Materials Horizons

Intrinsically Thermally Conductive Polymers

Journal:	*Materials Horizons*
Manuscript ID	MH-REV-10-2023-001796.R1
Article Type:	Review Article
Date Submitted by the Author:	23-Mar-2024
Complete List of Authors:	Roy, Rupam; University of Florida Stevens, Kaden; University of Florida Treaster, Kiana; University of Florida Sumerlin, Brent; University of Florida, Department of Chemistry; McGaughey, Alan; Carnegie Mellon University Malen, Jonathan; Carnegie Mellon University, Mechanical Engineering Evans, Austin; University of Florida,

Intrinsically Thermally Conductive Polymers

Wider Impact Statement

Thermal transport is a ubiquitous phenomenon with wide-reaching real-world relevance. Advancing many technologies will require new multifunctional thermal insulators and conductors. Despite significant progress in controlling thermal transport, combining high thermal conductivity with many other properties (*e.g.*, lightweight, electronically insulating, thermally conducting) remains inaccessible with contemporary material platforms. Polymers' synthetic versatility, processability, flexibility, scalability, low cost, and remarkable chemical stability have driven their deployment in nearly every technological domain. However, bulk polymers are nearly always thermal insulators (thermal conductivities of 0.1 – 0.3 W m^{-1} K^{-1}), which has reduced their deployment in thermal management applications. Thermal transport physicists have long understood that certain polymers, when processed under certain conditions, can host high thermal conductivities (>1 W m^{-1} K^{-1}). Unfortunately, there are still limited interactions between polymer chemists and experts from the thermal physics community, limiting the systematic exploration of thermal conductivity in polymeric materials. This review seeks to catalyze engagement between these often-siloed communities. We expect that establishing the design rules to achieve high thermal conductivity polymers (>1 W m^{-1} K^{-1}) will enable high thermal conductivity to be combined with previously unobtainable properties that will be widely useful in thermal management.

Intrinsically Thermally Conductive Polymers

Rupam Roy,[1] Kaden C. Stevens,[1] Kiana A. Treaster,[1] Brent S. Sumerlin,[1] Alan J. H. McGaughey,[2] Jonathan A. Malen,[2] Austin M. Evans[1,3,*]

[1]George and Josephine Butler Polymer Research Laboratory, Center for Macromolecular Science & Engineering, Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States. [2]Department of Mechanical Engineering, Department of Materials Science and Engineering, Carnegie Mellon University, 5000 Forbes Ave., Pittsburgh, Pennsylvania 15213, United States [3]Deparmtent of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611, United States

Abstract

Here, we describe the design features that lead to intrinsically thermally conductive polymers. Though polymers are conventionally assumed to be thermal insulators (<0.3 W m^{-1} K^{-1}), significant efforts by the thermal transport community have shown that polymers can be intrinsically thermally conductive (>1.0 W m^{-1} K^{-1}). However, these findings have not yet driven comprehensive synthetic efforts to expose how different macromolecular features impact thermal conductivity. Preliminary theoretical and experimental investigations have revealed that high k polymers can be realized by enhancing the alignment, crystallinity, and intermolecular interactions. While a holistic mechanistic framework does not yet exist for thermal transport in polymeric materials, contemporary literature suggests that phonon-like heat carriers may be operative in macromolecules that meet the abovementioned criteria. In this review, we offer a perspective on how high thermal conductivity polymers can be systematically engineered from this understanding. Reports for several classes of macromolecules, including linear polymers, network polymers, liquid-crystalline polymers, and two-dimensional polymers substantiate the design principles we propose. Throughout this work, we offer opportunities for continued fundamental and technological development of polymers with high thermal conductivity.

1. An Introduction to Thermally Conductive (>1 W m^{-1} K^{-1}) Polymers

Thermal transport is a ubiquitous phenomenon with wide-reaching real-world relevance. Developing next-generation microelectronics, energy storage devices, and extreme-environment materials requires new multifunctional thermal insulators and conductors.[1-4] A universal need for heat management has inspired a long-standing interest in the mechanistic underpinnings of thermal transport.[5, 6] This mechanistic insight has driven material designs that enhance or suppress thermal conductivity (k) while retaining other technologically desirable properties (*e.g.*, mechanical strengths, electrical conductivities). Despite significant progress in controlling thermal transport, many property combinations (*e.g.*, lightweight, electronically insulating, thermally conducting) remain inaccessible with contemporary material platforms.

Macromolecular materials can be engineered with a virtually limitless number of property combinations. Polymers' synthetic versatility, processability, flexibility, scalability, low cost, and chemical stability have driven their deployment in nearly every technological domain. However, a prevailing belief that polymeric materials are inherently thermally insulating (k = 0.1 – 0.3 W m^{-1} K^{-1}) has motivated research on composites of thermally conductive inorganic materials embedded in polymeric matrices and restricted the exploration of pure polymer constructs for thermal management.[7, 8] For a more in-depth exploration of thermally conductive polymer composites, we direct interested readers to the following references by Xu and coworkers and Gu and coworkers.[9, 10] Below, we consider only intrinsically thermally conductive polymeric materials.

Insights provided by Fermi, Pasta, and Ulam on thermal transport in one-dimensional lattices inspired computational work that suggested high k polymers (>1 W m^{-1} K^{-1}) may be obtainable.[11-15] However, these simplified models disregard much of the complexity that exists in bulk polymer samples. Over the past twenty years, the thermal transport community has experimentally demonstrated that bulk polymeric materials can host significantly higher thermal conductivities than previously assumed.[16] Unfortunately, there are still limited interactions between polymer chemists and experts from the thermal physics community, which has constrained the systematic exploration of thermal conductivity in polymeric materials. This review seeks to catalyze engagement between these often-siloed communities. It is clear that establishing the design rules to achieve high thermal conductivity polymers (>1 W m^{-1} K^{-1}) will enable previously unobtainable property combinations that will be widely useful in thermal management.

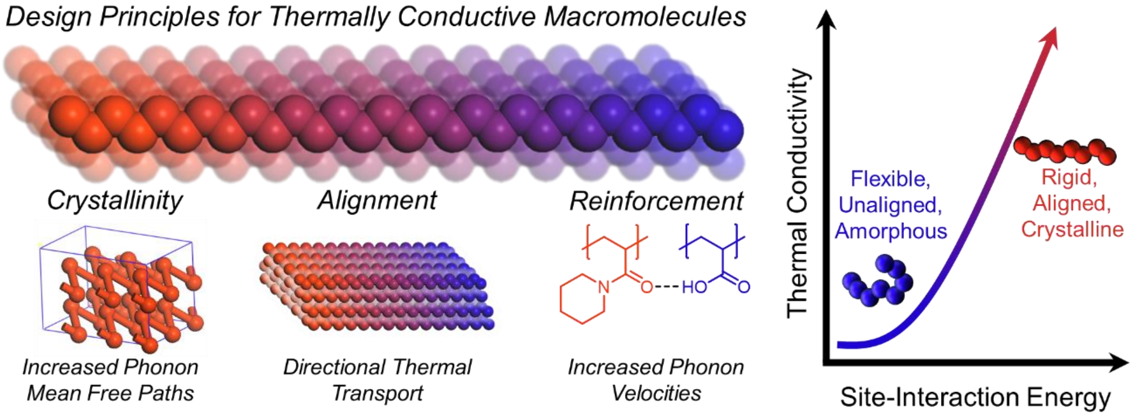


Figure 1| Material design elements that yield high thermal conductivity in polymeric materials.

The poor thermal conductivity observed in polymers is typically attributed to them being amorphous materials held together by weak intermolecular interactions.[17] While these features may limit the thermal conductivity of some polymers, they are not universal. Several recent reports have shown that highly thermally conducting polymers can be achieved (**Figure 1**) by (1) enhancing polymer crystallinity, (2) increasing macromolecular chain alignment, and (3) reinforcing inter-chain non-covalent interactions.[18-21] When these three features are combined, stiff, structurally ordered polymeric materials emerge. Preliminary observations reveal that high thermal conductivity manifests when polymers have these characteristics. While we consider these three features independently below for clarity, it is self-evident that alignment, crystallinity, and mechanical rigidity are invariably linked, and all collectively impact thermal conductivity. Luo and Zhang elegantly demonstrated this by performing molecular dynamic simulations on a prototypical polyethylene material and showed that as site-interaction energies increased, so too did the alignment, crystallinity, and rigidity of polymer systems (**Figure 1**).[22] These findings will generalize to large numbers of polymeric materials. Here, we describe a mechanistic framework based on phonon transport in crystalline materials, which we believe charts a roadmap to engineer polymers with high thermal conductivity.[23]

Thermally conductive polymers cannot be realized by chemical design alone. Appropriate processing conditions are essential for producing the well-ordered mesoscale structures important for bulk thermal transport.[10, 24] Due to the anisotropic structure of crystalline polymeric materials, it is reasonable to expect thermal conductivity to be anisotropic.[25, 26] For example, Luk and Chen provided evidence that aligned polymers have *k*'s >50 W m^{-1} K^{-1} and high *k* anisotropy ratios of >30. Chen and coworkers showed that polyethylene nanofibers processed *via* stretching yielded high thermal conductivity (104 W m^{-1} K^{-1}) along the alignment axis,[27] which was later shown to also improve the thermal conductivity in aligned polyethylene films (62 W m^{-1} K^{-1}).[28] These reports unambiguously demonstrated that phonon-like transport along aligned polymer chains can lead to high thermal conductivities,[29] revealing that developing thermally conductive polymers will require synergized covalent designs and processing strategies.

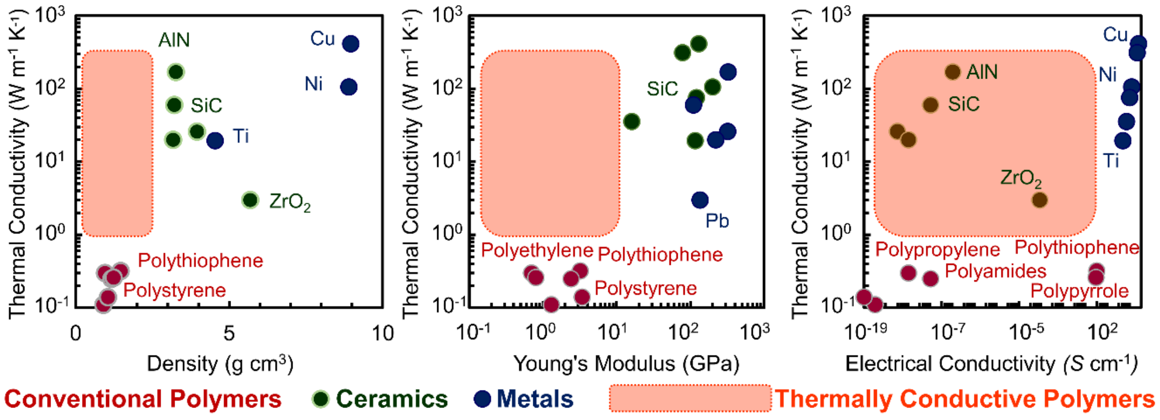


Figure 2| Potential multi-functionalities accessible by thermally conductive polymeric materials. Upper bound of potential thermal conductivity of polymers is assigned as the maximum thermal conductivity (computational report) reported for polyethylene (273 W m^{-1} K^{-1}).

Herein, we identify consistent polymer chemistry and processing elements currently reported to enhance intrinsic thermal conductivity in the absence of thermally conductive additives. Throughout this discussion, we draw on recent literature examples and highlight opportunities for continued exploration. We specifically aim to contextualize the proposed origins of high thermal conductivity in these reports within a broader discussion of the fundamental origins of high thermal conductivity in polymeric materials. While we do not aim to comprehensively cover all reports of thermal conductivity measurements in polymers, we do capture the key chemical and structural motifs that are prevalent across many reported materials. We also provide a brief tutorial on thermal transport mechanisms and outline challenges with obtaining thermal conductivity measurements, which are not frequently considered by the polymer chemists who are best positioned to prepare next-generation thermally conductive polymers. Similarly, we highlight synthetic design elements that lead to high thermal conductivities, which will inspire thermal transport experts who may be unfamiliar with polymer design and synthesis.

To-date, polymer thermal conductivity investigations have been primarily driven by the thermal transport community. We believe that future developments in polymer thermal conductivity will be driven by interactions between these experts and the macromolecular engineers who are trained to systematically vary polymer structures. We hope that the insight we provide here will help to bridge the gap between these often-siloed communities. This review provides a necessary nexus for chemists, materials scientists, and engineers to collaboratively target thermally conductive polymeric materials, which we view as a prerequisite to the successful deployment of polymers in thermal management. As these designs mature, we expect that thermally conductive polymers will host property combinations that are currently inaccessible (**Figure 2**).

2. Complex Thermal Transport Mechanisms in Polymeric Materials

The fundamental nature of thermal transport in macromolecular materials is not well understood,[16] making guided design of polymers with intrinsically high thermal conductivity challenging. A simple understanding of heat transfer in solid crystalline materials considers parallel contributions by electrons and phonons as the primary heat carriers (**Eq. 1**). This yields the equation:

$$k\ (T) = k_{\mathrm{p}} + k_{\mathrm{e}} \qquad \text{(Eq. 1)}$$

where k_{p} and k_{e} denote the contribution of phonons and electrons, respectively.[16] Given the limited electronic delocalization present in low-dielectric organic materials with low charge-carrier densities (*e.g.* 7.0 eV bandgap and 2.25 dielectric constant of polyethylene), the Weidermann-Franz law would lead one to the conclusion that the contribution from electron-based thermal transport is negligible in most polymer systems. As a rough approximation, to achieve a k_e of 0.1 W m^{-1} K^{-1} with the same Lorenz constant of Cu would require an electrical conductivity of 10^4 S m^{-1}, which is outside the range of many polymeric materials. However, there are notable examples of polymer systems that host high dielectric constants and significant charge-carrier densities, suggesting there may be cases where this assumption is invalid.[30] To our understanding, polymers with meaningful contributions of electron heat transport have yet to be identified. For this reason, we assume in the subsequent discussion that phonons are the primary heat carriers in polymeric systems. This interpretation is built on an imperfect assumption that thermally conductive polymers are at least partially crystalline. Nonetheless, we feel that a phonon model of thermal conductivity can be used as a guide to achieve high thermal conductivity polymers. Phonon-based models that assumed a mean free path that is comparable to the wavelength have been used by Slack and Cahill to define a lower limit to thermal conductivity of amorphous polymer systems of approximately 0.1 W m^{-1} K^{-1}.[34, 35].

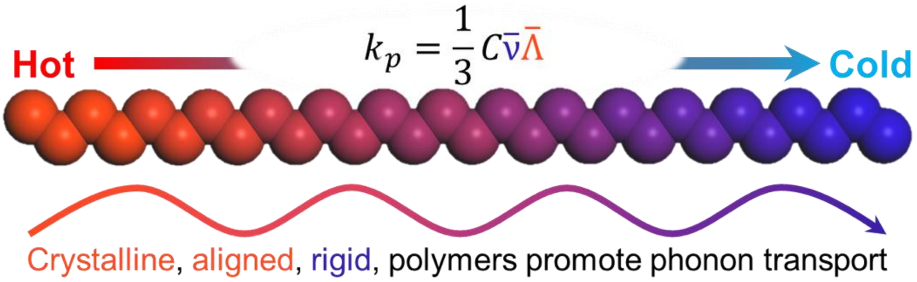


Figure 3| A phonon model of thermal transport in polymer materials and correlations between phonon propagation and structural design elements.

Phonons are emergent and quantized quasiparticles that describe collective structural oscillations in crystalline matter. Peierls showed that phonon propagation and scattering collectively describe heat transport in well-defined crystals.[17, 31] In polymer systems, phonons describe vibrations along the covalent polymer backbone, motion along pendent polymer functionality, non-covalent oscillations between chains, and collections of these movements. One feature distinguishing phonons in polymeric systems from those in typical inorganic crystals is that the bonding environment (*i.e.*, the covalent bonds that stitch the polymer chain together) is inherently anisotropic. This means that phonon-based thermal transport is also likely to be anisotropic. Given the high covalent bond strengths and similar masses of atoms in polymer backbones heat will often be transported primarily by phonons in the covalent polymer structure, which was first explored computationally by Young and coworkers.[32] It is important to realize that even in perfectly crystalline structures, phonon-phonon scattering prevents the realization of infinite thermal conductivity. Phonon-phonon (or perhaps more appropriately vibration-vibration) interactions in polymeric materials are not currently well-understood, but undoubtedly have a significant impact on thermal conductivity. We use a phonon-based model in our subsequent discussion to describe how polymers could host high, anisotropic thermal conductivities.

Phonon-based thermal transport is a simplified model to describe heat transport in polymeric materials.[17] Previous intuition for phonon-based transport has been derived from perfectly homogenous, single-crystalline, inorganic systems. Any degree of heterogeneity in the composition, structure, or local conformation will disrupt this periodicity. Amorphous and semicrystalline polymeric materials will unavoidably host these non-idealities. Strictly speaking, this would mean that it is no longer valid to describe thermal transport with phonon dispersions, defined wavevectors, or to assign phonon velocities. This has led the thermal transport community to introduce other quasi-particles, including propagons (delocalized and propagating vibrations), diffusons (randomized extended vibrations), and locons (localized vibrations).[33] In less ordered polymers, these descriptors may be more appropriate than a phonon model. A definitive and quantitative model does not exist to describe these other quasiparticles or capture the nuance of polymer thermal conductivity. We direct readers interested in recent theoretical descriptions of polymer thermal transport to the following references.[36-40] Going forward, it will be critical to develop models that can contend with the complex semi-crystalline structure of polymeric systems and their equally complex thermal transport carriers (see **Section 6**). The recently proposed Wigner formulation of thermal transport,[41, 42] which naturally includes phonon and diffuson effects, may provide insight, but challenges remain in applying it to disordered systems.[43] The mechanistic ambiguities surrounding thermal transport in polymers have constrained the systematic development of thermally conductive polymers. Despite these unresolved challenges, we propose that a phonon-based model is still useful for conceptualizing how one might engineer highly thermally conductive polymers (**Figure 3**).

Crystalline materials host higher thermal conductivities than their amorphous analogs.[44, 45] For this reason, crystalline polymers are a reasonable starting point towards the goal of producing highly thermally conductive polymers. Such an approach carries the advantage of drawing on a mechanistic understanding of phonon-based thermal transport in other crystalline systems to guide macromolecular designs. Specifically, we take inspiration from a simplified isotropic model (**Eq. 2**) of phonon-mediated thermal conductivity (k_{p}):

$$k_p = \frac{1}{3}\int C(\omega)v(\omega)\Lambda(\omega)d\omega = \frac{1}{3}C_v\bar{v}\bar{\Lambda} \qquad \text{(Eq. 2)}$$

where ω, C, $\overline{v}$, and $\bar{\Lambda}$ refer to the frequency, heat capacity, average phonon group velocity, and average phonon mean free path, respectively. In reality, there is a broad spectrum of phonons with different frequencies (ω) that display a wide range of values for these two properties (e.g., mean free paths may span from nanometers to microns).[46] This means that a narrow range of ω may dominate bulk thermal transport. From this equation, we derive the following objectives: (1) enhancing the phonon mean free path, Λ, can be achieved by increasing the crystallinity and producing polymers with physical lengths that exceed the intrinsic phonon mean free path set by phonon-phonon scattering, (2) increasing the phonon group velocity, v, can be achieved by making the polymer stiffer, which is known to increase thermal conductivity in inorganic materials. Modifying the volumetric heat capacity, C, is likely not a straightforward method to increase thermal conductivity given that it is non-trivial to increase the atomic number density in fully dense polymer materials. While this model does not account for much of the anisotropic, semi-crystalline nature in true polymer systems, we feel that it can be a useful starting point for considering design criteria to achieve thermally conductive polymers. We base our following exploration of stiff, aligned, and crystalline polymers on this description of thermal conductivity.

3. Molecular Features of High Thermal Conductivity Polymers

Contemporary studies that produce high thermal conductivity polymers have focused on enhancing the structural regularity and interchain interactions in polymer systems. Below, we provide examples that explore these features in various macromolecular materials. While we explore these features separately to focus our discussion, we stress that these features are intrinsically linked at the covalent, microstructural, and mesostructural scales.[22] No single theory or synthetic approach has systematically uncovered how these features are related in the context of thermal conductivity. In the future, engineering highly thermally conductive polymers will require controlling these structural elements simultaneously.

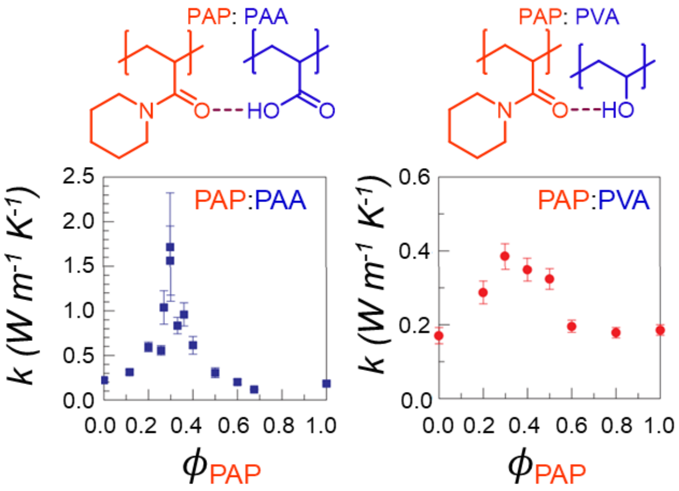


Figure 4| H-bonding in polymer blends leads to increased thermal conductivity. This graphic was adapted with permission from ref.(21). Copyright 2015 Nature Portfolio.

3.1 Supramolecular Reinforcement

3.1.1 Interchain Hydrogen-Bonding in Polymer Blends: Rigid materials generally host higher phonon group velocities that yield enhanced thermal conductivities.[17, 47] Some polymeric materials, such as isotactic polypropylene, are rigid without intentionally installed supramolecular reinforcement. This leads to modest thermal conductivities ($k > 0.5$ W m^{-1} K^{-1}) even in the absence of alignment or long-range crystallinity.[48, 49] These observations have motivated the exploration of engineered interchain supramolecular interactions to improve thermal conductivity. Pipe, Kim, and coworkers installed hydrogen bonding (H-bonding) units onto a series of polymers, which had interaction strengths one to two orders of magnitude higher than the van der Waals interactions that reinforce simple polyolefins, such as polypropylene.[50-54] Specifically, this report explored the thermal conductivity of polymer blends between a H-bond accepting poly(*N*-acryloyl piperidine) (PAP) and three different H-bond accepting polymers, poly(acrylic acid) (PAA), poly(vinyl alcohol) (PVA) and poly(4-vinyl-phenol) (PVPh) (**Figure 4**).[21] The authors postulated that by combining H-atom donors and acceptors, the composite material would exhibit high stiffnesses with a homogenous distribution of phonon percolation pathways. Fourier-transform infrared spectroscopy analysis of the C=O bond stretch revealed that the H-bond strength between these polymer blends decreased from PAP:PAA to PAP:PVPh to PAP:PVA. Cross-plane thermal conductivities performed in a differential 3ω configuration revealed that PAP:PAA polymers with the most robust interchain interactions had the highest thermal conductivities ($k = 1.5$ W m^{-1} K^{-1}), which was a substantial enhancement over pure PAP or PAA systems ($k = 0.19$ W m^{-1} K^{-1} and 0.22 W m^{-1} K^{-1}, respectively) (Figure 4). This concept was explored more deeply by Cahill and coworkers, who also showed that polymer blends with appreciable supramolecular interactions lead to enhanced thermal conductivity.[55] Moreover, these authors use mechanical property and sound speed measurements to show that the mechanical stiffness, sound speed, and thermal conductivity are all positively correlated. These findings underscore opportunities to compare widely available and easily measured polymer thermomechanical properties with thermal conductivity values, which we believe will yield important latent design insight for achieving high thermal conductivity polymers.

The measurements performed by Pipe, Kim, and coworkers were all performed on sub-100 nm thick films, which is routine practice for making polymer thin film samples to measure thermal conductivity . It is currently not understood if the experimentally observed thermal conductivities are influenced by the nanoscale dimensions of the samples studied or if these enhancements could also be observed in bulk materials with sufficient supramolecular reinforcement. An equilibrium molecular dynamics study by Tian and coworkers found that nanoscale confined amorphous polystyrene leads to decreased thermal conductivity.[56] This contrasts with crystalline polystyrene, which in the same computational work increased in thermal conductivity as nanoscale confinement is increased. The origin of this qualitatively different behaviour is ascribed to the different chain conformations that emerge in different polystyrene phases under confinement. As the authors of this study note, a generalized model for understanding nanoconfinement and thermal conductivity in polymer systems is not yet available. The high thermal conductivities experimentally observed by Pipe, Kim, and coworkers are even more impressive given that these polymer blends are amorphous and unaligned. Therefore, the systems with the same (or greater) degree of supramolecular reinforcement with improved structural regularity could exhibit even higher thermal conductivities.

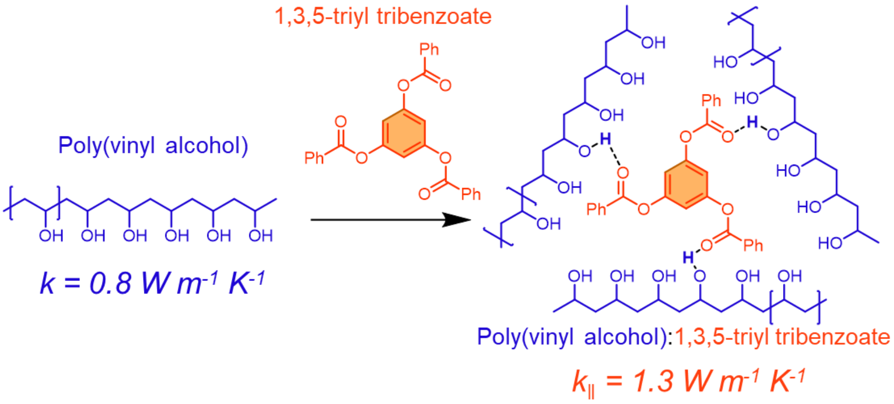


Figure 5| H-bonding from exogenous H-bonding molecules leads to increased thermal conductivity. This graphic was adapted with permission from ref.(57). Copyright 2022 John Wiley & Sons.

3.1.2 Molecular H-Bonding Dopants: Adding exogenous H-bonding molecular dopants can increase supramolecular reinforcement and thermal conductivity in polymer samples. For instance, Shi and coworkers used laser flash thermal diffusivity measurements to extract the k of poly(vinyl alcohol) films reinforced with H-bonding molecules. Specifically, the authors explored the H-atom acceptors 4,4'-dihydroxy diphenyl, 1,1'-biphenyl-4,4'-diyl hexanoate, and benzene-1,3,5-triyl tribenzoate,[57] finding that increasing amounts of each dopants increased the degree of crystallinity, tensile strength, and pyrolysis temperature of the resulting composites. Increasing the amount of H-bond mediator translated to an increase in their measured thermal conductivity from 0.80 W m^{-1} K^{-1} for native poly(vinyl alcohol) to a maximum of 1.3 W m^{-1} K^{-1} with the most potent H-atom bond acceptor, benzene-1,3,5-triyl tribenzoate (**Figure 5**). Interestingly, the authors reported that there was bulk anisotropic thermal conductivity with a $k_{\text{in-plane}}$ of 1.30 W m^{-1} K^{-1} and a $k_{\text{cross-plane}}$ of 0.64 W m^{-1} K^{-1}, which yields a k_{average} of 0.97 W m^{-1} K^{-1}. The origin of the purported k anisotropy in this system is not immediately apparent. The authors postulate that the increase in thermal conductivity arises from the stiffer, denser, and more ordered nature of the polymer-molecule composite, though experimentally determined densities were not reported. Future efforts for this and other supramolecularly reinforced systems should be directed towards understanding the interaction between materials design, mesostructural features, and resultant thermal conductivity. Despite the need for future study, this report suggests that increasing the H-bonding through incorporating H-bonding molecular dopants in poly(vinyl alcohol) may yield higher thermal conductivities.

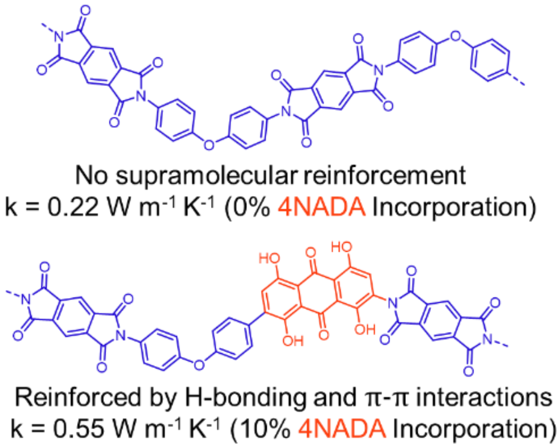


Figure 6| Copolymers exhibiting supramolecular reinforcement were observed to have higher thermal conductivities. This graphic was adapted with permission from ref.(58). Copyright 2023 Cell Press.

3.1.3 H-Bonding Engineering: Physically mixing multiple polymers into a single homogenous material is challenging to perform reliably. Xu and coworkers addressed this limitation by constructing copolymers with supramolecular motifs covalently tethered to the polymer backbone. Specifically, the authors prepared a rigid polyimide-based linear copolymer (**PMDA**) with variable incorporation of 2,4,5,7-tetraamino-1,8-dihydroxyanthracene-9,10-dione (**4NADA**) H-bonding moieties (**Figure 6**).[58] Following annealing, the polymers with 10 mol% H-bonding 4NADA motifs had a thermal conductivity three times higher (0.6 W m^{-1} K^{-1}) than the native PMDA polyimide as measured by a direct contact T-bridge method. This was accompanied by an exceptionally high glass transition temperature T_g = 434 °C. The authors hypothesize that these features emerged from H-bonding units minimizing the contortion of polymer chains, leading to enhanced copolymer packing densities. From this assumption, these authors propose that the phonon mean free paths are enhanced by supramolecular reinforcement. It could also be that the increased rigidity of the system leads to higher phonon group velocities. In either case, the "unit cell size" of the polymer units used to describe these phenomena have increased, which in crystalline solids would generally lead to lower thermal conductivities. This counterintuitive result highlights a limitation in describing thermal transport in amorphous systems with phonon-like heat transfer models. Uncovering the origin of high thermal conductivity in all polymer systems will require a more detailed mechanistic investigation into the nature of thermal transport and the synthetic designs that facilitate it. Presumably, understanding the impact of polymer microstructure on k could be driven by making correlations between thermomechanical characteristics (*e.g.*, T_g, thermal expansion coefficient, and tensile strengths) and thermal conductivity. Nonetheless, this work represents an exciting k enhancement by supramolecular reinforcement, which also gives these materials desirable multifunctionality in thermal conductivity, electronic insulation, mechanical strength, and high-temperature stability.

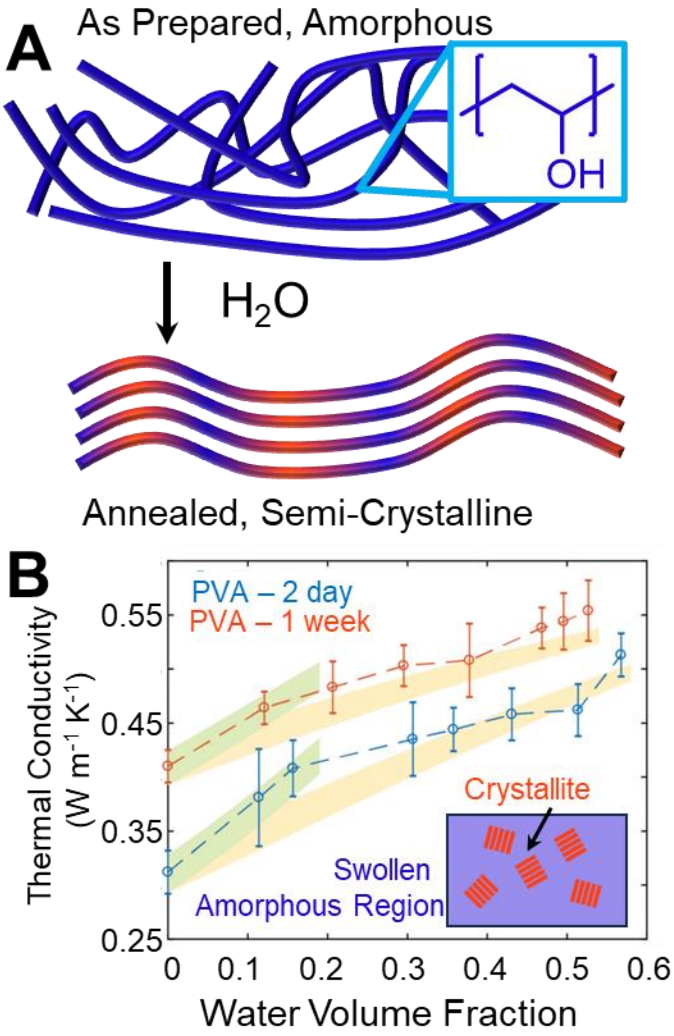


Figure 7| A. Poly(vinyl alcohol) can be annealed with water vapor to introduce crystallinity**. B.** Thermal conductivity data show that more annealed films have higher thermal conductivities. The green and yellow highlighted regions indicate fitting with different effective medium theory predictions. This data is consistent with a structure shown in the inset, where hydrated amorphous regions separate crystalline regions. This graphic was adapted with permission from ref.(59). Copyright 2020 Royal Society of Chemistry.

3.1.4 Dynamic Supramolecular Interactions: Supramolecular interactions can often be reversibly formed and broken. The dynamic nature of these interactions provides an exciting opportunity to engineer polymeric materials with switchable thermal conductivities. Chen and coworkers recently showed thermal switching in a poly(vinyl alcohol) system by the addition of water. The authors suggest that adding water vapor to poly(vinyl alcohol) increases the mobility of polymer chains, allowing more effective crystallization (**Figure 7A**).[59] This interpretation is supported by increased thermal conductivity to a maximum of 0.55 W m^{-1} K^{-1} after two weeks of annealing. Presumably, other structural features, such as the bound state of the water ($k_{\text{water, bulk}}$ = 0.6 W m^{-1} K^{-1}) or the supramolecular reinforcement from interchain H-bonding, also impacted the observed thermal conductivity (**Figure 7B**). The origin of thermal switching based on chemical stimuli will be complicated to unravel because of these chemostructural ambiguities. For this reason, we anticipate that stimuli-responsive switching based on non-chemical stimuli (such as photo, electrical, or thermally driven switching) will be more straightforward to understand. Nonetheless, this work demonstrates that supramolecular reinforcement, when combined with crystallinity, can give moderate thermal conductivities in low moduli networks. This is an exciting development because mechanically compliant materials are generally thermally insulating. As more switching mechanisms and thermal conductivity design principles are uncovered, we expect more unique multifunctionalities to naturally evolve.

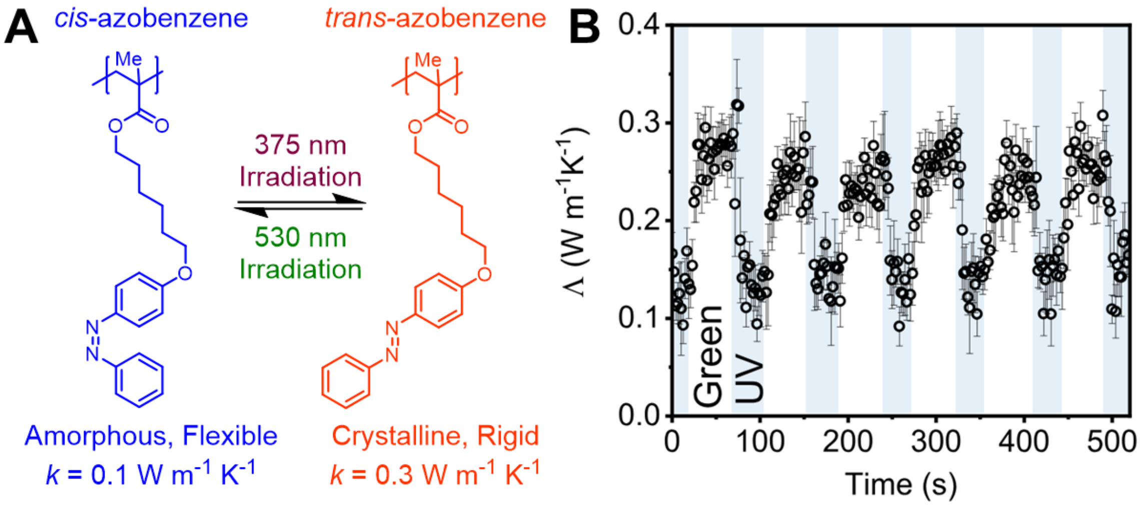


Figure 8| A. Photoinduced switching of azobenzene-functionalized polymers. **B.** Photoswitchable thermal conductivity over multiple switching cycles driven by different colors of light (UV = 375 nm and Green = 530 nm). This graphic was adapted with permission from ref.(60). Copyright 2020 National Academy of Sciences.

3.1.5 Photoswitchable Thermal Conductivities: Photoinduced switching of covalent bonds has also been used to modulate thermal conductivity in polymeric systems. Cahill and coworkers produced a poly(methyl methyacrylate) derivative containing photoswitchable azobenzene units.[60] *In situ* X-ray scattering experiments showed that as *trans*-azobenzene polymers were photoirradiated with 375 nm light, the semi-crystallinity of these supramolecular networks was disrupted and a phase change occurs due to the irregular folding of *cis*-azobenzene units (**Figure 8**). This transformation was fully reversible with irradiation of 530 nm light, which resulted in *trans*-azobenzene sidechains and full recovery of the original material phase and thermal conductivity. *In situ* time-domain thermoreflectance measurements showed that this crystalline-to-amorphous transition resulted in thermal conductivity switching from a *trans*-state thermal conductivity of 0.35 W m^{-1} K^{-1} to a *cis*-state thermal conductivity of 0.1 W m^{-1} K^{-1}. Shen and coworkers have also observed switchable thermal conductivity by taking polyethylene fibers through a melting phase transition.[61] Specifically, using a suspended platform measurement geometry to measure the thermal conductivity of approximately 100 nm thick crystalline polyethylene nanofibers at different temperatures allowed the authors to observe a maximum 10× thermal conductivity switching ratio from approximately 30 W m^{-1} K^{-1} to 3 W m^{-1} K^{-1}. Moreover, by producing asymmetric fibers by photoirradiation, they also demonstrated modest thermal rectification values of 50%.[62] This suggests that asymmetric polymeric structures might also host asymmetric thermal transport, which we consider to be an exciting direction for future research. We expect that future synthetic designs will lead to higher thermal conductivities and switching ratios by considering other elements of polymer systems, such as their propensity for alignment and their supramolecular reinforcement (which governs other important features in switchable thermal conductivity, such as T_g).

3.1.6 Perspective on Supramolecular Interactions in Thermal Transport: Targeted supramolecular interactions yield high thermal conductivities in polymeric systems. While the discussion here focuses heavily on H-bonding, other supramolecular interactions (*e.g.*, electrostatic or π-π interactions) can also facilitate increased thermal conductivities.[63, 64] Presumably, combinations of these intermolecular interactions will lead to higher thermal conductivities and new switching modalities that are yet to be explored. It is also unclear to what extent van der Waals contact (*e.g.*, between polyethylene chains) in all polymer systems impacts thermal transport. Currently, the interaction strengths of these supramolecular interactions are weak (<10 kJ mol^{-1}). Increasing the strength of these interactions may increase thermal conductivity beyond what has already been achieved. There may also be an upper threshold to how strong supramolecular interactions can be before they increase phonon-phonon scattering along a linear chain, which could reduce thermal conductivity. This may be why conventional H-bonding polymers, like Kevlar, are typically observed to be exceptionally thermally insulating.[65] Conclusions to this effect are challenging to assign definitively because reports demonstrate that Kevlar (and other high performance polymers) can be thermally conductive if they are appropriately aligned and crystallized by mechanical drawing.[47, 66] These competing findings underlie the importance of considering alignment, crystallinity, and supramolecular reinforcement holistically in polymer thermal transport. In the future, a more robust mechanistic understanding must be developed to understand how crystallinity and supramolecular interactions between chains collectively influence thermal conductivity.

3.2 Directional Alignment

3.2.1 Mechanical Drawing of Polyethylene: Structural regularity and directional alignment promote enhanced thermal conductivities. Polymer chain alignment can be achieved by spin-coating, templated-organization, spinning, or stretching (**Figure 9A**).[16, 19, 23, 27, 66-71] The origin of k increase in drawn polymer fibres is often attributed to the large-group velocity and long-lifetime longitudinal acoustic phonon modes that effectively transport heat along the aligned polymer backbones.[72, 73] Mechanical drawing has been heavily explored to produce highly thermally conductive polyethylene, a prototypical polymer system. Semicrystalline polyethylene thermal conductivities of >100 W m^{-1} K^{-1} have been achieved by a variety of processing methods (**Figure 9B**).[27] While the crystallinity certainly enhances thermal transport in drawn polyethylene fibres, mechanical drawing also aligns the amorphous regions of semi-crystalline polyethylene.[74] At this stage, it is not well-understood how alignment and crystallinity interact to yield high thermal conductivities.

The thermal conductivity of properly processed polyethylene is higher than many conventional thermal conductors, including GaAs ($k_p = 55$ W m^{-1} K^{-1}), TiO_2 ($k_p = 4.8$ W m^{-1} K^{-1}), Ni ($k_e = 62.4$ W m^{-1} K^{-1}). However, experimental measurements of polyethylene thermal conductivity are still lower than the upper limit predicted by molecular dynamic simulations of $k = 273$ W m^{-1} K^{-1} for single-crystal polyethylene.[75] We accept that mesostructural features, such as chain ends or local structural deviations, may lead to this disagreement in k values. An interesting feature of drawn polymer samples is that, in some cases, nanoscale dimensions are obtained.[76] At the absolute limit of single-molecule thermal transport, it is known that heat transfer happens extremely rapidly along the covalent backbone, with interfacial thermal resistances constraining the overall thermal diffusion.[77-79] Molecular dynamics simulations by Henry and coworkers show that system size effects reduce the upper limits to thermal conductivity in polyethylene. This was derived by first considering isolated polyethylene chains, then 2D sheets of polyethylene chains, and then 3D monoliths of polyethylene fibers of different diameters. Specifically, they show how adding vibrational modes (as they add dimensionality to a polyethylene system) increases two competing effects. The first effect is additional modes for thermal transport, which lead to increased thermal conductivity. The other is the increase in phonon-phonon scattering, which decrease thermal conductivity. For this polyethylene system, the increase in phonon-phonon scattering outcompetes the benefits of additional vibrational modes. This leads to the consequence that as more chains are added to the simulation, a decreased upper bound on thermal conductivity is observed. It is not yet clear if this is a general phenomenon amongst all polymeric materials or if the magnitude of this effect varies substantially. Collectively, extensive investigations into polyethylene demonstrate that high thermal conductivities naturally emerge if the crystallinity and alignment of macromolecules is optimized, which we expect will translate to other macromolecular structures.

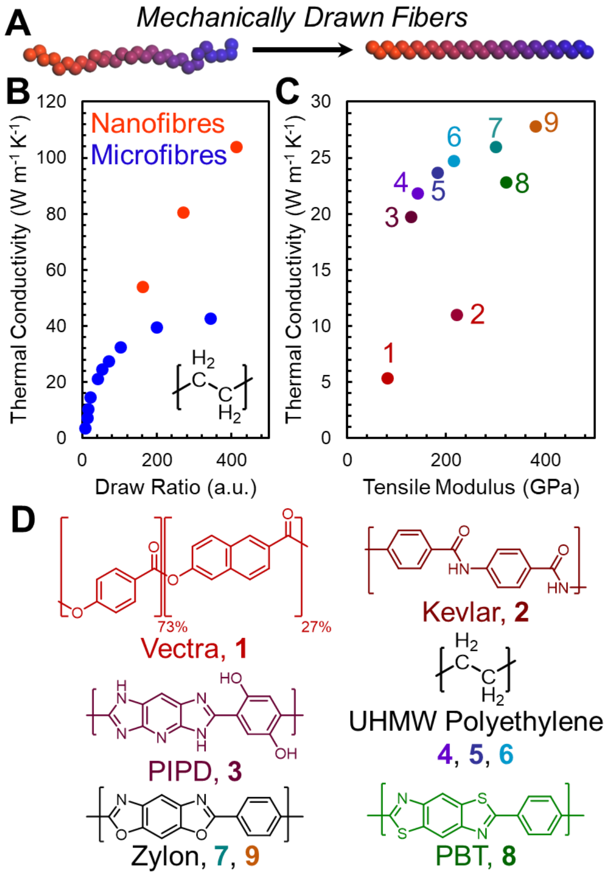


Figure 9| A. Schematic showing how mechanical drawing increases linear polymers' alignment and structural regularity. **B.** Thermal conductivity of polyethylene strands with high degrees of alignment and micron- or nano-scaled thicknesses. **C.** Thermal conductivities of various commercially drawn fibers and the **D.** structures of these polymers. Data from Panel B and C were taken from ref.(27) and ref.(66), respectively. Copyright 2010 Nature Portfolio and copyright 2013 American Chemical Society for ref.(27) and ref.(66), respectively.

3.2.1 Mechanical Drawing of Other Polymer Systems: To realize the scope of high thermal conductivity polymers it is imperative that the more complex chemical systems be explored. Cahill and coworkers expanded studies performed on aligned polyethylene by exploring the impact on *k* of these processing approaches on several high-modulus commercial fibres using time-domain thermoreflectance measurements (**Figure 9C-D**).[66] As one example, the thermal conductivity of drawn poly(*p*-phenylene benzobisoxazole)'s increased by nearly two orders-of-magnitude (20 W m^{-1} K^{-1}) over its unprocessed comparison. This increase in thermal conductivity was accompanied by significantly increased crystallization of the polymer chains, as demonstrated by X-ray scattering measurements. This study also used temperature-dependent thermal conductivity measurements to uncover an inverse $k(T) \propto 1/T$ dependence across a broad temperature range. This temperature dependence is analogous to temperature-dependent thermal transport in crystalline systems and suggests that Umklapp scattering rather than structural non-idealities govern the measured *k* at high temperatures. This finding suggests that a phonon thermal transport model can be valid in polymeric materials with sufficient structural order.

While postsynthetic mechanical drawing and aligning are undeniably valuable methods to access high thermal conductivities, these approaches have limitations. First, not all polymeric materials are amenable to crystallization by mechanical drawing, which may reduce the property combinations accessible by mechanically induced alignment. Second, post-processing methods to generate alignment are often only compatible with certain sample morphologies (*e.g.* fibers and films). To fully leverage the versatility of polymers, it will be necessary to identify how the accessible morphologies can be broadened to include structures such as bulk monoliths. Third, the relationship between chain alignment, polymer relaxation, and thermal conductivity has not been studied, which is essential to understanding the duration of high thermal conductivity in aligned polymer chains, especially in polymers with low T_gs. Presumably, some regions of aligned polymer materials slowly relax their alignment and lose their structural regularity over time. If true, this would motivate further investigations into thermodynamically stable, aligned polymers with high thermal conductivity. A more in-depth analysis of these transient structural dynamics in aligned polymers is needed to understand the absolute limitations of mechanically induced alignment. Regardless, the result of mechanical alignment shows that polymeric materials are not intrinsically thermally insulating. We expect this strategy and the mechanistic understanding it provides will feature prevalently as this field develops.

We direct readers interested in mechanical processing as a method to access high thermal conductivities to the following reference.[65]

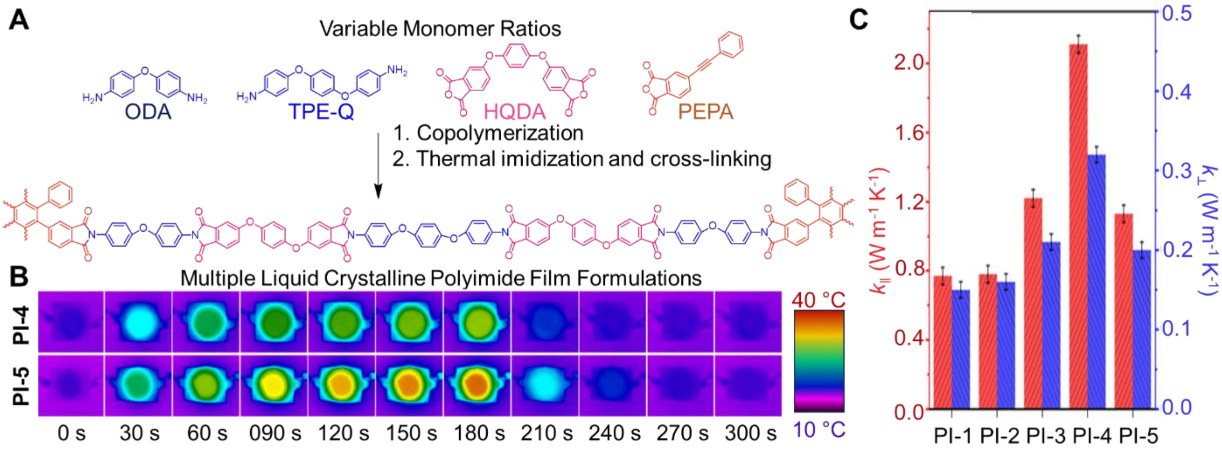


Figure 10| A. General monomer and polymer structure of liquid crystalline polyimides. Multiple polymer formulations are generated by altering the monomer feed ratios. **B.** Thermal imaging of heated two different liquid crystalline polymers heated over time. **C.** Extracted in-plane and cross-plane thermal conductivities from liquid crystalline polyimides generated from different monomer feed ratios. Data from Panels B and C are adapted from ref.(80). Copyright 2021 American Chemical Society.

3.3 Enhanced Crystallinity

3.3.1 Liquid Crystalline Polymers: Intrinsically crystalline polymeric systems offer clear opportunities for high thermal conductivity without mechanical alignment.[26] One approach to achieve high thermal conductivity without mechanical alignment is to use liquid crystalline polymer systems. For example, Gu and coworkers synthesized liquid crystalline polyimide copolymers by combining four reagents: 4,4'-diamino diphenyl ether (**ODA**), 1,4-bis(4-aminophenoxy) benzene (**TPE-Q**), 4,4′-(p-phenylenedioxy) bis[phthalic anhydride] (**HQDA**) and 4-phenylethynyl phthalic anhydride (**PEPA**).[80] By modifying the molar ratio of these components, the authors could tune the degree of crystallinity as evaluated by X-ray diffraction. The authors report that the thermal conductivity was positively correlated to the degree of crystallinity, with the most crystalline material exhibiting a maximum value of in-plane ($k_{\parallel}$) and cross-plane ($k_{\perp}$) thermal conductivity of 2.11 W m^{-1} K^{-1} and 0.32 W m^{-1} K^{-1}, respectively (**Figure 10**). These values were larger than the thermal conductivity values for entirely amorphous films with $k_{\parallel}$ = 0.77 W m^{-1} K^{-1} and $k_{\perp}$ = 0.15 W m^{-1} K^{-1}. The origin of this anisotropy is not immediately obvious. The authors postulate that phonon scattering was more prevalent in amorphous films, which reduced observed thermal conductivities. This conclusion is indicative of the challenges that arise in the absence of a unified model to describe thermal conductivity and heat carriers in polymer systems, because it is unclear if phonon scattering is increased or if the nature of the heat carriers has simply changed (as phonons do not conventionally exist in amorphous systems). Regardless, this work demonstrates the possibility of achieving high thermal conductivities without the need for mechanical alignment, though it is still unclear what approaches or material designs are best suited for intrinsically thermally conductive polymers and if these materials can match the ultra-high thermal conductivities of mechanically drawn macromolecules.

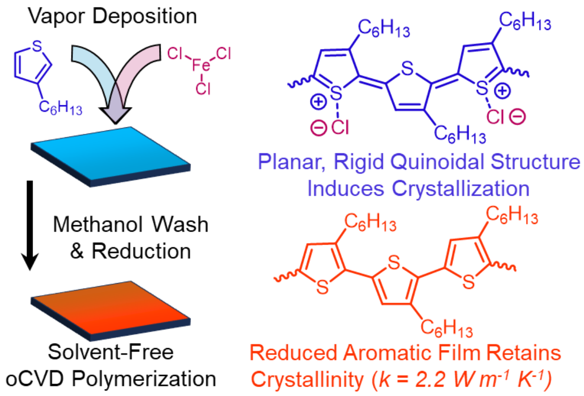


Figure 11| Oxidative chemical vapor deposition (oCVD) yields highly crystalline and aligned poly(hexylthiophene) with high thermal conductivities.

3.3.2 Oxidative Chemical Vapor Deposition Polymerization: Another approach to achieve high intrinsic thermal conductivities is for the polymerization method to directly yield crystalline structures. As one example of direct polymerization of crystalline samples, Chen and coworkers polymerized 3-hexylthiophene *via* oxidative chemical vapor deposition (oCVD) with iron chloride ($FeCl_3$) to directly produce highly crystalline poly(3-hexylthiophene) (**Figure 11**).[81] By adding $FeCl_3$, a quinoidal structure between adjacent thiophenes was generated leading to a rigid and highly planar nanostructure. Quinoidal formation was validated by UV-Vis. spectroscopy, which revealed a characteristic bipolaron feature in the 700-900 nm and 1800 nm regions. As a result of this quinoidal structure, the oxidized poly(3-

hexylthiophene) exhibited high crystallinities and supramolecular interchain reinforcement due to extensive π-π interactions. Time-domain thermoreflectance measurements demonstrated that films produced by oCVD exhibited a high room temperature thermal conductivity of $k = 2.2$ W m^{-1} K^{-1}. Variable-temperature thermal conductivity measurements revealed that the k value was positively correlated to the measurement temperature with a k value of 1.3 W m^{-1} K^{-1} at 200 K that increased to 2.2 W m^{-1} K^{-1} at 280 K. The authors ascribe this temperature-dependent behavior to the fact that both intra-crystallite phonon-transport and inter-crystallite interfaces with amorphous character both govern the observed k, each of which has its own temperature-dependence, making it complicated to assign the collective origin of thermal transport temperature-dependence. In future efforts of oCVD polymerization, it will be useful to definitively determine the crystal grain sizes studied to begin to disentangle the influence of these interfaces on bulk thermal transport. One limitation of this synthetic strategy is that there are a limited number of polymers and resultant material properties that oCVD can access. Future research should work to identify and expand the synthetic limitations of this approach. Nonetheless, given the desirable crystallinity produced by oCVD and its compatibility with large-scale manufacturing, we expect that directly producing crystalline thermally conductive polymers through this method will be a fruitful area of study.

3.3.3 Cross-Linked Networks: Alignment and crystallinity are often associated with linear polymer structures. Network polymers, which can also be structurally defined, have been overlooked in this design criteria. Complicating the situation further is that network polymers are less trivial to prepare as well-defined thin films, which are desirable for some thermal management applications. Cahill, Evans, and coworkers overcame this by studying liquid-crystalline epoxies, which they showed had thermal conductivities between 0.1 W m^{-1} K^{-1} to 1.0 W m^{-1} K^{-1}, which were positively correlated to the absolute crystallinity of these networks.[82, 83] The same authors more recently explored a dynamic covalent network, sometimes known as a vitrimer,[84] which can be processed as thin films. The particular inorganic-organic hybrid boronate-ester network explored in this report also exhibited slow crystallization kinetics, which allowed the authors to explore thermal conductivity as a function of total crystallinity.[82] Using time-domain thermoreflectance measurements, they showed that the thermal conductivity increased from 0.1 W m^{-1} K^{-1} to 1.0 W m^{-1} K^{-1} as the percent crystallinity increased over time. This work is unique in that it studies a single network polymer, with a defined chemical structure, and monitors thermal conductivity evolution as a function of crystallinity. This report provides an exciting demonstration of why cross-linked networks should not be ignored in the quest for highly thermally conductive polymer systems.

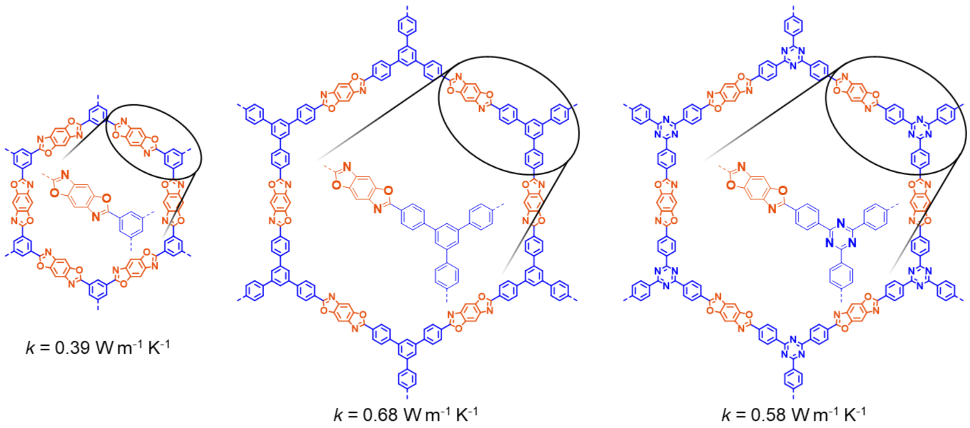


Figure 12| Structures and thermal conductivities of several benzo(bisoxazole)-based two-dimensional polymers. The thermal conductivities are qualitatively commensurate with more significant degrees of supramolecular reinforcement by π-π stacking.

3.3.4 Two-Dimensional Polymers: An emerging approach to create thermally conductive polymers relies on directly polymerizing single-crystalline systems comprised of multivalent monomers. The most common approach to this strategy is to produce layered two-dimensional polymers, sometimes called covalent organic frameworks, that are intrinsically crystalline and reinforced by non-covalent interactions. For instance, McGrier and coworkers measured thermal conductivity of benzobisoxazole (BBO)-based two-dimensional polymers (**Figure 12**).[85] Using longitudinal steady-state heat flow measurements, the authors showed that three different BBO-based two-dimensional polymers had isotropically averaged thermal conductivities of $k = 0.375 – 0.677$ W m^{-1} K^{-1}, 0.308 – 0.581 W m^{-1} K^{-1}, $k = 0.196 - 0.391$ W m^{-1} K^{-1} between 80 to 300 K. The authors hypothesized that more planar and strongly reinforced π-π stacking interactions could lead to higher thermal conductivities. A proportional temperature-dependent conductivity ($k \propto T$) was observed for all three BBO-based systems, which would be inconsistent with a phonon-based model of thermal conductivity. One challenge with definitively assigning the thermal conductivity mechanisms in this report is that the materials were studied as polycrystalline pressed pellets. For this reason, it is likely that domain boundaries, interfaces, and voids between crystallites in these samples all negatively impacted the thermal conductivity. This also suggests that the measured thermal conductivities are lower than what may be theoretically possible with higher-quality materials. As advanced processing methods are developed for two-dimensional polymers to access large single-crystals or highly uniform films,[86] we expect that design rules for high thermal conductivity will become clear.

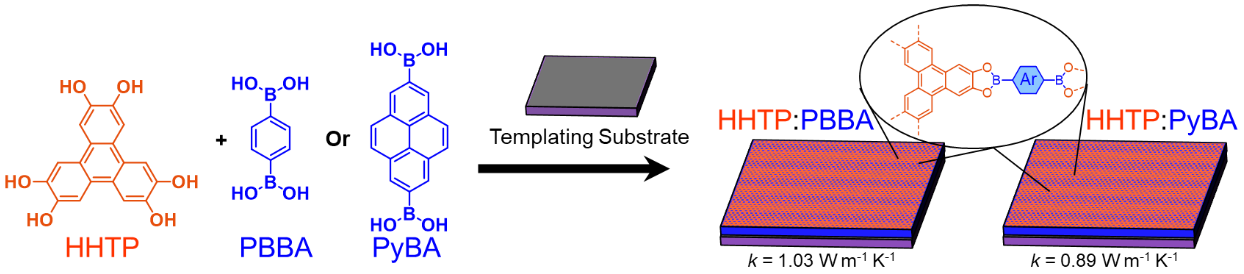


Figure 13| Synthetic approach and resultant thermal conductivities of two different two-dimensional polymer thin films synthesized atop a templating graphene substrate.

Synthesizing well-defined thin films of two-dimensional polymers is desirable for reliable thermal conductivity measurements. Dichtel and coworkers achieved this morphology by synthesizing two-dimensional polymers directly onto a templating graphene substrate using a colloidal growth method.[87] The two-dimensional polymers produced this way had desirable characteristics, including high crystallinity, well-ordered alignment, and a smooth surface. This enabled the reliable characterization of two different materials' cross-plane thermal conductivities of $k = 1.03 \pm 0.15$ W m^{-1} K^{-1} and 0.89 ± 0.14 W m^{-1} K^{-1} by thermoreflectance techniques (**Figure 13**). Molecular dynamics simulations revealed that the in-plane thermal conductivity of single-crystalline two-dimensional polymers could be four times higher than these experimental values. To date, no direct in-plane thermal conductivity measurements have been performed on two-dimensional polymers due to the challenges associated with preparing free-standing two-dimensional polymer films. We encourage other researchers to prioritize direct measurements of in-plane thermal conductivity as this field develops. The difference in thermal conductivity between these two two-dimensional polymer systems was attributed to the smaller unit cell of the more thermally conductive system. Interestingly, the longitudinal sound speed for both films was determined to be over 1900 m s^{-1}. This value is significantly higher than other framework-type (*e.g.*, metal-organic framework) materials, which are conceptually related but are held together through weaker non-covalent interactions. This suggests that fully covalent dimensional polymers may have uniquely high thermal conductivity performance compared to these other materials. Moreover, the low-polarizability of covalent bonds also made these materials function as low-κ dielectric materials, which are often thermally insulating. This highlights how technologically useful multifunctionality emerges as thermal conductivity is studied in polymer systems. As higher-quality thin films and more synthetically diverse two-dimensional polymer systems become available, we expect a rich number of design criteria to achieve high thermal conductivity will become apparent.[88]

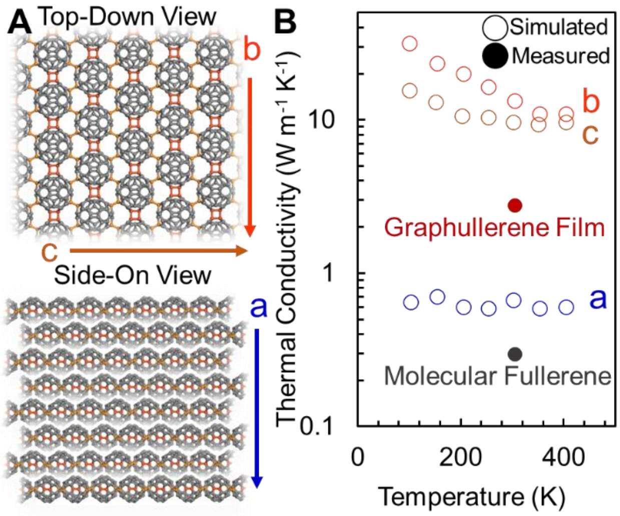


Figure 14| A. Structure of a multi-layer graphullerene two-dimensional polymer. **B.** Thermal conductivity of graphullerite with experimentally measured values in solid circles and thermal conductivities extracted from simulations shown in empty circles.

As new fully covalent macromolecular structures become available, we expect that ultra-high thermal conductivities in designed carbon-based materials will be accessed. Roy and coworkers recently produced a hybrid sp^2 and sp^3 carbon allotrope, graphullerene, by a chemical vapor transport approach.[89] Graphullerene is a two-dimensional polymeric version of

C_{60}, where C_{60} molecules are covalently interconnected with other homologs in a hexagonal array to create a graphene-like molecular sheet. The formation of the multi-layer graphullerite was validated by Raman spectroscopy, depicting the splitting of the C_{60} H_g peak into 1420 cm^{-1} and 1560 cm^{-1} because of the reduced symmetry in the polymerized structure. Transmission electron microscopy also provided evidence of stacked layers of graphullerene. The graphullerite material exhibited an enormous increase in experimentally measured time-domain thermoreflectance thermal conductivity (k = 2.7 W m^{-1} K^{-1}) over monomeric C_{60} crystals ($k_{\text{fullerene}}$ = 0.3 W m^{-1} K^{-1}) (**Figure 14**). The formation of intermolecular covalent linkages with highly rigid and ordered structures are critical attributes for the enhancement of thermal transport in the polymerized graphullerene. Molecular dynamics simulations were also performed to probe the thermal transport more deeply, illustrating the higher in-plane anisotropic thermal conductivity compared to the experimentally determined cross-plane k. Presumably, the intermediate thermal conductivity that was measured is representative of the sensitivity of time-domain thermoreflectance to the cross-plane "*a*" crystallographic direction. The authors postulated that creating covalent bonds between C_{60} units produced multiple vibrational modes that enhanced the intra- and inter-layer thermal transport. This exciting report demonstrates that as purely covalent, crystalline polymeric materials become available, higher thermal conductivities and unique multifunctionalities will also become apparent. We expect this not only to be true for two-dimensional polymers but for other macromolecular constructs as well.

4. Challenges with Determining Intrinsic Polymer Thermal Conductivity

Evaluating the thermal conductivity of polymeric systems presents unique challenges. Unprocessed polymer powders obtained from solution-based synthesis methods are unsuitable for the nanoscale, direct contact, and spectroscopic thermal transport characterization tools routinely used to characterize k. This is because nanoscale powder aggregates have ill-defined void spaces and complex geometries that complicate thermal transport in these systems. As a result, polymer samples must undergo postsynthetic processing before being measured. This requirement introduces ambiguities in the mesostructural features, such as the crystallinity and orientation of processed polymeric materials, which can alter k independent of molecular structure. For this reason, chemically identical polymer samples may yield different observed k values depending on the measurement or processing approach, which complicates the reproducibility of these measurements and makes establishing design principles from data acquired in separate studies challenging. Thermal conductivity measurements are also sensitive to minor fractions of residual solvent, unreacted monomers, oligomers, or other contaminants that can be introduced during synthesis and processing. Studies determining the reliability of different k measurement approaches on polymer samples would be a valuable addition to this area of study. Another postsynthetic complication arises from the fact that many thermal conductivity measurements (*e.g.*, thermoreflectance measurements or 3ω method) require the deposition of metallic contacts onto the material of interest. It is poorly understood if these deposition protocols lead to damage, undesirable cross-reactivity, or induce structural changes with the underlying material. Even if the polymer sample remains unchanged, different metal contacts will lead to different thermal boundary resistances, which need to be accounted for in evaluating the heterostructure's bulk thermal conductivity. Malen, McGaughey and coworkers recently showed that it is non-trivial to estimate how chemical features influence these thermal boundary resistances, which suggests that this may also complicate comparisons between thermal conductivity of different chemical systems or comparisons of identical chemical systems with different metallic contacts.[90]

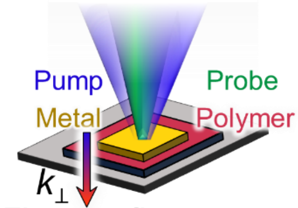
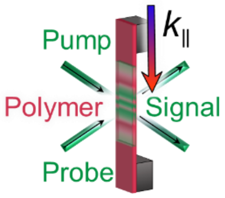
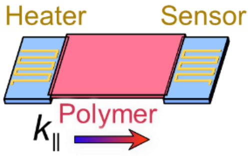
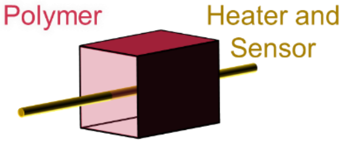
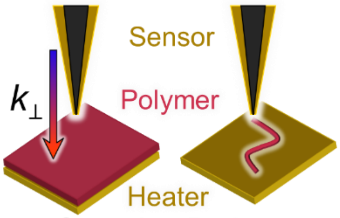
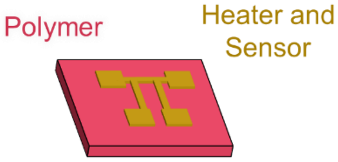
There are substantial opportunities to explore (and optimize) macromolecular processing and sample preparation methodologies to achieve accurate and reliable measurements of polymer thermal conductivity. Special consideration should be given to processing and fabrication approaches that are agnostic to polymer structure, as these would expedite the ability to explore and compare many synthetic designs in parallel.

Complicating the goal of defining a polymer's *k* further is the reality that polymers have several structural features that are synthesis dependent. It is currently not well-understood how macromolecular features such as the molecular weight, dispersity, tacticity, or chain end identity impact *k*. Independently isolating how each feature influences thermal conductivity should be a priority for near-term development. This will require polymer chemists, who specialize in controlling these features, to interface with experts who characterize these thermal transport phenomena.

A final consideration for determining the *k* of different polymers is that different thermal conductivity measurements are sensitive to different thermal transport directions (**Table 1**). Because the internal structures of crystalline polymeric materials can be anisotropic it is possible that different measurement techniques that are sensitive to different thermal transport directions can yield different measured *k* values on identical materials produced in identical ways. We expect resolving this anisotropy will most often be accomplished by combining different measurement techniques or joint simulation-experiment approaches to determine the directional dependence of thermal transport on a single polymer system. Understanding thermal transport anisotropy in polymeric systems will open many new opportunities for directionally guided thermal transport. As more polymer *k* measurements are performed, researchers must diligently work to understand the interaction between macromolecular structure, polymer processing, and the measurement approach used to evaluate *k*.

We offer the following suggestions for a theoretically optimal polymer thermal conductivity sample and preparation method. First, we stress that the polymeric material should be robustly characterized for their molecular weight, dispersity, and covalent structure. These data are often not made available, which constrains our ability to reach in-depth conclusions about macromolecular structure on polymer thermal transport. Another primary concern is void space or interparticle gaps that will lower thermal conductivity and will complicate the reproducibility of these samples. As such, polymer samples should be annealed (solvo-)thermally to relax the stress build up during processing. Otherwise, one runs the risk of evaluating the thermal conductivity of non-equilibrium polymer states. In some instances, one may seek to interrogate kinetically trapped polymer structures (*e.g.* drawn polyethylene) that have minimal voids or interparticle gaps as a function of processing. In these cases, annealing is not viable, so the density/void space should be characterized and reported. All thermal conductivity techniques require a robust understanding of the sample dimensions. For this reason, the thickness of polymer films/fibers/monoliths should be precisely characterized. Similarly, low roughness samples should be targeted to reduce the error associated with these measurements. Low roughness surfaces must also be prioritized for thermoreflectance techniques because light scattering associated with rough samples complicates the interpretation of these measurements. In all cases, the exact limits to roughness and thickness resolution will be determined by the sample morphology and measurement configuration. We provide more information on the techniques used to perform thermal conductivity measurements below (**Table 1**).

Table 1. Techniques used to evaluate thermal conductivities based on either temperature-dependent optical (thermoreflectance,[91-95] transient grating[96]) or electronic (suspended platform,[69, 97] transient hotwire,[98, 99] scanning probe thermometry,[27, 100] 3ω method[101, 102]) responses. Please see the references included in this caption to learn more about these tools.

Techniques	Description	Primary Usage
 **Thermoreflectometry**	Optoreflectance technique that measures the temperature-dependent reflectivity of a metal transducer on a polymer sample. Can be performed with a pulsed pump-probe (ps-μs) time-domain configuration (TDTR) or with a modulated continuous-wave laser (ns-ps) in the frequency-domain (FDTR).	Used to measure thin (10 nm to 1 micron) film or single-crystal cross-plane thermal conductivity or thermal boundary resistances between layers. Can be readily adapted to investigate thermal conductivities with a variety of stimuli. Sensitive to $k_\perp$.
 **Transient Grating**	Pump-probe pulsed laser technique used to measure thermal transport based on a diffraction grating created by interacting optical pulses. This optical signal interacts with samples and generates temperature-dependent optical characteristics (e.g. refractive index) at fast timescales (ns-μs).	Must be performed on suspended thin (few hundred nanometer) membranes. Requires that the material be mechanically robust. Sensitive to $k_\parallel$.
 **Suspended Platform**	Steady-state thermal conductivity measurement, where heat is driven through a suspended sample placed between two platforms where an ohmic heater and a temperature-dependent conductivity sensor are fabricated.	Generally performed on suspended thin films but is also amenable to suspended single-crystallites or fibers. Typical gap sizes are on the order of ~10s of microns. Sensitive to $k_\parallel$.
 **Transient Hot Wire**	Thermoresistance method where metal wire heater/thermometer is suspended in a sample and heavy side heated to measure thermal transport at moderate timescales (ms).	Used to measure thermal conductivity of monolithic polymer samples that can be fabricated surrounding the wire. Anisotropy can be measured if the sample is anisotropic.
 **Scanning Probe Thermometry**	Steady-state method where a scanning probe is used to draw and drive heat through a polymer sample, which is measured by an opposing thermometer. The nanoscale dimensions of the probe tip allows for nanoscale resolution of thermal transport.	Measurements of axial thermal conductivity in polymer nano/microfibers and single polymer chains. Can also be used to measure nanoscale thermal transport in films or crystallites.
 **3ω-method**	Thermoresistance method where a metal heater/thermometer is patterned directly onto a sample and heated periodically to measure thermal transport at moderate timescales (ms).	Can be used to measure film thermal conductivities cross-plane (by using a film on a substrate) or in-plane (by using a suspended membrane).

5. Applications of Intrinsically Thermally Conductive Polymers

Controlling heat transfer is of wide-reaching real-world relevance. Currently, it is challenging to reliably target thermal conductors with multifunctional properties such as low electronic conductivity, optical transparency, high mechanical toughness, or straightforward processability. The realization of thermally conductive polymers and a deep understanding of their structure-property relationships will enable their deployment in many applications.

For example, as microprocessor features continue to shrink, managing the thermal burden produced by their operation becomes paramount. For this reason, the Semiconductor Research Corporation has identified that thermally conductive materials will be critical in next-generation microelectronics and advanced packaging technologies. The high processability of polymeric materials and their ubiquity in current multi-layer semiconductor chips would make them valuable as thermal transport layers. Moreover, the inherently low electrical conductivity of polymer systems may enable them to be deployed in modalities (as conformed heat spreaders or thermal interface materials) that would be prohibitive for metallic thermal conductors. This raises another exciting possibility of chemical design to reduce interfacial thermal resistance of polymers with other materials, which is a current challenge in semiconductor chips. As such, it may not be critical for polymers to host extremely high bulk thermal conductivities to be technologically useful if they can circumvent limiting interfacial thermal processes. A deeper understanding of the structure-property relationships for thermally conductive polymers will accelerate the deployment of these materials in microelectronics.

Photonic devices are also susceptible to thermal management challenges. For example, light emitting diodes generate heat during their operation. However, increased temperatures modify the spectral profile and intensity of LED devices.[103] Additionally, even modest (10 °C) increases in temperature during operation can lead to severely decreased lifetimes (2X). Optical transparent high k polymer systems may be leveraged to remove heat from the emitting (as well as the non-emitting) side of the diode to improve the LED performance. Flexible photonic devices may also benefit from the mechanical compliance of polymer systems. Future efforts aimed at optimizing the multifunctionality of thermally conductive polymers will uncover the feasibility of using these materials in photonic devices.

The combination of fast extensional flows and rapid quenching have been shown to generate bulk materials with alignment among polymer chains in the direction of extension, raising the promise of industrial polymer processing techniques such as blow molding towards producing aligned polymeric materials in a variety of geometries.[104] However, it is currently not understood how well bulk materials in these morphologies can exhibit high thermal conductivity over extended periods of time. For example, at temperatures above T_g, polymer chains will attempt to adopt randomly coiled conformations, potentially erasing the alignment that enables high k in polymeric materials. A better understanding of how processing and chemical design can be synergized would drive the exploration of these applications.

Thermally conductive polymers are not currently used to address real-world thermal management challenges that require high k. However, the inherent processability, multifunctionality, and low cost of polymeric materials make them attractive as next-generation thermal conductors. To achieve high thermal conductivity polymers, it will be necessary to have uniformly high k within a material because thermal conductivity percolation effects are limited by the narrow range of thermal conductivity values and high interfacial thermal resistances between dissimilar materials. This is unlike electronic percolation effects, which can dominate macroscale behavior due to the large range of observable electrical conductivity (σ) values.[105] To realize the promise of these materials will require a more in-depth understanding of the structure-property relationships needed to enhance thermal conductivity. Within this goal, it will also be important to understand how these structure-property relationships interact with other desirable macromolecular optical, electronic, or mechanical properties. As this understanding matures, it will also become necessary to co-optimize chemical design and processing conditions so that thermally conductive polymers can be produced in many morphologies, which will expand the utility of these materials.

6. Multi-Disciplinary Opportunities in Thermally Conductive Polymers

Based on existing reports it is clear that supramolecular reinforcement, polymer alignment, and enhanced crystallinity will provide the high phonon velocities, directional thermal transport pathways, and large phonon mean free paths needed to access thermally conductive polymeric materials. Systematically uncovering what practical polymer designs can achieve high thermal conductivity requires deep interactions between chemists, material scientists, and engineers. Below, we identify opportunities for continued study.

A significant number of polymer systems should be explored to understand the structural and chemical features that lead to high thermal conductivity. Access to more defined polymer systems will provide opportunities to explore features such as chemical structure, molecular weight, dispersity, tacticity, and chain end identity on thermal conductivity. This will require the synthesis of bespoke polymers by controlled polymerization approaches. Understanding these relatively simple features will provide important insight as more complex polymer structures, such as higher-order block polymers or non-linear architectures, are explored. Simultaneously, new processing methods must be developed in parallel for reliable thermal conductivity measurements to be obtained. We feel that these studies will feature prevalently in the coming years.

An understanding of multi-length scale macromolecular structure must be developed for thermally conductive polymers. Sophisticated experimental characterization of polymer structure will drive this mechanistic insight. First, we must thoroughly understand the covalent polymer structures being studied and reported. Carefully characterizing and reporting polymer features such as molecular weight, dispersity, and chain ends with gel permeation chromatography, mass spectrometry, and nuclear magnetic resonance will significantly aid in the development of robust thermal transport models. Next, for research to progress in this area, researchers must couple an understanding of the covalent structures of polymers to their mesoscale arrangement using methods such as X-ray diffraction or electron microscopy measurements to determine their crystallinity and alignment. This will be complemented by strategies to characterize the phonon structure in these materials, such as by inelastic neutron spectroscopy. We also note that in many instances characterization and thermal measurements are performed on different samples. In some cases, the assumption that these two materials are identical may not be valid. In the future, structurally characterizing the same samples used for thermal transport measurements should be considered a priority, as a more reliable understanding of the polymer structure and chemistry will precede reliable thermal understanding. As this level of insight is achieved, it will become more critical to characterize thermal transport in multiple directions, often necessitating multiple sample morphologies or measurement techniques. Comparisons of different measurements of thermal conductivity that are sensitive to different directionalities will be informative in the context of anisotropic thermal transport, as has been preliminarily demonstrated for polyethylene and prototypical two-dimensional polymers.

A deeper mechanistic understanding of thermal conductivity in semi-crystalline polymers must be developed to engineer multi-functional thermally conductive polymers. As higher-quality materials and more robust characterization of polymeric thermal conductivity are achieved, a more reliable mechanistic understanding of thermal transport will naturally emerge. More comprehensive thermal conductivity measurements – such as those that vary temperature and sample dimensions – will be essential toward the goal of a mechanistic framework for polymer thermal conductivity. Furthermore, we believe that comparing diverse thermal conductivity measurements, each sensitive to specific directions, will enhance our understanding of anisotropic thermal transport. This has been demonstrated in initial studies with polyethylene and common two-dimensional polymers. The poor level of mechanistic understanding in thermal transport for polymer systems leaves a key question unanswered: *What level of molecular complexity can be embedded into a polymer system while retaining high thermal conductivity?* For example, it may be the case that polyethylene will be an unmatchable polymeric thermal conductor because it has a chemically homogenous backbone and no side-chain functionalities, both supporting long-wavelength phonon modes that carry significant heat. As more mechanistic insight is gained, it may be revealed that only chemically straightforward polymer systems can host high thermal conductivity, constraining the orthogonal functionalities one can design in highly thermally conductive systems.

Undeniably, computational modelling will be critical to the efforts of unravelling thermal transport effects in polymeric systems. If past experiences can predict the future, we expect that computational approaches to understanding and predicting thermal transport will predate robust experimentally derived thermal transport models. The development of interatomic potentials that can account for the multi-variant and anisotropic bonding environments in polymer systems are already underway and rapidly gaining in complexity. We expect that continued progress in these areas will inform the target structures that polymer chemists and thermal conductivity measurement experts target. Another challenge that must be addressed for semi-crystalline polymer systems, which are likely the most relevant for bulk thermally conductive materials, is that phonons and other heat carriers must be considered holistically. This requires methods that can combine the advantages of lattice dynamics-based methods that give reliable insight into phonon-based transport and molecular dynamics simulations, which can better tolerate amorphous materials or defective structures. These methods are already being developed and are rapidly gaining complexity for a variety of materials. We expect their deployment in the field of polymer thermal transport will greatly accelerate the development of this field.

Given the multi-dimensional nature of the challenges of designing intrinsically thermally conductive polymers in both an experimental and computational context, we expect that advanced machine learning approaches may help unravel the complexity of polymer thermal transport. Yoshida and coworkers showed how machine learning approaches could be used to evaluate a variety of reported and measured amorphous polymer thermal conductivities and develop intricate structure-property relationships.[106] In this report, the authors use transfer learning based on polymer properties that are straightforward to measure accurately (*e.g.* T_g) to predict polymer thermal conductivities, which they experimentally validated on a polymer with modest thermal conductivity (0.4 W m^{-1} K^{-1}). The authors note that heat transfer is enhanced in systems they studied with hydrogen-bonding, dipole-dipole interactions, or rigid covalent backbones, which suggests that design criteria provided by a phonon-based heat transfer model may be valid even in amorphous systems where the mechanisms of thermal transport are more complex. Given the large amount of non-thermal conductivity data available for many polymer systems and the ease at which this information can be obtained, understanding the correlations between these features would be practically useful. Moreover, understanding these correlations may also provide crucial information for a mechanistic framework for thermal conductivity. Critical to furthering this goal will be a robust method to compare results across different studies in the same material. For this reason, we encourage all data on polymers (molecular weight, dispersity, infrared spectroscopy, crystallography, etc) measured for their thermal conductivity to be published alongside the thermal transport measurements. In the longer term, it would be valuable to create a curated database for thermal conductivity studies that allows this information to be directly uploaded and organized for future investigation. Collaboratively developing insights derived from computational models, machine learning, and experimental investigation will be critical to producing robust polymer thermal transport models.

Preliminary observations suggest that polymers can be engineered to host high thermal conductivities through intentional molecular design and appropriate processing. As the design rules needed to achieve high thermal conductivity are developed, we expect many multifunctional thermal conductors to emerge. Multidisciplinary efforts in polymer synthesis and thermal characterization will drive these design rules. Interactions at the interface of these disciplines will also generate the mechanistic understanding needed to systematically develop thermally conductive polymers. As this mechanistic understanding evolves, we suspect that thermally conductive polymers with various combinations of mechanical, electronic, and optical properties will be readily accessed. Collectively, thermally conductive polymers are a unique and underdeveloped materials platform. We eagerly anticipate the realization of thermally conductive polymers and the potential of their associated devices.

Acknowledgements. We thank the Department of Defense for a Multidisciplinary University Research Initiative Award (W911NF2310260) that supported this work. K.A.T. was supported by the Department of Defense (DoD) through the National Defense Science & Engineering Graduate (NDSEG) Fellowship Program. A.M.E. is thankful for support from the 3M Non-Tenured Faculty Award.

Conflict of Interest. The authors declare no competing interests.

7. References

1. S. Hirano, in *Handbook of Climate Change Mitigation*, eds. W.-Y. Chen, J. Seiner, T. Suzuki and M. Lackner, Springer US, New York, NY, 2012, pp. 669-700.
2. Y. Zhao, Y. Cai, L. Zhang, B. Li, G. Zhang and J. T. L. Thong, *Adv. Funct. Mater.*, 2020, **30**, 1903929.
3. A. L. Moore and L. Shi, *Mater. Today*, 2014, **17**, 163-174.
4. Y. Li, W. Li, T. Han, X. Zheng, J. Li, B. Li, S. Fan and C.-W. Qiu, *Nat. Rev. Mater.*, 2021, **6**, 488-507.
5. S. R. Phillpot and A. J. H. McGaughey, *Mater. Today*, 2005, **8**, 18-20.
6. B. Zhang, P. Mao, Y. Liang, Y. He, W. Liu and Z. Liu, *ES Energy Environ.* , 2019, **5**, 37-55.
7. X. Xu, J. Chen, J. Zhou and B. Li, *Adv. Mater.*, 2018, **30**, 1705544.
8. Z. Wang, Z. Wu, L. Weng, S. Ge, D. Jiang, M. Huang, D. M. Mulvihill, Q. Chen, Z. Guo, A. Jazzar, X. He, X. Zhang and B. B. Xu, *Adv. Funct. Mater.*, 2023, **33**, 2301549.
9. Z. Wang, Z. Wu, L. Weng, S. Ge, D. Jiang, M. Huang, D. M. Mulvihill, Q. Chen, Z. Guo, A. Jazzar, X. He, X. Zhang and B. B. Xu, *Adv. Funct. Mater.*, 2023, **33**, 2301549.
10. Y. Guo, K. Ruan, X. Shi, X. Yang and J. Gu, *Compos. Sci. Technol.*, 2020, **193**, 108134.
11. E. Fermi, J. R. Pasta and S. M. Ulam, 1955.
12. S. Lepri, R. Livi and A. Politi, *Europhys. Lett.*, 1998, **43**, 271.
13. S. Lepri, R. Livi and A. Politi, *Phys. Rep.*, 2003, **377**, 1-80.
14. B. Li and J. Wang, *Phys. Rev. Lett.*, 2003, **91**, 044301.
15. A. Henry and G. Chen, *Phys. Rev. Lett.*, 2008, **101**, 235502.
16. X. Wei, Z. Wang, Z. Tian and T. Luo, *J. Heat Transf.*, 2021, **143**, 072101.
17. X. Qian, J. Zhou and G. Chen, *Nat. Mater.*, 2021, **20**, 1188-1202.
18. Y. Jia, Z. Mao, W. Huang and J. Zhang, *Mater. Chem. Phys.*, 2022, **287**, 126325.
19. R. Shrestha, P. Li, B. Chatterjee, T. Zheng, X. Wu, Z. Liu, T. Luo, S. Choi, K. Hippalgaonkar, M. P. de Boer and S. Shen, *Nat. Commun.*, 2018, **9**, 1664.

20. V. Singh, T. L. Bougher, A. Weathers, Y. Cai, K. Bi, M. T. Pettes, S. A. McMenamin, W. Lv, D. P. Resler, T. R. Gattuso, D. H. Altman, K. H. Sandhage, L. Shi, A. Henry and B. A. Cola, *Nat. Nanotechnol.*, 2014, **9**, 384-390.
21. G.-H. Kim, D. Lee, A. Shanker, L. Shao, M. S. Kwon, D. Gidley, J. Kim and K. P. Pipe, *Nat. Mater.*, 2015, **14**, 295-300.
22. T. Zhang and T. Luo, *J. Phys. Chem. B*, 2016, **120**, 803-812.
23. C. L. Choy, F. C. Chen and W. H. Luk, *J. Polym. Sci., Polym. Phys. Ed.*, 1980, **18**, 1187-1207.
24. H. Ma, B. Gao, M. Wang, Z. Yuan, J. Shen, J. Zhao and Y. Feng, *J. Mater. Sci.*, 2021, **56**, 1064-1086.
25. J. He and J. Liu, *J. Appl. Phys.*, 2021, **130**, 225101.
26. C. L. Choy, *Polymer*, 1977, **18**, 984-1004.
27. S. Shen, A. Henry, J. Tong, R. Zheng and G. Chen, *Nat. Nanotechnol.*, 2010, **5**, 251-255.
28. Y. Xu, D. Kraemer, B. Song, Z. Jiang, J. Zhou, J. Loomis, J. Wang, M. Li, H. Ghasemi, X. Huang, X. Li and G. Chen, *Nat. Commun.*, 2019, **10**, 1771.
29. N. Shulumba, O. Hellman and A. J. Minnich, *Phys. Rev. Lett.*, 2017, **119**, 185901.
30. Z. Li, L. An, S. Khuje, J. Tan, Y. Hu, Y. Huang, D. Petit, D. Faghihi, J. Yu and S. Ren, *Sci. Adv.*, 2021, **7**, eabi7410.
31. R. Peierls, *Annalen der Physik*, 1929, **395**, 1055-1101.
32. C. L. Choy, S. P. Wong and K. Young, *J. Polym. Sci.: Polym. Phys. Ed.*, 1985, **23**, 1495-1504.
33. P. B. Allen, J. L. Feldman, J. Fabian and F. Wooten, *Philos. mag. B*, 1999, **79**, 1715-1731.
34. G. A. Slack, *J. Phys. Chem. Solids*, 1973, **34**, 321-335.
35. D. G. Cahill, S. K. Watson and R. O. Pohl, *Phys. Rev. B*, 1992, **46**, 6131-6140.
36. M. C. Wingert, J. Zheng, S. Kwon and R. Chen, *Semicond. Sci. Technol.*, 2016, **31**, 113003.
37. D. G. Cahill, W. K. Ford, K. E. Goodson, G. D. Mahan, A. Majumdar, H. J. Maris, R. Merlin and S. R. Phillpot, *J. Appl. Phys.*, 2002, **93**, 793-818.
38. D. G. Cahill, P. V. Braun, G. Chen, D. R. Clarke, S. Fan, K. E. Goodson, P. Keblinski, W. P. King, G. D. Mahan, A. Majumdar, H. J. Maris, S. R. Phillpot, E. Pop and L. Shi, *Appl. Phys. Rev.*, 2014, **1**, 011305.
39. B. Li, F. DeAngelis, G. Chen and A. Henry, *Commun. Phys.*, 2022, **5**, 323.
40. S. Kommandur and S. K. Yee, *J. Polym. Sci., Part B: Polym. Phys.*, 2017, **55**, 1160-1170.
41. M. Simoncelli, N. Marzari and F. Mauri, *Nat. Phys.*, 2019, **15**, 809-813.
42. M. Simoncelli, N. Marzari and F. Mauri, *Phys. Rev. X*, 2022, **12**, 041011.
43. M. Simoncelli, F. Mauri and N. Marzari, *Npj Comput. Mater.*, 2023, **9**, 106.
44. W.-L. Ong, E. S. O'Brien, P. S. M. Dougherty, D. W. Paley, C. Fred Higgs Iii, A. J. H. McGaughey, J. A. Malen and X. Roy, *Nat. Mater.*, 2017, **16**, 83-88.
45. D. E. Kline, *J. Polym. Sci.*, 1961, **50**, 441-450.
46. K. T. Regner, D. P. Sellan, Z. Su, C. H. Amon, A. J. H. McGaughey and J. A. Malen, *Nat. Commun.*, 2013, **4**, 1640.
47. T. Zhang, X. Wu and T. Luo, *J. Phys. Chem. C*, 2014, **118**, 21148-21159.
48. P. Antonella and A. Domenico, in *Polypropylene*, eds. W. Weiyu and Z. Yiming, IntechOpen, Rijeka, 2019, DOI: 10.5772/intechopen.84477, p. Ch. 3.
49. M. Ono, *Polym. J.*, 2023, **55**, 1327-1334.
50. L. Zhang, M. Ruesch, X. Zhang, Z. Bai and L. Liu, *RSC Adv.*, 2015, **5**, 87981-87986.
51. X. Ran, Y. Wang, J. Lu, R. Sun, J.-B. Xu, N. Yang, H. Yin and C.-P. Wong, *Comput. Mater. Sci.*, 2022, **205**, 111191.
52. P. Hummel, A. M. Lechner, K. Herrmann, P. Biehl, C. Rössel, L. Wiedenhöft, F. H. Schacher and M. Retsch, *Macromolecules*, 2020, **53**, 5528-5537.
53. F. Jiang, S. Cui, N. Song, L. Shi and P. Ding, *ACS Appl. Mater. Interfaces*, 2018, **10**, 16812-16821.
54. A. Shanker, C. Li, G.-H. Kim, D. Gidley, K. P. Pipe and J. Kim, *Sci. Adv.*, 2017, **3**, e1700342.
55. X. Xie, D. Li, T.-H. Tsai, J. Liu, P. V. Braun and D. G. Cahill, *Macromolecules*, 2016, **49**, 972-978.
56. H. Ma and Z. Tian, *Appl. Phys. Lett.*, 2015, **107**, 073111.
57. H. Zheng, K. Wu, Y. Zhan, K. Wang and J. Shi, *J. Polym. Sci.*, 2023, **61**, 1622-1633.
58. B. Liu, Y. Zhou, L. Dong, Q. Lu and X. Xu, *iScience*, 2022, **25**, 105451.

59. J. Zhou, S. Lin, H. Zeng, J. Liu, B. Li, Y. Xu, X. Zhao and G. Chen, *Mater. Horiz.*, 2020, **7**, 2936-2943.
60. J. Shin, J. Sung, M. Kang, X. Xie, B. Lee, K. M. Lee, T. J. White, C. Leal, N. R. Sottos, P. V. Braun and D. G. Cahill, *Proc. Natl. Acad. Sci. U.S.A.*, 2019, **116**, 5973-5978.
61. R. Shrestha, Y. Luan, S. Shin, T. Zhang, X. Luo, J. S. Lundh, W. Gong, M. R. Bockstaller, S. Choi, T. Luo, R. Chen, K. Hippalgaonkar and S. Shen, *Sci. Adv.*, 2019, **5**, eaax3777.
62. R. Shrestha, Y. Luan, X. Luo, S. Shin, T. Zhang, P. Smith, W. Gong, M. Bockstaller, T. Luo, R. Chen, K. Hippalgaonkar and S. Shen, *Nat. Commun.*, 2020, **11**, 4346.
63. X. Wei and T. Luo, *Phys. Chem. Chem. Phys.*, 2022, **24**, 10272-10279.
64. W. Chen, K. Wu, Z. Qu and M. Lu, *Eur. Polym. J.*, 2019, **121**, 109275.
65. X. Pan, M. G. Debije and A. P. H. J. Schenning, *ACS Appl. Polym. Mater.*, 2021, **3**, 578-587.
66. X. Wang, V. Ho, R. A. Segalman and D. G. Cahill, *Macromolecules*, 2013, **46**, 4937-4943.
67. W.-X. Zhou, Y. Cheng, K.-Q. Chen, G. Xie, T. Wang and G. Zhang, *Adv. Funct. Mater.*, 2020, **30**, 1903829.
68. H. Ma, Y. Ma and Z. Tian, *ACS Appl. Polym. Mater.*, 2019, **1**, 2566-2570.
69. J. Ma, Q. Zhang, A. Mayo, Z. Ni, H. Yi, Y. Chen, R. Mu, L. M. Bellan and D. Li, *Nanoscale*, 2015, **7**, 16899-16908.
70. M. K. Smith, T. L. Bougher, K. Kalaitzidou and B. A. Cola, *MRS Advances*, 2017, **2**, 3619-3626.
71. A. Shi, Y. Li, W. Liu, J. Lei and Z.-M. Li, *J. Appl. Phys.*, 2019, **125**, 245110.
72. T. Kim, S. X. Drakopoulos, S. Ronca and A. J. Minnich, *Nat. Commun.*, 2022, **13**, 2452.
73. K. Utimula, T. Ichibha, R. Maezono and K. Hongo, *Chem. Mater.*, 2019, **31**, 4649-4656.
74. B. Zhu, J. Liu, T. Wang, M. Han, S. Valloppilly, S. Xu and X. Wang, *ACS Omega*, 2017, **2**, 3931-3944.
75. X. Wang, M. Kaviany and B. Huang, *Nanoscale*, 2017, **9**, 18022-18031.
76. A. Henry, G. Chen, S. J. Plimpton and A. Thompson, *Phys. Rev. B*, 2010, **82**, 144308.
77. Z. Wang, J. A. Carter, A. Lagutchev, Y. K. Koh, N.-H. Seong, D. G. Cahill and D. D. Dlott, *Science*, 2007, **317**, 787-790.
78. W. Lee, K. Kim, W. Jeong, L. A. Zotti, F. Pauly, J. C. Cuevas and P. Reddy, *Nature*, 2013, **498**, 209-212.
79. P. Reddy, S.-Y. Jang, R. A. Segalman and A. Majumdar, *Science*, 2007, **315**, 1568-1571.
80. K. Ruan, Y. Guo and J. Gu, *Macromolecules*, 2021, **54**, 4934-4944.
81. Y. Xu, X. Wang, J. Zhou, B. Song, Z. Jiang, E. M. Y. Lee, S. Huberman, K. K. Gleason and G. Chen, *Sci. Adv.*, 2018, **4**, eaar3031.
82. G. Lv, X. Li, E. Jensen, B. Soman, Y.-H. Tsao, C. M. Evans and D. G. Cahill, *Macromolecules*, 2023, **56**, 1554-1561.
83. G. Lv, C. Shen, N. Shan, E. Jensen, X. Li, C. M. Evans and D. G. Cahill, *Proc. Natl. Acad. Sci.*, 2022, **119**, e2211151119.
84. B. R. Elling and W. R. Dichtel, *ACS Cent. Sci.*, 2020, **6**, 1488-1496.
85. E. M. Moscarello, B. L. Wooten, H. Sajid, L. D. Tichenor, J. P. Heremans, M. A. Addicoat and P. L. McGrier, *ACS Appl. Nano Mater.*, 2022, **5**, 13787-13793.
86. A. M. Evans, M. J. Strauss, A. R. Corcos, Z. Hirani, W. Ji, L. S. Hamachi, X. Aguilar-Enriquez, A. D. Chavez, B. J. Smith and W. R. Dichtel, *Chem. Rev.*, 2022, **122**, 442-564.
87. A. M. Evans, A. Giri, V. K. Sangwan, S. Xun, M. Bartnof, C. G. Torres-Castanedo, H. B. Balch, M. S. Rahn, N. P. Bradshaw, E. Vitaku, D. W. Burke, H. Li, M. J. Bedzyk, F. Wang, J.-L. Brédas, J. A. Malen, A. J. H. McGaughey, M. C. Hersam, W. R. Dichtel and P. E. Hopkins, *Nat. Mater.*, 2021, **20**, 1142-1148.
88. A. Giri, A. M. Evans, M. A. Rahman, A. J. H. McGaughey and P. E. Hopkins, *ACS Nano*, 2022, **16**, 2843-2851.
89. E. Meirzadeh, A. M. Evans, M. Rezaee, M. Milich, C. J. Dionne, T. P. Darlington, S. T. Bao, A. K. Bartholomew, T. Handa, D. J. Rizzo, R. A. Wiscons, M. Reza, A. Zangiabadi, N. Fardian-Melamed, A. C. Crowther, P. J. Schuck, D. N. Basov, X. Zhu, A. Giri, P. E. Hopkins, P. Kim, M. L. Steigerwald, J. Yang, C. Nuckolls and X. Roy, *Nature*, 2023, **613**, 71-76.
90. S. Majumdar, J. A. Sierra-Suarez, S. N. Schiffres, W.-L. Ong, C. F. Higgs, III, A. J. H. McGaughey and J. A. Malen, *Nano Lett.*, 2015, **15**, 2985-2991.

91. D. G. Cahill, *Rev. Sci. Instrum.*, 2004, **75**, 5119-5122.
92. A. J. Schmidt, X. Chen and G. Chen, *Rev. Sci. Instrum.*, 2008, **79**, 114902.
93. A. J. Schmidt, R. Cheaito and M. Chiesa, *Rev. Sci. Instrum.*, 2009, **80**, 094901.
94. J. A. Malen, K. Baheti, T. Tong, Y. Zhao, J. A. Hudgings and A. Majumdar, *J. Heat Transf.*, 2011, **133**, 081601.
95. K. T. Regner, S. Majumdar and J. A. Malen, *Rev. Sci. Instrum.*, 2013, **84**, 064901.
96. A. B. Robbins, S. X. Drakopoulos, I. Martin-Fabiani, S. Ronca and A. J. Minnich, *Proc. Natl. Acad. Sci.*, 2019, **116**, 17163-17168.
97. L. Shi, D. Li, C. Yu, W. Jang, D. Kim, Z. Yao, P. Kim and A. Majumdar, *J. Heat Transf.*, 2003, **125**, 881-888.
98. J. J. Healy, J. J. de Groot and J. Kestin, *Phys. B+C*, 1976, **82**, 392-408.
99. M. D. Bartlett, N. Kazem, M. J. Powell-Palm, X. Huang, W. Sun, J. A. Malen and C. Majidi, *Proc. Natl. Acad. Sci.*, 2017, **114**, 2143-2148.
100. L. Cui, S. Hur, Z. A. Akbar, J. C. Klöckner, W. Jeong, F. Pauly, S.-Y. Jang, P. Reddy and E. Meyhofer, *Nature*, 2019, **572**, 628-633.
101. L. Qiu, X. H. Zheng, J. Zhu and D. W. Tang, *Rev. Sci. Instrum.*, 2011, **82**, 086110.
102. D. G. Cahill, *Rev. Sci. Instr.*, 1990, **61**, 802-808.
103. M. Hamidnia, Y. Luo and X. D. Wang, *Appl. Therm. Eng.*, 2018, **145**, 637-651.
104. Q. Huang, *Macromolecules*, 2022, **55**, 715-727.
105. I. Y. Forero-Sandoval, A. P. Franco-Bacca, F. Cervantes-Álvarez, C. L. Gómez-Heredia, J. A. Ramírez-Rincón, J. Ordonez-Miranda and J. J. Alvarado-Gil, *J. Appl. Phys.*, 2022, **131**.
106. S. Wu, Y. Kondo, M.-a. Kakimoto, B. Yang, H. Yamada, I. Kuwajima, G. Lambard, K. Hongo, Y. Xu, J. Shiomi, C. Schick, J. Morikawa and R. Yoshida, *Npj Comput. Mater.*, 2019, **5**, 66.