crystals

MDPI

Article

Solvent-Dependent Thermoelectric Properties of PTB7 and Effect of 1,8-Diiodooctane Additive

Mina Rastegaralam [1], **Changhee Lee** [1,*] **and Urszula Dettlaff-Weglikowska** [2,*]

[1] Department of Electrical and Computer Engineering, Inter-University Semiconductor Research Center, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Korea; mn.rstgrlm@gmail.com
[2] Materials Science Consulting and Management, 22113 Oststeinbek, Moellner Landst. 97B, Germany
* Correspondence: chlee7@snu.ac.kr (C.L.); udettlaff.w@gmail.com (U.D.-W.)

Academic Editor: George S. Nolas
Received: 19 August 2017; Accepted: 26 September 2017; Published: 29 September 2017

Abstract: Conjugated polymers are considered for application in thermoelectric energy conversion due to their low thermal conductivity, low weight, non-toxicity, and ease of fabrication, which promises low manufacturing costs. Here, an investigation of the thermoelectric properties of poly({4,8-bis[(2-ethylhexyl)oxy]benzo [1,2-b:4,5-b′] dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl) carbonyl]thieno[3,4-b] thiophenediyl}), commonly known as PTB7 conjugated polymer, is reported. Samples were prepared from solutions of PTB7 in three different solvents: chlorobenzene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene, with and without 1,8-diiodooctane (DIO) additive. In order to characterize their thermoelectric properties, the electrical conductivity and the Seebeck coefficient were measured. We found that, by increasing the boiling point of the solvent, both the electrical conductivity and the Seebeck coefficient of the PTB7 samples were simultaneously improved. We believe that the increase in mobility is responsible for solvent-dependent thermoelectric properties of the PTB7 samples. However, the addition of DIO changes the observed trend. Only the sample prepared from 1,2,4-trichlorobenzene showed a higher electrical conductivity and Seebeck coefficient and, as a consequence, improved power factor in comparison to the samples prepared from chlorobenzene and 1,2-dichlorobenzene.

Keywords: electrical conductivity; Seebeck coefficient; power factor; PTB7 polymer

1. Introduction

Thermoelectric materials are capable of the solid-state conversion between thermal and electrical energy. Such materials have attracted much attention due to their great potential for applications in power generation and refrigeration [1,2]. Thermoelectric materials are used in generating power from waste heat and in on-chip and larger-scale cooling modules [3–7]. Thermoelectric generators offer a number of advantages compared to other direct current sources of power. They usually have a compact module structure that does not require any moving parts [8].

The performance of thermoelectric materials is determined by a dimensionless quantity called the thermoelectric figure of merit ZT expressed by: $ZT = S^2\sigma T/\kappa$, where S, σ, T, and κ represent the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively.

In order to improve the figure of merit, it is necessary to increase the Seebeck coefficient and electrical conductivity simultaneously. However, it is a challenging task, as both parameters are inversely correlated. The electrical conductivity is calculated from $\sigma = en\mu$, with n being the carrier concentration, μ the carrier mobility, and e the electron charge. At the same time, by increasing n, the electrical conductivity of the material increases, while the Seebeck coefficient decreases. An alternative strategy is the enhancement of mobility while maintaining a constant n to increase electrical conductivity and Seebeck coefficient simultaneously [9].

Inorganic conductors and semiconductors are efficient thermoelectric materials, but they are associated with issues such as high production cost, toxicity, and scarcity [10]. In contrast, organic and polymeric semiconductors are advantageous over inorganic materials due to their relatively easy use, low thermal conductivity, low weight, non-toxicity, and the established thin layer technology, promising low fabrication costs. In addition to conventional polymers, conjugated polymers may also be used as thermoelectric materials since they have advantageous characteristics of conventional polymers. The low thermal conductivity, κ, of conjugated polymers (two or three orders of magnitude lower than in inorganic semiconductors) is a major factor when considering conjugated polymers for thermoelectric applications, besides their ease of fabrication via simple solution processability [8,11–13]. The fact that most conducting polymers can be manufactured in the form of thin films over large areas is a potential benefit for multilayered polymer thermoelectric modules. Thin films require less material than bulk, and can be more easily processed over large surfaces. Both factors contribute to lower fabrication costs. In addition, operating thermoelectric devices are usually modules composed of alternatively layered films of p- and n-type semiconducting materials. Therefore, the solution-processed thin film technology is beneficial for organic thermoelectric materials. If polymer thermoelectrics are produced on a large scale, the cost could be much lower than currently produced bismuth telluride thermoelectrics (~$7/watt) [14], which is the most commonly used material for thermoelectric applications with a ZT value close to 1.

To date, few conducting polymers have been studied for their thermoelectric properties [13,15–18]; therefore, samples of PTB7 polymer were prepared and investigated.

PTB7 is a p-type semiconducting polymer that is used in organic field effect transistors. This conjugated polymer is also widely used in bulk heterojunction polymer solar cells as a donor mixed with an acceptor material in the blend of their active layer. In an effort to improve the efficiency of PTB7-based polymer solar cells, DIO was added to the blend of donor-acceptor materials, giving power conversion efficiency (PCE) of 7.4%. This was the first polymer solar cell to show a PCE over 7% [19]. However, when DIO was mixed with only PTB7, it had, depending on the solvent, different effects on the polymer [20]. As has been shown by Guo et al., only the films made from 1,2,4-trichlorobenzene exhibited an improved crystallinity after addition of DIO compared to chlorobenzene and 1,2-dichlorobenzene [20].

Here, we explored the effect of different solvents and DIO on the thermoelectric properties of PTB7samples fabricated via drop casting. The following sections focus on the preparation of the samples, determination of their electrical conductivity, the Seebeck coefficient, charge carrier mobility, and a discussion of the results.

2. Materials and Methods

PTB7 and DIO were purchased from 1-Material and Tokyo Chemical Industry, respectively, and solvents were purchased from Sigma Aldrich. All materials were used as received. The PTB7 solutions were prepared by dissolving 15 mg of PTB7 in 1 mL (1000 μL) of chlorobenzene (CB), 1,2-dichlorobenzene (DCB), and 1,2,4-trichlorobenzene (TCB) under glove box filled with argon. For solutions containing DIO, 15 mg of PTB7 was dissolved in a mixture of 970 μL of solvent and 30 μL of DIO and stirred for more than 12 hours. Samples were formed by drop casting the solutions on glass substrates, which were cleaned via sonication in acetone, isopropyl alcohol, and water before use. The thickness of each sample was, on average, 10 μm, which was determined by a profilometer. The electrical conductivity was measured via the four-probe method using a Keithley SMU237 source measurement unit. The Hall mobility of the samples was measured in a magnetic field of 0.5 T at room temperature using the Van der Pauw method. The Seebeck coefficient was calculated from $S = -\Delta V/\Delta T$, where ΔV was the thermoelectric voltage generated along the sample when it was subjected to the temperature difference ΔT, as shown schematically in Figure 1. Two K type thermocouples were used to measure the temperature on both ends of the samples. From each solution, four samples were prepared, and electrical conductivity, carrier mobility, and the Seebeck coefficient were measured five times for each sample.

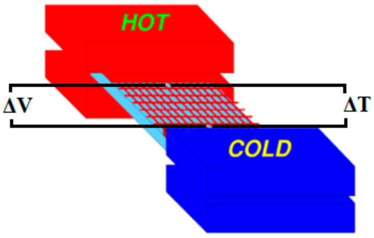

Figure 1. Schematic presentation of the Seebeck coefficient determination.

3. Results and Discussion

Figure 2 shows the molecular structure of the applied chemical materials, and Table 1 presents the boiling points of the solvents and DIO. Among these three solvents, 1,2,4-trichlorobenzene (TCB) has the highest boiling point (214) and chlorobenzene (CB) has the highest vapor pressure and the lowest boiling point (131). As shown in Figure 3, for both types of the samples (with and without DIO), the electrical conductivity value of the samples made of TCB is higher than two other samples made of DCB and CB.

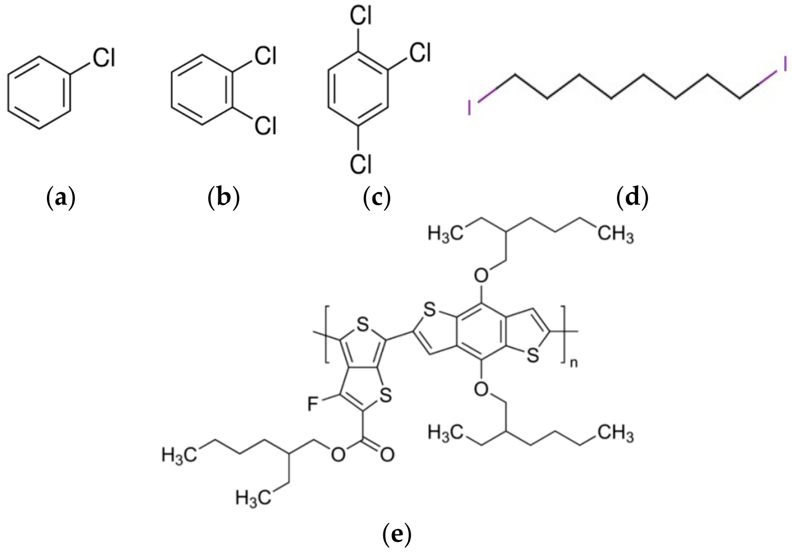

Figure 2. Molecular structure of (**a**) chlorobenzene (CB), (**b**) 1,2-dichlorobenzene (DCB), (**c**) 1,2,4-trichlorobenzene (TCB), (**d**) DIO (**e**) PTB7.

Table 1. Boiling point of the used solvents and 1,8-diiodooctane.

Material	Boiling Point (°C)
1,2,4-Trichlorobenzene ($C_6H_3Cl_3$)	214
1,2-Dichlorobenzene ($C_6H_4Cl_2$)	180
Chlorobenzene (C_6H_5Cl)	131
1,8-Diiodooctane($C_8H_{16}I_2$)	167–169

Considering the boiling point of the solvents, it is clear that samples made of a higher boiling point solvent need a longer time for drying to complete evaporation of the solvent. Slow evaporation of the solvent allows for better ordered molecular packing of the PTB7 polymer and therefore, its ability to transport charge carriers improves, leading to increased electrical conductivity [21].

As shown in Figure 3, the values of conductivities are 0.5 S/m, 0.8 S/m and 1.2 S/m for samples made of CB, DCB, and TCB without DIO, respectively. Furthermore, we observed that the addition of DIO improved the electrical conductivity only in the samples made of TCB, and failed to enhance the electrical conductivity of the samples prepared from CB and DCB. There seems to be a synergic effect in the interaction between the polymer, TCB, and DIO. However, in the solvents that evaporate faster, the introduction of DIO (which remains in the assembled polymer fibers) increases the impurity scattering due to collisions between charge carriers and DIO molecules, which may be the reason for decreasing the carrier mobility and as a consequence, electrical conductivity. By looking at the conductivity values, it is obvious that the addition of DIO has the worst effect on the conductivity of the sample prepared from chlorobenzene. The electrical conductivity values for samples containing DIO are as follows: 0.35 S/m, 0.6 S/m, and 1.78 S/m for samples made of CB, DCB and TCB, respectively.

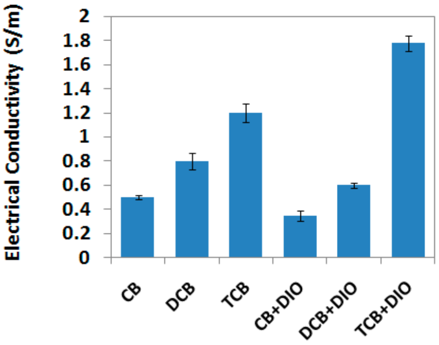

Figure 3. Electrical conductivity values of PTB7 samples prepared from different solvents with and without DIO.

The nature of charge carriers in the PTB7 samples was determined by thermoelectric power measurement. Corresponding Seebeck coefficients of the samples are shown in Figure 4. The positive Seebeck coefficient values indicate that the major charge carriers are holes, confirming PTB7 as a p-type semiconductor. The diagram reflects that the Seebeck coefficients increase with increasing boiling point of the solvent for both types of samples (with and without DIO) as was already observed in the electrical conductivity measurements. For both types of the samples, the highest Seebeck coefficient value was obtained from the samples made of TCB. This simultaneous enhancement in electrical conductivity and the Seebeck coefficient is attributed to an increase in the carrier mobility of the samples, in which a solvent with a higher boiling point was used. Table 2 presents the Hall mobility values of the samples. The changes in the mobility of the samples prepared from different solvents closely correlate with the corresponding measurements of electrical conductivity and the Seebeck coefficient.

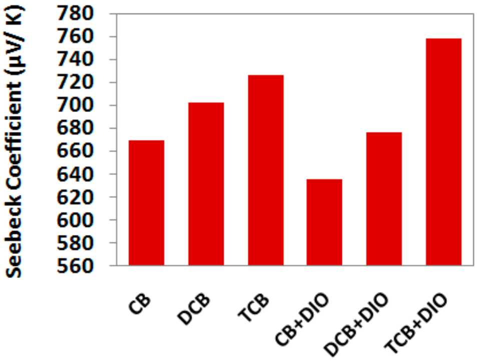

Figure 4. Seebeck coefficient values of PTB7 samples prepared from different solvents with and without DIO.

Table 2. Mobility of the samples.

Sample	Mobility (cm^2/Vs)
PTB7: TCB	1.09×10^{-1}
PTB7: TCB + DIO	1.69×10^{-1}
PTB7: DCB	7.15×10^{-2}
PTB7: DCB + DIO	5×10^{-2}
PTB7: CB	3.9×10^{-2}
PTB7: CB + DIO	2.66×10^{-2}

Upon addition of DIO, Seebeck coefficient values in the samples made of CB and DCB decrease, showing that DIO plays a negative role in increasing mobility in CB and DCB samples. The Seebeck coefficient values of the samples are: 670 μV/K, 702 μV/K and 726 μV/K for CB, DCB and TCB samples without DIO and 636 μV/K, 676 μV/K and 758 μV/K with DIO, respectively.

Figure 5 shows the AFM images of the PTB7 samples. As seen in Figure 5a–c, all the neat PTB7 samples are rather homogeneous as is expected for homopolymer films. For both types of samples, surface roughness decreases when the boiling point of the solvent increases, which is consistent with increasing the mobility. As shown in Figure 5d–f, polymer aggregation is clearly visible when DIO is added. Obviously, the addition of DIO decreases the solubility of polymer in the neat solvents leading to aggregation of polymer fibers and formation of lateral structures in the ternary system (polymer, solvent, DIO). Considering the volatilities of the used solvents that decrease from CB (131 °C) to DB (180 °C) and TB (214 °C), the observed differences in the structure can be explained. The root-mean-square (RMS) surface roughness was found to be 1.1, 0.92 and 0.82 for CB, DCB and TCB samples without DIO and 3.8, 3.2 and 0.7 for CB, DCB and TCB samples with DIO, respectively.

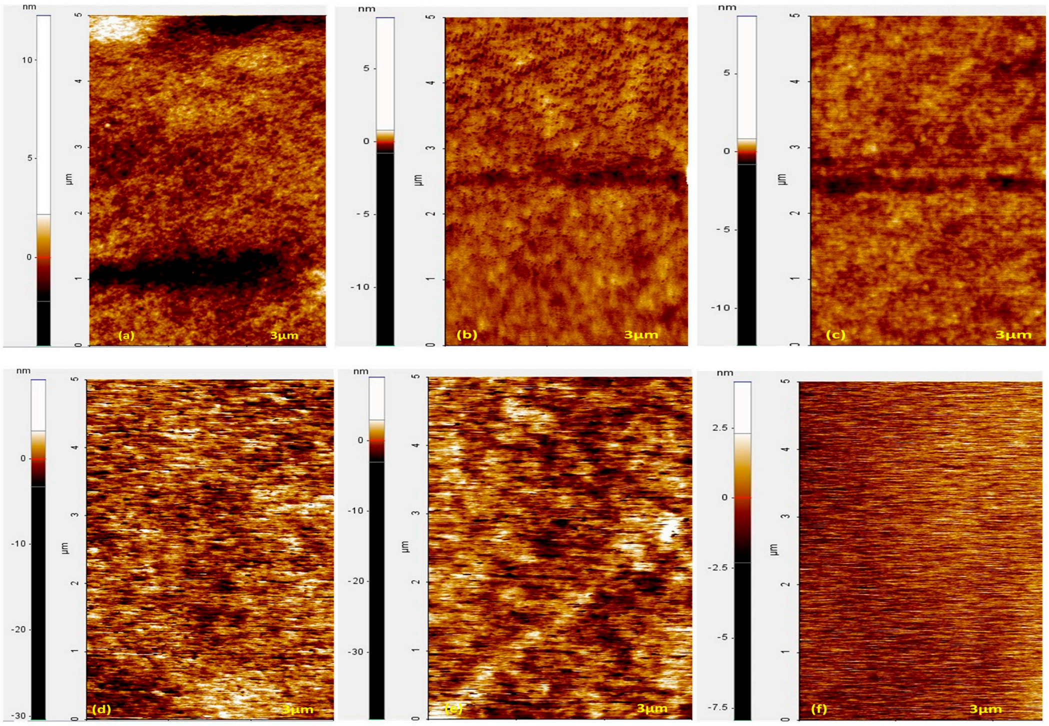

Figure 5. AFM images of PTB7 samples prepared from different solvents with and without DIO: (**a**) CB; (**b**) DCB; (**c**) TCB; (**d**) CB-DIO; (**e**) DCB-DIO; (**f**) TCB-DIO.

Figure 6 shows the thermoelectric power factor values of our samples calculated from $P = S^2\sigma$, where S is the Seebeck coefficient value and σ is the electrical conductivity. For both types of samples (with and without DIO), the highest power factor was obtained from the 1,2,4-trichlorobenzene sample that shows among these 3 solvents, 1,2,4-trichlorobenzene is the best one for preparing PTB7 solutions in order to obtain samples with higher thermoelectric power factor and addition of DIO has a positive effect on that, while reduces power factor of the CB and DCB samples. The calculated values of the power factor are: 0.00224 ($\mu WK^{-2}cm^{-1}$), 0.0039 ($\mu WK^{-2}cm^{-1}$) and 0.0063 ($\mu WK^{-2}cm^{-1}$) for samples made of CB, DCB and TCB without DIO and 0.00141 ($\mu WK^{-2}cm^{-1}$), 0.00274 ($\mu WK^{-2}cm^{-1}$) and 0.01 ($\mu WK^{-2}cm^{-1}$) with DIO, respectively.

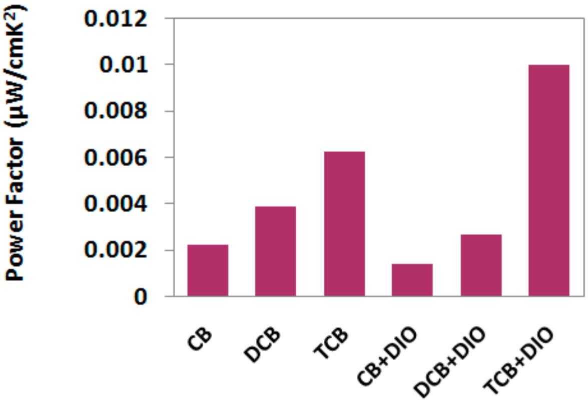

Figure 6. Power factor values of PTB7 samples prepared from different solvents with and without DIO.

It is worth noting that both the electrical conductivity and the Seebeck coefficient and therefore, the power factor values of PTB7 samples are higher than some previously reported conducting polymers such as poly [3-hexylthiophene] (P3HT) [13], poly [N-90-heptadecanyl-2,7-carbazole-alt-5,5-(40,70-di-2-thienyl-20,10,3-benzothiadizole)] (PCDTBT) [16], poly carbazolenevinylene derivative, poly paraphenylene, poly *p*-phenylenevinylene [22] and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) [23]. However, we believe that any changes in chemical structure of the conducting polymers, lead to a modification in their electrical conductivity and influence the thermoelectric effect. The replacement of the functional groups by different side chains in PTB7 will affect the assembly of polymer fibers in the solution-processed layers and polymer solubility and thus, modify their thermoelectric behavior. For this purpose, detailed computer simulations followed by experimental studies are required to find out which kind of side chains will have a positive effect on the thermoelectric properties of the modified PTB7.

Assuming that the thermal conductivity of the PTB7 samples is comparable to the value provided for polypyrrole (0.1) [22], the figure of merit (ZT) values for our samples are estimated to be 0.000673, 0.00118 and 0.0019 for samples made of CB, DCB and TCB without and 0.000424, 0.00082 and 0.003 with DIO, respectively, which is still some orders of magnitude lower than that of bismuth telluride. However, thin layer technology established for conductive polymers enables the fabrication of multi-layered structures. In future work, we aim to investigate multiple element modules composed of alternatively layered films with PTB7 as an electron-donating polymer and films of an n-type semiconducting polymer. The thermoelectric voltage generated by such modules would be the sum of contributions from each layer, resulting in increased power output.

4. Conclusions

We investigated the effect of different solvents and 1,8-diiodooctane additive on the thermoelectric properties of PTB7 polymer. Our data demonstrate that a suitable solvent leads to the improvement of thermoelectric properties and the enhancement of the figure of merit. Dissolving PTB7 in a solvent with a higher boiling point leads to obtain higher electrical conductivity and Seebeck coefficient values due to a better ordering of polymer fibers which is beneficial for charge carrier mobility. We observed that addition of DIO improves the electrical conductivity and the Seebeck coefficient of PTB7 only in the sample prepared from 1,2,4-trichlorobenzene, while for the samples prepared from chlorobenzene and 1,2-dichlorobenzene, DIO has a negative effect on the thermoelectric properties reflected by the power factor.

Acknowledgments: This work was supported by the National Research Foundation of Korea (NRF-2016R1A2B3009301) and LG Chem, Ltd.

Author Contributions: Mina Rastegaralam conceived, designed and performed the experiments; Urszula Dettlaff-Weglikowska coordinated scientific work and interpreted the experimental results and Changhee Lee wrote the paper. All authors read and approved the final version of the manuscript to be submitted.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Poudel, B.; Hao, Q.; Ma, Y.; Lan, Y.; Minnich, A.; Yu, B.; Yan, X.; Wang, D.; Muto, A.; Vashaee, D.; et al. High-Thermoelectric Performance of Nanostructured Bismuth Antimony Telluride Bulk Alloys. *Science* **2008**, *320*, 634–638. [CrossRef] [PubMed]
2. Zhao, W.; Fan, S.; Xiao, N.; Liu, D.; Tay, Y.Y.; Yu, C.; Sim, D.; Hng, H.H.; Zhang, Q.; Boey, F.; et al. Flexible Carbon Nanotube Papers with Improved Thermoelectric Properties. *Energy Environ. Sci.* **2012**, *5*, 5364–5369. [CrossRef]
3. Adroja, N.; Mehta, S.B.; Shah, P. Review of thermoelectricity to improve energy quality. *Int. J. Emerg. Technol. Innov. Res.* **2015**, *2*, 847–850.
4. Sharp, J.; Bierschenk, J.; Lyon, H.B. Overview of Solid-State Thermoelectric Refrigerators and Possible Applications to On-Chip Thermal Management. *Proc. IEEE* **2006**, *94*, 1602–1612. [CrossRef]
5. Bell, L.E. Cooling, heating, generating power, and recovering waste heat with thermoelectric systems. *Science* **2008**, *321*, 1457–1461. [CrossRef] [PubMed]
6. Snyder, G.J.; Toberer, E.S. Complex thermoelectric materials. *Nat. Mater.* **2008**, *7*, 105–114. [PubMed]
7. Karni, J. Solar energy: The thermoelectric alternative. *Nat. Mater.* **2011**, *10*, 481–482. [CrossRef] [PubMed]
8. Xu, L.; Liu, Y.; Chen, B.; Zhao, C.; Lu, K. Enhancement in thermoelectric properties using a P-type and N-type thin-film device structure. *Polym. Compos.* **2013**, *34*, 1728–1734. [CrossRef]
9. Petsagkourakis, I.; Pavlopoulou, E.; Portale, G.; Kuropatwa, B.A.; Dilhaire, S.; Fleury, G.; Hadziioannou, G. Structurally-driven enhancement of thermoelectric properties within poly 3,4-ethylenedioxythiophene) thin films. *Sci. Rep.* **2016**, *6*, 30501. [CrossRef] [PubMed]
10. Dubey, N.; Leclerc, M. Conducting Polymers: Efficient Thermoelectric Materials. *J. Polym. Sci. B Polym. Phys.* **2011**, *49*, 467–475.
11. Lodha, A.; Singh, R. Prospects of manufacturing organic semiconductor- based integrated circuits. *IEEE Trans. Semicond. Manuf.* **2001**, *14*, 281–296. [CrossRef]
12. Goodson, K.E.; Ju, Y.S. Heat conduction in novel electronic films. *Annu. Rev. Mater. Sci.* **1999**, *29*, 261–293. [CrossRef]
13. Sun, J.; Yeh, M.L.; Jung, B.J.; Zhang, B.; Feser, J.; Majumdar, A.; Katz, H.E. Simultaneous increase in Seebeck coefficient and conductivity in a doped poly (alkylthiophene) blend with defined density of states. *Macromolecules* **2010**, *43*, 2897–2903. [CrossRef]
14. Hewitt, C.A.; Kaiser, A.B.; Roth, S.; Craps, M.; Czerw, R.; Carroll, D.L. Multilayered carbon nanotube/polymer composite based thermoelectric fabrics. *Nano Lett.* **2012**, *12*, 1307–1310. [CrossRef] [PubMed]
15. Ma, W.; Shi, K.; Wu, Y.; Lu, Z.Y.; Liu, H.Y.; Wang, J.Y.; Pei, J. Enhanced molecular packing of a conjugated polymer with high organic thermoelectric power factor. *ACS Appl. Mater. Interfaces* **2016**, *8*, 24737–24743. [CrossRef] [PubMed]
16. Maiz, J.; Rojo, M.M.; Abad, B.; Wilson, A.A.; Nogales, A.; Borca-Tasciuc, D.A.; Borca-Tasciuc, T.; Martín-González, M. Enhancement of thermoelectric efficiency of doped PCDTBT polymer films. *RSC Adv.* **2015**, *5*, 66687–66694. [CrossRef]
17. Mateeva, N.; Niculescu, H.; Schlenoff, J.; Testardi, L.R. Correlation of Seebeck coefficient and electric conductivity in polyaniline and polypyrrole. *J. Appl. Phys.* **1998**, *83*, 3111–3117. [CrossRef]

18. Toshima, N. Conductive polymers as a new type of thermoelectric material. *Macromol. Symp.* **2002**, *186*, 81–86. [CrossRef]
19. Liang, Y.; Xu, Z.; Xia, J.; Tsai, S.; Wu, Y.; Li, G.; Ray, C.; Yu, L. For the bright future-bulk heterojunction polymer solar cells with power conversion efficiency of 7.4%. *Adv. Mater.* **2010**, *22*, E135–E138. [CrossRef] [PubMed]
20. Guo, S.; Herzig, E.M.; Naumann, A.; Tainter, G.; Perlich, J.; Muller-Buschbaum, P. Influence of solvent and solvent additive on the morphology of PTB7 films probed via X-ray scattering. *J. Phys. Chem. B* **2014**, *118*, 344–350. [CrossRef] [PubMed]
21. Foote, A.L. Investigation of Solvent-Dependent Properties of Donor and Acceptor Materials for Photovoltaic Applications. Available online: http://corescholar.libraries.wright.edu/etd_all/1451/ (accessed on 29 July 2015).
22. Xuan, Y.; Liu, X.; Desbief, S.; Leclère, P.; Fahlman, M.; Lazzaroni, R.; Berggren, M.; Cornil, J.; Emin, D.; Crispin, X. Thermoelectric properties of conducting polymers: The case of poly(3-hexylthiophene). *Phys. Rev. B* **2010**, *82*, 115454. [CrossRef]
23. Gao, F.; Liu, Y.; Xiong, Y.; Wu, P.; Hu, B.; Xu, L. Fabricate organic thermoelectric modules use modified PCBM and PEDOT:PSS materials. *Front. Optoelectron.* **2017**, *10*, 117–123. [CrossRef]