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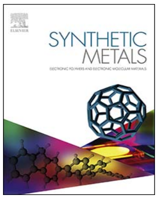

Solution-fabrication dependent thermoelectric behavior of iodine-doped regioregular and regiorandom P3HT/carbon nanotube composites

Murat Tonga[a], Lang Wei[a], Eugene Wilusz[b], Ljiljana Korugic-Karasz[c], Frank E. Karasz[c], Paul M. Lahti[a,*]

[a] Department of Chemistry, University of Massachusetts, Amherst, MA, 01003, USA
[b] Natick Soldier Research, Development and Engineering Center, Natick, MA, 01760, USA
[c] Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA, 01003, USA

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ABSTRACT

Thermoelectric (TE) measurements were compared for iodine-doped composites of carbon nanotubes (CNTs) with poly(3-hexylthiophene-2,5-diyl) (P3HT) having different degrees of regioregularity. Regioregular P3HT gave much higher power factors, showing the need of regioregularity in the polymer for best TE results. TE power factors (PFs) up to $148\,\mu\mathrm{W\,m^{-1}\,K^{-2}}$ were obtained by optimizing multiple factors, including: (i) P3HT sample type, (ii) relative amount and type of CNT, (iii) sample fabrication solvent, and (iv) composite doping duration. The TE performance improvements in the composites arose from greatly increased electrical conductivity by doping and CNT addition, coupled with limited decreases in Seebeck thermopower. Extensive network formation was seen by scanning electron microscopy (SEM) in composites with higher CNT fraction, which is believed to provide better charge transport pathways to improve PFs. Multiwall CNT composites showed much lower PFs compared to singlewall CNT composites, attributable (at least in part) to poor nanotube dispersion.

1. Introduction

The search for sustainable energy sources has impelled efforts to harvest electricity from waste heat, including development of new thermoelectric (TE) materials. Most work has focused on inorganic TE materials, but their development is challenging for large-scale preparation due to their high costs and limited fabrication choices, as well as their toxic natures and scarce earth abundance of some promising elements [1]. As a result, organic TE materials, especially ones based on conjugated polymers, have gained considerable research interest in recent years. These materials can have intrinsically low thermal conductivity (typically $< 1\,\mathrm{W\,m^{-1}\,K^{-1}}$) [2] with tunable electronic behaviors [3], as well as ready processibility by multiple methods [,4].

TE efficiency can be expressed by the dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, using the Seebeck thermopower coefficient S, electrical conductivity σ, thermal conductivity κ and temperature. The power factor ($PF = S^2\sigma$) is also frequently used to report TE performance due to the difficulties of measuring thermal conductivity. These relationships show that *simultaneous* increases in σ and S — while maintaining low κ – are best to maximize TE. However, these properties typically have strong interdependence in bulk materials. Doping to give more charge carriers and increase σ is usually accompanied by decreased S [5].

The conformation and interchain morphological arrangements of polymer chains have a big impact on charge carrier mobility [6]. For example, poly(3-hexylthiophene-2,5-diyl) (P3HT) has been used heavily in electronic materials research due to its good solubility in common organic solvents (*e.g.,* chloroform, chlorobenzene, and tetrahydrofuran), its good chemical and thermal stability, and its high charge carrier mobility when p-doped in morphologies produced from some fabrication solvents. P3HT morphology depends strongly on regioregular (*rr-*) versus regiorandom (*ra-*) connectivity (Scheme 1), yielding a wide range of doped carrier mobilities (*e.g.,* for *rr*-P3HT $\sim 0.1\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$, for *ra*-P3HT $\sim 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) [7]. We have been particularly interested in conjugated polymers whose TE performance is enhanced by compositing with electrically conductive fillers. Carbon nanotubes (CNTs) have been very promising in this role, due to their high charge transport capabilities [8] and growing commercial availability. Nanotubes (NTs) can form interconnected networks in a composite material, enhancing electrical conductivity while keeping nearly constant the Seebeck thermopower and thermal conductivity relative to a polymer without CNT additive [9]. Phase separated

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[*] Corresponding author.
E-mail address: lahti@chem.umass.edu (P.M. Lahti).

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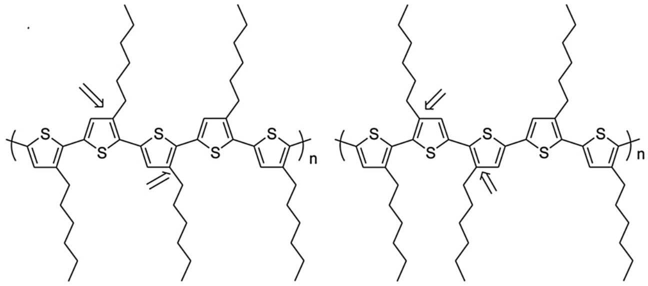

Scheme 1. Chemical structure of regioregular P3HT (left) and regiorandom P3HT (right). Arrows emphasize alkyl chain attachment points.

polymer-rich and CNT-rich regions in polymer/CNT composites thereby can enable simultaneous increases in σ and *S* for higher PFs. Müller *et al.* reported a PF of 95 $\mu W \cdot m^{-1} \cdot K^{-2}$ in drop-cast composite films of CNTs with P3HT doped by $FeCl_3$ [10]. Jang *et al.* reported that P3HT films using singlewall CNTs (SWNT) gave PFs of 105 $\mu W\, m^{-1} K^{-2}$ to 325 $\mu W\, m^{-1} K^{-2}$ in composites processed by different procedures [11–13]. These and other [14] studies show the promise of CNT/P3HT composites.

Although the promise of all-organic TE composites is clear, less work has focused on TE performance of polymer regioregularity by systematically varying in a single study the blend composition, fabrication solvent, doping times and variation of the CNT additive (*e.g.*, singlewall CNT [SWNT] versus multiwall CNT [MWNT]). We recently noted the substantial TE gains to be realized by such a multi-variable optimization of iodine-doped poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV)/CNT composites [15]. In the present work, we similarly investigate TE performance in composites of P3HT with SWNT and MWNT subjected to iodine (I_2) doping. In addition to polymer regioregularity, effects were tested of blend composition, fabrication solvent, doping time, and different types of CNTs including SWNTs versus MWNTs. Substantial variation in sample surface morphologies was found by scanning electron microscopy (SEM). Working with readily-handled, 2.5 cm × 0.5 cm samples under ambient conditions, best performance was obtained for 87 – 90 kDa *rr*-P3HT/SWNT composite films. A 1:1 w/w ratio of polymer to SWNT gave PFs up to 148 $\mu W\, m^{-1} K^{-2}$ after 2.5 h of doping, about 50 times higher than PFs of *ra*-P3HT/SWNT composite films. The higher PF results are comparable to the highest values reported in the recent literature for P3HT/CNT composites. The multivariable optimization process shows a strategy for further improvement.

2. Experimental

2.1. Materials

Iodine was purchased from Fisher Scientific and used as received. Regioregular-P3HT (molecular weight of 87 kdalton with 98% regioregularity) and regiorandom-P3HT (molecular weight of 95 kdalton) polymers were purchased from Sigma-Aldrich. Another regioregular-P3HT (molecular weight of 90 kdalton with 96% regioregularity) was purchased from Rieke Metals, Inc. Two grades of SWNTs purchased from Sigma-Aldrich were tested: (1) ≥50 – 70% carbon basis with 1.2 – 1.5 nm diameters, (2) ≥80% carbon as nanotubes with 0.7–1.4 nm diameters. MWNTs were tested from Wako Pure Chemical Industries (3–20 nm diameters), and from Sigma-Aldrich (outer diameter 6–13 nm, inner diameter 2–6 nm, length 2.5–20 μm). Spectral grade chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), chlorobenzene (CB), and 1,2-dichlorobenzene (DCB) purchased from Fisher Scientific were used as received.

2.2. Sample preparation

P3HT and P3HT/nanotube composite solutions were prepared in spectral grade solvents at concentrations of 6 – 7 mg/mL for P3HT blends with varying weight/weight (w/w) percentages of SWNTs or MWNTs. The solutions were thoroughly mixed by sonication for 2 h, stirred at room temperature for 18 h, poured into casting wells incised into a polytetrafluoroethylene sheet, then allowed to air-dry overnight. The resulting films were removed and cut into rectangles of about 2.5 cm × 0.5 cm × (25–50) μm. A micrometer was used to determine sample thickness, by averaging several measurements across the sample.

Doping was carried out by placing pristine film samples into capped vials with a few crystals of iodine (I_2) for set times. Electrical conductivity and thermoelectric measurements were then carried out as quickly as possible after sample removal from the doping chamber. Additional details are given in supporting material.

2.3. Sample analyses

Sample specific conductivity was measured using a standard four-probe setup with platinum wire contacts. A Keithley 2440 5A source meter was used for conductivity measurements, and a Keithley 2182A nanovoltmeter for voltage measurements. Thermoelectric performance was evaluated using a custom-built apparatus described previously [15]. A Mannix DT8852 digital dual input thermometer was used to measure sample temperatures and confirm establishment of a stable thermal gradient, using K-type thermocouples coated with polyvinylchloride. Thermoelectric potentials were measured for thermal gradients $\Delta T = 0.1 - 10\,^{\circ}C$. Seebeck coefficients were determined by plotting measured thermoelectric potentials versus applied ΔT. Only single composite strips ("tabs") were used for measurements – no multistrip, laminated-stack samples were used. Further details are given in supporting material.

Scanning electron microscopy (SEM) using an FEI Magellan 400 instrument was used to obtain EM images at acceleration voltages of 1 – 5 kV using the same, free-standing samples used to carry out thermoelectric testing. Prior to analysis, SEM samples were attached to a flat geometry sample holder using conductive double-faced adhesive tape. All the SEM analyses were carried at room temperature.

3. Results and discussion

3.1. Maximizing sample electrical conductivity

Commercial *rr*-P3HT samples of molecular weight (MW) 87 kdaltons with 98% regioregularity and MW 90 kdaltons with 96% regioregularity were tested, as well as *ra*-P3HT of MW 90 kdalton and reported 1:1 head-to-head:head-to-tail regioconnectivity. Conditions to maximize electrical conductivity σ versus iodine-doping time for *rr*- and *ra*-P3HT films (without added CNTs) were tested for samples cast from different solvents. Testing focused on halogenated solvents, since these gave best results in our previous TE optimization study [15] of compositing MEH-PPV with CNTs. Film doping times up to 19 h were tested, but extended doping gave lower σ and reduced TE performance. Doping for 2 – 4 h gave maximum σ for *rr*-P3HT, and 5 – 8 h for *ra*-P3HT; these and the consequent PFs are reported in Table 1.

The electrical conductivity was higher for films cast from lower boiling point solvents like $CHCl_3$ or CCl_4. The *rr*-P3HT samples gave σ at least an order of magnitude higher than *ra*-P3HT under corresponding conditions, and *ra*-samples took roughly twice as long to reach maximum σ. This is consistent with the higher intrachain planarity and better interchain packing expected [16] for solvent-cast *rr*-P3HT versus *ra*-P3HT. The doped *rr*-samples all had similar, positive (p-doped) thermopowers $S \sim 35 - 50\,\mu V\, K^{-1}$, rather lower than in *ra*-samples that had $S \sim 45 - 70\,\mu V\, K^{-1}$. Since the two similar *rr*-P3HT sample types

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