Blending poly(3-hexylthiophene) for controlled thermal conductivity

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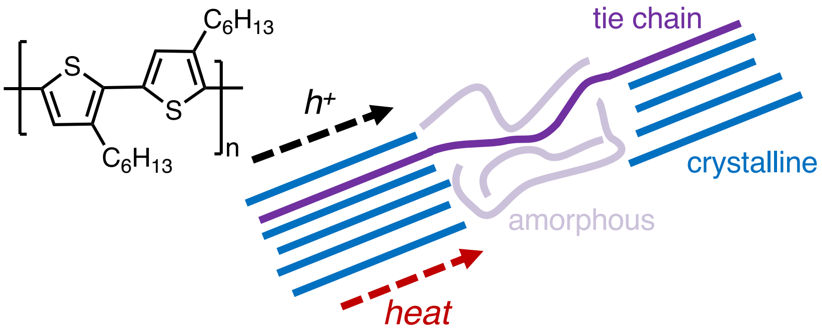
Abstract

Semiconducting polymers have transport properties that can be tuned by both synthetic design and processing techniques. Their thermopower, electronic conductivity, and low lattice thermal conductivity make them particularly attractive in thermal management and thermoelectric applications, especially in form factors unfit for comparable inorganic ceramics. The effects of blending differing molecular weights and regio-regularities on the thermal conductivity of poly(3-hexylthiophene) (P3HT) doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane were investigated in order to develop design rules for the co-optimization of thermal and electronic properties. The thermal conductivity of blended P3HT films was found to be controlled by engineering the distribution of molecular weights and regioregularities of chains to achieve room-temperature thermal conductivities. The resulting thermal conductivity of P3HT was found to span 0.2-0.85 W/mK without significant synthetic modification of the monomer or specialized processing. Upon electrical doping, a significant decrease in thermal conductivity was found at all blending compositions despite comparable electronic conductivity. These results suggest blending of molecular weights and regioregularities as a rational means to optimize thermal conductivity while maintaining desired electronic properties in polymeric semiconductors.

TOC Image



Semiconducting polymers are an attractive choice for development in a large range of electronic applications,[1] including thermal management and thermoelectrics. However, while the impacts of blending, doping, backbone structure, and side chain choice[2–8] have been extensively documented in mapping the structure-function relationship for semiconducting polymers, relatively little is known about the effect of these processes on the thermal properties. Thermal conductivity is a critical material property in overall performance of thermal management and thermoelectric generators; it is important to understand its optimization when designing polymeric systems for these applications. The thermal conductivities of organic semiconducting polymers tend to be low compared to inorganic compounds, typically in the range of 0.1-1.0 W/mK,[9,10] and like all electronically conductive materials, the thermal conductivity in principle has contributions from charge carriers and lattice vibrations. Electronic contributions to thermal conductivity are typically well described by the Wiedemann-Franz law in both organic and inorganic conductors, so the primary benefit of polymeric materials is in their low lattice thermal conductivity. Their propensity for polycrystallinity within a glassy, disordered matrix makes their thermal properties simultaneously attractive for application, and difficult to derive models from which to develop design rules.[10,11]

The lack of a satisfying foundational theory for the thermal conductivity of polymers, the ~~immense~~ diversity of chemical structures and molecular architectures, and the difficulty in measuring thermal properties as compared with inorganic materials have resulted in relatively poor understanding of how to reliably control thermal conductivity and how to co-optimize it with other critical material properties. For example, poly(3-hexylthiophene) (P3HT) is one of the most studied semiconducting polymers with much known about the variation of electronic and structural properties with molecular weight, crystallinity, and processing history.[12] The same cannot be said about the thermal conductivity of P3HT with varying values across studies with significant differences in the behavior upon electrical doping. (See Supporting Information, Table S1).[13–16] It is difficult to make direct comparisons across studies because they differ in material properties such as molecular weight and also in the processing conditions used to form the undoped and doped samples. These changes impact the aggregation and crystallization of polymers which are known to strongly influence the thermal conductivity.[17,18] Our understanding of thermal transport is beginning to change with advances in computational techniques and modeling that provide a means to better understand the behavior of polymers.[11,19] Recent experimental work across semiconducting polymers has also begun to reveal systematic changes in thermal properties as a function of electrical doping and processing showing significant nonlinear response to doping level and also anisotropies in thermal and mechanical properties from alignment of polymer chains.[4,17,20,21] Other key properties affecting aggregation and crystallization, such as regioregularity and molecular weight, have not been explored for their impact on thermal conductivity, signifying the need for more work to develop a full understanding of these systems and design rules for their application.

In this work, we explore the effect of blending different molecular weights and regioregularities of a single polymer to extract the impact of the polymer blends polycrystalline structure on their thermal conductivity. We employ P3HT in this study as the effects of electrical doping, especially with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ), and molecular weight on physical properties, such as the structure,[22–25] heat capacity and melting temperatures,[26] and electronic conductivity[5,6,8] , have been well studied. Low molecular weight regioregular (RRe) P3HT forms highly crystalline films with thermal and structural properties changing sharply with molecular weight.[22,26] The variation of these properties slows with increasing molecular weight, as polymer chains approach their infinite-chain statistics. Studies have shown that blends with controlled distributions of molecular weights and regioregularities of P3HT can tune their electrical conductivity[27] and mechanical performance.[28] By considering the impacts of blending on the electronic, structural, and thermal properties of the resultant thin films we probe the impact of polycrystalline structure on thermal conductivity in films with well controlled electronic properties.

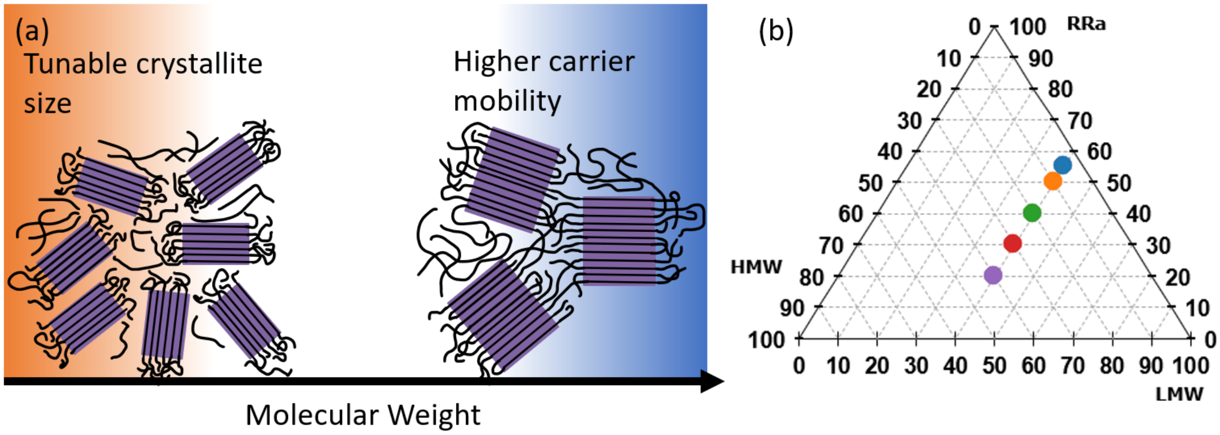


Figure 1. (a) The structural and electronic properties of poly(thiophenes) depend on their molecular weight and polydispersity. With increasing molecular weight homopolymers the charge carrier mobility tends to saturate. **(b)** The three-component P3HT blends here are tuned by regioregularity and the molecular weight of the regioregular fraction across a compositional region expected to yield highly interconnected films.

Here we use blends of varying molecular weight and regioregularity to examine changes in the thermal conductivity of P3HT while still maintaining typical electronic conductivities (≈1 S/cm) achieved at high carrier concentration. We employed a combination of short and long chain RRe P3HT to tune the crystalline fraction, as well as the frequency of chains participating in multiple different crystallites, known as tie-chains. In semicrystalline polymers, there are three characteristic distances associated with the behavior of tie-chain molecules – the characteristic size of crystallites, the characteristic separation between crystallites, and the radius of gyration of the tie-chain polymer. These features have been applied to examine the carrier mobility of P3HT using blends of P3HT with varying MW based on a model developed by Huang and Brown to describe effect of tie chains on the mechanical properties of semicrystalline polymers.[27] We use a similar approach here to examine thermal transport by incorporating a low molecular weight (LMW), whose conformational length is less than the persistence length (M_n=4.5 kDa, PDI of 1.6), a higher molecular weight (HMW) RRe P3HT, which is long enough to span amorphous regions between crystallites forming tie-chains (M_n=22 kDa, PDI of 1.8), and a regiorandom P3HT (M_n=16.3 kDa, PDI of 2.54), which is not expected to significantly incorporate in crystalline regions of the LMW P3HT (See Supporting Information, Figure S1 and S2). This three component blend associates one constituent material per salient distance to the formation of tie-chains. This framework allows us to target fractions of tie-chain molecules associated with high electronic conductivities while varying the amount of RRe material and fraction of crystallites in the blend in order to study their effect on the thermal conductivity. Based on modeling (see Supporting Information, Figure S3) we found that blends with a constant 40 wt% of LMW RRe P3HT and increasing fractions (5-40 wt%) of HMW RRe P3HT should probe films with varying crystallinity but high electronic conductivity. We report the compositions of the films as “LX:HY:RaZ” where X, Y and Z are the mass fractions of LMW RRe and HMW RRe, and RRa P3HT in the blend (Figure 1b).

We carried out structural, spectroscopic, and electronic characterization on the P3HT blends to determine the impact of the three components on the overall behavior of thin films (See Supporting Information for experimental details) and to verify they conformed with the expectations for P3HT thin films. Both neat films and films electrically doped with F_4TCNQ infiltrated from the vapor phase were examined. The resulting grazing incidence wide angle x-ray scattering, UV-Vis absorption spectra of undoped films (spectra for doped films are in Figure S4), and thermopower and electronic conductivities of doped films prepared from these blends are shown in Figure 2. The UV-Vis absorption spectra show an increase in the relative intensity of peaks associated with vibronic transitions with increasing HMW wt% in undoped films as expected (Figure 2(a)). Radially integrated GIWAXS scattering on un-doped polymer films is shown in the inset of Figure 2(a) and demonstrates a clear increase in the intensity of lamellar and π- π stacking peaks associated with scattering from polymer crystallites with increasing wt% HMW RRe P3HT. These results clearly indicate that blending has the intended effect of increasing the aggregate and crystalline fractions within these materials. Measurements of the blend films doped with F_4TCNQ show that the electronic conductivity of these blends is near 1 S/cm and their thermopowers are near 200 μV/K, with decreasing thermopower as the electronic conductivity increases (Figure 1(b)). This increase in electronic conductivity was associated with increasing the fraction of HMW material and was relatively small as compared with the effect of doping. These observations are consistent with the expectations from the selection of these blending ratios with increasing aggregation and crystallization with higher blending ratios of HMW RRe P3HT, but relatively stable electronic conductivity based on the Huang-Brown model. The least interconnected film, H40:L05:Ra55, showed a statistically significant deviation in the trend seen in the other blends, with larger thermopower than films of a comparable electronic conductivity. At low crystallinities, it is expected that hopping transport will contribute significantly to the overall transport in the bulk of the film: we can expect to see slightly different transport behavior represented at this low blending ratio than in the more crystalline, more interconnected films. Overall, these results are consistent with our expectations for the structural and electronic properties of P3HT thin films.

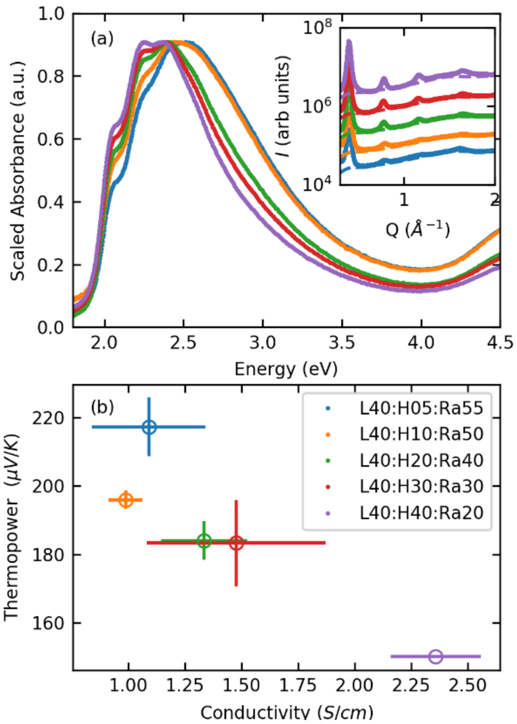


Figure 2. (a) UV-Vis spectra of undoped films of the P3HT blends. Each spectrum has been scaled to facilitate comparison of the relative contribution between aggregate peaks (around 2.0-2.3 eV) and the amorphous contribution (peak around 2.5 eV). *(inset)* GIWAXS scattering data collected on blended undoped films. Measurements are offset by decades for clarity of presentation. **(b)** Thermopower of doped films plotted as a function of thin film electronic conductivity.

The thermal conductivities of the blend films, both before and after doping with F_4TCNQ, were measured using time domain thermoreflectance (TDTR), a highly sensitive technique for measuring low thermal conductivities.[29] The doping level, film thicknesses, and annealing conditions for films were selected to minimize the complexity of the modeling process and subsequent extraction of thermal conductivity values (See Supporting Information for detailed information on experimental methods and models, Figure S5 to S9). TDTR measurements were performed on films approximately 300 nm thick, larger than the thermal penetration depth at our TDTR modulation frequency reducing the impact of the polymer-air interface on fitting. While de-doping at the Al:P3HT interface can occur, the thickness of de-doped region decreases rapidly with dopant concentration.[30] We expect at the doping level used here which is high (~10^{20} cm^3), the thickness of a depletion layer would be below the thermal penetration depth (~50 nm). As such, we expect measured thermal conductivity values are close to the bulk values relevant for applications. To obtain the thermal conductivity of these blends from TDTR measurements it is necessary to know the volumetric heat capacity in both the neat and doped state for each blending composition; the values and details of their derivation are presented in the Supporting Information along with an analysis of the sensitivity of the model used (Figure S10). The results of these measurements are shown in Figure 3, with error bars representing the modelling uncertainty. The films were characterized before and following their vapor doping with F_4TCNQ, and in both cases demonstrated significant variation in thermal conductivities between different blending ratios. In undoped films we observed thermal conductivities ranging approximately from 0.2-0.85 W/mK with thermal conductivity increasing with fraction of HMW P3HT in the blend. We observed no qualitative differences in the TDTR signal from these films in their neat and doped states (See Supporting Information, Figure S6). This trend was repeated for doped films but with lower measured values of the thermal conductivity compared with their undoped values. All compositions demonstrated a decrease in thermal conductivity following doping. The decrease in thermal conductivity following doping of films is consistent with other reported measurements of vapor-doped semiconducting polymers,[20] although there is evidence that with other methods of doping that P3HT can exhibit increases, as opposed to decreases, in thermal conductivity.[31,32] Given that there can be changes in morphology of semiconducting polymer depending on whether doping is carried out in solution prior to deposition of films or induced by swelling with solvents, it is possible that such differences in thermal conductivity are due to morphological changes as opposed to electronic effects. Here, the thermal conductivity of P3HT blends varies smoothly with the composition of the blend in both the as-prepared and vapor doped states demonstrating the importance of the ordered aggregate fraction and the tie chains between them. As such, we have demonstrated the ability to tune the thermal conductivity of P3HT across the range of typically observed polymer thermal conductivities (0.2 to near 1 W/mK) by rationally modifying the distribution of chain size and structure.[10,18]

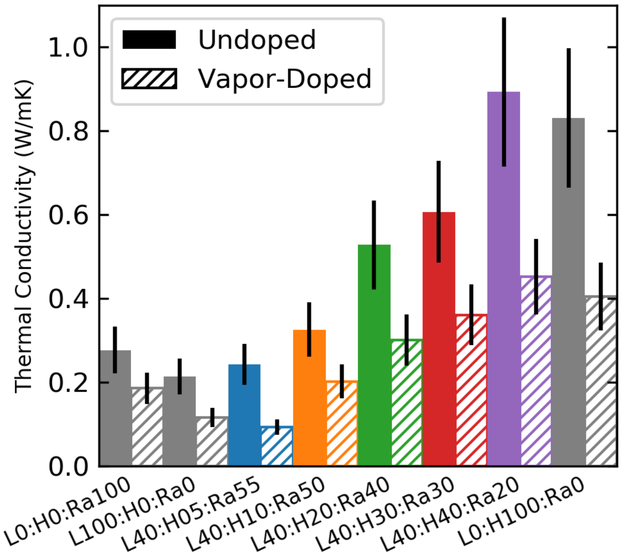


Figure 3. Thermal conductivities of thermally thick films of each blend composition, RRa, LMW, and HMW P3HT for comparison. Vertically hatched bars represent measurements made on undoped films while diagonally hatched bars in the same color denote the thermal conductivity of the same films after vapor doping with F_4 TCNQ. Error bars denote the combined measurement and fitting uncertainty.

To assess the difference between the effects of the total blending ratio of RRe and RRa P3HT and interconnections between crystallites, we also measured the thermal conductivity of a blend with no HMW P3HT. This bi-polymer film, consisting of LMW P3HT and RRa P3HT is expected to have similar aggregation but significantly less interconnection of the crystallites. Both the radially integrated GIWAXS data for a L50:H0:Ra50 film and a L40:H10:Ra50 film in addition to the phase data from TDTR measurements of the same blends are shown in Figure 4. The GIWAXS exhibited similar ratios of the primary alkyl stacking peak with respect to the background, indicating similar crystallinities. The bi-polymer blended film exhibited a thermal conductivity of 0.24 W/mK as compared with 0.33 W/mK in the tri-polymer blended film. Across all blends, we observe consistently that the fraction of high regioregularity, higher molecular weight chains confer significantly larger thermal conductivities as compared with lower molecular weight and lower regularity P3HT. The low thermal conductivity of LMW RRe and observed increase in thermal conductivity when blends include HMW RRe material indicate that longer polymer chains contribute significantly to the resulting thermal conductivity. This enhancement can be attributed to the more interconnected network expected by the addition of HMW RRe chains, but we note that the MW of the RRe chains is higher than the RRa fraction so we cannot perfectly rule out an impact of MW independent of regioregularity. Regardless of the mechanism, this work does demonstrate the importance of the distribution of molecular weights and regio-regularities in determining the thermal conductivity of semiconducting polymers, and that large differences in thermal properties can be achieved with relatively straightforward design rules.

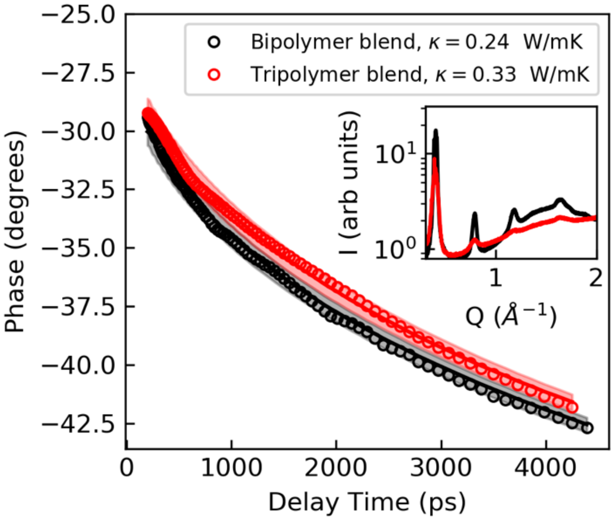


Figure 4. Phase information from TDTR measurements made on films with the same composition, including data (circles), theoretical fit (solid line), and estimation of 20% relative error (shaded region) taken on bi-(50:0:50) and tri-polymer (40:10:50) films.(inset) Radially integrated GIWAXS data with intensity scaled to account for differences in scattering volume and exposure, and demonstrate substantially similar scattering especially in the ratio of the (100) peak near 0.4 Å^{-1} and the background scattering.

For specific use-cases like thermoelectric generators, we can consider the effect blending has on the overall performance. In thermoelectric generators, the efficiency of a thermoelectric module is typically expressed via the figure of merit $zT = \alpha^2\sigma T/\kappa$ which is related to the thermodynamic efficiency. The results for the P3HT blends here are shown in Figure 4. We expect that the thin film geometries employed in our electronic characterization are representative of the bulk conductivity by virtue of the lack of in-plane alignment. Ultimately, the morphology of all films can be described as polycrystalline with a high degree of interconnectivity that influences the electronic conductivity. It is possible that there could be processing dependent changes in the precise values of σ, but we do not expect that this would impact our observed trends. We observe that in such blended materials, those with lower fractions of HMW P3HT may perform significantly better as compared with higher HMW blend ratios. This suggests that a strategy of incorporating amorphous fill material and low thermal conductivity molecular weights can be used to effectively optimize device performance. As we can see in the inset of Figure 5, the change in thermal conductivity is around 0.6 W/mK across the measured blends. While there is evidence of variations from a conventional Lorenz number to an order of magnitude larger values and several reported mechanisms for potential deviations from the Sommerfeld number,[17,33–35] the change in observed electronic conductivity are still insufficient to explain this increase in thermal conductivity, which is expected to be of order 10^{-3} W/mK near room temperature. Even in polymer semiconductors with significantly larger electronic conductivities like PEDOT:PSS (c.a. 2000 S/cm), we would expect that changes in the lattice thermal conductivity as observed here could significantly impact the total thermal conductivity and thus thermoelectric performance. Another important feature is the change in thermal conductivity observed upon doping in this system. As has been recently observed in other systems,[20] changes in lattice thermal conductivity should be considered when doping semiconducting polymers for use in applications sensitive to the ratio σ/κ, and that blending is one way to do so. Other applications may call for different optimization, but these results indicate that thoughtful design can be used to improve the performance of these materials without added processing or synthetic complexity.

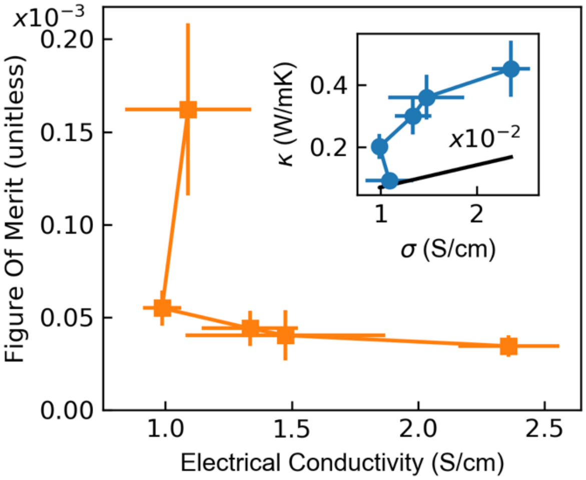


Figure 5. Thermoelectric performance as determined by the figure of merit zT at room temperature (orange) of the same blends plotted as a function of electronic conductivity. Connecting lines indicate the series of increasing wt% HMW RRe P3HT, with the 40/05 in the lower left, proceeding to 40/40 in the upper right. (inset) Thermal conductivity (blue) of the same blend compositions plotted against their electronic conductivity. The solid black line corresponds to the expected increase in thermal conductivity corresponding to the change in electronic conductivity as predicted by the Wiedemann-Franz law with the Sommerfeld Lorenz number, scaled by 100 for readability.

Due to their reported low thermal conductivities, polymer semiconductors have been a material of significant interest in thermal management and thermoelectrics. In applications such as these it is crucial to be able to co-optimize between material properties such as the electronic conductivity, thermal conductivity, and the thermopower. While we have reliable design rules from which to control electronic transport in semiconducting polymers,[4–6,9,24] our understanding of how to control thermal conductivity in these materials is still evolving.[17,20,21,36] We have observed changes in thermal conductivities of blended P3HT films controlled only by the blending of differing molecular weights and regioregularities. These blends exhibit thermal conductivities across the entire typically measured range for polymers,[10,18] the tuning of which is associated with relatively small changes in other material properties, and relatively small changes in the materials themselves. Previous reports of the thermal conductivity of P3HT homopolymers vary within the range we have observed, reporting κ = 0.189,[13] 0.48,[14] and 0.185 W/mK.[15] However these studies do not report the material properties to make quantitative comparison to the values here. Our work demonstrates that significant differences in thermal conductivity can occur due to variation in the distribution of molecular weight and crystallinity without significant change to the electronic properties observed by spectroscopy or electrical conductivity measurements. These results highlight the need for careful consideration of the impact of processing and design decisions on the thermal conductivity in these materials and a route to optimize performance.

The observation of thermal conductivities over the range of typically observed polymer thermal conductivities, achieved solely through blending varying MW and regioregularities of the same polymer, has significant implications for the design and processing of new polymer semiconductors for thermal applications. While we have identified the abundance of higher molecular weight chains as the salient variable in tuning thermal conductivity of blends of P3HT, it is worthwhile to note that these results may not extrapolate to systems in which lower electronic or significant ionic conductivity is preferable, or where the contribution of counterions and polymer sidechains to the thermal conductivity may be substantially different. Other effects especially those concerning the structure of dopant counterions, could have profound effects on the overall morphology and warrant further study. However, these results do demonstrate that careful design of molecular weight distributions in polymer thin films can have a significant effect on their resulting thermal conductivity with profound implications on their performance in specific applications.

Experimental Methods

Suitable polymers for the preparation and measurement of the blends considered in this work were sourced commercially as possible and synthesized when not. RRA P3HT was sourced from Sigma-Aldrich (M_n=16.3 kDa, PDI of 2.54). HMW RRe P3HT was purchased from Ossila with M_n=23 kDa, PDI=1.8. Both commercial polymers were used in the state in which they were received. A suitable low molecular weight RRe P3HT was not commercially available, and thus was synthesized following a GRIM procedure. The resultant P3HT was characterized via H^1-NMR (Figure S1) and GPC (Figure S2). It was found to have M_n=4.5 kDa and a PDI of ~1.6.

Samples for GIWAXS, 4 point probe electronic conductivity, thermopower, UV-Vis spectroscopy, and thermal conductivity were all prepared via spin coating following previously reported procedures to reliably control the thickness via spinning solution concentration. Films of ~40 nm were used in GIWAXS, electrical conductivity, thermopower, and UV-Vis while films of ~300 nm were used for TDTR samples. Full experimental and fabrication details can be found in the Supporting information.

Supporting Information

Experimental details of materials synthesis, processing methods, electrical measurements, and time-domain thermoreflectance. Details of modeling of thermoreflectance data. Table of literature values of thermal properties of P3HT.

Acknowledgements

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