-1}), sp^3 C-H stretching ($2942, 2849\text{ cm}^{-1}$), C=C ring stretching ($1518, 1456$ and 1425 cm^{-1}) and phenylene C-H bending (823 cm^{-1}) vibrations. The result of the elemental analysis showed that the found C, H content of the new polymer (C: 90.94 ± 0.03 ; H: 7.74 ± 0.04) was in the order of the calculated content of C and H for PPX (C: 92.26; H: 7.74). To reaffirm the formation of PPX, the new polymer was subjected to solid state ^{13}C cross magic angle spinning (CP-MAS) NMR analysis.¹³ Figure 2 shows the ^{13}C (CP-MAS) NMR spectrum of the polymer. It shows signals at 40.3, 129.6 and 141.6 ppm. The signal positions of the new polymer are the same as the signal positions of PPX prepared from paracyclophane as reported by Greiner *et al.*⁵ The signal at 40.3 ppm is assigned to the aliphatic C_1 atom, the one at 129.6 ppm to the aromatic C_3 atom and the one at 141.6 ppm to the aromatic C_2 atom.

The thermal properties of the same polymer were studied by the differential scanning calorimetry (DSC) under a stream of N_2 gas at the heating and cooling rate of $10\text{ }^\circ\text{C}/\text{min}$. The thermogram on the heating cycle exhibited peaks at 217, 273 and $416\text{ }^\circ\text{C}$. It is well known that PPX is polymorphic and each crystal structure shows solid-to-solid transitions before the final melting. According to the literature,¹³⁻¹⁵ the peak at $217\text{ }^\circ\text{C}$ corresponds to the α -crystal (monoclinic)- β_1 (hexagonal) transition, and the one at $273\text{ }^\circ\text{C}$ to the β_1 crystal- β_2 crystal (hexagonal) transition. The last peak at $416\text{ }^\circ\text{C}$ corresponds to thermal decomposition on melting. According to thermogravimetric analysis of the same sample, this polymer started to undergo the initial thermal decomposition at about $280\text{ }^\circ\text{C}$ and a fast weight loss at $480\text{ }^\circ\text{C}$. The cooling DSC curve showed a strong exothermic peak at $261\text{ }^\circ\text{C}$ responsible for crystallization of the β_1 form from the β_2 form. The small peak at $216\text{ }^\circ\text{C}$ corresponds to the β_1 - α transition. The high temperature peak at $391\text{ }^\circ\text{C}$ must be from crystallization (β_2 form) from the melt.

Concerning about the side products, the liquid collected in the deposition zone was analyzed by GC/MS spectroscopy. The result reveals that CVDP of PPX from the monomer **1**, similarly as reported by Greiner *et al.*⁹ of CVDP of diester monomers, is accompanied by production of a wide variety of side products. As far as the reaction mechanism (see eq.

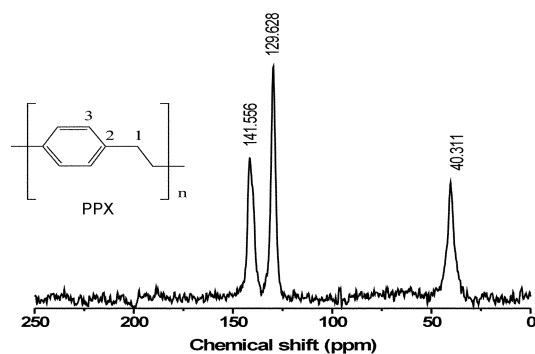


Figure 2. ^{13}C (CP-MAS) NMR spectrum of the CVDP polymer prepared from monomer **1**.

1) for the present CVDP process is concerned, it is conjectured that thermolysis of monomers results in formation of quinodimethane, which undergoes polyaddition. This mechanism is basically the same as that¹⁶ proposed for the CVD reaction of *p*-xylene and paracyclophane to PPX. The other three monomers behaved more or less the same way as monomer **1** did. The only difference observed was that the deposition of PPX from monomer **3** and **4** was slower at the substrate temperature of $50\text{ }^\circ\text{C}$. Therefore, we collected the polymer on the substrate surface at the temperature of $10\text{ }^\circ\text{C}$. The lower the substrate temperature, the faster the deposition rate became. The major advantage of using monomers **1** and **2**, when compared with diesters reported by others,⁹ lies in the fact that their vapor pressures are higher and they are hydrolytically more stable.

In summary, we observed that PPX is easily formed from α,α -diether of *p*-xylene by chemical vapor deposition polymerization. This observation makes it possible to synthesize PPX and derivatives from readily available compounds.

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