Thin Films of Insoluble Poly(Oligothienylene vinylenes) Prepared by Chemical Vapor Deposition Polymerization**

By Sung-Hoon Joo, Chun-Young Lee, Donghyuk Park, Jinsoo Joo, and Jung-Il Jin*

A series of poly(oligothienylene vinylenes) (PT_{m}Vs, m = 2–4) with a varying number of consecutively bound thienylene rings are successfully prepared in thin films by chemical vapor deposition polymerization (CVDP) using the corresponding bis(halo-methyl)thiophenes as starting materials. The chemical and electronic structures are studied spectroscopically and also by cyclic voltammetry. Top-gate field-effect transistors are fabricated by two consecutive CVDP cycles of PT_{m}V and poly(p-xylylene) followed by the deposition of a Au gate electrode. In the case of a PT_{3}V active layer, a field-effect mobility value of 0.5 × 10^{-4} cm^{2} V^{-1} s^{-1} is obtained.

1. Introduction

The preparation of insoluble and infusible polyconjugated polymers with controlled shapes at the nanoscale has always been a challenge to synthetic polymer chemists because the polymers precipitate out of the reaction medium as they are formed or form intractable solid masses during polymerization. One method of overcoming this challenge is to utilize a synthetic route that proceeds through an intermediate step where a precursor polymer that is soluble in water or organic solvents is formed. The precursor is ultimately transformed to the final polymer in the last synthetic step. One example of this strategy is the Wessling–Zimmerman synthesis[1,2] of poly(p-phenylene-vinylene), PPV, as shown in Scheme 1. Such an approach, however, can leave behind remaining reaction solvents and byproducts that can contaminate the final product, which is a significant disadvantage to a multistep method.

We have recently reported[3–5] the facile preparation of PPV by a chemical vapor deposition polymerization (CVDP) method, where 1,4-bis(chloromethyl)benzene was vaporized in an inert gas such as argon, and the vaporized monomer was passed through a hot zone (600–850 °C) to prepare an activated intermediate. This intermediate was polymerized on a surface to prepare thin films, tubes, rods, and fibers.[3] In order to ensure the complete conversion to PPV, the deposited polymer was subjected to a final thermolysis step at 250–350 °C to remove remaining halogen atoms by an elimination reaction. The simplified reaction pathway is given in Scheme 2. As reported by Vaeth and Jensen,[6] the reaction is much more complicated than what is shown in Scheme 2. Moreover, the final polymer contains detectable amounts of saturated units resulting from another minor intermediate, quinodimethane. This synthetic method was described earlier by European groups[7,8] and also reviewed by Greiner et al.[9] The fact that the PPV prepared by this method could be easily carbonized to graphitic carbon made this approach very attractive.[5,10] We have prepared well-aligned graphitic carbon nanotubes[10] exhibiting high field-emission properties[10] and bilayer nanotubes and nanofilms consisting of carbonized PPV and PPV layers displaying highly efficient photoconductivity values.[5,11] Recently, we have also successfully prepared poly(thiénylenevinylene) via the same CVDP method by using 2,5-bis(chloromethyl)thiophene as the starting material.[11]

Polyconjugated polymers have been studied since the late 1940s[12] and a large number of their experimental and theoretical studies have been published. Recently, the demonstration of organic electroluminescent diodes[13,14] and organic thin-film transistors (OTFTs)[15–19] based on either small organic molecules[13,16] or π-conjugated polymers[14,15,17] and the significant improvements in device performance and efficiency[20–23] have attracted much interest not only from academics but also from industry. Most of the research on organic transistors has focused on π-conjugated polymers soluble in common organic solvents. Regioregular poly(3-alkylthiophenes)[24–27] are representative examples. When regioregular poly(3-alkylthiophenes) (P3HT)[28] consisting of 98.5 % or more head-to-tail (HT) linkages was used in the fabrication of field-effect transistors (FETs), a dramatic increase in mobility was observed relative to regiorandom poly(3-alkylthiophenes).[29] For the latter, the reported field-effect mobility was 10^{-5}–10^{-4} cm^{2} V^{-1} s^{-1}, whereas a mobility as high as 0.045 cm^{2} V^{-1} s^{-1} was achieved for the former.

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In this report, we describe the CVDP synthesis and characterization of poly(oligothienylenevinylene) (PT$_m$V) thin films, where $m$ corresponds to the number of consecutively bound thiophene rings between the vinylene linkages. These polymers belong to a new class of polyconjugated polymers. We also discuss the preparation of thin films of PT$_2$V and PT$_3$V on patterned substrates and report their transistor properties.

2. Results and Discussion

Figure 1 compares the Fourier transform (FT) IR spectra of three polymers, PT$_2$V, PT$_3$V, and PT$_4$V, from KBr disks. To obtain high quality polymer films, it was necessary to activate the monomers at high temperatures, and the temperatures used increased with increasing number of thiophene rings (see Table 1).

There are several points worthy of special attention. All of the IR absorption spectra (Fig. 1) show sp$^3$ C–H stretches near 2910 cm$^{-1}$ in addition to the sp$^2$ C–H stretching mode at 3010 cm$^{-1}$. The relative intensity of the saturated sp$^3$ C–H stretch increased with increasing number of thiylene-ring repeat units. At the same time, the intensity of the absorption peak at 930 cm$^{-1}$ for the trans vinylene C–H out-of-plane bending mode diminished with increasing number of rings because of the progressively reduced proportion of vinylene groups in those structures with multiple ring repeat units.

The trend described above can be attributed to two different possible factors: monomer activation temperature and relative stability of the two reactive intermediates, A and B, shown in Scheme 3.

The C–H str corresponding to the thiophene rings appear at 1450 cm$^{-1}$, and the thiophene overtone bands are observed at 1500–1750 cm$^{-1}$ in the IR spectra of the polymers.

Figure 1. The IR spectra of PT$_m$Vs (films on KBr discs; the activation temperatures and film thicknesses are shown in parentheses).

Table 1. CVDP conditions for the preparation of PT$_m$V and PPX polymer films.

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>PT$_2$V</td>
<td>120</td>
<td>700</td>
<td>4 × 10$^{-2}$</td>
<td>25</td>
</tr>
<tr>
<td>PT$_3$V</td>
<td>140</td>
<td>750</td>
<td>8 × 10$^{-3}$</td>
<td>15</td>
</tr>
<tr>
<td>PT$_4$V</td>
<td>170</td>
<td>800</td>
<td>7 × 10$^{-4}$</td>
<td>5</td>
</tr>
<tr>
<td>PPX</td>
<td>140</td>
<td>750</td>
<td>4 × 10$^{-1}$</td>
<td>50</td>
</tr>
</tbody>
</table>

[a] Standard cubic centimeters per minute. [b] Time calculated on the assumption that the system is in the standard state (25 °C, 1 atm, 1 atm = 101.325 kPa).

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The polymer films were prepared on quartz plates by the CVDP method. The first member of the polymer series, PTV, exhibited a broad absorption peak (ca. 325–700 nm) for the \( \pi-\pi^* \) transition of the backbone system, whereas the other polymers had two absorption peaks, one for the thiophene rings and the other for the complete chain structure. The results are summarized in Table 2. The spectral data indicate that the \( \pi \) electrons of PTV are most efficiently delocalized among the units and that the thiophene rings in the repeat unit are not coplanar. Thus, the bandgap energy increased from 1.7 eV for PTV to 2.0 eV for PT3V and PT4V, as estimated from the absorption edges of the corresponding UV-vis absorption spectra. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels were obtained from optical bandgaps and cyclic voltammetry (CV) results.

We attempted to determine the molecular weights of the precursor polymers, but to our surprise, all of the precursor polymers were insoluble in the organic solvents tested. It appears that partial crosslinking between the polymer backbone occurred. But the major UV-vis absorption peaks observed were due to typical \( \pi-\pi^* \) transitions of \( \pi \)-conjugated polymers. We speculate that the average degree of polymerization of the present polymers is not very low. Moreover, if the polymers had very low molecular weights, it would not have been possible to obtain good quality films.

Table 2. Spectral data and HOMO and LUMO levels for the PTmV series.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>( \lambda_{\text{max}} ) [nm]</th>
<th>( \lambda_{\text{edge}} ) [nm]</th>
<th>Eg [eV] [c]</th>
<th>HOMO [eV]</th>
<th>LUMO [eV]</th>
</tr>
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<tbody>
<tr>
<td>PTV [11]</td>
<td>— 523</td>
<td>729 1.7</td>
<td>5.3 3.6</td>
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<td></td>
</tr>
<tr>
<td>PT2V</td>
<td>358 455</td>
<td>663 1.9</td>
<td>5.8 3.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PT3V</td>
<td>367 457</td>
<td>605 2.0</td>
<td>5.7 3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PT4V</td>
<td>414 472</td>
<td>621 2.0</td>
<td>5.6 3.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PT [28]</td>
<td>— 593</td>
<td>593 2.1</td>
<td>5.4 3.3</td>
<td></td>
<td></td>
</tr>
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</table>

[a] Absorption (\( \pi-\pi^* \)) from thiophene rings. [b] Absorption from the conjugated main-chain. [c] 1 eV = 1.602 × 10^{-19} J.

Present homologous series. The polymer films were prepared on quartz plates by the CVDP method. The first member of the polymer series, PTV, exhibited a broad absorption peak (ca. 325–700 nm) for the \( \pi-\pi^* \) transition of the backbone \( \pi \) system, whereas the other polymers had two absorption peaks, one for the thiophene rings and the other for the complete chain structure. The results are summarized in Table 2. The spectral data indicate that the \( \pi \) electrons of PTV are most efficiently delocalized among the units and that the thiophene rings in the repeat unit are not coplanar. Thus, the bandgap energy increased from 1.7 eV for PTV to 2.0 eV for PT3V and PT4V, as estimated from the absorption edges of the corresponding UV-vis absorption spectra. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels were obtained from optical bandgaps and cyclic voltammetry (CV) results.

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The CVDP method, for the first time, could be successfully applied to fabricate ‘top-gate’ field-effect transistors (FETs). Both the active layer and the poly(p-xylylene) (PPX) insulating layer\(^\text{[21–33]}\) could be directly formed by CVDP. The dielectric...
constant of PPX is 2.65, and this value is nearly constant over a large frequency range from 60 Hz to 1 MHz. PPX also had a high crystalline melting temperature of 420 °C.[33] To prepare the device, the active layer (95 nm thick) was first deposited by the CVDP of PT3V and PT2V on a source (S) and drain (D) electrode pattern on a silicon oxide plate made by vapor deposition on a positively doped silicon wafer, on which the PPX layer was deposited. Finally, the gate Au electrode was deposited by vapor deposition on top of the PPX layer. The process is represented in Figure 5 together with a scanning electron microscopy (SEM) image of a fabricated device. These devices belong to the so-called “top-gate” structures.

The dependence of current on the electric field \( I_d \) on \( V_d \) between the S and D electrodes for PT3V and PT2V is shown in Figure 6a and c, respectively. Figure 6b contains a semilogarithmic plot of \( I_d \) versus \( V_g \), and Figure 6b and d show the root of \( I_d \) versus \( V_g \) for PT3V and PT2V, respectively. Figure 6a reveals the saturation behavior in the \( I_d-V_g \) curve and the enhancement of current with increasing gate voltage, which implies a clear transistor behavior for the PT1V device. The field-effect mobility \( (\mu) \) of the devices can be calculated from

\[
I_d = \frac{W e C}{2L} \left( \frac{V_g - V_t}{V_d} \right)^2
\]

where \( C \) is the unit area capacitance (\( \varepsilon/export thickness, \( \varepsilon_{\text{ppx}} = 2.65 \times 10^{-13} \text{ F cm}^{-1} \) of the insulating layer, \( V_t \) is the threshold voltage, \( V_d = -20 \text{ V} \), \( L \) (channel length or the distance between source and drain electrode) = 5 \( \mu \text{m} \), and \( W \) (channel width between source and drain electrode) = 1.5 mm. The field-effect mobility \( (\mu) \) and current on–off ratio \( (I_{\text{on}}/I_{\text{off}}) \) estimated from the plot of Figure 6b are 0.53 \( \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) and ca. 10\(^3\), respectively, which is considered to be significant but not satisfactory for practical applications. The saturation behavior seen from the \( I-V \) curve (Fig. 6c) was not observed for the device containing PT3V in the active layer. The device, however, showed a gate voltage dependence of the current between source and drain (Fig. 6d). The experimental data shown in Figure 6 implies that positive holes were the major carriers.

3. Conclusions

We have determined from this investigation that the CVDP method is an extremely versatile synthetic method applicable to the preparation of insoluble poly(oligothienylenevinylene)s as thin films. This method provided us with cleaner polymers because solvents and catalysts were not utilized in the process. For the first time, we have demonstrated that the CVDP method could be utilized to fabricate both the active and dielectric layers in FET devices. We fabricated top-gate FET devices by using PT2V and PT3V as the active layers and PPX as an insulating layer. The device made with PT3V showed a saturation regime in \( I-V \) curves, and its field-effect mobility was 0.53 \( \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \). If we could increase the crystallinity or molecular orientation of the polymer chains in the films, it is expected that the field-effect mobility would be enhanced.

4. Experimental

Chemicals and Instruments: Bithiophene-5,5′-dicarbaldehyde [34] and 5,5′-bis-tributylstannanyl-2,2′-bithiophene [35] were prepared by reported methods. 2,2′-5′,2″-Thertihiofine-5,5′-dicarbaldehyde, 5-bromothiophene-2-carbaldehyde, [2,2]paracyclophane, and tetrakis(triphenylphosphine)palladium were purchased from Aldrich Chemical Company, Inc. (WI, USA) and used without any further purification. All other chemicals were obtained commercially from Tokyo Kasei Kogyo (Tokyo, Japan) or ACROS Organics (Geel, Belgium). Solvents were dried by standard methods [36]. Infrared spectra were recorded on an FTIR Bomem Michelson instrument (Genova, Switzerland). \(^1\)H NMR spectra were recorded on a Varian Gemini 300 spectrometer (California, USA). Elemental analyses were performed by the Korea Basic Science Institute (KBSI), Seoul, Korea, by using a Flash EA 1112 Series elemental analyzer (Milan, Italy). X-Ray diffraction (XRD) patterns were obtained by using a Rigaku tabletop rotating anode X-ray generator (RINT 2000 series, Nagoya, Japan). A nickel-filtered Cu Kα line (\( \lambda = 0.1542 \text{ nm} \)) was utilized as a radiation source. Cyclic voltammograms were obtained on
an Amagel 2049 (Pasadena, USA) potentiostat and Power Lab (Chicago, USA) system (4sp). The redox behavior of the compounds was investigated with a standard three-electrode electrochemical cell in a 0.10 M tetrabutylammonium tetrafluoroborate solution in acetonitrile at room temperature under nitrogen with a scanning rate of 20 mV s⁻¹. An indium working electrode, a counter electrode, and a Ag/AgCl (0.1 M in acetonitrile) reference electrode were used.

Synthesis of Bis-Chloromethyl Monomers: Three monomers, 5,5′-bis-chloromethyl-2,2′-bithiophene (2), 5,5′-bis-chloromethyl-2,2′,5,5′-terthiophene (4), and 5,5′-bis-chloromethyl-2,2′,5,5′,2′,5′-quaterthiophene (7) were prepared via multistep synthetic routes as shown in Scheme 4. As compounds 3, 4, and 7 were prepared in the same manner, a detailed synthetic procedure is given only for the preparation of 1, 2, and 5.

5,5′-Bis(Hydroxymethyl)-2,2′-Bithiophene (1): 2,2′-Bithiophene-5,5′-dicarbaldehyde (1.00 g, 4.50 mmol) was dissolved in 30 mL dry tetrahydrofuran (THF), and sodium borohydride (1.60 g, 45.00 mmol) was added to the solution. The mixture was stirred for 5 h at room temperature under a dry nitrogen atmosphere. The mixture was poured with vigorous stirring into an aqueous solution of ammonium chloride (514 mg, 2.69 mmol) in 10 mL DMF with a gas-tight syringe. The temperature of the resulting solution was increased to 80 °C and stirred for 8 h. The resulting fluorescent red solution was cooled to room temperature and poured into 300 mL of cold n-hexane. The red precipitate was separated by filtration and dried under vacuum (456 mg, 88 %). 1H NMR (300 MHz, DMSO-d₆, δ): 7.33–7.34 (d, 2H, Ar–H), 7.41–7.46 (q, 4H, Ar–H), 7.80–7.81 (d, 2H, Ar–H), 9.85 (s, 2H, Ar–CH=O). Anal. calcd. for C₁₀H₈Cl₂S₂: C 45.63, H 3.06, S 24.36; found: C 45.62, H 3.08, S 24.38.

2,2′,5,5′,2′,5′-Quaterthiophene-5,5′-Dicarbaldehyde (5): To an oven-dried 100 mL Schlenk flask equipped with a magnetic stirring bar was added 5,5′-bis-triethylstannanyl-2,2′-bithiophene (1.00 g, 1.34 mmol) and tetrakis(triphenylphosphine)palladium (15 mg, 0.013 mmol). The system was evacuated and backfilled with argon three times. Anhydrous dimethylformamide (DMF, 50 mL) was added to the mixture followed by the slow addition of 5-bromothiophene-2-carbaldehyde (514 mg, 2.69 mmol) in 10 mL DMF with a gas-tight syringe. The temperature of the resulting solution was increased to 80 °C and stirred for 8 h. The resulting fluorescent red solution was cooled to room temperature and poured into 300 mL of cold n-hexane. The red precipitate was separated by filtration and dried under vacuum (598 mg, 98 %). 1H NMR (300 MHz, DMSO-d₆, δ): 4.57–4.59 (d, 4H, Ar–CH₃), 5.50–5.54 (t, 2H, Ar–CH₂–OH), 6.87–6.88 (d, 2H, Ar–H), 7.06–7.06 (d, 2H, Ar–H). Anal. calcd. for C₁₀H₈O₂S₄: C 55.93, H 2.61, O 8.28, S 33.18; found: C 55.95, H 2.59, O 8.29, S 33.17.

5,5′-Bis(Chloromethyl)-2,2′-Bithiophene (2): 5,5′-Bis(hydroxymethyl)-2,2′-bithiophene (1) (100 mg, 4.42 mmol) was dissolved in 40 mL dry chloroform, and the solution was added to a 100 mL round-bottomed flask. Purified thionyl chloride (0.5 mL) was added to the solution by using a syringe. After this mixture was stirred for 2 h, the residual thionyl chloride and chloroform were removed under reduced pressure by using a rotary evaporator. This crude solid was redissolved in 5 mL chloroform and poured with stirring into 100 mL dry hexane. The precipitate was separated by filtration, washed with cold hexane, and dried under a reduced pressure. The resulting 5,5′-bis(chloromethyl)-2,2′-bithiophene was gold in color (1.13 g, 97 %). 1H NMR (300 MHz, CDCl₃, δ): 4.47 (s, 4H, Ar–CH₂–Cl), 6.99 (s, 4H, Ar–H). Anal. calcd. for C₁₀H₈Cl₂S₂: C 45.63, H 3.06, S 24.36; found: C 45.62, H 3.08, S 24.38.

Chemical Vapor Deposition Polymerization: The experimental setup was similar to the procedure described by Schäfer et al. [3,8]. A sili-
con wafer, KBr disk, and quartz plate were utilized as substrates for IR, UV-vis spectrometry, and XRD measurements. A monomer (50–150 mg) placed on a tungsten boat was vaporized at 120 °C for compound 2, 140 °C for compound 4, and 170 °C for compound 7 in a steady stream (5–2 standard cubic centimeters per minute, sccm) of argon at pressures of 4 × 10⁻², 8 × 10⁻³, and 7 × 10⁻⁴ Torr (1 Torr = 133.32 Pa), respectively. The vaporized monomer was allowed to pass through the pyrolysis zone preheated to 700–800 °C for 2 h. Detailed CVDP conditions are shown in Table 1.

The precursor polymer deposited on the substrate was thermally treated at 250 °C for 10 h to convert it into the final PTnV. The polymers on substrates were washed with anhydrous chloroform and THF several times and dried. The final films on substrates were stored under argon.

Scheme 4. Synthesis of PTnV monomer.

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