

Chemical Vapor Deposition Polymerization for Conducting Polymer Thin-Film Coating

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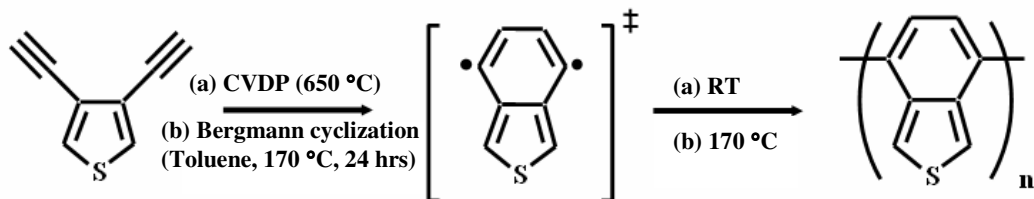
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EXTENDED ABSTRACT

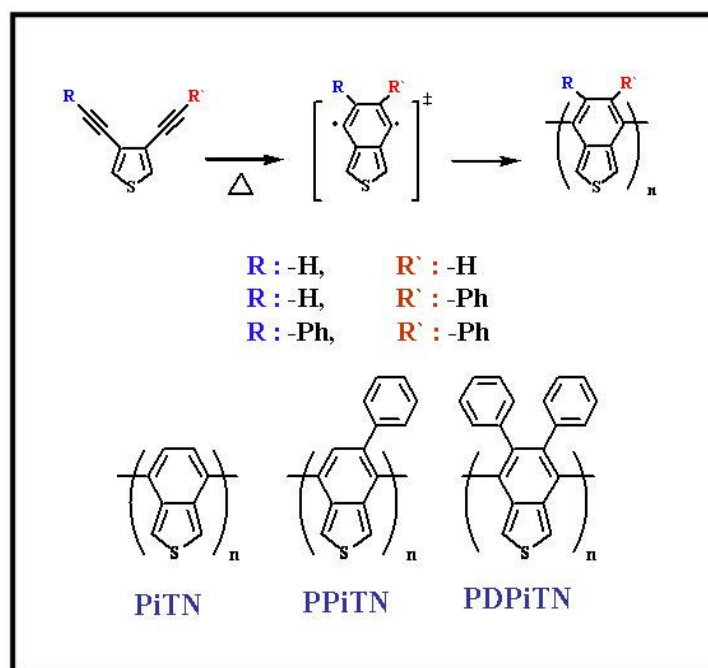
Power conversion efficiency of the polymer solar cells is reaching over 5% in research laboratory [1-7], and there is great interest in exploring their potential in the market in coming years. Among many studies of polymer solar cells, a bulk heterojunction where random mixture of electron-donating and electron-accepting molecules is most often used as a primary absorber layer. In general, the mixture of the two different small organic molecules is prepared by thermal co-evaporation process under vacuum [1] and the mixture between electron-donating conjugated polymer molecules and nano-scale electron-accepting organic or inorganic molecules is prepared by spin-coating process under inert gas [2-7]. Although PCE over 5 % has been achieved by both processes, more emphasis has been made on the bulk heterojunction solar cells with conjugated polymers due to the advantage of solution process over vacuum thin-film process. It should be noted that the world-record PCE over 6 % has been reported utilizing a double polymer bulk heterojunction solar cell fabricated by the solution process [7].

So far, most conducting polymer thin-film coatings for photovoltaic applications are made by solution processes such as spin-coating, doctor blade, and several printing techniques. While the solution processes provide a very simple, cost-effective way to fabricate the solar cells, simple thermal chemical vapor deposition polymerization (CVDP) thin-film coating will provide more options for different device structures and applications because of their superior conformal coating capability down to nano scale. CVDP, as a gas-phase CVD method, it produces uniform, conformal coating in very controlled manner - conformal coating on any non-conventional platform like bi-facial coating on flat plates, coating on fibers, nano/micro trenches with a high aspect ratio is possible. The deposition temperature is typically below 100 °C and any flexible polymer substrate could be used. Clearly, there is no catalyst and solvent involved in the coating process eliminating possible sources for contamination and any other complications.

In our recent work, we have successfully deposited a new thiophene-derivative conjugated polymer thin films using CVDP. For example, we have deposited a new family of poly(isothianaphthene)-based conjugated polymers from various diethynylthiophene monomer. Thiophene-based monomers studied in this work directly polymerize into thin-films via free radical polymerization. Results have confirmed that 3,4-diethynylthiophene monomers can be thermally excited (activated) transforming into free radicals. Subsequently, polymerization occurs among ethynyl radicals forming phenyl rings (scheme 1) at relatively low temperature (< 100 °C). This new polymer, poly(isothianaphthene-3,6-diyl) (PITN(3,6)) has never been synthesized previously, and a number of modified versions of the biethynyl monomers and their polymers have been prepared (scheme 2) using CVDP. In CVDP, the monomer molecules are thermally vaporized, pass through hot zone transforming into radicals, and eventually polymerize on the surface of substrate (figure 1). A monomer sample (30 ~ 200 mg) of



Scheme 1. Synthesis of poly(isothianaphthene-3,6-diyl) (PITN(3,6)) using (a) chemical vapor deposition polymerization and (b) Bergmann cyclization.



Scheme 2. Examples of PITN(3,6) derivatives.

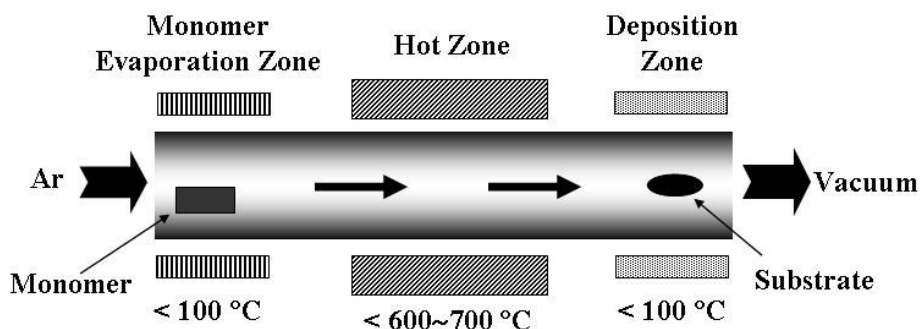


Fig. 1. Schematic diagram of basic thermal chemical vapor deposition polymerization set-up.

purified 3,4-diethynylthiophene was placed on a tungsten boat and vaporized at 60 °C in a steady stream of argon (40 SCCM). The pressure was typically maintained at about 0.01 torr during the process. The vaporized monomer was allowed to pass through the activation zone (hot zone in the figure) preheated to 650 °C. Then, polymerization occurred when activated monomers arrived on the surface of the substrate located in the deposition zone from the figure. The substrate was typically at room temperature. As expected, the final thin-film was not soluble in organic solvents. For Bergmann cyclization (Figure 1b), the solution of 3,4-diethynylthiophene (0.175 g, 1.3 mmol) in 2 ml toluene was placed in a screw pressure cap tube and heated at 170 °C for 24 hours under darkness. After cooling down to room temperature, the product was obtained by filtration and was cleaned by chloroform. Finally the black solid of PITN(3,6) (77% yield) was obtained after Soxhlet extraction with tetrahydrofuran.

In addition to the proton nuclear magnetic resonance performed (not shown here), Fourier transform infrared spectroscopic (FTIR) results verified the structure of PITN(3,6). Figure 2 shows FTIR spectra and further structural analysis of PITN(3,6) synthesized by two methods – CVDP and Bergmann cyclization. Two main absorption bands at 740 cm^{-1} and 3060 cm^{-1} correspond to the thiophene ring's $\text{C}_{\text{sp}^3}\text{-H}$ out-of-plane bend and the stretching modes, respectively. Hence, the polymerization did not occur through the thiophene rings, but through phenyl rings instead. In contrast, PITN(3,6) prepared by Bergmann cyclization contained terminal alkyne group (dashed circle in the figure) and five-membered rings, that generally results a weak chemical structure reported by Johnson *et al.*[8]. This structure was verified by two absorption bands at 2104 cm^{-1} and 3298 cm^{-1} and the bands were indicated in dashed circles (spectrum b in the figure). These results indicate PITN(3,6) prepared by CVDP has a cleaner structure than the polymer from Bergmann cyclization within experimental window explored.

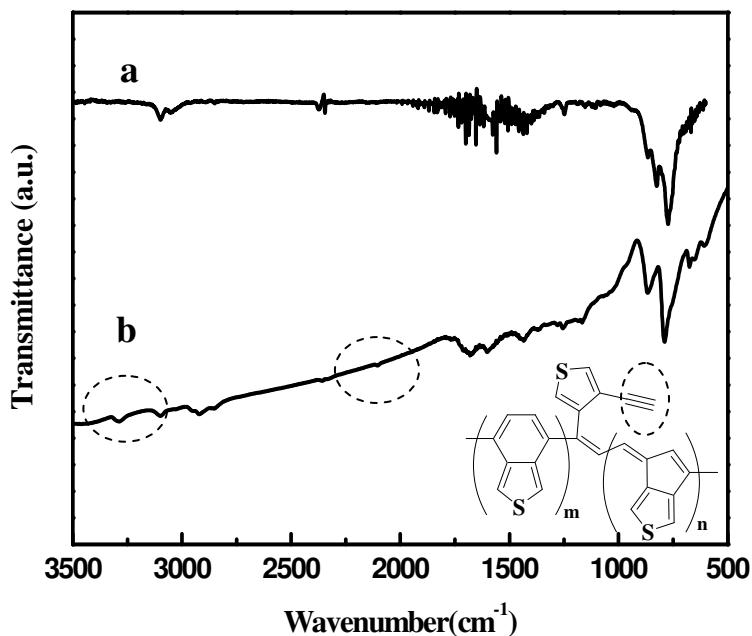


Fig. 2. FTIR spectrum of PITN(3,6) prepared by (a) CVDP and (b) Bergmann cyclization. The molecular structure of the polymer prepared by Bergmann cyclization is included in the figure - the terminal alkyne group and associated absorption bands are indicated by dashed circles.

Figure 3 shows the absorption spectrum and cyclic voltammogram of a PITN(3,6) film deposited by CVDP. The optical band-gap of PITN(3,6) is about 1.8 eV, which is comparable to the band-gap of P3HT, more commonly used for polymer solar cells [7]. The synthesis of PITN(3,6) was partially motivated by both theoretical and experimental research of more commonly known PITN(2,7) showing its low band-gap of about 1.1 eV [9,10]. In those studies, the low band-gap was explained by the polymer backbone (conjugation) formed through thiophene rings, which tends to stabilize the electronic quinoid state effectively. Similar effect is expected to be present for PITN(3,6) as the repeating units are linked through the phenyl ring although the band gap of PITN(3,6) is bigger than that of PITN(2,7) as measured. The highest occupied molecular orbital (HOMO) level of the film was calculated from the onset of the oxidation measured from cyclic voltammetry of the PITN(3,6) film [11] and, the lowest unoccupied molecular orbital (LUMO) level was estimated from the band-gap and HOMO level. Optical and electrochemical properties of PITN are summarized in Table 1.

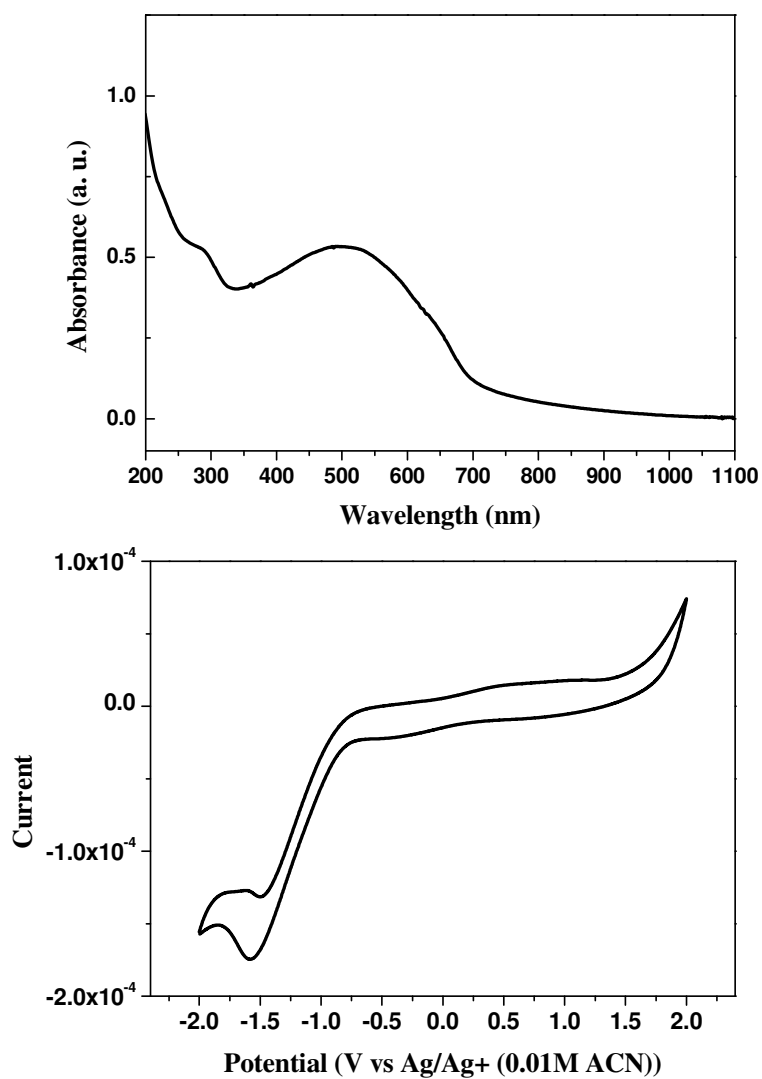


Fig. 3. (a) Absorbance spectrum and (b) cyclic voltammogram of PITN(3,6) thin-film deposited by CVDP.

Table 1. Optical and electrochemical properties of PITN(3,6) thin-film deposited by CVDP.

$\lambda_{\max}^{\text{abs}}$ (nm)	E_g (eV)	E_{onset} (V)	HOMO (eV)	LUMO (eV)
540	1.8	0.6	5.0	3.2

A layered heterojunction solar cell with a stacking order of carbonized poly(p-phenylenevinylene) (CPPV)/PITN(3,6)/Al is fabricated (Figure 4). First, PPV film (300 nm) was prepared by CVDP on the quartz substrate, and the PPV film was subsequently carbonized at 1000 °C for an hour under argon stream. CPPV was considered as both a junction layer and an anode. On top of the CPPV layer made, a 40 nm thick PITN(3,6) thin-film was deposited by CVDP. Finally, Al layer (30 nm) was deposited by thermal evaporation.

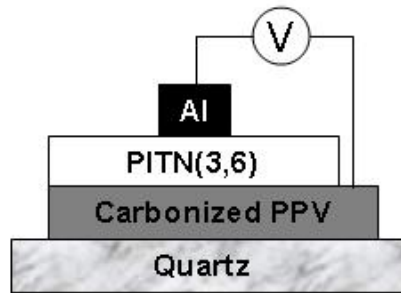


Fig. 4. Photovoltaic device structure of a layered PITN(3,6) heterojunction solar cell.

The PITN(3,6) solar cell yielded an open circuit voltage of about 300 mV as shown in Figure 5. At this writing, its short circuit current is quite low. The low current can be partially ascribed to a very thin absorber layer and unoptimized electrode configuration and probing mechanism – light was shine from Al side instead of quartz substrate side due to the mechanical limitation of the probe station. This demonstration simply intended to show Further optimization of the device structure and the probing method is under progress to improve the performance of solar cells.

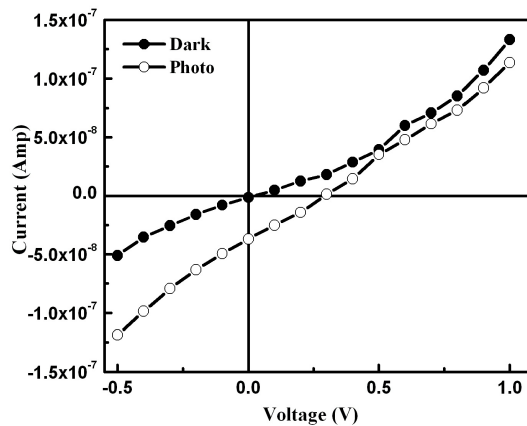


Fig. 5. Dark and photo I-V characteristics of a layered PITN(3,6) heterojunction solar cell.

In summary, poly(isothianaphthene-3,6-diyl) (PITN(3,6)), new thiophene-based pristine conjugated polymer and their derivative thin films have been successfully synthesized from tailor-made monomer precursor molecules for photovoltaic applications. The thin-films were deposited by chemical vapor deposition polymerization (CVDP) at substrate temperatures typically lower than 60 °C. Structural analysis using proton NMR and FTIR verified the chemical vapor reaction under CVDP was clean. It is also shown that the same polymer can be synthesized from the reaction in liquid-solution synthetic process (Bergmann cyclization) using the same monomer although some side reaction occurs and need to be avoided. The optical band-gap of PITN(3,6) was about 1.8 eV and its HOMO and LUMO levels were found to be 5.0 eV and 3.2 eV respectively. A layered heterojunction between carbonized PPV and PITN(3,6) thin-films was fabricated and an open circuit voltage of about 300 mV was measured under simulated AM0 condition. As demonstrated in this study, CVDP is a strongly viable option for multi-junction polymer thin-film devices including solar cells. It further provides a capability to deposit conformal polymer thin-films on any platform that has an irregular shape used for unique photovoltaic applications. Deposition of various PITN-derivatives is in progress and further emphasis will be made on the optimization of solar cell performance in future studies.

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