Preparation of nano-thin films from conducting polymer by chemical vapor deposition method and its application for light emitting diodes (LED) and organic solar cells

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Abstract. It was demonstrated that a series of copolymers consisting of p-phenylenevinylene (PV) and p-phenyleneethylene (PE) units could be prepared from a single monomer, p-(methoxymethyl)benzyl chloride, via chemical vapor deposition polymerization (CVDP) method. The composition of the copolymers can be varied by altering the monomer activation temperature; the higher the temperature, the lower the content of the PV units becomes. The sufficient incorporation of the PE units into the poly(p-phenylenevinylene) backbone caused a significant blue shift in both photoluminescence and electroluminescence. The luminescence properties of the copolymer strongly depend on the amount of the PE units incorporated. The external quantum efficiency of the electroluminescence devices having the configuration of ITO/PEDOT-PSS/copolymer/Al-Li increased as the content of the PV units increased in the copolymer, which can be ascribed to the improved confinement of excitons. For the solar cell based on PPV derivative, the effect of the PCBM concentration on the performance of the solar cell is investigated. The results show that there is no interaction between the MEH-PPV and PCBM phase and the photoluminescence of MEH-PPV is quenched by the incorporation of PCBM. With increasing PCBM concentration, the short circuit current density and the overall energy conversion efficiency of the solar cell have been strongly improved.

Keyword: Copolymers, CVDP, organic solar cell.

1. Introduction
π-Conjugated polymers such as poly(p-phenylenevinylene) (PPV) and its derivatives [1,2] and polyfluorenes and their copolymers [3-5] have attracted much interest over the past decade due to their potential usages in optoelectronic devices such as light-emitting diodes (LED) [6-9], lasers [10] and solar cell [11-13]. The first green LED of PPV were reported by the Cambridge group [6]. Color tuning of such devices has been realized via many approaches: increasing or decreasing the band gap energy ($E_g$) of a light-emitting polymer by increasing or decreasing the effective conjugation length of the main chain, which causes red shift or blue shift in the emitted light. Decreasing the $E_g$ value can be achieved by placing electron-donating substituents on polymer backbone whereas the $E_g$ value increases when the polymer backbone [14, 15] is forced to twist out of plane with bulky pendants [16] or by disrupting the conjugated structure of the polymer through copolymerization with a second unconjugated monomer [17]. Although the solution polymerization methods are widely utilized to modify the structure of a polymer, their limitation lies in the problem of side reactions and possible contamination from the solvents used.

The alternative method to the preparation of the insoluble PPV in various shapes is the chemical...
vapor deposition polymerization method (CVDP). The potential advantages of CVDP compared to the solution processing method include good control of film uniformity, easy elimination of side products, and the potential to control the film architecture and composition on the molecular level. So far, the main starting materials for CVDP preparation of PPV are α, α'-dihalo –p-xylene. But the use of these starting materials suffers the evolution of hydrogen halide gases, which can affect the indium-tin oxide (ITO) electrode and cause worsened device efficiency [18, 19].

In this work, nano-thin film from PPV and its derivative have been prepared by CVDP method for LED application and by spin-coating for solar cell application. The optoelectronic properties of the materials were investigated and discussed.

2. Experimental

The monomer for the CVDP (p-(methoxyethyl)benzyl chloride) and MEH-PPV was synthesized in our Lab. The other chemicals were purchased from Merck Company and were used without purification.

Chemical vapor deposition polymerization and characterization

The experimental setup for the CVDP process is practically the same as described earlier by us [21]. The monomer (0.2 ml) placed on a tungsten boat was vaporized at the temperature of 80-85 °C. The CVD-process was performed under a steady stream (8 ml/min) of argon gas at the pressure of 1.0 Torr. The vaporized monomer was allowed to pass through the pyrolysis zone preheated varying from 650oC to 800°C. The substrate temperature was maintained at the temperature of 50°C.

The IR, UV-VIS and photoluminescence (PL) spectra of the materials were recorded by using BOMEM, MB-104 Instrument, HEWLETT PACKARD 8453 Instrument and AMINCO Bowman Series 2 Instrument, respectively. The excited wavelength for PL study was 360 nm. The differential scanning calorimetry (DSC) (Mettler–Toledo DSC 821 Instrument) and the thermogravimetric analysis (TGA) (Mettler-Toledo TC 15 Instrument) were performed under the stream of N2 at the heating rate of 10°C/min. The device configuration of LED was ITO / PEDOT-PSS (40 nm) / polymer (90 ± 5 nm) / Al-Li (100 nm). The Al-Li alloy contained 0.3 wt % of lithium. The characterization of the devices was performed by assembly instrument consisting of a PC-based DC power supply (HP6623A), digital multimeter (HP 34401) and a light power meter (Newport Instrument, Model 818-UV). The electroluminescence spectra of the devices were measured at room temperature (AMINCO Bowman Series 2 Instrument).

3. Results and Discussion

3.1. Structure analysis

We first examined the IR spectra of the intermediates and the final polymer obtained in the process of CVDP of p-(methoxyethyl)benzyl chloride. Figure 1 shows the changes of IR spectra during the CVDP process after activating the monomer at 650 °C.

It was noted that some side products in the form of liquid were observed in the deposition zone after the CVDP process. The sample obtained by the CVDP process was carefully washed with methylene chloride. By comparing the IR spectrum of the sample obtained right after the CVDP process (figure 1b) with that after washing (figure 1c), we clearly see that two strong peaks at 1701 and 1609 cm\(^{-1}\) and many other peaks in the region from 1400 cm\(^{-1}\) to 600 cm\(^{-1}\) in the spectrum 1b disappeared after washing. The peak at 1701 cm\(^{-1}\) is assigned to the carbonyl C=O stretching vibration and the one at 1609 cm\(^{-1}\) to an aliphatic C=C stretching vibration mode. It seems that the side products are the same as those formed in the CVDP of α, α'-dialkoxy-p-xylene reported in our previous paper [23]. The IR-spectrum of the washed precursor polymer exhibits absorption peaks characteristic of sp\(^2\) C-H stretching (3017 cm\(^{-1}\)), sp\(^3\) C-H stretching (2926 and 2853 cm\(^{-1}\)), aromatic C=C stretching (1519, 1452 and 1415 cm\(^{-1}\)) and phenylene C-H bending (823 cm\(^{-1}\)) modes. The absorption peak of C-Cl stretching mode appears as broad peak at 727 cm\(^{-1}\). And then, the sample was subjected to thermal treatment at 250°C under vacuum for 5 hours converting the precursor polymer to the final copolymer. A new absorption peak at 965 cm\(^{-1}\) was observed in the IR-spectrum after thermal treatment, which is probably attributable to the formation of C=C stretching vibration.

In summary, the results obtained in this work clearly demonstrate the potential of the CVDP method for the preparation of high-quality thin films of PPV and its derivatives. The optoelectronic properties of the materials prepared by this method will be further investigated in future studies.
from the characteristic out-of-plane C-H bending mode of trans vinylene units newly formed and, thus, the absorption peak of the C-Cl stretching mode simultaneously disappeared (figure 1d). The characteristic feature of the IR spectrum of the final polymer is basically the same as that of the copolymers consisting on PV and PE units as described earlier by Vaeth and Jensen [24] and a superposition of PPX and PPV spectra.

**Figure 1.** Comparing the IR spectra of monomer, precursor polymer and the final polymer prepared after activating the monomer at 650°C. (a): Monomer; (b): precursor polymer; (c): after washing the precursor polymer with methylene chloride; and (d): after thermal treatment of the washed precursor polymer at 250°C for 5 hours.

We studied the thermal properties of the precursor polymer obtained from the present CVDP followed by washing with CH₂Cl₂. The DSC and TGA thermograms obtained under N₂ atmosphere at the heating rate of 10 °C/min are given in figure 2.

**Figure 2.** DSC and TGA thermograms of the precursor polymer obtained after the CVDP process followed by washing with CH₂Cl₂.

On the DSC curve, a broad endothermic peak is observed in the region of 160°C to 300°C. A concurrent weight loss is observed over the same temperature range in the TGA thermogram. The result indicates that an endothermic reaction takes place in this temperature region. This behavior of the precursor polymer is similar to the thermal dehydrochlorination of the PPV precursor as observed in the preparation of PPV from α, α'-dihalo -p-xylene and also as described by Iwatsuki et al. [26]. Assuming all the weight loss mentioned about, is due to elimination of HCl, we estimate that this polymer contains 52 wt % of the PV units. Therefore, the IR spectroscopic and thermal analysis results confirm that the deposited polymer is a copolymer consisting PV and PE units.

The possible mechanism for the formation of the precursor and the final copolymer is given below:
Thermolysis or thermal activation of the monomer at an elevated temperature produces two different quinodimethanes, one with chlorine and the other without chlorine. Condensation of the two active species on a substrate surface will result in a copolymerization reaction to form a precursor copolymer consisting of two different repeating units, one of which is to be further converted to the final PV units on thermal treatment under vacuum. The side products, although not completely identified, can be removed by washing with methylene chloride.

### 3.2. Photo-electroluminescent properties

Figure 3 shows the UV-VIS and photoluminescence (PL) spectra of PPV, the precursor obtained after activating the monomer at 650°C and the final copolymer.

For the sake of comparison, PPV was prepared in the same condition as described earlier by us [21]. Comparing the UV-VIS spectrum of the final polymer to the UV-VIS spectrum of the precursor polymer, it is clearly seen from figure 3 that a new strong broad absorption bands appeared at 324, 400 and 434 nm. The UV-VIS spectrum of the copolymer is basically identical to the UV-VIS spectrum of the partially converted PPV precursor, or not fully conjugated polymer, reported by Gagnon [27]. The fully conjugated PPV has a broad continuous absorption band with the maximum absorption peak at 410 nm. It is interesting to note that the absorption edge of PPV at 512 nm (optical band gap $E_g = 2.4$ eV) blue-shifted to 497 nm (optical band gap $E_g = 2.5$ eV) by the copolymerization. The present copolymer exhibits light emission at three positions: 496, 530, and 573 nm at the excitation wavelength of 360 nm. The PL spectrum of the copolymer when compared to the PL spectrum of PPV is significantly blue-shifted. For example, the $S_{0,0}$ transition peak shifted from 510 to 496 nm. Since poly(p-phenyleneethylene) or poly(p-xylylene) is not a luminescent polymer in the visible region, the incorporation of the unconjugated PE units along the backbone shortens the effective conjugation
length of the resulting polymer causing a blue-shift in UV-VIS absorption and also in PL behavior.

Figure 4 compares the PL spectra of the copolymers prepared at different monomer activation temperatures.

![Figure 4](image)

**Figure 4.** Comparison of PL spectra of the copolymers prepared at different monomer activation temperatures.

It is clearly seen from the figure that with increasing monomer activation temperature from 650 to 800°C, the $S_{0,0}$ transition peak shifted from 496 nm to 479 nm. We observed a similar trend in their UV-VIS absorption spectra. The PV contents estimated from TGA due to the weight loss are 52, 35, 31 and 26 wt.% respectively for the monomer activation temperature of 650, 700, 750 and 800°C. The estimated PV contents after TGA analysis are lower than the estimated PV contents after analysis of the transmittance intensity by IR spectra proposed by Vaeth and Jensen [20] about 5 wt. % till 20 wt. % but the tendency is the same. This indicates that the formation of the unsubstituted quinodimethane intermediate is favored over the formation of the chlorine-substituted activated species as one increases the monomer activation temperature. Increasing of the PE content in the copolymer would shorten the conjugation length of the polymer backbone resulting in a blue-shift in PL as we have observed in this investigation.

Figure 5 shows the electroluminescence (EL) spectra for the devices of ITO / PEDOT-PSS (40nm) / polymer (90 ± 5 nm) / Al-Li (100nm).

![Figure 5](image)

**Figure 5.** Comparison of the EL spectra of the devices fabricated with PPV and copolymers prepared at different monomer activation temperature.

The general feature of the EL spectra is about the same as the corresponding PL spectra, although less vibronic details are visible in EL spectra. As observed in their PL spectra, the wavelength of the maximum emission intensity decreased from 505 nm for the PPV device to 480 nm for the device of the copolymer obtained after monomer activation at 750°C.

Figure 6 shows the light output vs. electric field and the current density vs. electric field curves for devices.
Figure 6. Light output vs. electric field (a) and current density vs. electric field (b) curves for the devices of ITO / PEDOT-PSS (40 nm) / polymer (90 ± 5 nm) / Al-Li (100 nm).

The numbers represent PPV (1), and polymers (2, 3 and 4) prepared after activating the monomer at 650, 700 and 750°C, respectively. The turn-on electric field of the devices fabricated with PPV and copolymers prepared after monomer activation 650, 700 and 750 °C are steadily increased from 0.28 to 0.84, 1.38 and 1.62 MV/cm. The device with polymer 4 showed very little electroluminescent. The same tendency was also observed for the current density of the devices (figure 6b). The enhancement of the turn-on electric field by higher monomer activation temperature is to be expected because of the increased incorporation of the saturated PE units in the backbone leading to diminished electrical conductivity of the resulting copolymers. The external quantum efficiencies of the copolymers devices, however, were higher (6×10^{-3}, 3.4×10^{-3} and 1.1×10^{-3} % respectively for the copolymers prepared at the activation temperature of 650, 700 and 750°C) than that (8×10^{-4} %) of the device fabricated with PPV. The confinement of excitons in the conjugative structure disrupted by the saturated PE units in the polymer backbone appears to be responsible for this observation [19]. It is also noted that the external efficiency drops down in a regular fashion as the content of the PE units in the copolymers increases, which can be ascribed to the decreased concentration of the light emitting PV units in the backbone.

3.3. Solar cell based on PPV derivative

Figure 7 shows the UV-VIS spectra of MEH-PPV, PVBM and their composite in different PCBM concentration.
The characteristic π-π* absorption peak of MEH-PPV is observed around 510 nm in the pure MEH-PPV and its composites. From the UV-VIS spectra, we can see that the three characteristic peaks in UV range (at 339, 260 and 211) of PCBM are overlapped with the absorption peaks of pure MEH-PPV (335, 260 and 211 nm). The absorption peaks of the composite are just superposition of the characteristic peaks of pure MEH-PPV and PCBM. This result confirms that there is no significant interaction between the two materials in the ground state.

Evidence of photoinduced charge transfer in MEH-PPV/PCBM composite can be provided by PL quenching. Figure 8 shows the PL spectra of MEH-PPV and its composite. For the pure MEH-PPV, the characteristic PL peaks are observed around 589 and 625 nm. With increasing PCBM concentration this peaks are significantly quenched.

Figure 8. PL spectra of MEH-PPV and its composite (Excitation wavelength: 488 nm).

Figure 9 shows the dependence of the open photovoltage on the MEH-PPV/PCBM ratio. With increasing MEH-PPV/PCBM ratio, the open circuit photovoltage of the solar cell only slightly increases from 0.6 V to 0.64 V. In contrast, with increasing MEH-PPV/PCBM ratio, the short circuit current density strongly decreases from 4.3 mA/cm² by the ratio of 0.2 to 1.7 mA/cm² by the ratio of 0.5 (figure 10).

Figure 9. Dependence of the open photovoltage on the MEH-PPV/PCBM ratio.
According to [11], higher concentration of PCBM favors the formation of a phase separated interpenetrated network with sizable domains, which in turn favors effective charge separation. Thus, the short circuit current density is enhanced by higher PCBM concentration or lower MEH-PPV/PCBM ratio. The same tendency comparing to the short circuit current density has been observed by the overall energy conversion efficiency depending on the MEH-PPV/PCBM ratio (figure 11). By the MEH-PPV/PCBM ratio of 0.2, the solar cell reaches the highest overall energy conversion efficiency of 1.1%. This result indicates that the MEH-PPV/PCBM composite has significantly improved the performance of the solar cell comparing to the solar cell using only MEH-PPV as active material.

### 4. Conclusion

It was demonstrated that a series of copolymers, poly(p-phenylenevinylene –co- p-phenyleneethylene), could be prepared from a single monomer, p- (methoxymethyl) benzyl chloride, via the CVDP method after activating the monomer at the different temperatures. Incorporation of p-phenyleneethylene units in the polymer backbone resulted in a blue-shift in both photoluminescence and electroluminescence when compared with those PPV. The luminescence properties of the copolymers strongly depended on the CVDP condition, especially, on the monomer activation temperature, which controlled the amount
of the PE units incorporated in the copolymer backbone. A higher monomer activation temperature led to inclusion of a higher level of the PE unit in the deposited copolymer resulting in bigger blue shift in EL and PL spectra.

We have also successfully fabricated the organic solar cell based on the MEH-PPV/PCBM composite. Through the PCBM phase, the photoluminescence of the MEH-PPV was strongly quenched due to the photoinduced charge transfer from MEH-PPV onto fullerene. The incorporation of PCBM phase into MEH-PPV phase had strong effect on both the short circuit current density and the overall energy conversion efficiency of the solar cell. With increasing PCBM concentration, the two parameters above steadily increased. The effect of the PCBM concentration on the open photovoltage was insignificant.

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