

ORGANIC MATERIALS FOR ELECTRONIC AND THERMOELECTRIC APPLICATIONS

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Abstract: In this invited review article, we give a comprehensive account of the existing literature on the electronic properties of organic materials. The main focus of this article is the rich and extensive literature on the electronic transport in organic materials, particularly conjugated polymers, as they offer numerous advantages over inorganic materials. Consequently, they have found widespread application in photovoltaics, light-emitting displays, and even, more recently, in thermoelectric energy conversion. This literature review will be useful to researchers starting in the field of organic electronics as well as experts seeking to broaden their understanding of transport in polymers.

Keywords: thermoelectric materials, polymers

INTRODUCTION

For decades, societal demand for advanced electronics, ranging from portable personal devices to large servers and data centers, had grown hand-in-hand with the overall demand for electrical energy. The constant increase in global energy need forced the emergence of cheaper and environmentally friendly alternatives for energy production and retrieval. More than a half of all energy produced is wasted in the form of heat during production or transmission to the end consumer. Similarly, more than half the energy consumed by electronics is dissipated into heat, leaving enough space to significantly reuse that waste heat. Thermoelectric (TE) devices have emerged as a possible solution to this need as they allow direct conversion of waste heat into electric energy without moving parts. They rely on the closely related Seebeck and Peltier effects. Semiconductors as thermoelectric materials are a perfect choice for those purposes and the concurrence of *n*-type (negatively) and *p*-type (positively) doped semiconductors increases the efficiency of thermoelectric conversion to satisfactory levels. However, the shortage for inorganic semiconductors, their noxiousness to environment, toxicity, and high production cost, justified the idea of seeking new materials. Organic materials rely on considerably cheaper and more environmentally friendly carbohydrates.

Among them, conjugated polymers, consisting of long chains with a conjugated carbon backbone, are an exceptional replacement as substitute materials for modern electronic devices [1]. Their properties span a broad range, but several polymers have emerged as platforms for electronics, including flexible electronic

devices for wearables, organic solar cells, and even thermoelectric energy converters for low-grade heat sources at moderate temperatures near room temperature. Polymers are now widely used in various devices as thin-film transistors (TFTs) [2], photovoltaic (PV) cells [3], [4], organic light-emitting diodes (OLEDs) [5], and are finding increased utilization as materials for thermoelectric conversion [6]-[7]. Efforts to understand and engineer polymers properties in the past two decades established the appearance of arrays of diverse phenomena in these materials and answered as well as opened many questions.

One of the key differences between organic materials such as conjugated polymers and their inorganic counterparts such as silicon is their lack of long-range order and crystalline structure. Polymers are typically either amorphous or semicrystalline, consisting of small crystalline domains of well-aligned polymer chains separated by regions of amorphous tie-chains connecting the crystalline domains. This lack of structural order translates into partial or complete localization of charge carriers and a broadening of the electronic states, typically termed energetic disorder. Another key difference is that polymers are not doped by substituting donor or acceptor atoms into the crystal structure of the host, like inorganics, but are doped by charge transfer in a blend of host polymer with a small-molecule dopant. Doping is necessary in order to raise the concentration of free carriers and, with it, electrical conductivity. The presence of ionized dopant molecules implies a random array of charges that induce strong Coulomb interactions with charge carriers that reside on the backbone of the polymer,

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which further exacerbates energetic disorder. Doping organic materials, which is necessary to control their conductivity, is therefore challenging as doping can both raise carrier concentration and lower the mobility of carriers by creating coulomb traps. Consequently, carrier mobility in organic materials remains well below their inorganic counterparts. Developing novel combinations of host polymers and dopants in a way to maximize both free carrier concentration and mobility remains a formidable challenge. Nonetheless, their amorphous structure also lowers thermal conductivity, which is highly advantageous to TE conversion, thus making polymers potentially interesting candidates for TE applications.

1. EFFICIENCY, FIGURE OF MERIT AND POWER FACTOR OF THERMOELECTRIC MATERIALS

The efficiency of thermoelectric materials is given by the figure of merit that is defined as

$$zT = \frac{\sigma \cdot \alpha^2}{\kappa} T \quad (1)$$

where σ represents the electrical conductivity, α Seebeck coefficient, κ the thermal conductivity and T the temperature. Materials that exhibit the best thermoelectric properties are semiconductors with a figure of merit zT exceeding 1. Achieving higher values of the figure of merit is possible with doping, and the same procedure is also conducted in polymers for the purpose of obtaining higher conductivities [8], [9]. However, reaching values above 3 is a highly desirable target and a challenge that has been approached but not yet reached.

The denominator of the figure of merit is thermal conductivity, which consists of electronic and lattice (phononic) contributions $\kappa = \kappa_e + \kappa_{ph}$. The link between the electronic contribution to thermal conductivity and electrical conductivity is given by Wiedemann-Franz's law that states

$$\kappa_e = L\sigma T \quad (2)$$

where L is the Lorentz number that is related to the open circuit electronic thermal conductivity κ_e as $L = \kappa_e / \sigma T \alpha^2$ and can be obtained from the variance of excess energy [10].

Electrons dominate thermal transport in highly conductive materials such as metals. This coupling between electrical and thermal conductivities makes it impossible to decouple them and optimize the figure of merit. Consequently, most metals perform very poorly as TE converters. In contrast, thermal conductivity in semiconductors, including polymers, is dominated by the contribution of lattice vibrations and electrons only make a moderate contribution. This decoupling allows for further

optimization of the figure of merit by raising electrical conductivity through doping without simultaneously raising thermal conductivity. Furthermore, the Lorentz number in polymers changes with doping [11] - [13], but remains in the range of Sommerfeld's value at high doping. With their overall low thermal conductivity and advanced Seebeck coefficient in general, the main issue regarding the use of polymers as thermoelectric materials remains low electrical conductivity. Thermal conductivity of polymers is remarkably low even with high doping, so that the efficiency of thermoelectrics is rather measured by their power factor

$$PF = \sigma \cdot \alpha^2 \quad (3)$$

which is the numerator of the figure of merit. However, increasing the conductivity of polymers leads to a decrease in the Seebeck coefficient, so that the overall value of the power factor would represent a tradeoff between these two quantities. Since this is the case, the PF has a maximum that typically occurs at higher doping levels.

The conductivity of polymers is often calculated using Mott's formula [14]

$$\sigma = \int \sigma(E) \left(-\frac{df}{dE} \right) dE \quad (4)$$

where $\sigma(E)$ is often referred to as the transport distribution function (TDF) and contains microscopic details of transport. For a crystalline material with delocalized electrons having well-defined crystal momenta $\hbar\vec{k}$ and group velocities $\vec{v}$, it is related to velocity and relaxation time τ between scattering events through

$$\sigma(E) = \int d\vec{k} v^2(\vec{k}) \tau(\vec{k}) \delta(E_{\vec{k}} - E) \quad (5)$$

where the delta function represents a contour integral over all momenta having energy E . If velocity and relaxation time only depend on momentum indirectly through energy, as would be the case in materials with an isotropic electronic structure, then the above simplifies to

$$\sigma(E) = v^2(E) \tau(E) D(E) \quad (6)$$

Here $D(E)$ is the density of states, obtained from $D(E) = \int d\vec{k} \delta(E_{\vec{k}} - E)$, which plays a major role in both the Seebeck coefficient and conductivity in all materials.

In polymers, carriers are largely localized and thus lack a well-defined crystal momentum and velocity. Instead of the above, they transport by phonon-assisted hopping from one localized state to its neighbors. Its solution for hopping in three dimensions, which is elaborated in the next section, is approximated by

$$\sigma(T) = \sigma_0 \exp \left[-\left(\frac{T_0}{T} \right)^\gamma \right] \quad (7)$$

where σ_0 would represent a low temperature limit, T_0 is a constant dependent on the density of localized states at the Fermi level and $\gamma=1/(d+1)$, with d being the dimensionality. This leads to a $\gamma=1/4$ in most cases when transport is three-dimensional, while $\gamma=1/2$ has also been observed in some experiments and associated with the one-dimensional nature of polymer chains.

Based on the previous formalism, the Seebeck coefficient is then given by:

$$\alpha = -\frac{k_B}{e} \frac{\int \frac{E-E_F}{k_B T} \sigma(E) \left(-\frac{df}{dE}\right) dE}{\int \sigma(E) \left(-\frac{df}{dE}\right) dE} \quad (8)$$

where the integral in the denominator represents the overall conductivity, k_B Boltzmann's constant, $\sigma(E)$ the energy E dependent conductivity, e elementary charge, E_F the energy at the Fermi level and f Fermi-Dirac distribution function. Dividing the integral in the numerator into two parts where one contains E and the other E_F , the Seebeck coefficient becomes:

$$\alpha = -\frac{1}{eT} \frac{\int E \sigma(E) \left(-\frac{df}{dE}\right) dE}{\int \sigma(E) \left(-\frac{df}{dE}\right) dE} + \frac{E_F}{eT} = -\frac{E_T - E_F}{eT} \quad (9)$$

The so-called transport energy E_T , as emphasized by the previous equation, represents the mean energy of a conducting carrier, so that the Seebeck coefficient can be considered as the average energy relative to the Fermi level that a carrier transfers at a certain temperature. This fact is very important for understanding polymer properties and, in particular their electronic properties, which we shall discuss further in the following sections.

2. DENSITY OF STATES

The density of states (DOS) in general represents the distribution of available energy levels that carriers can fill in a solid. In crystalline inorganic materials, the carriers are delocalized and electronic bands have approximately a quadratic dispersion, resulting in a broad DOS that follows the square root of energy away from the conduction and valence band edges, separated by a bandgap. The DOS in polymers differs markedly from that in inorganic semiconductors due to the presence of localized electronic states with modest overlap and relatively weak interaction. The shape of the DOS denotes the properties of semiconducting materials and numerous studies concentrate on revealing the actual energetics of states inside polymers [15], [16]. It is well accepted that the intrinsic DOS, both at the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) level, has a Gaussian shape [17], [18]. This is sometimes termed the gaussian disorder model (GDM).

Doping, for example, changes the structure of the DOS and quantities as the dielectric constant of the polymer [19] or dopant clustering [20], are affecting the broadening of the DOS, as shown in Figure 1. More details about the doping impact can be read in section four. The width of the DOS, termed energetic disorder, was expected to be dependent on polymer structure and morphology, where a crystalline material would have a narrow DOS with low energetic disorder. In contrast, there are studies with opposing observations [21], [22]. For a long time, increasing the crystallinity and planarization of polymer backbones was thought to be key in the design of polymers with optimized charge transport properties. This general belief had to be revisited with the emergence of apparently amorphous organic conjugated polymers exhibiting only short-range order [18], [23], [24]. Nevertheless, larger energetic disorder can lead to an improvement of polymer properties in blends [25] but is still assigned to disordered systems and despite both experimental and computational studies [7], [22], [26], predicting energetic disorder from morphology remains challenging. Several methods, usually using Urbach tails in solid-state absorption spectra, charge transport studies or Kelvin probes of band bending are used to measure DOS widths [27], but other methods, such as using photogenerated charge-separation efficiency [17] have been shown to be useful as well.

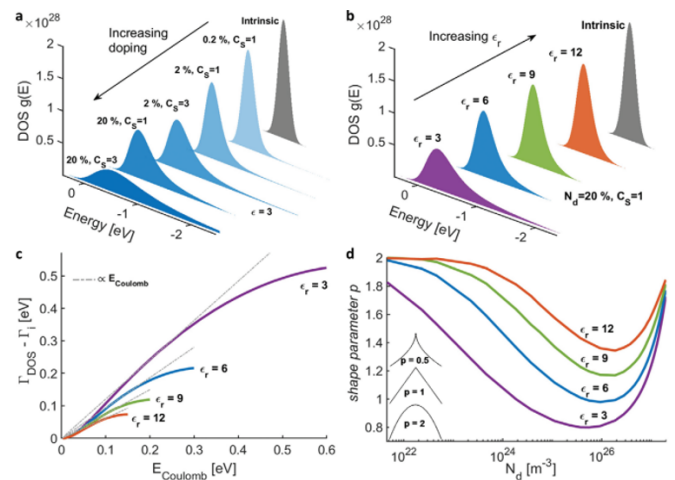


Figure 1: Increasing the dielectric permittivity counteracts the broadening of the DOS. a) The effect of doping and clustering on the DOS distribution with 100 meV intrinsic Gaussian width. b) Increasing the dielectric constant counters the broadening of the DOS by mitigating the Coulomb carrier-dopant interactions c) Additional energetic disorder caused by doping as a function of Coulomb energy for the standard $\epsilon_r = 3$ and elevated dielectric constants. The grey dashed lines are linear fits showing that the amount of energetic disorder closely follows the Coulomb interaction energy. d) Generalized Gaussian shape parameter p versus doping concentration showing that increasing the dielectric constant keeps the shape parameter more Gaussian ($p \approx 2$) even at higher doping concentrations (adapted from [19]).

The doping process, undertaken to improve conductivity by increasing carrier concentration, dramatically changes the shape of the DOS and increases energetic disorder,

while dopant aggregation may destroy the crystalline morphology, inducing an exponential tail [28], [29].

Electrical conductivity and Seebeck coefficient are highly reliant on the DOS. Therefore, understanding the physics behind dopant induced disorder and the final DOS shape is necessary to engineer polymers with desired properties [30]. Penetrating the polymer, dopants can ionize fully or partially. Both result in charge separation forming free carriers and polarons, where charge transfer complexes, integer or partial, can occur. Ionized dopants act as traps, hindering charge transport through the polymer, and generally, resulting in increase in energetic disorder caused by Coulomb potentials interacting with charge carriers. This is considered analytically using a hopping model in doped and disordered organic semiconductors (OSCs) [28]. An important conclusion is that the trade-off between increasing densities of charge carriers and Coulomb traps, is controlled by the intrinsic DOS width and external field strength. Deep traps strongly suppress the hopping rate causing lower contributions to the mobility with doping and the dominant process governing transport is the competition between the formation of a deep tail in the host DOS and state filling [8]. Modifying this dopant-induced disorder, e.g. by controlled exchange of counter-ions [30], can lead to high thermoelectric power factors. A one-dimensional nearest neighbor tight-binding model with a correlated Gaussian distribution of on-site energies and constant off-site coupling elements efficiently described the main features of electronic structure in these systems [17]. The tail of the DOS is typically described by an exponential distribution and the position and localization length of states are mainly determined by disordered electrostatic potential, and not by conjugation breaking as previously thought.

3. ELECTRICAL TRANSPORT PROPERTIES

Electric transport in polymers is widely considered as a 3D hopping process, where carriers have to overcome a binding potential. Using Pauli's master equation to calculate site occupational probabilities, the hopping of localized carriers is usually calculated from Miller-Abrahams rates [31]. Also, quantum expressions based on the Fermi Golden Rule [32] and the classical approximated Marcus formula [33] were widely used together with the Pauli master equation or kinetic Monte-Carlo algorithm [34], [35] to calculate hopping mobility. Lastly, mean field theory [36] proved to work well for charge transfer rates but failed to account for the temperature dependence of mobility in large aggregates. Although the mean field simulation neglecting system-bath interaction can reproduce thermally activated transport, the role of additional nonlocal electron-phonon couplings cannot be properly characterized, and the mean field theory must be used with caution when studying charge transport in the hopping regime.

Mott's formula describes electric conductivity through the energy change of the Fermi-Dirac distribution. By considering the distribution for not too high temperatures, its change with respect to energy can be approximated as a delta function at the Fermi level, since:

$$\begin{aligned} \frac{df}{dE} &= \frac{1}{k_B T} \frac{e^{\frac{E-E_F}{k_B T}}}{\left(1 + e^{\frac{E-E_F}{k_B T}}\right)^2} = \frac{1}{k_B T} \frac{1}{\left(e^{\frac{E-E_F}{2k_B T}} + e^{\frac{E-E_F}{2k_B T}}\right)^2} \\ &= \frac{1}{4k_B T} \left(\sec h \frac{E-E_F}{2k_B T} \right)^2 \end{aligned} \quad (10)$$

where the hyperbolic secant has a peak at zero. Therefore, the largest contribution to conductivity is at the Fermi level (where $E=E_F$), that is, at energies that have free as well as occupied states. That way, the existence of carriers and empty states that carriers can occupy after hopping, is ensured. In the limiting case when $-df/dE \approx \delta(E-E_F)$, the only contribution to electrical transport is at the Fermi level and qualitatively, as a quantity dependent on carrier number, conductivity refers to the density of states at the Fermi level. Developments of this formulation by relating the constant in Mott's equation for disordered systems to the critical density of a certain dimensionless percolation problem, lead to a better description of hopping conductivity, where the applicability to real systems is discussed as well [37].

An accurate ab initio approach for simulation of carrier transport in large disordered systems enabled to obtain rich microscopic details of carrier motion in conjugated polymers [26]. Here, calculations for the macroscopic mobility of disordered poly(3-hexylthiophene-2,5-diyl) (P3HT), a commonly used polymer, agree well with experimental results from the literature. Anyhow, direct calculations of carrier hopping rates in strongly disordered conjugated polymers, show that the dependence of hopping rates on distance and the dependence of mobility/conductivity on temperature, are significantly different than the ones originating from Miller-Abrahams model [38]. Additional to the electronic DOS, the phonon density of states and the spatial overlap of the wave functions are necessary to properly describe carrier hopping. Dependence of conductivity, Seebeck coefficient and power factor with doping concentration for different spatial overlap and hopping rates can be seen in Figure 2.

It is worth mentioning that there are two regimes that are distinguishable regarding the conductivity behavior upon doping and temperature change. Increasing the temperature and/or doping level, the conductivity slope changes signs, reminding on metallic behavior. Therefore, this regime is sometimes called metallic and the other one nonmetallic. At high doping, which is achieved without degrading the structural order, the thermoelectric power factor exhibits a peak between the boundary of metallic

and nonmetallic electrical transport processes. Doping increase causes noticeable deployment of this metal-to-insulator transition to lower temperatures [39].

Recently, the semi-localized transport (SloT) model was proposed [40] and, as an improvement of Kang-Snyder's model [41], it defines the transport function's energy independent term as a function of concentration and temperature.

Temperature dependent electrical conductivity and Seebeck coefficient are measured and system-dependent parameters, such as the mentioned amount of dopant required to achieve metal-like conductivity, have been determined. The origin of this band-like transport was investigated using optical spectroscopy of gate-induced charge carriers [42], where the measurements showed at low temperature and small lateral electric field that charges become localized onto individual molecules in shallow trap states.

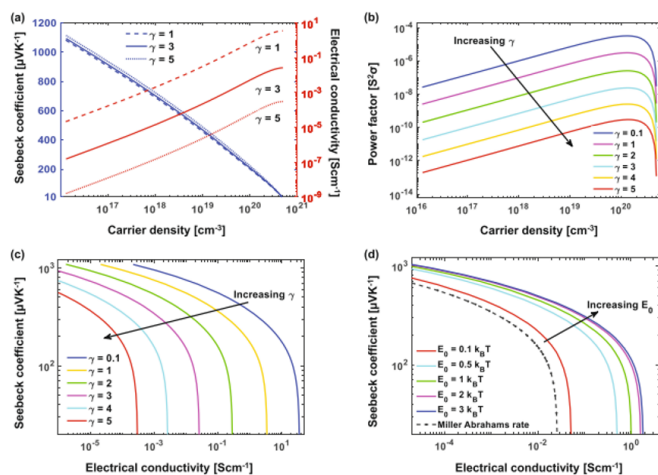


Figure 2: (a) Seebeck coefficient, electrical conductivity and (b) power factor as a function of carrier density at different overlap parameter values. We note that the highest power factor is obtained at a carrier density of $2 \times 10^{20} \text{ cm}^{-3}$, corresponding to 20% of sites being occupied. (c) Seebeck coefficient vs. Electrical conductivity showing the increase in electrical conductivity and Seebeck coefficient with stronger electronic orbital overlap. (d) Comparison of the conductivity vs. Seebeck plot for hopping rates computed using Miller-Abrahams and Marcus rate equations (adapted from [10]).

Localized transport limited by thermal lattice fluctuations appears to be the cause of negative temperature coefficient of the mobility at high fields. Taking P3HT as an example, the occurrence of negative field dependence of mobility above ~250 K in highly regioregular P3HT is attributed to small energetic and high spatial disorder [43]. The comparison of experimentally obtained conductivity and their temperature dependence between regioregular and regiorandom P3HT doped with iodine enabled a deeper insight into the structural dependence of the doping and hopping process [44]. This temperature and field dependence is studied by the time-of-flight technique and the transition temperature

appears to be lower than in previous studies because of mobility overestimation in the former [43]. Note that mobility measurements can show different values depending on the used method [45] and of course molecular weight [3], [46]. The discrepancies were found between mobilities extracted from hole-only diodes and field effect transistors and believed to originate from the significant dependence of hole mobility on charge carrier density.

An accurate description of conductivity of p-doped conjugated polymers with doping can be reproduced with a power law dependence with doping concentration [47]. The behavior is explained by introducing an energy-dependent localization length in the hopping model. The conductivity for one doped polymer is here split into three regimes, all with different slopes, where the exponent ranges from 2 to 5. Another good correlation between paracrystallinity and conductivity lead to a conclusion that structural and dynamic disorder control the conductivity of highly doped conducting polymers, rather than the ionic trapping/size of dopant [7], [48]. Although the authors used different doping concentrations with differently shaped molecules and compared different materials, the conclusion that crystallinity has a greater impact on conductivity than dopant size at high doping is fairly justified. Anyways, there are works stating that polymer crystallinity is less important for achieving high conductivities [49].

4. IMPACT OF CRYSTALLINITY AND DOPING

Electrical conductivity can be improved without affecting the Seebeck coefficient with stronger overlap between sites [11]. In this study, it was found that the positional disorder aids the formation of new conduction paths with more carriers in high energy sites. This in turn increases the electrical conductivity and leaves the Seebeck unchanged. Overall, by reducing energetic, while increasing positional disorder, higher thermoelectric power factors are obtained (Figure 3).

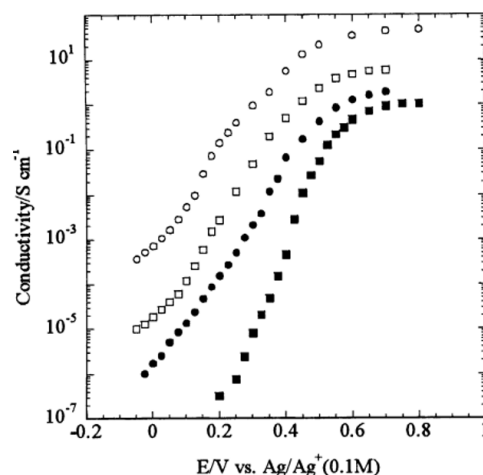


Figure 3: Semi-logarithmic plots of the in-situ conductivities of P3HT films versus doping potential with regioregularities of (○) 97%, (□) 81%, (●) 70% and (■) 54% (adapted from [52]).

Using again P3HT as an example, where with a higher degree of side-chain disorder regiorandom P3HT is expected to have lower conductivities, but above a certain doping level, the conductivities of regioregular and regiorandom P3HT are very similar [44]. For lower doping, a significant impact on carrier mobilities (and conductivities) is observed, that are measured as a function of doping level, for electrochemically evaluated P3HT films with different regioregularities [50], as in Figure 3.

The study of the effect of disorder on thermoelectric properties using regioregular and regiorandom P3HT doped with F₄TCNQ from the vapor phase, has shown a dependence of Seebeck coefficient with structural ordering. Also, the electrical conductivity and power factor are more strongly correlated with the long-range connectivity of ordered domains [52] (Figure 4, adapted from [51]). Here, vapor phase doping induces order in disordered regions and increases the long-range connectivity in films. The conductivity of solution sequential processing F₄TCNQ doped P3HT also increases with crystallinity [53].

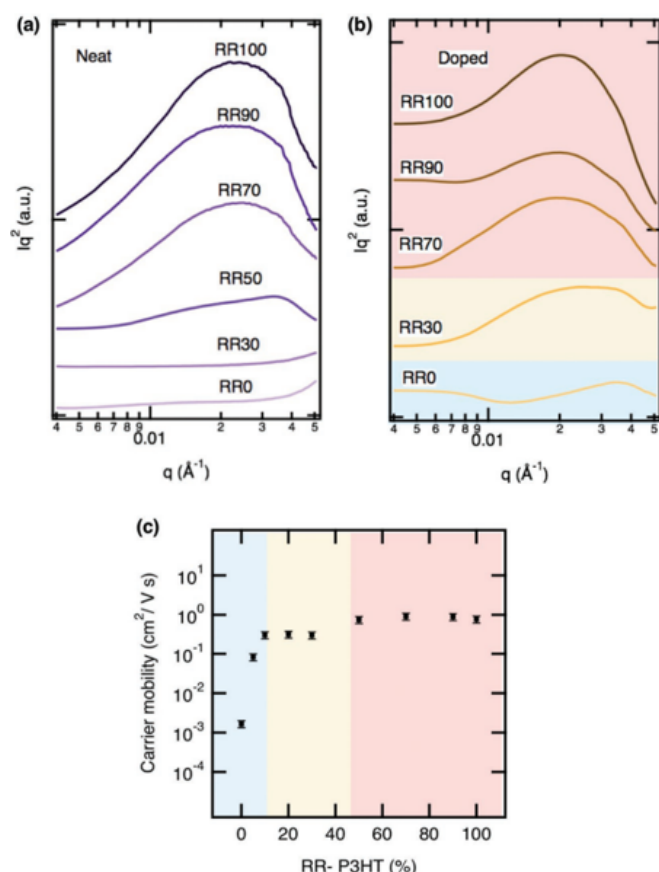


Figure 4: Lorentz corrected RSoXS profiles of a) neat and b) doped films of RR-:RRa-P3HT blends at resonant energy (285.4 eV). c) Carrier mobility as a function of % RR-P3HT. The highlighted regions in (b) and (c) correspond to the same films (adapted from [51]).

Three distinct degrees of crystallinity were obtained by synthetical improvement of the films regioregularity, where their observations suggest that the F₄TCNQ anions infiltrate the crystalline lamellar regions and afterwards begin to incorporate into the polymer amorphous regions, but do not π -stack in the polymer crystallites. The additional disorder introduced by doping can compensate the intrinsic disorder of the material, so that the total disorder remains constant or is even reduced [54] and the position of the Fermi level and electrical conductivity are controlled by disorder compensation. Doping causes increased ordering from the need to delocalize charge in the polymer in more than one dimension, which is observed for regiorandom P3HT [49] comparing its optical, electrical and structural properties by changing the dopant. Interestingly, films are doped with F₄TCNQ and FeCl₃ and only infiltrated by TCNQ. If the infiltrated atoms and molecules, as TCNQ here, do not dope the polymer, the polymer displays similar properties as the crude and undoped one. Increased ordering is found only for the dopants, where simple space filling would leave the polymer almost unchanged. Changes in host's morphology occur for systems with a difference in dopants LUMO and host's HOMO level above about 0.5 eV [8]. For dopants with a LUMO within ~ 0.5 eV to the host's HOMO, the dominant process governing transport is the competition between the formation of a deep tail in host's DOS and state filling. For relatively amorphous hosts the latter can even lead to a suppression of deep traps, causing a surprising mobility increase by 1–2 orders of magnitude. On the other hand, an *n*-type conjugated polymer with a single dominant planar backbone conformation, high torsional barrier at each dihedral angle and zigzag backbone curvature promises high tolerance to dopant induced disorder [55]. Those highly dopable polymers are reaching extremely high conductivities compared to polymers with similar chemical structure. Some dopants, such as dodecaborane-based ones [56], electrostatically shield counterions from carriers by effectively intercalating into the lamellae, far from polarons on the polymer backbone. Thus, the importance of choosing the right dopant [9] for a certain host is crucial to obtaining good conductivity.

5. STRATEGIES TO IMPROVE THE THERMOELECTRIC POWER FACTOR

The spatial distribution of dopants has an important impact on charge transport, where their clustering is not desirable [20]. The temperature at which the polymer is doped, displays a significant change of the Seebeck coefficient. Other advantageous effects as lowering dopant-carrier Coulomb interactions by increasing polymer's permittivity [19] as shown in Figure 5, are predicted to occur upon high doping [57] as the system approaches dielectric instability.

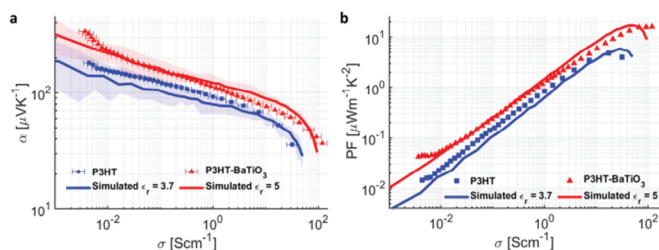


Figure 5: Higher dielectric permittivity leads to a higher power factor in OSCs. a) Plot of simulated α versus σ values and experimental values of BaTiO₃-P3HT composite and pristine P3HT. BaTiO₃-P3HT composite shows a fit to $\epsilon_r = 5$ while pristine P3HT fits $\epsilon_r = 3.7$. The simulations were iterated 25 times; the solid lines represent averaged values and the shaded region represents the minimum and maximum values. The horizontal error bars represent the error in the experimental electrical conductivity due to the variation in film thicknesses. b) Power factor as a function of carrier density. There is an approximately four-fold increase in power factor from 4.8 to 16.2 as ϵ_r is increased (Figure 5, adapted from [59]).

Low band gap and high-mobility polymers are accomplishing highly desirable thermoelectric properties with a reported power factor of $276 \mu\text{W m}^{-1} \text{K}^{-2}$ [58]. FeCl₃ and spin-coating doped P3HT shows only a narrow range of dopant concentrations with a high power factor, whereas PDPP3T exhibits a broad concentration range, which is shown in Figure 6 with illustrative reasoning why this is the case. Reaching surprisingly high conductivities of 3000 S cm^{-1} became possible by, seemingly, doping the amorphous domains of P3HT where the crystalline were almost unaltered [59]. This approach showed to be effective for reaching high power factors, which can be reached by engineering dopant induced disorder [30], choosing dopants with suitable energy offsets relative to the host [60] or possibly in blends [25], [61]. Improvement of power factor in polymer blends compared to single polymers is proved to be possible under certain conditions.

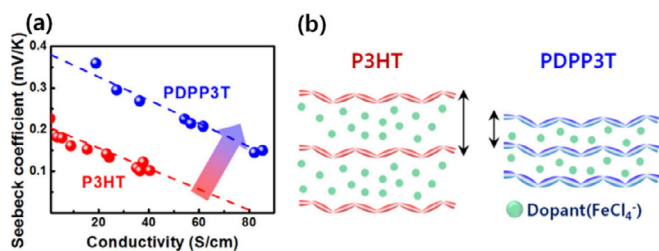


Figure 6: (a) Seebeck coefficients of the doped P3HT and PDPP3T films as a function of electrical conductivity (the dashed lines were inserted to stand out the difference of Seebeck coefficients more clearly), and (b) the scheme of the doped P3HT and PDPP3T with optimal thermoelectric performances (copied from [61]).

The final DOS was computed as a weighted sum of the two separate DOS curves originating from individual polymers with a shift in their HOMO energy levels. A

narrow DOS at higher energies and a broad DOS at lower energies with a larger correlation length is required to increase the power factor of the blend. The model had not taken into account dopant-induced disorder, which for a 3D hopping model leads to significant changes of the tail of the DOS.

A synergy of computational and experimental studies is further required to efficiently predict polymer behavior on one hand because of the lack of theoretical description and on the other difficulties to accurately measure quantities as mobility or carrier density.

6. CONCLUSIONS AND FUTURE OUTLOOK

Organic materials remain a vibrant and active area of research, with work spanning chemistry, materials science, physics, and applications unfolding at a rapid pace. Among organic materials, conjugated polymers have found applications as electronic materials for flexible electronics, organic photovoltaics, thermoelectric energy conversion, and numerous other related applications that take advantage of their unique properties, which are chiefly their low cost, ability to be solution processed, and their environmentally friendly composition. These stand in contrast to inorganic materials, which require extensive chemical processing, etching, and sometimes rely on materials with low abundance.

Here we have reviewed the extensive literature on the electronic properties of organic materials, with a particular focus on the interdependence between electronic properties and doping, which is necessary to increase electrical conductivity of polymers. We have also reviewed the literature on the closely related thermoelectric properties, as electrical conductivity and the thermoelectric Seebeck coefficient that can be viewed as two complementary windows into charge transport in polymers. Both have a close relationship on the density of electronic states, which are typically localized and have a Gaussian distribution, but are also highly dependent on the coulomb interactions between the charge carriers and the static dopants.

We conclude that much work remains to be done on understanding the interdependence between polymer structure, morphology, doping, and transport. Furthermore, future research in this area will likely involve the co-design of dopant-host polymer pairings that simultaneously optimize multiple targets, such as morphology, dopant placement relative to the polymer backbone where carriers are transporting, and the resulting shape of the DOS. This will likely have as its goal to minimize the deleterious impact of dopants on transport via carrier trapping, while maintaining good interconnections among polymer chains or domains for good carrier mobility. Another simultaneous target can be to maximize the asymmetry between the heavy tail and narrow middle of the DOS, which is expected to improve

the Seebeck coefficient. Taken together, we anticipate organic electronics to remain a vibrant research area for years to come.

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