

Research Article

Effect of Microwave Radiation on the Synthesis of Poly(3-hexylthiophene) and the Subsequent Photovoltaic Performance of CdS/P3HT Solar Cells

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Poly(3-hexylthiophene) (P3HT) is a semiconductor polymer that has been proved to be a good electron donor in organic or hybrid solar cells. In this work, a detailed study of P3HT synthesis in CH_2Cl_2 solvent by oxidative method with and without MW assistance has been conducted. Effects of synthesis process parameters on the physical properties of P3HT products and their application in hybrid CdS/P3HT photovoltaic devices were studied. It is observed that the use of MW as well as the reaction time affected the reaction yield and properties of the polymer products. It was found that, by the traditional method (without MW), the maximum yield and the properties of the polymer products were similar after 2 h or 24 h of synthesis. The optimal reaction time with MW for P3HT polymerization in CH_2Cl_2 solvent was 1 h, and the obtained P3HT product showed similar or better properties than those P3HT polymers synthesized by the traditional method in the same solvent. The effect of using MW during the synthesis was to increase yield and crystal size of P3HT. Larger energy conversion efficiency of ITO/CdS/P3HT/CP-Au devices was obtained when the P3HT product had higher molecular weight and head/tail-head/tail (HT-HT) triad contents.

1. Introduction

Conductive polymers have attracted significant attention in recent decades because of their potential applications in various fields of chemistry, physics, electronics, optics, materials, and biomedical sciences [1]. In particular, polythiophene and its derivatives stand out as the most promising members of conjugated polymer family because of their unique electrical behavior, excellent environmental and thermal stability, solubility, low-cost synthesis, and mechanical strength [1]. In particular, polythiophenes have been used in organic photovoltaics (OPV) [2–4], rechargeable batteries [5], optical windows [6], fuel cells [7], electrochromic devices [8], and so forth. OPV is a rapidly emerging renewable energy alternative that offers the advantage of being of

lower cost than existing technologies due to the ability to be printed on a mass scale [9]. For solar cell applications, poly(3-hexylthiophene) (P3HT) is one of the most promising candidates due to its high absorption coefficient ($\sim 10^5 \text{ cm}^{-1}$) in the visible region of the solar spectrum as well as the high mobility of the photogenerated holes [10]. Oxidative coupling polymerization has a great advantage, especially in large-scale preparation. P3HT can be obtained as precipitate by oxidative polymerization of the monomer at low or room temperature and inert atmosphere [11, 12].

During the chemical synthesis, heat is mostly required to accelerate the reaction rate and is commonly supplied by conduction through warm plate or recipients. Microwave (MW) radiation is another and very efficient way to heat the reaction solution [13]. The beginning of the rapid growth

of MW-assisted organic synthesis procedures was started in 1986 by pioneers Gedye et al. [14] and Giguere et al. [15]. MW heating is a promising technique in sustainable chemistry (green chemistry); several methods have been developed for performing reactions using MW, including the use of less solvent compared to the traditional method and even solvent-free conditions [16, 17]. With the use of modern scientific MW devices, high temperatures can be achieved in an easy, safe, and reproducible manner, the reaction times can often be decreased, and product yields and purity can be increased in comparison with the conventional heating methods [18]. However, several questions are still open concerning the different effects of MW irradiation in organic and macromolecular chemistry [19]. It is now recognized that, during the MW heating, the MW irradiation is transferred directly to the reactive species, causing the migration of ions and rotation of dipoles. These molecular movements generate molecular collisions and friction, causing the heating of the material [20].

In a previous work, MW radiation technology had been used for the chemical synthesis of poly(3-hexylthiophene) (P3HT) with CoolMate [16]. The synthesis was carried out by direct oxidation of 3-hexylthiophene monomer in chloroform solvent, and an optimum MW radiation time of 1 h was determined in that work. As an alternative solvent, the reaction was carried out in dichloromethane (CH_2Cl_2) under the same MW irradiation, but the radiation time was only of 1 h. The polymerization in CH_2Cl_2 solvent resulted in a higher yield, better homogeneous morphology with smaller grain size (determined by AFM), and greater HT coupling, but the optimum reaction time in CH_2Cl_2 solvent was not carried out. As a continuation of that investigation, in this work, a detailed study was carried out in the MW-assisted synthesis of P3HT in CH_2Cl_2 solvent. P3HT was synthesized by oxidative method with and without MW assistance for comparison. Effects of process parameters such as MW radiation and reaction time on the properties of the products were studied. The P3HT products were characterized by FTIR, ^1H NMR, TGA, GPC, XRD, photoluminescence, and UV-Vis spectroscopy. Once the materials were characterized, some of them were selected for manufacturing of photovoltaic devices with CdS/P3HT as active layers. The effect of P3HT properties on photovoltaic performance of the solar cells was also discussed.

2. Experimental

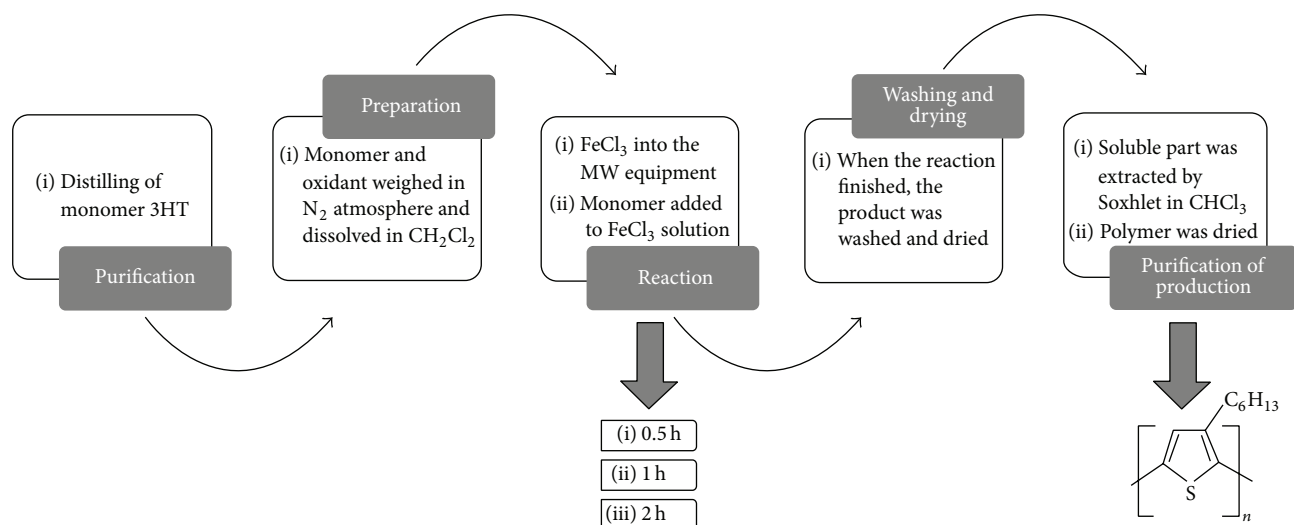
P3HT was obtained by two methods in CH_2Cl_2 solvent: (1) by direct oxidation of distilled 3-hexylthiophene (3HT) monomer using FeCl_3 as oxidant at 0°C and under N_2 atmosphere [21], called the "traditional method," and (2) by MW-assisted synthesis [16]. Briefly, in the first case, 3HT monomer was added to FeCl_3 , both previously dissolved in CH_2Cl_2 . The mixture was stirred at 0°C at different reaction times. The product was precipitated in methanol, filtered, and washed with methanol, HCl solution, acetone, NH_4OH solution, EDTA solution, and distilled water. The polymer was dried and extracted in chloroform. For the case of MW-assisted synthesis (monomode microwave CEM Discover apparatus at -40°C with a Discover CoolMate apparatus, with

a power output ranging from 0 to 300 W), the FeCl_3 solution in the reactor was placed inside the MW equipment and the experimental conditions were programmed to obtain a 0°C reaction temperature, 100 W of power, and different reaction time. When the reaction temperature was reached, 3HT solution was added to the reactor (Scheme 1). The reaction time was varied (24 h, 2 h, 1 h, and 0.5 h) to determine the optimal reaction time in this solvent for each synthesis method (MW-assisted and traditional). The amount of solvent used in the MW-assisted synthesis of P3HT was lower with respect to traditional synthesis (approximately one-sixth of the amount of solvent used in the traditional synthesis without MW). Once the polymers were obtained, films were prepared on Corning glass substrates by spin-coating technique at a concentration of 16 mg/mL toluene. Uniform films were obtained in the red coloration (nondoped state).

The number average (M_n) and weight average (M_w) molecular weights and polydispersity (PD) were determined by a size exclusion chromatograph (SEC, Hewlett Packard HPLC 1100) equipped with in-line vacuum degasser, autosampler, and UV detector. The SEC equipment was fitted with three PLgel 5–10 mm columns (pore size: 106, 105, and 103; 300 mm \times 7.5 mm) and one PLgel 10 mm guard column (50 mm \times 7.5 mm) (Polymer Laboratories) and operated using tetrahydrofuran as eluent at 1.0 mL/min at 40°C . The instrument was calibrated with polystyrene standards, and molecular weights are expressed as polystyrene equivalents (standards 1×10^6 –400 Da). Dyads (HH and HT) and triads (HT-HT, HT-HH, TT-HT, and TT-HH) configuration was determined by ^1H NMR (Varian Inova 400 instrument) using CDCl_3 as solvent. Their contents in P3HT polymer were estimated from the peak areas that appeared around $\delta = 2.55$ (HH), 2.8 (HT), 6.98 (HT-HT), 7.00 (HT-HH), 7.02 (TT-HT), and 7.05 (TT-HH) ppm in the ^1H NMR spectrum [22, 23].

Thermal stability and decomposition temperature of the polymers were determined by thermogravimetric analysis (TGA TA Q500). The samples were heated at $10^\circ\text{C}/\text{min}$ rate under nitrogen atmosphere. Changes in optical absorption of P3HT films were probed by recording ultraviolet-visible (UV-Vis) spectra using a Shimadzu 3101 PC spectrophotometer. Fourier transform infrared spectroscopy (FTIR) spectra of samples were recorded in a FTIR Spectrometer GX, PerkinElmer. X-ray diffraction (XRD) patterns were recorded in a Rigaku Ultima IV X-ray diffractometer ($\text{CuK}\alpha$ radiation; $\lambda = 0.154$ nm), with a scanning rate of $1^\circ/\text{min}$ from 10° to 40° in 2θ range (mode: parallel beam and grazing angle: 1). For XRD measurement, P3HT was deposited on Corning glass. Photoluminescence characterization was performed in a UV-Vis spectrophotometer of absorption-emission (LAMBDA 650, PerkinElmer) at excitation wavelengths of 430 nm. P3HT was characterized in form of thin films, prepared by spin-coating.

For solar cells fabrication, a 50 nm CdS film as window layer (CdS-f) was deposited by chemical bath deposition for two hours at 60°C on clean ITO coated glass substrates (Delta Technologies, sheet resistance $R_s = 8$ –12 Ω). The composition of the chemical bath solution for the window layer consists of 12.5 mL of cadmium nitrate (1 M), 7.5 mL of sodium citrate (1 M), 1 mL of concentrated ammonium hydroxide, 2.5 mL of thiourea (0.1 M), and finally 26.5 mL of



SCHEME 1: MW-assisted synthesis of poly(3-hexylthiophene).

distilled water [24]. To prepare the polymer film, P3HT was dissolved in 1,2-dichlorobenzene (DCB) with a concentration of 2.5 mg/mL and magnetically stirred. After this, the solution was deposited on top of the CdS-f window. The ITO/CdS-f/P3HT structure was then annealed at 190°C for 10 min. For the hole-collecting contact, a film of conductive carbon paint (CP, SPI Chem) was deposited through an aluminum shadow mask with an area of 0.1 cm². Finally, a 40 nm thick gold (Au) electrode was deposited by evaporation [25]. The final device configuration was ITO/CdS-f/P3HT/CP/Au. At least 6 cell samples were prepared for each type of solar cell. All the cell preparation procedure was carried out in air (except for the evaporation of Au) and the final devices were not sealed. The solar cell samples were irradiated from the ITO side with a solar simulator (Oriel) with 100 mW/cm² radiation intensity. The current-voltage (*I-V*) measurement was recorded in ambient conditions.

3. Results and Discussion

The P3HT products were completely soluble when they were synthesized with MW for reaction times of 0.5 and 1 h. However, when the reaction time was up to 2 h, an insoluble precipitate was present in the final product that the Soxhlet extraction was required to separate the soluble part of the product. In the case of P3HT synthesized without MW, the products were soluble for reaction times of 0.5 and 1 h, and longer reaction times (2 and 24 h) led to the formation of insoluble precipitates. The insoluble parts of P3HT should be those macromolecules with higher molecular weight or cross-links. Reaction yields based on soluble polymer were calculated and listed in Table 1. For the three reaction times, 0.5 h, 1 h, and 2 h, P3HT products synthesized without MW showed a lower yield than P3HT products synthesized with MW, indicating, as expected, that the MW radiation promotes a faster reaction.

When the reaction time was shorter like 0.5 h, both synthesis methods gave a low yield (49 to 54%), suggesting that

the reaction was not completed for that reaction time. Longer reaction times led to larger yield, and the use or disuse of MW affected the reaction time for the maximum yield. Without MW, the maximum yield was obtained for 2 h of reaction. Longer reaction time such as 24 h only maintained the same yield without further increase. Thus, in the synthesis without MW, a reaction time of 24 h is not required as conventionally the reaction is performed. On the other hand, the use of MW reduced the reaction time to reach the maximum yield. With a reaction time of 1 h under MW radiation, maximum yield of P3HT products was obtained (92%), similar to that obtained in the previous study for 1 h in CH₂Cl₂ (93%) [16]. It is evident that the use of MW helped to reduce the reaction time and increase the yield. Furthermore, reagent consumption was monitored using thin-layer chromatography and 1 h was determined as the optimum time in the case of P3HT polymerization in CH₂Cl₂ solvent. In the previous work, the optimal polymerization time was also 1 h by using chloroform as solvent [16], suggesting that both solvents were effective as MW heating medium.

Thermal stability of the P3HT products was analyzed by TGA technique and the results were shown in Figure 1. It is observed that the samples synthesized without MW were thermally more stable than those synthesized in the presence of MW. Up to 200°C, all samples showed similar stability, but above that temperature the samples synthesized with MW showed a small weight loss from 200°C to 340°C (about 7%), which could be the loss of the low-molecular-weight fraction of the P3HT product [26]. The second and the largest decomposition stage of P3HT products occurred at temperatures between 476 and 500°C (Table 1). P3HT synthesized for 24 h without MW showed the highest degradation temperature (500°C) among all the polymer products, because of the highest molecular size or weight that product contained, as it will be shown in Table 2.

Table 2 gives the measurements of molecular weights and polydispersity for the P3HT products. The results showed that, by increasing the reaction time, the molecular weight

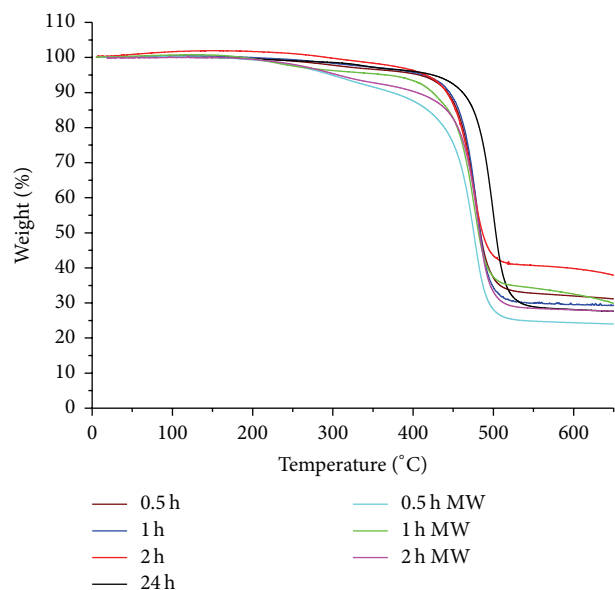


FIGURE 1: TGA curves of the P3HT products synthesized with or without MW radiation.

TABLE 1: Reaction yield and maximum decomposition temperature of P3HT products synthesized with or without microwave radiation (MW) for different reaction times.

Reaction time (h)	Yield (%)	Maximum decomposition temperature (°C)
0.5	49	478
1	84	480
2	86, extraction	476
24	86, extraction	500
0.5 (with MW)	54	476
1 (with MW)	92	476
2 (with MW)	88, extraction	481

TABLE 2: Molecular weight and polydispersity data of P3HT products synthesized with or without microwave (MW) radiation.

Reaction time (h)	Mn	Mw	PD
0.5	17816	40436	2.27
1	29089	65016	2.24
2	29454	71163	2.42
24	32662	80295	2.46
0.5 with MW	13662	40295	2.95
1 with MW	14648	40438	2.76
2 with MW	31069	92008	2.96

of the products increased with or without MW. Up to 1 h of the reaction time, the molecular weight was smaller when the synthesis was carried in the presence of MW. With 2 h of reaction time, the molecular weight of MW synthesized product was similar to that obtained without MW with a reaction time of 24 h. On the other hand, the P3HT polymers synthesized with MW showed higher polydispersity compared with those

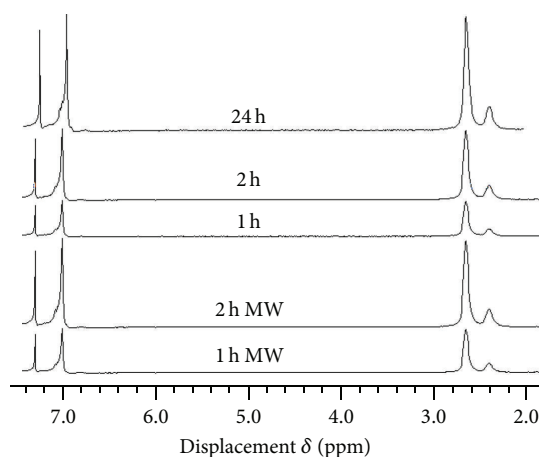


FIGURE 2: ^1H NMR spectra of P3HT polymers synthesized with or without MW radiation.

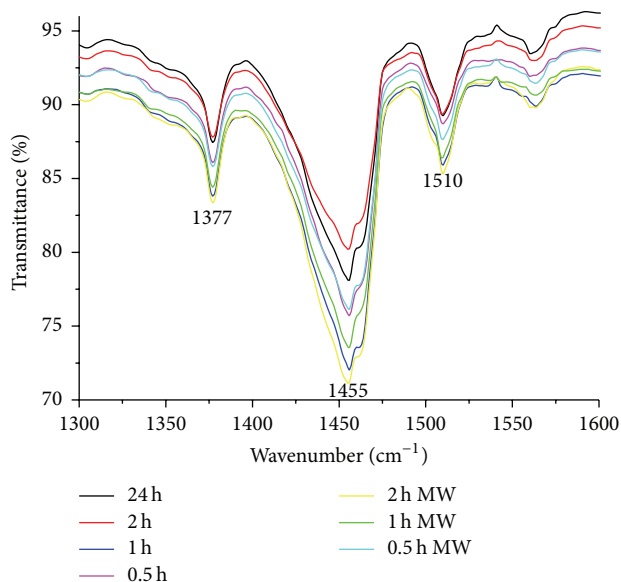
synthesized in the absence of MW, which could result from the rapid polymerization kinetics under MW irradiation. Larger polydispersity in MW P3HT products implies that they contained a larger percentage of the macromolecules with lower molecular weight, which confirmed the TGA results of the same samples. Finally, from the application point of view, the polymer molecular weight is an important parameter in the fabrication of efficient organic photovoltaics (OPV) devices [9]. For the bulk heterojunction devices, the device performance increases with P3HT molecular weight. This result will be probed later on.

The structural regularity of the P3HT products was examined by ^1H NMR spectroscopy (Figure 2). The spectra showed two peaks in the 2.4–2.9 ppm region (2.54 ppm and 2.78 ppm), due to the $\alpha\text{-CH}_2$ protons that are directly connected to the thiophene ring. Thus, the signal at 2.78 ppm corresponds to the head/tail (HT) dyad configuration and that at 2.54 ppm to head/head (HH) one. The signals between 6.9 and 7.1 ppm correspond to β -protons (or protons on the 4-position) on the thiophene ring and reveal the triad configuration. Triads were estimated from the ratio of peak areas that appeared around 6.98 (head/tail-head/tail, HT-HT), 7.00 (head/tail-head/head, HT-HH), 7.02 (tail/tail-head/tail, TT-HT), and 7.05 (tail/tail-head/head, TT-HH) ppm [23]. The dyad and triad contents of different P3HT products are shown in Table 3.

The P3HT products obtained by both synthesis methods showed the maximum content of the HT dyads with reaction time. In the case of P3HT synthesis without MW, the increase of dyads was given up to a reaction time of 2 h, giving the maximum dyads percentage of 79.5%. Above 2 h of reaction, that percentage decreased with longer reaction time. In the case of the MW-assisted synthesis of P3HT, the maximum percentage of dyads was given for reaction time of 1 h (79.1%) and then decreased for longer reaction time, giving a decrease of 4.8% for 2 h of reaction. As for the triad content, the maximum HT-HT content was obtained for 24 h of reaction in the case of the P3HT products synthesized without MW. The maximum of the same triad content for P3HT products

TABLE 3: Dyad (HT and HH) and triad (HT-HT, TT-HT, HT-HH, and TT-HH) contents of P3HT products synthesized in CH₂Cl₂ with or without MW radiation.

Reaction time in CH ₂ Cl ₂ (h)	HT (%)	HH (%)	HT-HT (%)	TT-HT (%)	HT-HH (%)	TT-HH (%)
0.5	77.6	22.4	67.36	12.76	13.28	6.6
1	77.5	22.5	66.92	10.74	9.64	12.7
2	79.5	20.5	68.72	13.28	9.36	8.64
24	78.2	21.8	70.42	14.32	7.53	7.73
0.5 MW	77.3	22.7	66.55	14.35	7.54	11.56
1 MW	79.1	20.9	68.97	10.16	10.12	10.75
2 MW	74.3	25.7	62.36	9.46	11.32	16.86

FIGURE 3: FTIR spectra of the P3HT products in the range of 1300 to 1600 cm⁻¹.

with MW was obtained for a reaction time of 1 h. Since the HT-HT triads are the uninterrupted conjugation segments, they are conductive phases inside the P3HT products. As a result, the reaction time for optimum conductivity should be 1 h if P3HT products were synthesized under MW radiation. If the same products were synthesized without MW, the optimum time should be 24 h.

From the FTIR spectra of the P3HT products (Figure 3), it is affirmative that MW radiation did not generate the formation of any subproduct. The same FTIR spectra, on the other hand, can help to estimate the conjugation length in the P3HT molecular chains, as suggested by the literature [27]. Figure 3 shows the FTIR spectra of the P3HT products in the range of 1300 to 1600 cm⁻¹. The intensity ratio of the symmetric ring stretch at 1455 cm⁻¹ to the asymmetric ring stretch at 1510 cm⁻¹ ($I_{\text{sym}}/I_{\text{asym}}$) of each P3HT product is listed in Table 4. In the literature [27], it is affirmed that longer conjugation length in the polymer backbone results in smaller $I_{\text{sym}}/I_{\text{asym}}$ ratio. According to that, the conjugation length was similar in most P3HT products synthesized with and without MW ($I_{\text{sym}}/I_{\text{asym}} = 3.0$ to 3.2), except for that sample synthesized for 0.5 h without MW ($I_{\text{sym}}/I_{\text{asym}} = 3.9$)

that contained shorter conjugation length. Compared to the HT-HT triad contents (Table 3) of the same products, which varied from 62 to 70%, it seems that the estimation of conjugation lengths by FTIR spectra was close to the results of the ¹H NMR spectroscopy.

The optical properties of P3HT thin films were studied by analyzing their UV-Vis and photoluminescence (PL) spectra, Figures 4(a) and 4(b), respectively. The maximum absorption peaks of all the P3HT films were at about 513 nm (2.41 eV), corresponding to π - π^* band, and two vibronic absorption shoulders appeared at 550 nm (2.25 eV) and 600 nm (2.07 eV) (Figure 4(a)). The appearance of the vibronic features is the signature of the close packing of P3HT polymer chain in the condensed phase [28], indicating that there is small ordering in the chains of all the P3HT films. Furthermore, a shift of the 513 nm absorbance peaks towards higher wavelengths was given for the samples synthesized for 1 h with and without MW, suggesting a decrease in energy gap related to increased conjugation chain [29]. It seems that MW radiation had no effect on the optical absorbance of the P3HT products.

Figure 4(b) shows the normalized PL spectra of the same P3HT films as in Figure 4(a) in the wavelength region from 600 to 800 nm under excitation of 430 nm incident light at room temperature. Below 600 nm, there were sharp peaks from the cut-off filter of the fluorophotometer that did not correspond to the P3HT samples. The PL spectra give vibronic emission with maximum peaks located at wavelength of 656 nm (0-0 emission peak) and shoulders at 702 nm (0-1 emission peak). The vibronic structure of the solid is related to the ordered crystalline phase [30]. The vibronic structure observed in the PL spectra is due to the radiative recombination of excitons near the bottom of the $\bar{\nu} = 0$ band, and the 0- ν ($\nu = 0, 1, 2, \dots$) peak corresponds to emission terminating on the electronic ground state with ν vibrational excitations [31].

The optical energy gap (E_g) values of P3HT thin films can be determined as the low energy onset of the absorption peaks in Figure 4(a) [32, 33], which were 1.85 for P3HT synthesized for 1 h, with or without MW, and 1.88 to 1.89 eV for the rest of the P3HT samples. In the PL spectra, on the other hand, the E_g values of the same P3HT films correspond to the wavelengths of the maximum emission peaks (Figure 4(b)), giving the same numbers as in the case of absorption spectra. The second method to estimate E_g values is by Tauc plots if P3HT is considered as a semiconductor material of direct transition: $(\alpha h\nu)^2$ versus $h\nu$ [34], giving

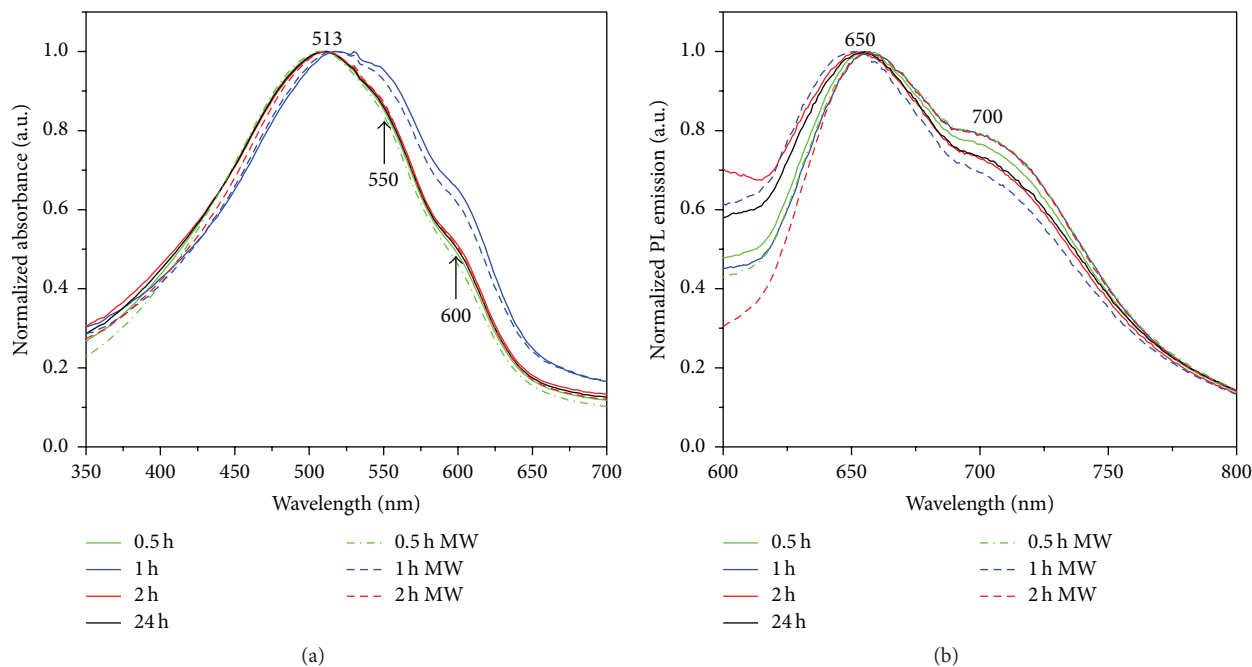


FIGURE 4: Normalized (a) UV-Vis and (b) photoluminescence (PL) spectra of pristine P3HT thin films. P3HT products were synthesized with or without MW radiation.

TABLE 4: Intensity ratios of the symmetric ring stretch at 1455 cm^{-1} to the asymmetric ring stretch at 1510 cm^{-1} ($I_{\text{sym}}/I_{\text{asym}}$) of the P3HT products synthesized with or without MW for different reaction times.

Reaction time (h)	$I_{\text{sym}}/I_{\text{asym}}$
0.5	3.9
1	3.1
2	3.0
24	3.0
0.5 (with MW)	3.1
1 (with MW)	3.1
2 (with MW)	3.2

values of 1.92 to 1.93 eV for P3HT products synthesized for 1 h with and without MW and 1.95 to 1.96 eV for the rest of the polymer samples. The slightly higher E_g values estimated by Tauc method could come from the imprecision in determining the intersection of linear plots on the abscissa axis. However, the consistent smaller band gap values for 1 h P3HT samples are indicative that these films contained more crystalline structure or longer conjugation lengths than the rest of the P3HT products.

To confirm the microstructures of 1 h P3HT samples, their XRD patterns are shown in Figure 5, together with a 24 h sample (without MW). Well-defined diffraction peaks with maximum intensity at $2\theta = 10.6^\circ$ and 15.9° and a wide peak at 23.4° were manifested by the three P3HT samples. These peaks correspond to the Miller indices (2 0 0), (3 0 0), and (1 2 0), respectively (identified with the card of P3HT Powder Diffraction: 00-054-2080; the crystal system:

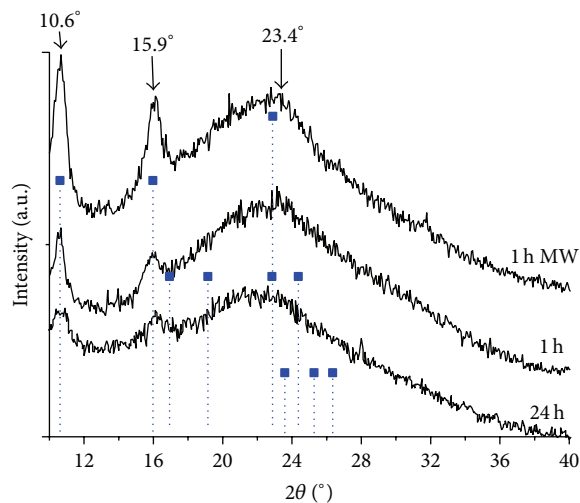


FIGURE 5: X-ray diffraction patterns of P3HT products and their comparison with card of P3HT for orthorhombic crystal system (00-054-2080).

orthorhombic). The two low-angle peaks at $2\theta = 10.6^\circ$ and 15.9° correspond to second- and third-order reflections from the interlayer spacing, respectively, and the corresponding values of d -spacing calculated using Bragg's law are 8.4 \AA and 5.6 \AA , respectively [35]. Chen and Ni proposed that the broad peak at $2\theta = 23.4^\circ$ (d -spacing: 3.8 \AA) could be attributed to the spacing between two successive stacking planes of coplanar subchains (or intraplanar packing) [35]. Furthermore, crystal sizes of P3HT samples can be estimated with the full width at

TABLE 5: Crystal size values using the Scherrer equation and full width at half-maximum peak at $2\theta = 10.6^\circ$.

Sample	FWHM (deg.)	Crystal size (nm)
P3HT 1 h	0.8775	10.5
P3HT 1 h MW	0.7904	11.8
P3HT 24 h	1.1052	8.1

TABLE 6: Photovoltaic parameters of CdS/P3HT hybrid solar cells with different P3HT products.

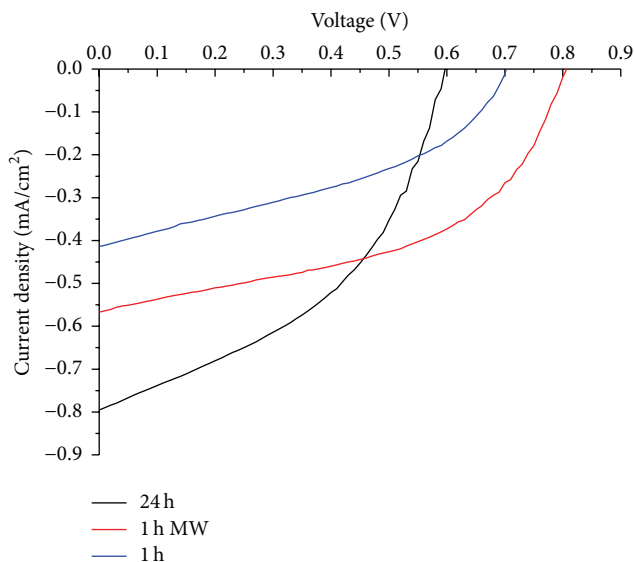
Reaction time	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η
24 h	0.795	0.599	0.55	0.268
1 h	0.440	0.701	0.4	0.15
1 h MW	0.563	0.803	0.44	0.198

half maximum (FWHM) at a selected diffraction peak in their XRD patterns using Scherrer equation [36]. By choosing the peak at $2\theta = 10.6^\circ$, it is found that 1 h P3HT with MW had an average crystal size of 11.8 nm, the 1 h P3HT sample without MW had an average crystal size of 10.5 nm, and the P3HT sample synthesized for 24 h without MW had an average crystal size of 8.1 nm (Table 5).

XRD results suggested that both parameters, the synthesis time and MW radiation, influenced the P3HT crystallinity. First, when the synthesis is carried out without MW, a shorter synthesis time produced higher crystallinity. Second, the MW radiation produced higher crystallinity in the synthesized product in comparison with those without MW. The crystallinity is related to molecular weight, according with Kline et al. [37]. They found that low-molecular-weight films have a higher degree of crystallinity than high-molecular-weight films. The results of this work support that observation. The direct correlation between lower molecular weight (Table 2) and larger crystal size (Table 5) is present for the three mentioned P3HT samples.

The three samples analyzed by XRD were selected to build photovoltaic devices and their photovoltaic performance was evaluated using the following configuration: ITO/CdS-f/P3HT/CP-Au. Figure 6 shows J - V curves, and the values of open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and efficiency (η) of the different PV devices are listed in Table 6. P3HT synthesized for 1 h without MW showed the lowest J_{sc} , while the sample synthesized for 24 h without MW showed the highest. Moreover, P3HT synthesized in MW for 1 h showed the highest V_{oc} . As a result, the highest efficiency was obtained in the device based on P3HT synthesized for 24 h without MW.

Conventional theory on charge transport in organic semiconductors would predict that the more-ordered or crystalline films should have higher charge carrier mobility than their less-ordered, high-molecular-weight counterparts. However, Kline et al. [37] showed that in reality the opposite is true. The less-ordered films had higher mobility. The charge carrier mobility of regioregular P3HT spin cast from

FIGURE 6: J - V curves of CdS/P3HT based solar cells with P3HT products synthesized for 1 h with and without MW and for 24 h without MW.

chloroform decreases by four orders of magnitude when the molecular weight is reduced by one order of magnitude [37]. Kline et al. commented that intergrain transport is severely limited in the low-molecular-weight films due to the poor connectivity between grains and the large number of insulating grain boundaries. In the case of the high-molecular-weight films, there are no well-defined grain boundaries. Since the molecules are much longer than the size of the ordered domains, individual molecules are expected to be part of several domains. These bridging molecules limit the amount of misorientation between neighboring domains and provide a possible pathway for charges to go between neighboring domains [38, 39]. This trend of increasing mobility with molecular weight was also observed in diodes by Goh et al. [40]. The 24 h P3HT sample without MW is one that has the highest molecular weight (Table 2) among the three cell samples, which corroborates the fact that the device performance increases with P3HT molecular weight due to the improved charge mobility [9], originated from the enhanced intermolecular ordering (p-stacking) of the P3HT phase. Comparing the two 1 h P3HT samples, the one without MW had a higher molecular weight. However, it contained lower HT and HT-HT contents (Table 3), which probably affected the device efficiency. In summary, high molecular weight plus high regioregularity in P3HT improves the photovoltaic performance of CdS/P3HT based solar cells.

4. Conclusions

Poly(3-hexylthiophene) (P3HT) was synthesized by oxidative method using CH_2Cl_2 as solvent with and without microwave (MW) radiation. P3HT synthesized with MW showed a higher yield than those obtained in the absence of MW. Maximum dyad configuration was determined for the synthesis of P3HT with MW for 1 h and without MW for

2 h. The molecular weight was directly proportional to the reaction time in both synthesis methods (with and without MW); 2 h of reaction time in the synthesis of P3HT with MW is required to reach the molecular weight comparable with those products obtained for 24 h in the absence of MW. Polydispersity of P3HT synthesized with MW was higher than that synthesized without MW. UV-Vis characterization determined that the largest blue-shift was shown by P3HT synthesized for 1 h with and without microwave, suggesting a decrease in energy gap, probably caused by higher molecular arrangement. Furthermore, the MW presence in the P3HT synthesis allowed better arrangement of the polymer chains in P3HT, resulting in larger crystal size. Finally, energy conversion efficiency of CdS/P3HT based photovoltaic devices increased with the molecular weight in combination with the percentage of HT-HT triads in the P3HT products synthesized with both methods. The optimization of polymerization process of conducting polymer plays an important role in photovoltaic performance of hybrid solar cells.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

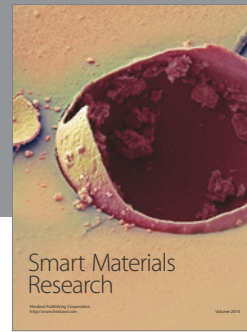
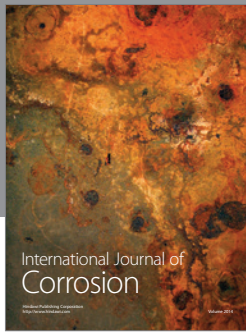
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