Thermoelectric Properties of Semiconducting Polymers

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Keywords:

thermoelectrics, semiconducting polymers, organic electronics, doping, morphology, charge transport

Abstract:

Semiconducting polymers have the potential to be used in thermoelectric devices that are lightweight, flexible, and fabricated using solution processing. Because of their structural and energetic disorder, the relationship between the structure and thermoelectric properties of semiconducting polymers is complex. We review the interconnection between processing routes and doping methods on the thermoelectric properties of polymers. These studies have led to correlations between thermopower and electrical conductivity that are under investigation by theory. With greater understanding of the materials properties behind their performance, semiconducting polymers can be used in future power generation or cooling devices.

1. Introduction

Thermoelectrics are materials that can readily interconvert electrical and thermal energy. While thermoelectric devices are currently made with inorganic materials,(1) there is emerging interest in applications where integration of these materials into systems is challenging. For example, modules operating near room temperature that are mechanically flexible are interesting for wearable devices for health sensing.(2) This driver has led to the investigation of semiconducting polymers as thermoelectric materials. The electronic properties of semiconducting polymers suggest significant potential as thermoelectric materials with the benefit of simple processing routes, such as printing or extrusion.(3, 4)

Thermoelectric materials take advantage of the Seebeck effect, where an electric potential is generated in response to an applied thermal gradient, or the Peltier effect, where a thermal gradient is generated in response an applied electric potential.(1) The magnitude of the Seebeck effect is given by the Seebeck coefficient, or thermopower, S, where ΔV is the electric potential, and ΔT is the temperature gradient (Eq. 1).

$$S = -\frac{\Delta V}{\Delta T} \tag{1}$$

In *n*-type materials, the Seebeck coefficient is negative, while S is positive in *p*-type materials. In addition to the Seebeck coefficient, the thermoelectric performance of a material depends on its electrical conductivity, σ, and thermal conductivity, κ. Thermal conductivity has two components, the thermal conductivity from electrons, κ_{el}, and that from phonons, or vibrations of the lattice, κ_{ph} (Eq. 2).

$$\kappa = \kappa_{el} + \kappa_{ph} \tag{2}$$

These properties contribute to the performance of a material through the figure of merit, ZT, that can be used with the Carnot cycle to predict the ultimate efficiency of thermoelectric energy conversion (Eq. 3).

$$ZT = \frac{S^2 \sigma T}{\kappa} \tag{3}$$

The performance of a thermoelectric material can be improved by increasing the numerator of Eq. 3, where $S^2\sigma$ is referred to as the power factor, or by reducing the total thermal conductivity. In practice, optimization of ZT is challenging because, as the electrical conductivity of a material increases, the Seebeck coefficient tends to decrease while the thermal conductivity increases. If one considers doping of a semiconductor, peak ZT tends to occur at a relatively high charge carrier concentration but before the material reaches degeneracy.(5) Because each of the fundamental properties is temperature dependent, ZT will vary with temperature, leading to a peak temperature of performance.

Inorganic thermoelectric materials are commercially used in specialized power generation and cooling applications, but these materials are typically stiff, made from relatively rare elements,

and can reach peak efficiency at high-temperature.(5, 6) The performance of inorganic materials, such as binary tellurides, chalcogenides, and skutterudites, has been improved by efforts to decrease their thermal conductivity while maintaining their electrical properties.(7, 8) Strategies to decrease thermal conductivity by increased scattering of phonons include alloying and introduction of grain boundaries in polycrystalline samples.(5, 9) Conversely, because polymeric thermoelectrics have lower thermal conductivity than inorganic materials in their insulating state, different approaches are necessary to optimize their thermoelectric performance.

Doped semiconducting polymers provide a route to form thermoelectric devices. Foundational research on materials such as polyacetylene and polyaniline demonstrated that doped semiconducting polymers, also referred to as conducting polymers, can have high electrical conductivities (>1000 S/cm).(10–13) Thermopower of these polymers was examined mainly as a means to study the fundamental transport properties and were found to be relatively low (e.g. ~1 μV/K for highly conductive polyaniline). Their application as thermoelectric materials was not extensively explored due to issues with stability in the ambient. Recent work on the stable polymer poly(3,4-ethylenedioxythiophene) (PEDOT) has revealed relatively high thermopowers at electrical conductivities of ~100 S/cm in thin films, spurring the interest in the thermoelectric behavior of polymers.(14)

This review will focus on recent work that has aimed to identify structure-property relationships for thermoelectric behavior of polymers. While record performance has been obtained using various forms of PEDOT, it is very difficult to characterize because of its low solubility. This characteristic limits measurement of even the most basic information about the polymer, such as the molecular weight of the polymer chains. We focus mainly on *p*-type polymers because of the large number of such materials, but point out that comparable behavior has been found in *n*-type polymers.(15)

2. Basics of Semiconducting Polymers

2.1. Molecular Structure and Electronic Properties

Semiconducting polymers have conjugated backbones with alternating single and double carbon-carbon bonds (Figure 1). This pattern allows the unoccupied *p* orbitals of the carbon atoms to form delocalized π and π^* symmetry molecular orbitals along the polymer chain that are the valence and conduction bands of the single polymer chain. In the solid state, intermolecular interactions modify the energies of the single chain states, but the electronic interactions are weak and the electronic states are frequently described in terms of molecular levels. The ionization energy (IE) is associated with the highest occupied molecular orbital (HOMO), and the electron affinity (EA) is associated with the lowest unoccupied molecular orbital (LUMO). For example, the homopolymer poly(3-hexylthiophene) (P3HT) has an approximate IE level of 5.1 eV and EA level of ~3.0 eV, giving an energy gap of 2.1 eV.(16) The band gap can be modified by choice of monomers or by synthesizing copolymers with alternating electron-donating and electron-accepting units.(17) Judicious design of the donor and acceptor units allows the IE and EA to be tuned separately, which is helpful for chemical stability in the ambient.(17)

A wide range of semiconducting polymers have been developed with varying band gaps and solution processabilities. The use of cyclic conjugated units and heterocycles in the backbone of

the polymer provides the ability to rationally modify the IE and EA, but this structure leads to difficulties in processing because of the stiffening of the polymer backbone. To improve the processability of semiconducting polymers, side chains are added to the backbone to lower the melting point and to improve solubility in common solvents. These side chains are usually formed from functionalities that do not interact strongly with the π-orbitals on the backbone, but they can help to tune the IE and EA by withdrawing or donating electron density. Semiconducting polymers with linear or branched alkyl side chains, such as P3HT and poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT), have been the most widely studied as thermoelectrics.

The interplay between the side chains and backbones helps to control the organization and properties of semiconducting polymers in the solid state. Electronic interaction between the planar backbones of polymers leads to co-facial arrangement referred to as π-π stacking. These π-π stacks form lamellae that are separated by the side chains, commonly referred to as alkyl stacking for materials with alkyl sidechains (Figure 2). This structural motif leads to crystallization for polymers with regioregular backbones. Regioregular (RR-) polymers have their monomers connected in the same isomeric sequence, i.e. "head-to-tail". Regioregular polymers, such as RR-P3HT, can crystallize because of the translational symmetry along the backbone. In contrast, regiorandom (RRa-) polymers have monomers connected in a random arrangement, where some monomers are connected "head-to-head" and others "tail-to-tail." In regiorandom P3HT (RRa-P3HT), the alkyl side chains will not have a regular spacing, making the polymer more soluble but unlikely to form crystallites in films. In regioregular polymers that form semicrystalline films, such as P3HT and PBTTT, charge transport within the crystallites can be highly anisotropic. Electronic transport is fastest along the conjugated backbones, and the π-π stacks facilitate electron transport, as well. However, transport is inhibited in the alkyl, or lamellar, stacking direction due to the insulating side chains (Figure 2). This anisotropy complicates the measurement of the thermoelectric properties. For example, in thin films, the backbone of conjugated polymers tends to lie parallel to the substrate. Crystallites with the alkyl stacking direction perpendicular to the substrate are called "edge-on," while those with the π-π stacking direction perpendicular to the substrate are called "face-on." Measurements of electrical and thermal transport taken in the in-plane and out-of-plane directions can differ because of the anisotropy of the polymer chains.

2.2. Structural Order and Disorder

Both structural and electronic disorder are inherent to semiconducting polymers. Structural disorder can originate from polymer synthesis, e.g. chain defects and the polydispersity of the molecular weight of the polymer molecules, or from the kinetics of solidification from solvent or the melt state. Because polymers have a limited amount of time to crystallize during solidification, polymers chains form an amorphous structure outside of the crystallites. The amorphous and crystalline regions exhibit different electronic properties. The band gap arises from the interaction of the π and π* orbitals of the repeat units along the chain; therefore, conformational changes will modify the electronic levels. For example, the IE of regiorandom P3HT, which is thought to be mostly amorphous, is ≈5.25 eV, while that of regioregular P3HT, which contains more crystalline domains, is ≈5 eV.(18) The conformational disorder disrupts intermolecular interactions, further modifying the electronic levels. Overall, the structural and electronic disorder broaden the electronic density of states (DOS), leading to trap states that reduce the carrier mobility.

The majority of recent studies of the thermoelectric properties of polymers have been carried out on thin (~100 nm thick) films rather than in bulk samples. Thin films have advantages over bulk samples because physical characterization methods, such as optical spectroscopy and X-ray scattering, can be carried out without further steps that could perturb their morphology, e.g. sectioning.(19) These studies have revealed that alignment and connectivity of ordered domains is critical for charge transport because these ordered domains have the least electronic disorder and hence have a higher carrier mobility than disordered regions.(20) The connectivity of ordered domains is accomplished by domain boundaries and tie chains, which are polymer chains that extend that connect crystallites or ordered aggregates together through the amorphous regions.(20, 21) It is critical that the molecular weight of a polymer is high enough such that tie chains can sufficiently connect crystallites by spanning intervening amorphous domains.(21) Charge carrier mobility is further improved if crystallites are aligned in one direction over a length scale several times the crystallite size. Processing strategies that increase chain alignment therefore tend to increase the carrier mobility of polymers.(22) The length scale of crystallite alignment can be observed using high resolution electron microscopy (HR-TEM) or small angle X-ray scattering. Recently, resonant soft X-ray scattering (RSoXS) has proven helpful to define an orientational correlation length (OCL) for the length scale over which backbones maintain comparable directionality.(23)

2.3. Doping Semiconducting Polymers

Doping is required to increase the conductivity and to optimize the power factor of semiconductors because most semiconducting polymers are highly insulting as synthesized. While inorganic semiconductors can be doped by substitution of atoms, organic semiconductors are doped by introducing molecular species that can remove or add electrons to the conjugated backbone. For polymers synthesized in an insulating state, several mechanisms exist to introduce charge carriers. The most straightforward doping method involves charge transfer between the dopant and the polymeric backbone, where the resulting charged dopant acts as the counter-ion to the carrier on the polymer. In the case of *p*-type doping, charge transfer is energetically favorable when the HOMO energy level of the polymer is above the LUMO level of the dopant. Examples of *p*-type charge transfer dopants include tetrafluorotetracyanoquinodimethane (F_4TCNQ) and organometallic oxidants (Figure 3). In contrast, chemical doping involves a chemical reaction leading to charge transfer with the polymer and formation of a charge balancing counter-ion. For example, the salt $NOPF_6$ reacts by charge transfer followed by evolution of NO gas leaving PF_6^- as the counter ion. Strong acids, such as such as 4-ethylbenzenesulfonic acid, can protonate the backbone followed by subsequent reactions between chains to form charge carriers. Examples of *n*-type dopants include the charge transfer reductant tetrakis(dimethylamino)ethylene (TDAE), the hydride transfer reagent 4-(2,3-Dihydro-1,3-dimethyl-1*H*-benzimidazol-2-yl)-*N*,*N*-demthylbenzenamine (N-DMBI),(24) and organometallic species (Figure 3).(25, 26) Semiconducting polymers can also be synthesized in doped form; PEDOT is commonly synthesized in an oxidized state that is stabilized by polystyrenesulfonic acid (PSS), forming a water-processable dispersion, PEDOT:PSS.(27) Independent of doping method, a counter-ion is present in a doped polymeric semiconductor to maintain charge neutrality.

An important question is how the charge carriers introduced on polymer chains interact with each other. The initial oxidation (or reduction) of the backbone leads to formation of a singly

charged species that can be localized, i.e. a polaron.(28) Polarons form because of the changes in bonding upon introduction of charge carriers. The structural disorder also leads to energetic disorder, further localizing the charge carriers through broadening of the electronic DOS. The formation of charge carriers leads to bleaching of the main optical absorption of the neutral polymer and the appearance of sub-optical gap transitions that are assigned to the polaronic levels. The energies of these transitions have been modeled and shown to depend on the separation of the counter ion and charge carrier.(29, 30) Recent theoretical work suggests that shifts in the optical transition can be correlated to the distance of anions from polarons, with greater polaron delocalization arising from increases in separation.(31) In addition to polarons, electron spin resonance (ESR) spectroscopy has suggested the formation of spinless carriers. When solutions with increasing doping levels were measured using ESR, the concentration of charge carriers first showed an increase in the concentration of spins with increasing doping but turned over at high concentrations.(32) The formation of spinless carriers has historically been attributed to the formation of bipolarons, but the nature of the carriers is still debated.(33, 34) The combination of spinless carriers and structural disorder makes determination of the carrier concentration using conventional methods, such as the Hall effect, difficult.(35, 36)

Dopants cause significant changes in the processability and solid-state structure of polymers.(37) The charged counterions must be relatively close to the carriers on the backbone because of the low dielectric constant of the material. Additionally, the formation of charge carriers can stiffen the polymer chains as the charge delocalizes along the backbone.(31, 38) These changes lead to a strong dependence of the thermoelectric properties on the processing and doping route used to form solid films.

To overcome the challenges associated with casting doped polymers, several methods to introduce dopants after film processing have been developed. If polymer chains are doped in solvent ("solution doping"), charged polymer-dopant aggregates can precipitate from non-polar solvents.(39) The model system of P3HT and F_4TCNQ has been widely studied in this context. Films cast from doped solutions tend to be relatively inhomogeneous and have relatively low electrical conductivity (< 1 S/cm).(40) Sequential processing methods have been developed to prevent aggregation during film deposition. Sequential processing methods involve casting a neutral polymer film and then adding dopants in a second processing step. This second step often involves dissolving the dopant in an antisolvent for the polymer, i.e. an orthogonal solvent, so that the dopants can penetrate the polymer film without re-dissolving and washing off the film. For example, the polymer film can be immersed in a dopant solution in an orthogonal solvent ("immersion doping"). Dopant solution from an orthogonal solvent can also be spun cast on the polymer film ("sequential casting").(40) Finally, volatile dopants, such as F_4TCNQ, can be diffused into polymer films from the vapor phase ("vapor doping") without using a second solvent.(41) These two-step methods take advantage of the ability to process the neutral semiconducting polymer into morphologies that are known to improve charge transport.

Dopants further affect the morphology of semiconducting polymers because of conformation changes in the backbone and through their electrostatic and steric interactions. P3HT, the most widely studied model system, demonstrates the changes in morphology because of its combination of crystalline and amorphous domains. Smaller dopants like F_4TCNQ have been found to become incorporated into the alkyl chain portions of P3HT crystallites, as well as in the amorphous regions

of the films.(40, 42) For F_4TCNQ sequentially cast on P3HT films, the optical transition energy of the polaron in the infrared region was consistent with simulations of anions 6 – 8 Å away from the P3HT polarons, indicating that anions were located in between alkyl chains or outside of crystallites.(30) Measurements of RRa-P3HT films with sequentially cast F_4TCNQ suggest that anions can be located even closer to polarons in amorphous regions of films, further localizing charges.(43, 44) Dopants that are too large to be incorporated into alkyl stacking regions are located outside of polymer crystallites, potentially increasing the anion distance from the polaron.(45, 46) F_4TCNQ doping also causes P3HT backbones to increase in planarity.(47) This dopant-induced backbone stiffening can even cause amorphous regiorandom P3HT films to order into "edge-on" crystallites.(43, 44, 48) These results show how the electrostatic and steric effects of dopants are interrelated and change polymer film morphology.

Despite the understanding of the basic behavior, some aspects of doping remain to be elucidated. Contrary to intuition about driving forces for charge transfer, "uphill" doping, where the dopant EA is slightly less than the polymer IE, has been observed in commonly-used semiconducting polymers.(39) Conversely, common charge transfer dopants such as F_4TCNQ have been shown to form partial charge transfer complexes with polymers where integer charge transfer was seemingly favorable.(49, 50) In a charge transfer complex, only a partial charge transfer is completed between the donor and acceptor.(51) Because the donor and acceptor share electron density, charge transfer complexes do not provide free carriers for electrical conduction. P3EHT, a polythiophene with branched side chains, forms a charge transfer complex with F_4TCNQ, even though integer charge transfer would be energetically favorable based on its IE.(49) Due to the electronic and morphological complexities involved in doping semiconducting polymers, much still remains to be studied in order to optimize doping for thermoelectric applications.

3. Thermoelectric Properties of Semiconducting Polymers

3.1 Background

Determining the ultimate thermoelectric properties of semiconducting polymers is challenging because of their structural and energetic disorder. Disorder can contribute differently to the electrical conductivity, thermal conductivity, and thermoelectric power factor. PEDOT:PSS, the highest-performing polymeric thermoelectric, is a prototypical example of a heterogenous system, where films consist of both PEDOT-rich and PSS-rich domains.(27) However, morphological control in PEDOT:PSS is difficult to achieve. Alternative synthesis methods use a polymer template with a tosylate counter ion to make PEDOT:Tos, which is also difficult to characterize with parameters such as the molecular weight being ill-defined.(27) Recent effort has focused on understanding the relationship between the electrical conductivity and thermopower of polymers in an effort to optimize the power factor (Table 1). Because polymers have lower thermal conductivities than inorganic materials, the general assumption is that enhancing the power factor is the most likely route towards well-performing polymer thermoelectrics.

Thermoelectric performance is best related to the carrier concentration of a material. In practice, it is difficult to measure the precise carrier concentration in semiconducting polymers. Due to the disorder and lower conductivities of semiconducting polymer films, typical methods used to

measure carrier concentration in inorganic materials, such as Hall effect measurements, are not possible with many polymers.(41) Because of these experimental challenges, thermoelectric properties of polymers are often tracked with respect to the amount (concentration or time) of doping or by comparing the thermopower and conductivity with the assumption that higher carrier concentrations lead to higher electrical conductivities.

3.2. Electrical Conductivity

3.2.1 Role of Side Chains

The design of sidechains can strongly influence the thermoelectric properties of polymers because of their influence on solubility, molecular ordering, and interactions with the counterion to the charge carrier. For ordered polymers, the free volume near the sidechains provides space to host the counterion to the charge carriers that reside on the backbone. Despite the less favorable interaction of ions with non-polar alkyl chains, F_4TCNQ anions have typically been found to be located in the alkyl chains between lamellae in crystalline regions of P3HT and PBTTT.(22, 30, 41, 42, 52) X-ray scattering of sequentially doped films of P3HT showed that the alkyl spacing increased in the doped films while the π-π stacking distance compressed, suggesting that F_4TCNQ anions are located in the side chains.(30, 42) Polarized UV-Vis-IR absorption spectroscopy of sequentially doped, aligned P3HT films showed that F_4TCNQ anions were oriented perpendicular to the π-face of the backbone of the polymer chains.(22) These results contrast many computational studies where charge transfer dopants are modeled as having a co-facial orientation with the π-face of the backbone.(53) The counterions from electrochemical doping, such as bis(trifluoromethane)sulfonimide ($TFSI^-$), have also been found to be located near the sidechains of the polymer (Figure 4).(54, 55) Because small dopants are incorporated into the side chain regions of crystallites, the design of side chains can affect doping efficiency and dopant miscibility, as well as the crystallite packing.

The need to solvate the counterion in doped semiconducting polymers has led to significant investigation into polar sidechains. One example of designing polymer side chains to improve the miscibility of dopants with their host polymer is the *n*-type system of copolymer P(NDIOD-T2) and dopant N-DMBI. This system was found to have very limited miscibility, with phase-separated dopant aggregates forming on the surface of the film.(56) Only 1% of N-DMBI molecules were estimated to have introduced a free carrier to P(NDIOD-T2), limiting the power factor to 0.6 $\mu W/(m \cdot K^2)$.(56) In contrast, P(NDIOD-T2) with polar side chains based on poly(ethylene glycol) (PEG) showed greater miscibility and doping efficiency with N-DMBI, although the power factor was slightly lower at 0.4 $\mu W/(m \cdot K^2)$.(57, 58) Polar side chains can increase polymer-dopant miscibility, but they can also change the aggregation behavior of polymer chains. This change was observed in a non-aggregating poly(3,4-propylenedioxythiophene) derivative with PEG side chains, P(ProDOT-EG).(59) P(ProDOT-EG) maintained planarity in relatively polar solvents and was efficiently doped by F_4TCNQ, but films cast from doped solutions had an amorphous morphology.(59) Finally, polar side chains can affect the electronic levels of the polymer backbone. PBTTT was compared to derivatives with alkoxy side chains (p(a2T-TT)) and with oligoglycol side chains (p($g_4$2T-TT)).(60) The polar side chains decreased the IE from 5.2 eV for PBTTT to 4.9 eV for p(a2T-TT) and to 4.5 eV for p($g_4$2T-TT). When these lower ionization energy polymers were mixed with dopant 1,3,4,5,7,8-hexafluoro-tetracyanonaphthoquinodimethane

(F_6TCNNQ), the polymers were oxidized twice because the first and second EAs of F_6TCNNQ, 5.3 and 4.8 eV, are greater than or close to the IEs of the polymers. The formation of a dianion was also observed when p($g_4$2T-TT) was mixed with F_4TCNQ (EA^0 = 5.2 eV, EA^- = 4.7 eV). Through transfer of two electrons, the doping efficiency reached by p($g_4$2T-TT) with F_4TCNQ was much higher than 100%.(60) These results show that design of polymer side chains can affect their ionization energy and doping efficiency. Dopants that can accept (or donate) multiple charges can potentially be used to improve thermoelectric performance because fewer dopants would be needed to achieve high conductivity, which minimizes the microstructural disruption of the dopant ion.

3.2. Microstructural Ordering

Most high performance semiconducting polymers are semi-crystalline with amorphous and crystalline domains.(20) The morphology of the film strongly affects its conductivity, but the process of doping has the potential to change the morphology of the polymer if the incorporation of small molecules interrupts the short- and long-range order of the crystallites. As a result, confounding variables arise from increasing the concentration of carriers while altering carrier mobility.

P3HT has been an important model system to explore the effect of crystallinity on conductivity and thermoelectric power factor, as there are several synthetic and processing handles to control its crystallinity. Processing methods including changing the casting solvent, thermal annealing and the doping route offer another way to control morphology.(37) Blending regioregular (RR-) P3HT with RRa-P3HT is an alternative method to increase the amorphous fraction of the film.(48) The composition of aggregated and amorphous domains in P3HT can be determined by a combination of X-ray scattering and UV-visible spectroscopy(31, 61) We note that crystallinity and aggregation are not equivocal with the latter term used for regions where the polymer chains extend, but do not form true crystallites.(62)

The method through which a dopant is mixed with a polymeric semiconductor impacts the ultimate properties of the resulting film. Early studies that explored the impact of doping method on polymeric thin-film properties found that the homogeneity and electrical conductivity of a sequentially F_4TCNQ-doped film of P3HT is higher than a P3HT film cast from a doped solution.(63) This improvement was likely due to avoiding the decrease in solubility of charged P3HT that causes precipitation from solvent by incorporating dopants in P3HT in its solid state. Further improvements in conductivity, up to 48 S/cm, were realized by diffusing F_4TCNQ vapor into P3HT films.(42) Because little change in OCL was observed between neat, solution doped, and vapor doped films, the improvement in conductivity was attributed to short-range differences in crystal texture and fibril length.(42)

To study the effect of crystallinity on thermoelectric properties, P3HT films with varying fractions of aggregates and amorphous regions have been examined. In one study, P3HT films were cast from several different solvents and subsequently vapor doped with F_4TCNQ.(64) Altering the casting solvent was found to influence the fraction of aggregates and their free exciton bandwidth, which scaled with the electrical conductivity and thermoelectric power factor. Choice of solvent was shown to increase the charge carrier mobility and thermoelectric power factor by

approximately one order of magnitude. There was no clear trend in thermopower with the degree of solid-state order, indicating that the entropy per carrier is less sensitive to the film morphology at a given carrier concentration. As a result, improvements in thermoelectric properties from increased crystallinity were attributed to improvements in carrier mobility.(64) Blends of RR- and RRa-P3HT provided an alternative method to control the film crystallinity. The conductivity of the F_4TCNQ vapor-doped blend films yielded a similar trend of increasing electrical conductivity with crystallinity.(48) Increasing amounts of RRa-P3HT decreased the crystallinity of the film without changing the long-range order or texture of the crystallites, as evidenced by RSoXS and wide angel X-ray scattering. A measurable OCL was observed through RSoXS only at approximately 30% RR-P3HT content, the same point at which a stark increase in carrier mobility was measured. This correlation further justifies the need for increasing long-range order within doped polymeric semiconductors to achieve high electrical conductivity and power factor. Similar to other work, no trend was found between thermopower and percent crystallinity.(48)

The limitations of using short-range order to explain thermoelectric properties were shown through the use of the highly ordered polymer PBTTT.(65) Unlike P3HT, PBTTT has liquid crystalline phases that can be controlled using thermal annealing and the surface chemistry of the substrate.(52) PBTTT was sequentially doped with two different doping methods: vapor phase (Tridecafluoro-1,1,2,2,-tetrahydrooctyl)-trichlorosilane (FTS), which dopes through an interfacial protonic mechanism, and immersion in 4-ethylbenzene sulfonic acid (EBSA) solution. At similar values of electrical conductivity, the thermopower of an FTS-doped film of PBTTT was greater than that of an EBSA-doped film, with thermopowers of 33 and 14 μV/K, respectively. Both doping methods similarly preserved the edge-on PBTTT crystallites, so changes in the crystalline ordering of the PBTTT could not fully explain the difference in thermopower. Instead, the FTS-doped film may have had an increased vibrational or domain boundary scattering contribution to its thermopower.(65) These results show that, while short-range ordering is critical to understanding conductivity, it cannot explain all morphology-dependent changes in thermoelectric performance.

PBTTT also acts as a model system to examine the importance of long-range ordering of films on thermoelectric properties. The short- and long-range order of the polymeric films of PBTTT were controlled using thermal processing followed by infiltration of F_4TCNQ from the vapor phase.(52) Neat PBTTT films annealed at 180 °C had an OCL of 180 nm. After vapor doping with F_4TCNQ, the OCL increased slightly to 220 nm. In contrast, solution doping yielded films with poor long-range order, with an OCL of 44 nm. The power factor increased with the OCL because the long-range order continuity yielded the highest electrical conductivity (Figure 5). The electrical conductivity in the longest OCL films was nearly two orders of magnitude higher than conductivity in the shortest OCL films.(52) This conductivity vs. OCL trend was also found to be consistent with P3HT.(42) When F_4TCNQ solution and vapor doped samples of P3HT were compared, the conductivities were 2.3 and 48 S/cm, respectively. The difference in electrical conductivity was less dramatic in P3HT than in PBTTT films, due to the comparable OCL of the solution and vapor-doped films of ~10 nm. Surprisingly, the OCL and electrical conductivity of the vapor-doped P3HT films was consistent with the predicted σ vs. OCL trend from the results on PBTTT.(42) These studies solidified the concept that long-range ordering must be considered in understanding polymer film conductivity and morphological changes during doping.

Processing methods that increase chain alignment in polymer films act as another route to dramatically improve the power factor of doped polymers. High-temperature rubbing is one tool that orients polymeric crystallites parallel to the rubbing direction.(22) Aligned P3HT films were doped with F_4TCNQ by sequential casting. Both electrical conductivity and thermopower were higher when measured parallel to the alignment direction. Because of the crystallite alignment, the highest film conductivity was 22 S/cm,(22) compared to 3 S/cm for spun cast sequentially doped films.(40) This alignment method was also used to increase the conductivity of PBTTT-C_{12}.(66) While aligned P3HT films still had a semicrystalline morphology, aligned PBTTT-C_{12} films formed a liquid crystal-like morphology. When doped by immersion in $FeCl_3$ solution, the PBTTT-C_{12} films reached a conductivity of 2.2 x 10^5 S/cm and power factor of 1.94 mW/(m·K^2) measured parallel to the alignment direction.(66) This dramatic improvement in conductivity and power factor upon alignment suggests a path forward for understanding the limiting properties of thermoelectric polymers.

These studies highlight the need for unique transport models that capture the behavior of heterogenous polymeric materials. Although the DOS of amorphous and crystalline regions of a polymer are expected to be different, the Seebeck coefficient varies by less than ~20% for films of starkly different crystallinity at the same doping level.(42, 52) However, the carrier mobility increases as the long-range order of the crystallites improves, which increases the power factor. An added complexity of carriers imbued through doping is that the long-range order of a film can change, which justifies the need for a dynamic model that accounts for doping-induced order.

3.3 Relationship between Thermopower and Electrical Conductivity

As noted, the thermopower of a material usually decreases as the electrical conductivity increases. This behavior can be understood in a number of ways but can simply be thought of in terms of the energy of a carrier relative to the Fermi energy (chemical potential) of the material. The connection between thermopower and the electrical conductivity can be given by Eq. 4 that describes the contributions of carriers at energy E to charge transport by a transport function, $\sigma(E)$, and $f(E, E_f, T)$ is the Fermi function at a given temperature T and Fermi energy E_f.

$$\sigma = -\int \sigma(E) \frac{df\left(E, E_f, T\right)}{dE}\, dE \tag{4}$$

The Seebeck coefficient can be determined using the same formalism and yields Eq. 5 where k_B is Boltzmann constant, and e is the unit charge.

$$S = -\frac{k_B}{e} \int \left(\frac{E - E_f}{k_B T}\right) \frac{\sigma\,(E)}{\sigma} \frac{df\left(E, E_f, T\right)}{dE}\, dE \tag{5}$$

Because the Fermi level approaches the transport states as more carriers are added, the energy per carrier decreases. While the general trends of thermopower and electrical conductivity are clear, the details are not. Carriers are introduced by doping, which strongly perturbs the electronic structure of the neat material. Significant structural changes occur, and the amount of ordered and disordered material will shift upon doping. For PEDOT:Tos, it has even been argued that the

thermoelectric performance is related to a shift to semi-metallic behavior at high carrier concentration.(33)

Given assumptions about the mechanism of charge transport, the expected behavior of the thermopower can be determined. For example, if states within a few k_BT near the Fermi level contribute to transport, then the Seebeck coefficient is expressed by Eq. 6, which is typical of metallic conduction.

$$S = \frac{\pi^2}{3}\frac{{k_B}^2 T}{e}\left.\frac{d(\ln(\sigma))}{dE}\right|_{E_f} \tag{6}$$

In contrast, when the Fermi energy is far from the energy of highly mobile states, then the Seebeck coefficient is given by Eq. 7. Eq. 7 is for hole conduction, where E_V is the energy of the valence level and A is a constant that depends on the precise form of the conductivity function.

$$S = \frac{k_B}{e}\left(\frac{E_f - E_V}{k_BT} + A\right) \tag{7}$$

The thermopower of heavily doped semiconducting polymers tends to follow a form close to that of Eq. 6, where the Seebeck coefficient increases with temperature. Lightly doped materials (< 10^{18} carriers/cm^3) have been shown to follow the temperature independent form similar to Eq. 7. However, there are few measurements for any given material to determine a clear switch-over in the functional form between these two limits.

For semiconducting polymers, a striking empirical relationship between thermopower and electrical conductivity has been observed (Figure 6).(67) Across a range of materials and within materials systems, the two are related by a power law given by Eq. 8 where σ_0 and s are fitting parameters.

$$S = \frac{k_B}{e}\left(\frac{\sigma}{\sigma_0}\right)^{-1/s} \tag{7}$$

This behavior was observed for polyacetylene and more recently shown to be followed for a variety of materials systems.(67–69) What is surprising about this behavior is that it holds over a broad range of electrical conductivities where the doping level varies substantially. One would expect different transport mechanisms between materials with high and low conductivity; typically, more insulating samples exhibit Arrhenius temperature-dependent behavior in electrical conductivity, while more conductive materials follow variable range hopping. The observation of a power law over a wide range is particularly surprising given the change in transport mechanism. The power law relationship has been rationalized using models with varying assumptions on the nature of transport.

Using a power law form of the conductivity function, which was previously examined for disordered inorganic semiconductors,(70) a simple relationship between the electrical conductivity

and thermopower can be determined. This formalism assumes that there is a minimum transport energy E_t, below which electronic carriers will not contribute to transport, and above which transport occurs (Figure 7). The form of the conductivity function given by Eq. 8, where s is a parameter that describes different charge transport models (i.e. s=0 for a mobility edge or higher values in other cases) and $\sigma_{E0}(T)$ is a temperature-dependent transport parameter.(71)

$$\sigma(E) = \begin{cases} \sigma_{E_0}(T) \times \left(\frac{E - E_t}{k_b T}\right)^s & (E > E_t) \\ 0 & (E < E_t) \end{cases} \tag{8}$$

When the material is heavily doped such that E_f is much larger than E_t, then the electrical conductivity and thermopower can be related to the difference between the two energy levels, given by $\eta=(E_f-E_t)/k_bT$, resulting in Eq. 9 and 10.

$$S = \frac{\pi^2}{3}\frac{k_b}{e}\, s\eta^{-1} \tag{9}$$

$$\sigma = \sigma_{E_0}(T)\eta^s \tag{10}$$

The exact energy dependence above the transport edge for this model depends on the materials system and remains difficult to predict; however, the model captures transport behavior for a wide range of polymeric semiconductors, including PEDOT:PSS, near room temperature.(71) An issue with the model is that the temperature dependence of the conductivity is assumed to follow a form comparable to variable range hopping, whereas the conductivity deviates from this relationship over the range where the empirical relationship holds.

Another approach to rationalize the empirical power law relationship between thermopower and conductivity is by a change in the electronic DOS by doping. Because of electrostatic interactions between the charge carrier and counterion, the DOS likely changes as a function of charge carrier density. Such changes in the DOS has been posited by some research efforts utilizing a Gaussian DOS and comparison to electrically doped polymers.(69, 72) Using simulations, hopping models were found to yield a power law dependence over a range of electrical conductivities. While successful, this model does not describe the extended state transport that has been observed for high performance polymers like PBTTT and IDTBT.(35, 41, 73)

Because doping of semiconducting polymers can strongly perturb their morphology, quantitative modeling of thermopower as a function of charge carrier density can be challenging. One approach to studying transport while maintaining a constant morphology is to use either field-effect or electrochemical gating of semiconducting polymers. A significant benefit of gating measurements to measure thermoelectric properties is that the carrier concentration is easily controlled and quantifiable. This idea was first demonstrated by measuring thermopower as a function of gate voltage using an oxide dielectric.(73, 74) In this case, the carrier concentration was limited by the dielectric strength of the gate oxide. Using an electrochemical transistor for transport measurements provides a larger window of carrier concentration through the creation of a

conducting channel throughout the film thickness. Results using a polymeric ionic liquid (PIL) as the gate dielectric found that, in an electrochemical transistor, PBTTT followed the power law relationship between electrical conductivity and thermopower.(75) Additional information about the carrier concentration revealed that the presence of the counter-ions from the PIL dielectric broadened the electronic DOS and reduced the magnitude of the thermopower (Figure 8). Thus, the assumption of a constant pre-factor in Eq. 8 as a function of carrier concentration is likely not valid.(75) This study suggests that a quantitative model needs to incorporate a non-constant conductivity function due to the changes in energetic disorder.

3.4. Thermal Conductivity

The thermal conductivity of doped polymers has a component due to vibrations of the polymer chains, κ_{ph}, and a component related to the heat carried by charge carriers, κ_{el}. The electronic portion can be estimated by the Wiedemann-Franz law (Eq. 11) where L is the Lorenz number, with a predicted Sommerfeld value of 2.44×10^{-8} WΩ/K^2. Doping may change both terms if the microstructure changes, e.g. through stiffening of the polymer chains, making it difficult to perfectly separate the two effects.

$$\kappa_{el} = LT\sigma \tag{11}$$

Accurate measurements of the thermal conductivity of electrically conductive polymers are still difficult to achieve. One challenge for precise measurements of thermal conductivity arises from different contributions from amorphous and ordered regions of semi-crystalline polymers. In ordered regions, there is anisotropy in the bonding, with covalent bonding along the chain direction and van der Waals interactions between chains. The disorder in amorphous regions and the variation in the length of polymer chains from synthesis is expected to limit propagation of phonons.(76) The orientation of the chains can vary based on processing methods and sample size. For example, the backbone of the polymer chains in thin films is frequently preferentially oriented parallel to the substrate for both semicrystalline and glassy materials. The lack of single crystals makes it important to know the morphology to interpret values of the thermal conductivity for both in-plane and out-of-plane directions.

The thermal conductivity of insulating polymers varies significantly with morphology and structural order. The thermal conductivity of amorphous, random coil polymers is typically ~0.2 to 0.3 W/m·K and is attributed to weak intermolecular coupling of the polymer chains.(76) The thermal conductivities of fibers of rod-like polymers, e.g. poly(p-phenylene benzobisoxazole) (PBO, Zylon), is ~20 W/m·K along the fiber axis but lower than amorphous polymers in the radial direction.(77, 78) For comparison, the thermal conductivity of melt-processed P3HT in nanoporous matrices has been reported to be ~7 W/m·K, but there are no reports of bulk samples with similar alignment.(79) Most studies of semiconducting polymers have been done on semicrystalline or glassy thin films. The in-plane thermal conductivity of thin films of P3HT and PBTTT are ~0.3 to 0.4 W/m·K, with slightly smaller values ~0.2 W/m·K in the out of plane direction.(80) Whether these values are due to scattering between ordered and more glassy regions or to distributions of orientations of ordered regions is not known.

The majority of measurements of thermal conductivity as a function of electrical conductivity have been done on versions of PEDOT. Overall, the electronic contribution to thermal conductivity is significant only above electrical conductivities of ~10 S/cm.(81, 82) The electronic component to thermal conductivity of PEDOT:PSS in the in-plane and through-plane directions was determined on thick films (>50 μm) treated with varying concentration of DMSO. The data obey the Wiedemann-Franz law (Figure 9) with a typical Lorenz factor of 2.4×10^{-8} WΩ/K^2 and a lattice thermal conductivity of ~0.6 W/m·K at room temperature. Here, the phonon contribution of PEDOT:PSS was higher than that of neat PSS pointing out how blends can strongly modify properties of their components. In another study, PEDOT:Tos films with electrical conductivity varied by de-doping (range 240 S/cm to ≈25 S/cm) had in-plane thermal conductivity from 0.86 W/m·K to nearly 0.6 W/m·K.(81) The electronic contribution was found to be greater than that predicted by the Sommerfeld value of the Lorenz number in this study, leading to relatively high thermal conductivities, ~1.5 W/m·K at electrical conductivity of ~ 500 S/cm. The sample preparation was different in each study, making it difficult to determine the origin of the variation, but the data point out the significant variance even for a model system. None of these studies are close to predictions from nonequilibrium molecular dynamics simulations for an ideal crystal of PEDOT, which produced a thermal conductivity along the chain direction of ~40 W/m·K.(83)

3.5 Figure of Merit ZT

Despite significant progress in understanding the power factor of polymeric thermoelectrics, assessment of ZT is incomplete for many materials. Because of the anisotropies of the transport characteristics of polymers, values of all of the thermoelectric properties measured along the same direction are required to obtain an accurate ZT. The thermal and electrical properties should be obtained from films with the same morphology, which can be challenging due to the varying needs of sample preparation for each measurement. Oftentimes, thermal conductivity of a material is assumed in order to calculate ZT, despite the uncertainty of the electrical contribution and anisotropic transport properties.

The majority of data evaluating ZT is related to PEDOT:PSS and PEDOT:Tos.(27) One of the highest reported values of ZT is 0.42 for an ethylene glycol-treated PEDOT:PSS film.(84) This value is based on thermal conductivity measurements where no significant electronic contribution was found in PEDOT:PSS, despite a number of other studies showing a significant electronic contribution. In a study of PEDOT:Tos, where all parameters were measured in the same direction of the sample, a power factor of ≈10 μW/m·K^2 with a thermal conductivity of 0.8 W/m·K yielded a ZT of 0.005.(81) However, higher power factors for PEDOT:Tos have been reported in literature, suggesting that 0.005 is not an upper bound for this system. The variance in the properties of PEDOT:PSS and its analogs result from the complexity of the morphology and the contribution of water in the samples.(85, 86) There is continuing work to control these properties towards a better understanding of this high performing materials system.

The potential ZT of semiconducting polymers can be estimated using the best power factors and a thermal conductivity based on a standard value for the Lorenz number.(71) The in-plane thermal conductivity of both amorphous polymers and semiconducting polymers in thin films is near 0.3 W/m·K. The addition of an electronic contribution gives a total thermal conductivity near 1

W/m·K at electrical conductivities ~500 S/cm. If the power factor is near 100 to 270 μW/m·K^2, as observed at room temperature for a range of polymers (Table 1), then the ZT would be ~0.03 to 0.06. If the lattice contribution to the thermal conductivity were higher, the ZT would be lower, ~0.01. This estimate is not likely an upper bound, however. The report of rubbing-aligned PBTTT with a power factor close to 2 mW/m·K^2 suggests that ZTs around 10x higher than these estimates may be possible for polymer thermoelectrics.(66) The majority of studies emphasize optimizing the power factor rather than ZT and the trade-off between enhancing the power factor and increasing the thermal conductivity is still not known. There has also been little exploration of the optimal temperature for polymeric thermoelectrics with the observation of increasing performance towards 100° C in some studies.(87) One therefore can expect that reaching ZT of greater than 0.1 is certainly within reach for many materials systems.

4. Future Directions

The thermoelectric properties of semiconducting polymers are still under active investigation to develop clear structure-property relationships. The dependence of thermoelectric properties on the processing methods used to cast and electrically dope polymers complicates the prediction of ultimate properties, but routes have been developed that have significantly increased the ability to predict their behavior. For example, improving structural order clearly benefits both the thermopower and electrical conductivity, as shown in experimental observations and theoretical predictions. It is unclear if the electronic structure of the backbone can be modified to rationally enhance the thermopower using mechanisms such as contributions from multiple electronic levels. Recent work on blends of semiconducting polymers suggest that tuning the electronic DOS is a potential route to modify the thermoelectric properties of polymers.(88)

One of the most important questions is whether routes to increase the power factor will be accompanied by changes in the thermal conductivity. If improvements in the charge carrier mobility result from alignment of the polymer backbones, then one expects that the lattice component of the thermal conductivity may significantly increase. Design rules for controlling the thermal conductivity of polymers are poorly understood and are an area for future exploration.

The power factor of many polymers is close to that needed for applications, suggesting that enhancements do not need to be dramatic. With known materials, a ZT near 1.0 at low temperatures (room temperature to 100°C) is likely within reach for *p*-type materials. Solution processable *n*-type systems have been less-studied due to the lower air stability of dopants for *n*-type polymers.(15) The highest power factor demonstrated in solution processable *n*-type systems was 28 μW/m·K^2 for a fluorinated benzodifurandione-phenylenevinylene derivative (FBDPPV) solution doped with N-DMBI.(89) If comparable thermoelectric performance can be achieved for both *p*- and *n*- type polymers, practical applications such as energy harvesting and efficient temperature control in low-cost modules should be possible.(90)

Acknowledgement.

The authors acknowledge support for work on transport properties and doping of thermoelectric polymers from NSF DMR 1808622 and on ionic interactions in semiconducting polymer from Department of Energy Office of Basic Energy Sciences under grant no. DE-SC0016390. E.M.T. gratefully acknowledges support from the NSF Graduate Fellowship (DGE-1650114).

Figure Captions

Figure 1. Chemical structures of widely-studied *p*-type and *n*-type polymers.

Figure 2. Thin films of semiconducting polymers have structural order over multiple length scales and directions that must be considered for interpretation of thermoelectric properties.

Figure 3. Chemical structures of charge transfer and chemical reactive dopants for polymeric semiconductors.

Figure 4. (a) Schematic representing the typical location of counterions (shown by green ellipsoids) to charge carriers (holes, h^+) on the backbone within crystallite regions. This structrure can be observed through GIWAXS (b), where the alkyl stacking distance shifts to lower q (higher real-space distance) when doped. Adapted with permission from Thomas EM, et al. 2018. *Adv. Funct. Mater.* 28(44):1803687. Copyright (2018) WILEY-VCH.

Figure 5. (a) The orientational correlation length (OCL) is defined as the distance over which polymeric backbones retain alignment with one another. The electrical conductivity of PBTTT doped with F_4TCNQ from the vapor phase increases dramatically with OCL of the PBTTT chains (b), while the thermopower is less sensitive to the OCL (c). Adapted with permission from Patel, et al. 2017. *Sci. Adv.* 3(6):e1700434. Copyright 2017 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science.

Figure 6. An empirical trend was found between thermoelectric power factor and electrical conductivity for semiconducting polymers ($S^2\sigma \propto \sigma^{1/4}$) (blue circles) that spans over eight orders of magnitude in electrical conductivity, despite clear differences in the primary transport mechanism. Interestingly, PEDOT:PSS was one polymer that seemed to deviate from the relationship (brown symbols). Adapted with permission from Zevalkink A, Smiadak DM, Blackburn JL, Ferguson AJ, Chabinyc ML, et al. 2018. *Appl. Phys. Rev.* 5(2):021303

Figure 7. The thermoelectric properties of polymers can be modeled with a power law function for the conductivity function. The contribution of carriers to charge transport is governed by the energetic difference between the Fermi level and the transport edge, below which carriers do not conduct (a). This transport model captures thermopower and electrical conductivity behavior over several orders of magnitude where more conventional models considering predictions from variable range hopping or a mobility edge do not (b). Adapted with permission from Kang, S., et

al. 2017. *Nat. Mater.* 16(2):252-257. Copyright (2017) Macmillan Publishers Limited, part of Springer Nature.

Figure 8. (a) Electrochemical gating provides a large transport window to study the thermoelectric properties of semiconducting polymers. Using PBTTT gated by a polymeric ionic liquid, the power law relationship between thermopower and electrical conductivity was observed. Carrier concentration was also quantifiable with electrochemical gating, providing insight into how transport evolves as a function of carrier concentration (b). Adapted with permission from Thomas EM, et al. 2018. *Chem. Mater.* 30(9):2965-72. Copyright (2018) American Chemical Society.

Figure 9. In-plane and through-plane thermal conductivity of PEDOT:PSS. This polymeric composite obeyed the Wiedemann-Franz law in the in-plane direction whereas the through plane thermal conductivity was relatively constant with electrical conductivity. The lattice thermal conductivity was found to be ~0.6 W/m·K at room temperature. Reprinted with permission from Liu, J. et al. 2015. *Macromolecules* 48(3):585-591. Copyright (2015) American Chemical Society.

Table 1. Processing-dependent thermoelectric properties of solution processable polymers.

Polymer	Dopant	Processing	σ (S/cm)	S (μV/K)	Power Factor (μW/(m·K^2))	Ref.
PEDOT	PSS	De-doped by ethylene glycol immersion	880	73	469	(84)
PEDOT	Tos	Synthesized in solution with $Fe(Tos)_3$, pyridine, and a triblock copolymer template	1355	79.8	862.9	(91)
P3HT	F_4TCNQ	Solution doping	2	76	1.15	(42)
P3HT	F_4TCNQ	Vapor doping	37	85	27	(42)
PBTTT	F_4TCNQ	Solution doping	3.51	60	1.3	(67)
PBTTT	FTS	Vapor doped in vacuum oven	1,000	33	110	(65)
PBTTT	F_4TCNQ	Cast on OTS-coated quartz; vapor doped	670	42	120	(52)
PBTTT-C_{12}	$FeCl_3$	Rubbing aligned film; immersion doped; measured parallel to rubbing direction	2.2 x 10^5	9.4	1944	(66)
P(NDIOD-T2)	N-DMBI	Solution doping	8 x 10^{-3}	-850	0.6	(56)
FBDPPV	N-DMBI	Solution doping	14		28	(89)

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