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John C. Duda, Patrick E. Hopkins, Yang Shen, and Mool C. Gupta

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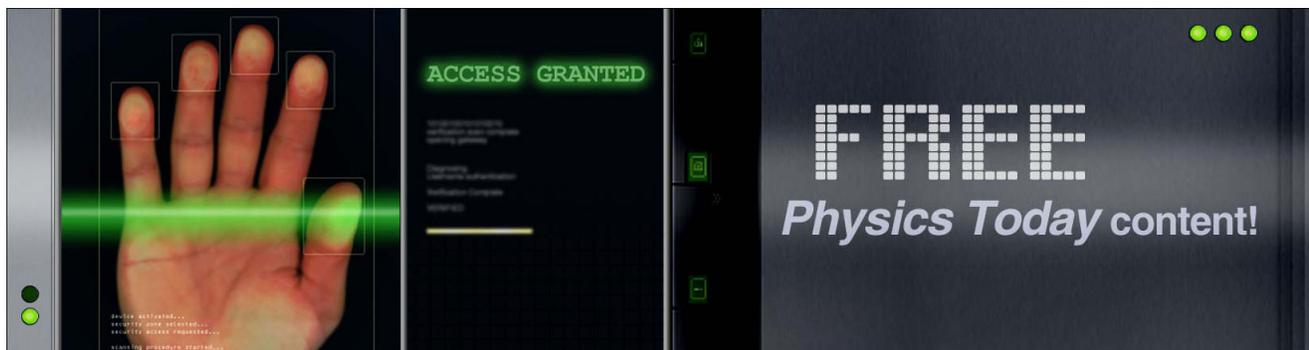
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Thermal transport in organic semiconducting polymers

John C. Duda,^{1,2} Patrick E. Hopkins,^{1,a)} Yang Shen,³ and Mool C. Gupta^{3,b)}

¹Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia 22904, USA

²Seagate Technology, Bloomington, Minnesota 55435, USA

³Department of Electrical and Computer Engineering, University of Virginia, Charlottesville, Virginia 22904, USA

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We report on the thermal conductivities of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM), poly(3-hexylthiophene-2,5-diyl) (P3HT), and P3HT:PCBM blend thin films as measured by time domain thermoreflectance. Thermal conductivities vary from 0.031 ± 0.005 to 0.227 ± 0.014 W m⁻¹ K⁻¹ near room temperature and exhibit minimal temperature dependence across the range from 319 to 396 K. Thermal conductivities of blend films follow a rule of mixtures, and no percolation threshold is found. Thermal annealing of blend films has a variable effect on thermal conductivity. Finally, the thermal conductivities of P3HT films do not vary with changes in film thickness from 77 to 200 nm. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4812234>]

Despite their low carrier mobilities, organic polymers have attracted attention in photovoltaics applications due to their strong optical absorption coefficients ($>10^5$ cm⁻¹)¹⁻³ and their ability to be deposited on flexible substrates, thus allowing for high-speed and readily scalable manufacturing processes.³⁻⁵ Bulk heterojunction solar cells comprised of P3HT (poly(3-hexylthiophene-2,5-diyl)) and PCBM ([6,6]-phenyl C₆₁-butyric acid methyl ester) have shown particular promise, and a significant effort has been put forth to electrically characterize these materials in device configurations.⁶⁻¹⁰ In addition, organic polymers have very recently received attention as plausible thermoelectric materials,¹¹⁻¹³ stemming from the fact that they are both semiconducting and that they should exhibit relatively low thermal conductivities, i.e., disordered polymeric chains often exhibit thermal conductivities an order of magnitude smaller than that of silica glass.¹³⁻¹⁹ Regardless of application, adequate thermal characterization of these materials is critical, whether it be to properly account for the I^2R losses in photovoltaic configurations^{6,9} or maximize the figure of merit in thermoelectric applications.^{20,21}

Thermal characterization of polymeric thin films is often a non-trivial task due to the fact the polymer thermal properties are very sensitive to the arrangement of the molecules within. For example, well-aligned polymeric chains can exhibit exceptionally high thermal conductivities,^{22,23} in stark contrast with the disordered polymeric chains described above.¹³⁻¹⁹ In disordered polymeric films, thermal conductivities exhibit temperature-dependencies that are typical of amorphous solids, and heat transfer is limited by a random walk of localized energy on the time and length scales of atomic vibrations and interatomic spacing, respectively.²⁴⁻²⁶ The issue of molecular arrangement is of particular interest in the context of the present material systems (e.g., P3HT:PCBM blends) as thermal annealing of common bulk heterojunction blends can lead to the alignment of polymer

chains and the formation of large crystallites,²⁷⁻³⁰ further demonstrating a need for the adequate thermal characterization of these materials. Even so, reports on the thermal conductivities of these materials in thin-film or device configurations are limited.

Recently, Losego *et al.*¹⁶ measured the thermal conductivities of PMMA thin films via time domain thermoreflectance (TDTR) and noted that thermal conductivities did not vary as a function of film thickness for thicknesses greater than 5 nm and that interface conductances between PMMA and the underlying substrate (Si) were in excess of 300 MW m⁻² K⁻¹. With regard to organic semiconductors, several studies have reported on room-temperature thermal transport behaviors. For example, Jin *et al.*¹⁷ measured the thermal conductivity of copper phthalocyanine (CuPc) as a function of film thickness via the 3ω technique and reported conductivities that were nearly constant for films from 12 to 39 nm thick. Furthermore, the interface conductance between CuPc and C₆₀ was reported to be 450 MW m⁻² K⁻¹. In addition, Malen *et al.*¹⁸ used fiber-aligned frequency domain thermoreflectance to measure the room-temperature thermal conductivity of a 1.6 μm thick P3HT film and reported a value of 0.17 W m⁻¹ K⁻¹, while Rausch *et al.*¹⁹ measured the room-temperature thermal conductivity of spin cast P3HT films ranging in thickness from 83 to 800 nm via the 3ω technique and reported minimal dependence of conductivity on film thickness. Finally, Bubnova *et al.*¹³ measured the room-temperature thermal conductivity of spin cast poly(3,4-ethylenedioxythiophene) tosylate thin films 175 ± 25 nm thick via the 3ω technique; the in-plane and cross-plane thermal conductivities were 0.37 and 0.33 W m⁻¹ K⁻¹, yielding an anisotropy ratio of 1.11.

In this letter, we report on the thermal conductivities of PCBM, P3HT, P3HT:PCBM blend, and PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)) thin films as a function of temperature from 319 to 396 K. The thermal conductivities of these films were measured by TDTR, a non-contact, pump-probe optical thermometry technique.³¹⁻³⁴

a) phopkins@virginia.edu

b) mgupta@virginia.edu

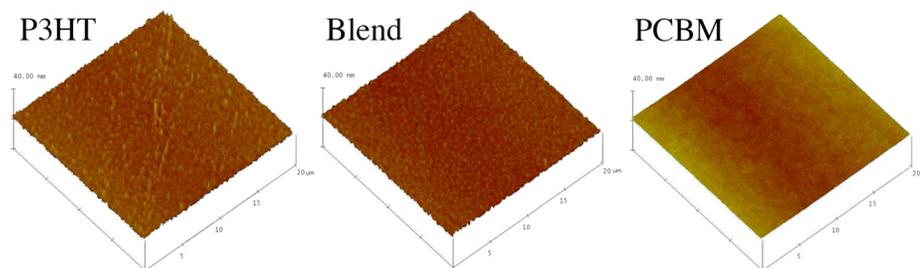


FIG. 1. AFM images depicting the surface morphology of P3HT, P3HT:PCBM blend, and PCBM thin films.

The thermal conductivities of these films span nearly an order of magnitude near room temperature, but exhibit negligible temperature dependence across the range presently considered. Furthermore, thermal conductivities of blend films follow a rule of mixtures, and no percolation threshold is found despite the large difference in the conductivities of the constituent phases. In addition, thermal annealing of P3HT:PCBM blends has a variable effect on thermal conductivity, but can lead to an increase in excess of 40 % in 45:55 blends. Finally, it is found that the thermal conductivities of P3HT are insensitive to changes in film thickness from 77 to 200 nm, thus demonstrating that size effects are not responsible for the low measured thermal conductivities. We speculate that the localization of vibrational energy is responsible for a majority of the observed behaviors.

The organic thin film semiconductors were prepared according to the following procedure: indium tin oxide (ITO) coated glass substrates (provided by Delta Technologies) were first cleaned with acetone and isopropyl alcohol and, subsequently, dried with air. Highly conductive PEDOT:PSS provided by H.C. Starck was then spin-cast (4000 rpm) on these substrates from aqueous solution. The PEDOT:PSS films had average thicknesses of 56 nm and were baked for 15 min at 110 °C in air. Of these substrates, one was set aside to serve as the PEDOT:PSS reference sample, while the others received further processing. For the PCBM, P3HT, and blend films, P3HT and PCBM (provided by Sigma-Aldrich and Nano-C, respectively) were dissolved in chlorobenzene for 24 h before fabrication. The PCBM, P3HT, and blend solutions were 1 wt. %, and the blend solutions were composed of a variable ratio of P3HT to PCBM (10:90, 45:55, or 90:10). The solutions were then spin-cast at various speeds on the PEDOT:PSS coated substrates producing film thicknesses from 25 to 200 nm. All but one series of P3HT:PCBM blend films were annealed in air at 130 °C for 2 min. A nominally 80 nm thick Al film was then deposited on the films (including on the PEDOT:PSS reference sample) via electron beam evaporation. The electrical resistivities of devices prepared in identical fashion were measured via a procedure, which we outlined previously, where the only variations in geometries were the film thicknesses; they ranged from 7.4×10^5 to $3.1 \times 10^6 \Omega \text{ cm}$.⁹ The surface morphologies of representative PCBM, P3HT, and blend films were measured by atomic force microscopy (AFM), the results of which are shown in Fig. 1. The results suggest that the average aggregate size is largest in the P3HT film, as surface roughness has been shown to correlate with molecular aggregation.^{29,35}

The thermal conductivities of these organic, semiconducting polymer films were measured with TDTR.³⁶ Time-domain thermoreflectance and appropriate analyses accounting for

pulse accumulation when using a Ti:sapphire oscillator have been detailed previously by several groups.^{31–33,37} In short, TDTR is a pump-probe technique in which 100 fs laser pulses emanate from a Spectra Physics Tsunami at an 80 MHz repetition rate. We delay the time in which the probe pulse reaches the sample relative to the pump pulse by way of a mechanical delay stage (for a maximum delay of ≈ 5.2 ns). In this study, we modulate the pump at 11.39 MHz and monitor the ratio of the in-phase to out-of-phase signal of the probe beam from a lock-in amplifier ($-V_{\text{in}}/V_{\text{out}}$). Our pump and probe spots are focused to $1/e^2$ radii of 25 and 12 μm at the sample surface; at these sizes and at the 11.39 MHz pump modulation frequency, we are negligibly sensitive to any in-plane transport in the films, thus decreasing the uncertainty associated with determining the cross-plane thermal conductivity.^{37,38} We take a total of six TDTR measurements on each film at ambient temperatures from 294 to 375 K in a cryostat with optical access that is kept under vacuum (< 1.0 mTorr). We limit the maximum temperature to 375 K to prevent the melting of or structural changes to the polymers.^{28,29} In addition, we limit the total incident laser power to ≈ 20 mW; still due to the low thermal conductivity of our thermal sink (glass), the temperature rise due to the incident laser beams is ≈ 22 K.³¹

We fit the TDTR data with a thermal model that accounts for pulse accumulation in a layered system. At our modulation frequency, we are sensitive to thermal effusivity, $\sqrt{\kappa C}$, where κ is the thermal conductivity and C is the volumetric specific heat.^{31,39} Consequently, in order to determine thermal conductivities, the volumetric specific heats must be known. We assume literature values for the specific heats of the Al (Ref. 40) and P3HT.^{18,41} We approximate the specific heat of PCBM from data on C_{60}/C_{70} fullerite microcrystals (Ref. 42), as they exhibit a very similar crystal structure to PCBM films processed via chlorobenzene solution (both exhibit fcc-like lattices with a center-to-center distance between fullerene moieties of $\approx 10 \text{ \AA}$).^{28,43} This assumption is addressed in more detail in the supplementary material.⁴⁴ We assume a rule of mixtures with weighted averaging, when calculating the heat capacity of the PCBM:P3HT blend. Finally, we take the heat capacity of PEDOT:PSS to be $2.0 \pm 0.5 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$, which spans the range of the other polymers considered. Despite this large window, this range correlates to less than a 15 % variation in the measured thermal conductivity of PEDOT:PSS (reflected in error bars in Fig. 2). In addition, all reported uncertainties reflect 5% variations in film thicknesses and uncertainties in PCBM heat capacity, as well as the repeatability of the measurement on each sample. The thicknesses of the Al films are confirmed via picosecond acoustics.^{45,46} Finally, despite the relative “thinness” of the polymer films, their thermal

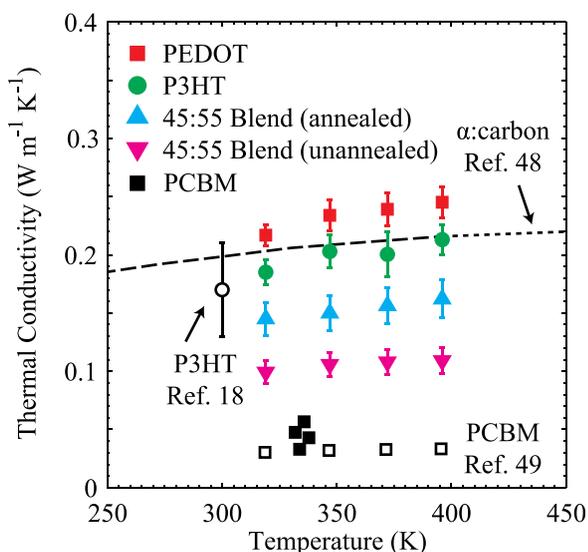


FIG. 2. Thermal conductivities of the PEDOT:PSS, P3HT, PCBM, and P3HT:PCBM films, along with previously published thermal conductivities of amorphous carbon (dashed line, Ref. 48), thin film PCBM (open squares, Ref. 49), and P3HT (open circle, Ref. 18). The PCBM data near 335 K have been offset horizontally for clarity.

conductivities are low enough that we are not sensitive to the underlying layers of PEDOT:PSS, ITO, or glass at our modulation frequency. This is confirmed by appropriate sensitivity analyses⁴⁷ and by the fact, we observe no dependence of thermal conductivity on film thickness. Thus, thermal conductivity of the film is the only free parameter in our thermal model.

Thermal conductivities of the PEDOT:PSS, P3HT, and P3HT:PCBM blend films are shown in Fig. 2. In addition, we plot the thermal conductivity of amorphous carbon from Ref. 48 ($\rho = 0.9 \text{ g cm}^{-3}$), thin film PCBM from Ref. 49, and a previous room temperature measurement of P3HT from Ref. 18. The thermal conductivities of P3HT ($0.185 \pm 0.011 \text{ W m}^{-1} \text{ K}^{-1}$) near room temperature are in good agreement with those previously reported (see Refs. 18 and 19). Also in Fig. 2, we report data on PCBM films with different thicknesses and processing conditions than those reported in Ref. 49 (details in supporting information). At this time, we do not understand the origin of the variation in thermal conductivities of the different PCBM films, however, we speculate that the different processing conditions and substrates can lead to different packing densities or inhomogeneities in the structure or composition in the spin cast PCBM films.⁵⁰ This could be reflected in the variation in heat capacities that we inferred from our TDTR data, as discussed in the supporting information. Even still, PCBM films represent ultra-low thermal conductivity solids, as we discuss in detail in Ref. 49.

Overall, the thermal conductivities of these materials do not exhibit any significant temperature dependence. Furthermore, it is interesting to note that while all these films are nearly twice as atomically dense as the amorphous carbon films investigated in Ref. 48, they have conductivities on-the-order-of or less-than that of the amorphous carbon films. One plausible explanation for this behavior is that the large, repeated unit cells in each of these polymeric films leads to Einstein-like behavior, where the oscillations of each unit cell are localized and uncoupled with those of their

neighbors (as has been suggested for both C_{60} and PCBM films in Refs. 42 and 49, respectively). In addition, this could further explain the lower thermal conductivity of P3HT relative to that of PEDOT:PSS. While both P3HT and PEDOT:PSS have similar molecular weights, the number of oscillators (unit cells) per unit volume, N , will be higher in the case of PEDOT:PSS than in P3HT due to the fact that the number of atoms per unit cell is lower in PEDOT:PSS than in P3HT. In Einstein's model, thermal conductivity scales as $N^{1/3}$, suggesting this behavior could be expected.

Also shown in Fig. 2 is that annealing P3HT:PCBM blend films can lead to an increase in thermal conductivity of approximately 40%. This correlates to the evolution of P3HT:PCBM morphology during annealing insofar as increased molecular mobility will lead to P3HT crystallite formation and PCBM aggregation.^{29,30,51} However, we believe that any increase in thermal conductivity is due to alignment alone and not aggregation; a reduction in interface density should have little effect on the thermal conductivity of blend films, as the Kapitza conductances at fullerene-polymer interfaces are exceptionally high.¹⁷ Quantitatively, one may consider the Kapitza length, which is often used as a metric for determining the degree to which interfaces dictate thermal transport properties of composite films. Assuming a film conductivity of $\kappa = 0.25 \text{ W m}^{-1} \text{ K}^{-1}$ and the thermal interface conductance between CuPc and C_{60} reported in Ref. 17 ($h_K = 450 \text{ MW m}^{-2} \text{ K}^{-1}$), the Kapitza length, $l_K = \kappa/h_K$, is 5.56 \AA . This implies that if interfaces were to dominate thermal resistance of the blend films presently studied, aggregates would have to be less than one nanometer in size. However, investigations into the morphologies of similar films prepared in identical fashion indicate that aggregates are significantly larger.^{29,35} Furthermore, the fullerene moieties of PCBM molecules are roughly 10 \AA in diameter themselves.^{28,43}

In Fig. 3, thermal conductivities of annealed and unannealed P3HT:PCBM blends are plotted as a function of P3HT concentration, and the dashed line is a linear interpolation of between the conductivities of pure PCBM and P3HT thin films. From the plot, it is clear that while thermal annealing can lead to increase in the thermal conductivity, this effect is variable and a large discrepancy is found among the thermal conductivities of 45:55 blends (which are horizontally offset in the figure for clarity). At present, we are unsure of the cause for this variability, though we hypothesize that our annealing procedure led to different degrees of polymer alignment within those films.⁵¹ Also of interest is the fact that a rule of mixtures holds for the thermal conductivity of polymer-blend thin films, as opposed to the dramatic decrease in thermal conductivity observed in bulk and thin-film semiconductor alloys.^{52,53} Furthermore, no sign of a percolation threshold is observed despite the order of magnitude difference in the thermal conductivities of the constituent phases (as one might expect in two-phase polymeric thermal interface materials, for example).⁵⁴ However, this behavior could be expected in a system where vibrations are localized.

Finally, the thermal conductivities of P3HT films near room temperature (319 K) are plotted as a function of film thickness in Fig. 4; conductivities of films 77 to 200 nm thick

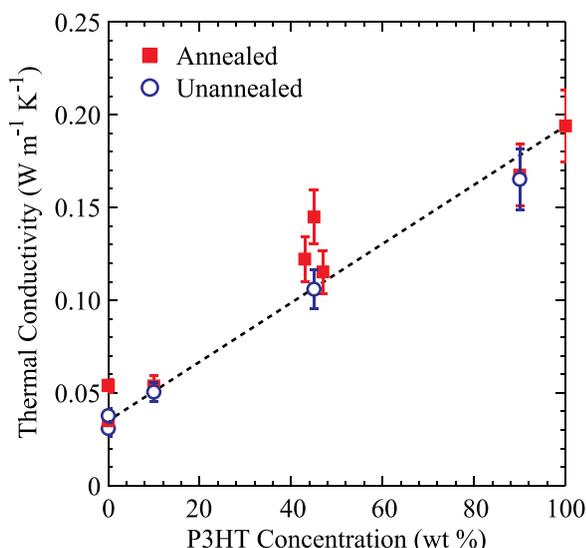


FIG. 3. Thermal conductivities of the P3HT:PCBM blend films as a function of weight percent P3HT. Filled squares represent data taken on annealed samples and hollow circles on unannealed samples. The dashed line is a linear interpolation between the conductivities of pure PCBM and P3HT thin films fabricated in identical fashion. The data suggest that a rule of mixtures applies, where thermal conductivity is a linear function of film composition. The three measurements taken on annealed 45:55 blends have been (horizontally) offset slightly for clarity.

range from 0.185 ± 0.011 to $0.213 \pm 0.013 \text{ W m}^{-1} \text{ K}^{-1}$. The relatively small changes in conductivity with film thickness, together with the non-monotonic trends, suggest that the “thinness” of the films is not responsible for the low thermal conductivities (boundary effects would scale with thickness). This lack of size dependence is consistent with earlier observations of the thermal conductivities of CuPc (Ref. 17) and PCBM (Ref. 49) thin films. Furthermore, this reaffirms our treatment of the polymer films as semi-infinite in our thermal model despite their relative thinness (the thermal penetration depth at our modulation frequency is roughly 60 nm in the P3HT films). The data are thus consistent with the picture that thermal transport in polymeric films is dominated by a random walk of vibrational energy.

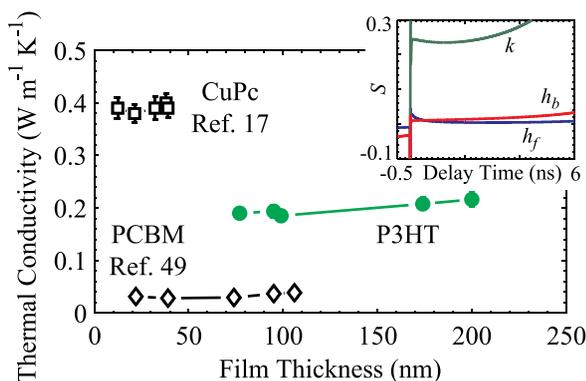


FIG. 4. Thermal conductivities of P3HT (filled circles), CuPc (hollow squares, Ref. 17) and PCBM (hollow diamonds, Ref. 49) films as a function of film thickness. The data indicate that size effects are not responsible for the low thermal conductivities. The inset is a plot of measurement sensitivity as a function of delay time, and shows that we are overwhelmingly sensitive to the thermal conductivity of the films even in a “worst-case-scenario,” where the film is 50 nm thick, and interface conductances are low, i.e., $50 \text{ MW m}^{-2} \text{ K}^{-1}$.

In summary, we have reported on the thermal conductivities of PEDOT:PSS, PCBM, P3HT, and P3HT:PCBM blend thin films as measured by time domain thermoreflectance. From 319 to 396 K, the thermal conductivities of these films are insensitive to changes in temperature. The thermal conductivities of blend films follow a rule of mixtures, and thermal annealing of these films leads to a variable increase in thermal conductivity, which we attribute to changes in morphology that result from the anneal. Finally, the thermal conductivities of P3HT thin films exhibit no sign of size effects down to film thicknesses of 77 nm. The data suggest that localization may play a large part in the thermal transport behaviors of these films.

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