Low, high, and switchable thermal conductivity in soft materials

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I-MRSEC

ONR, Altana Institute

Low, high, and switchable thermal conductivity in soft materials

Motivation and extremes of the thermal conductivity of materials

Molecular structure and the thermal conductivity of soft materials

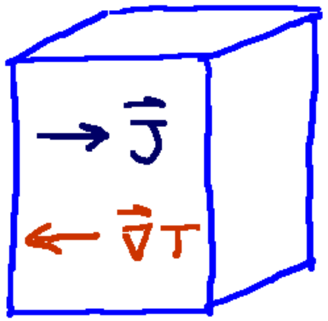
New high-throughput techniques: frequency-domain probe beam deflection for thermal diffusivity

Search for thermally functional materials

Thermal transport coefficients

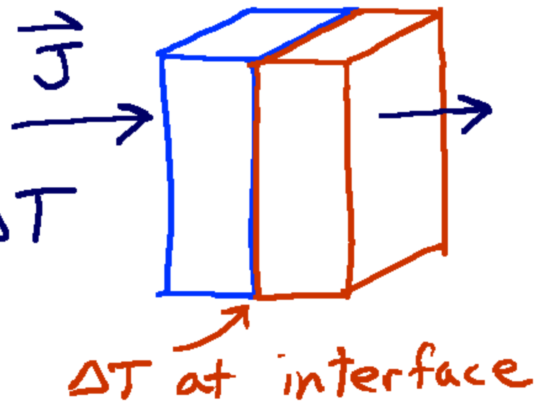
- Thermal conductivity Λ is a property of the continuum

$\vec{J} = -\Lambda \vec{\nabla} T$



$$\Lambda = \frac{1}{3 V k_B T^2} \int_0^\infty \langle \vec{j}(t) \cdot \vec{j}(0) \rangle \, dt$$

- Thermal conductance (per unit area) *G* is a property of an interface



$J = G \Delta T$

$$G = \frac{1}{A k_B T^2} \int_0^\infty \langle q(t) q(0) \rangle \, dt$$

Motivation

For an efficient heat engine, we want to minimize irreversible processes. We want the working fluid to carry the heat and **minimize thermal losses**.

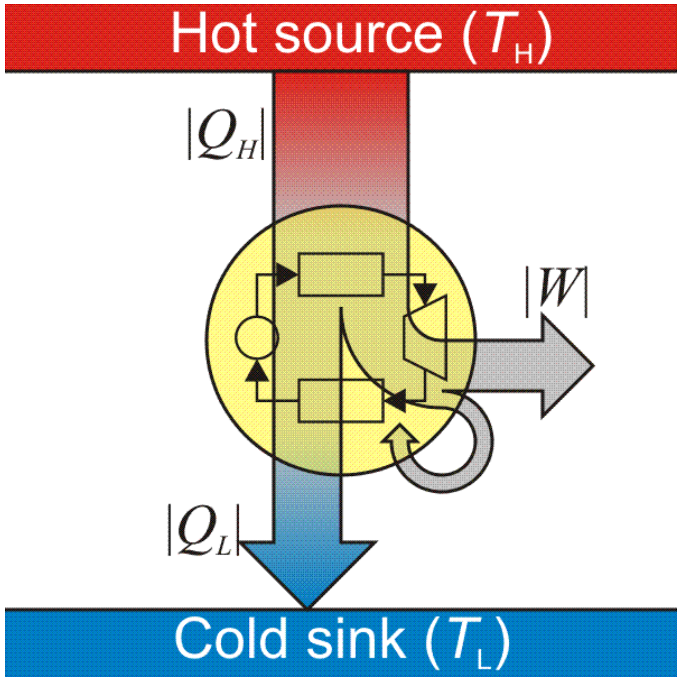
A solid-state thermoelectric material is a specific example. We want the **vibrational thermal conductivity to be as small as possible** so that the electrons and holes carry a larger fraction of the heat.

$$ZT = \frac{S^2 \sigma T}{\Lambda_l + \Lambda_{el}}$$

$$ZT = \frac{S^2 / L}{1 + \frac{\Lambda_l}{\Lambda_{el}}}$$

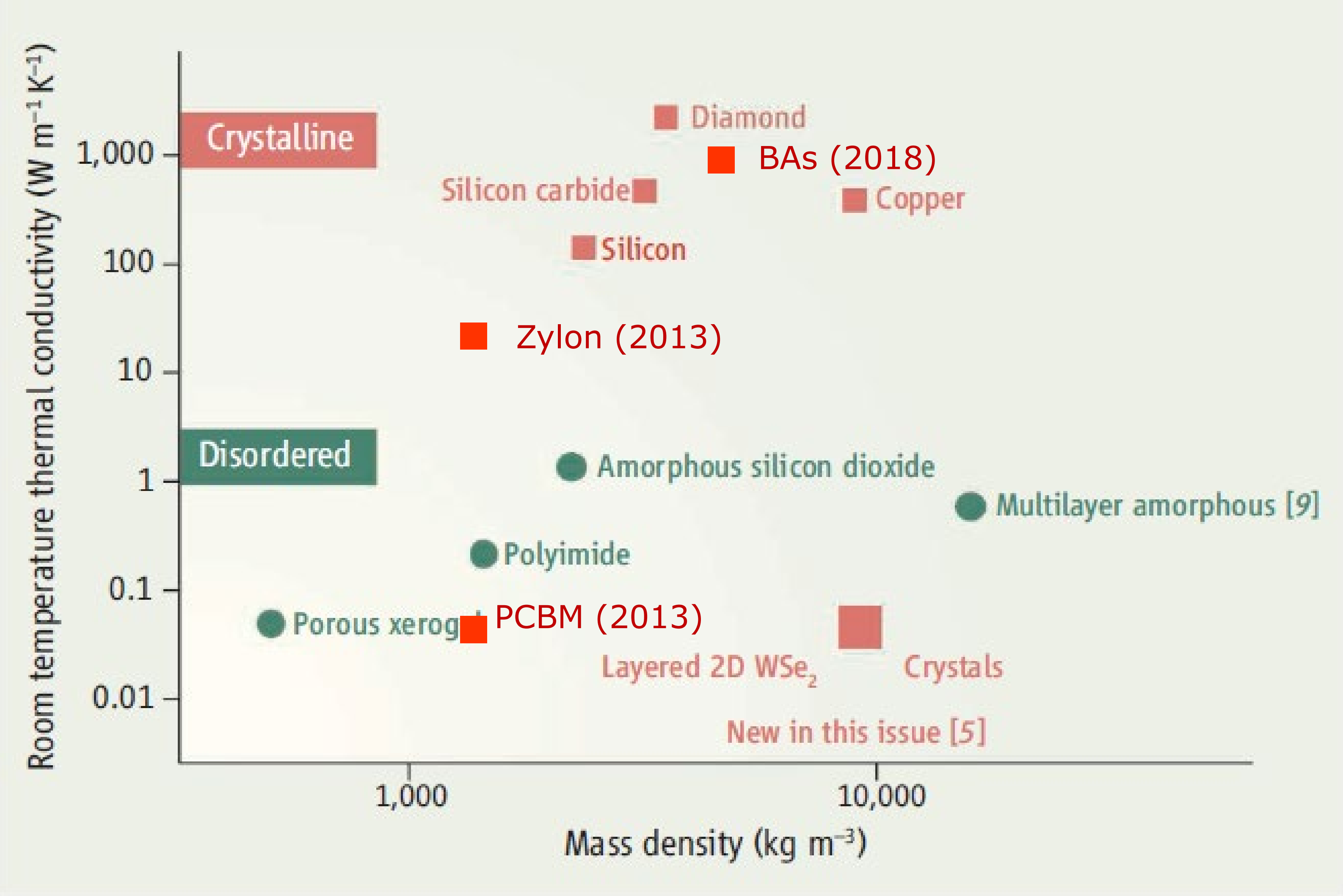
Motivation

We want to minimize the temperature drop in the heat exchangers, another source of dissipation. Thus, we want **high thermal conductivity** soft materials to construct lightweight, flexible heat exchangers.



Gonfer at English Wikipedia

Thermal conductivities of dense solids span a range of 40,000 at room temperature



Adapted from Goodson, *Science* (2007)

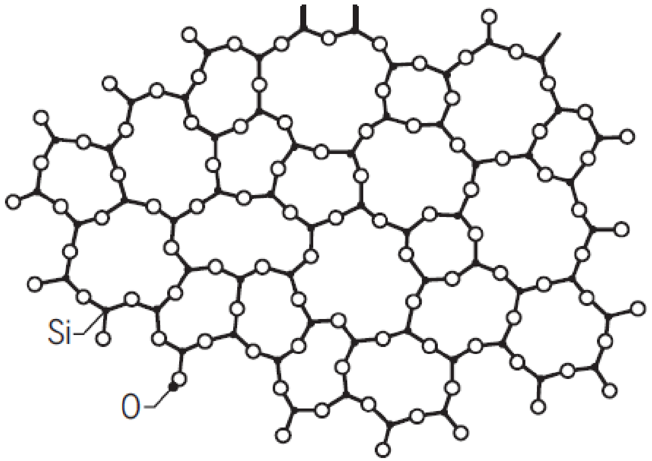
Theory and computation for thermal conductivity of simple inorganic crystals is relatively mature

1st principles theory for phonon processes beyond third order.

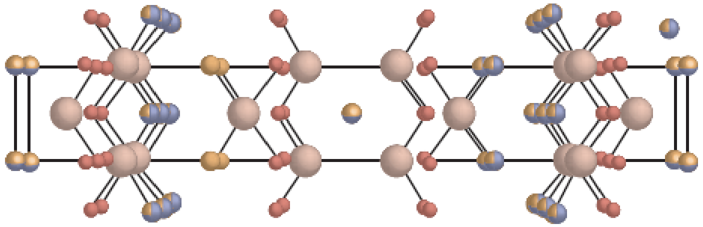
Complex crystal structures require greater computational resources.

Recent theory (Simoncelli et al. 2019) bridges the gap between harmonic glasses and anharmonic crystals.

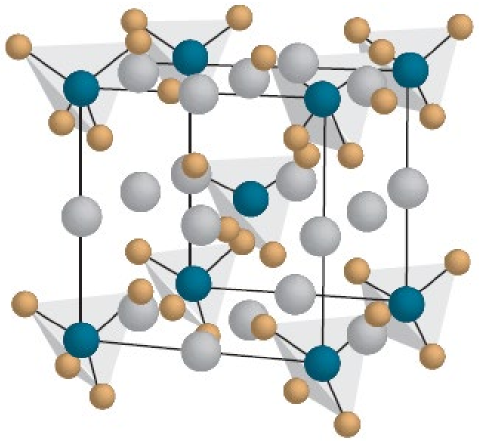
Harmonic glasses



Anisotropy



Anharmonicity



Kim and Cahill, Science (2021)

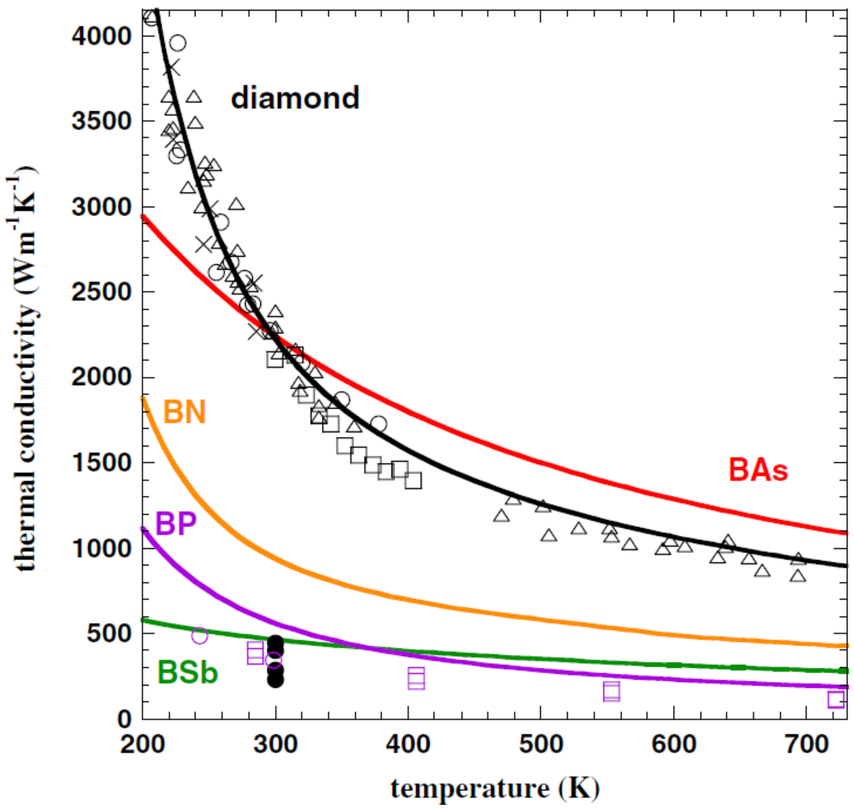
New (past decade) capabilities for calculations of thermal conductivity of crystals from 1st principles

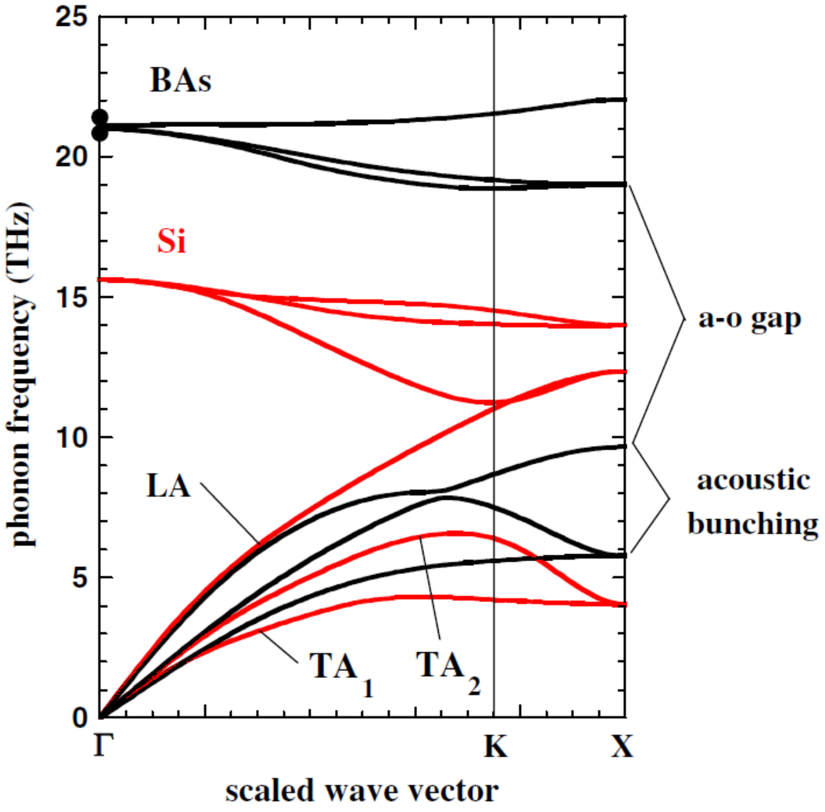
Selected for a Viewpoint in *Physics*

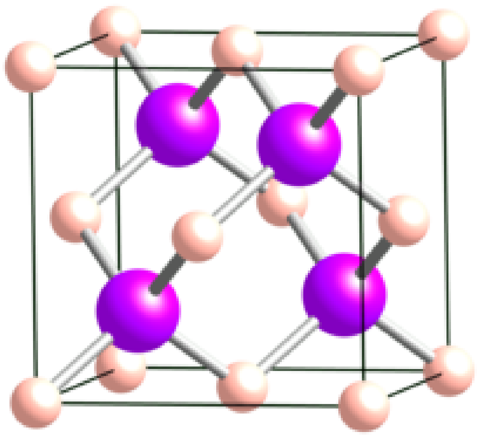
PRL **111**, 025901 (2013) PHYSICAL REVIEW LETTERS week ending 12 JULY 2013

First-Principles Determination of Ultrahigh Thermal Conductivity of Boron Arsenide: A Competitor for Diamond?

L. Lindsay,[1] D. A. Broido,[2] and T. L. Reinecke[1]

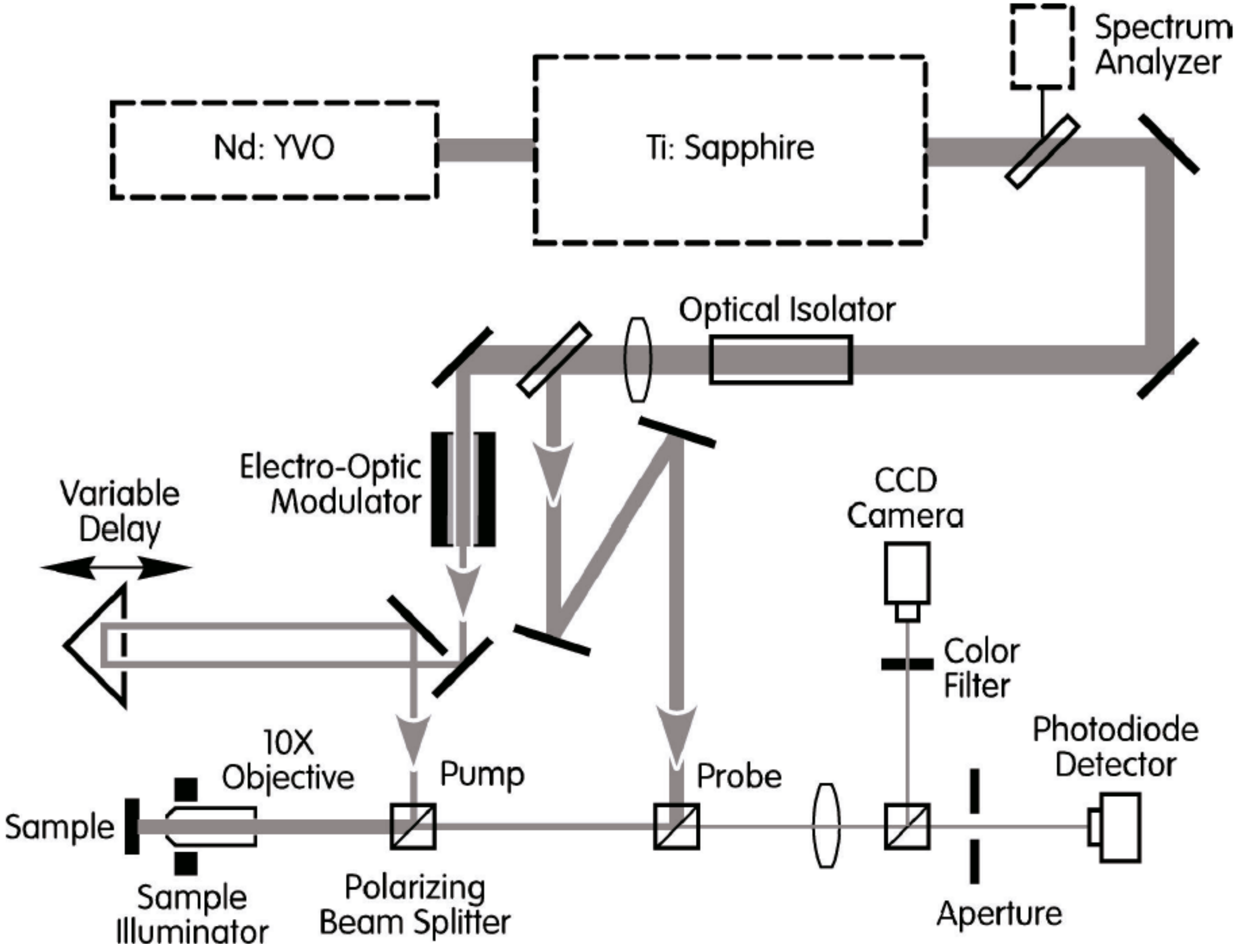




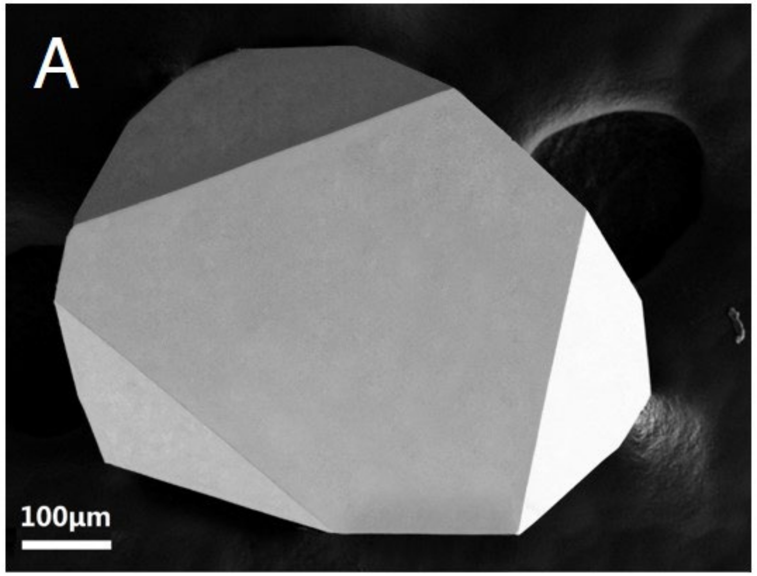


High-throughput pump-probe measurements of thermal conductivity, heat capacity, and elastic constants of polymers

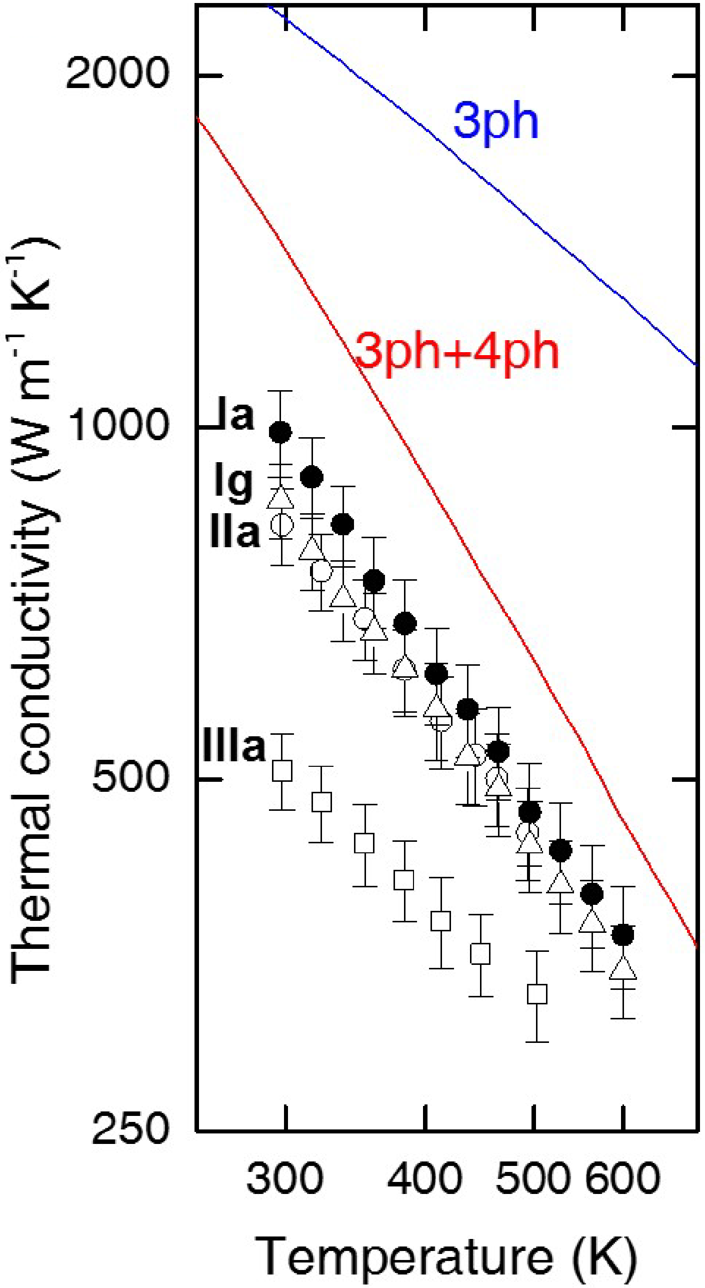
- Applicable to thin (100 nm) layers.
- TDTR for heat capacity and thermal conductivity.
- Picoseconcd acoustics and surface acoustic wave velocities for C_{11} and C_{44} elastic constants.



Thermal conductivity of BAs is limited by four-phonon scattering



Li, Zheng *et al.*, *Science* (2018)



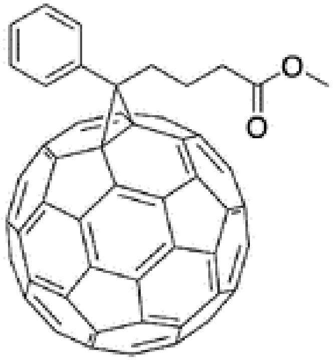
Predictive understanding of the thermal conductivity of polymers is much less mature

Overlapping challenges of disorder, uncertainty in the molecular structure, non-bonding interactions, and lack of systematic data.

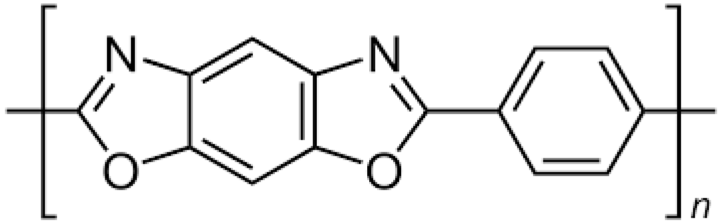
We know that the thermal conductivity of polymers can span a large range.

0.06 W/(m-K) → ×300 → 20 W/(m-K)

PCBM



ZYLON

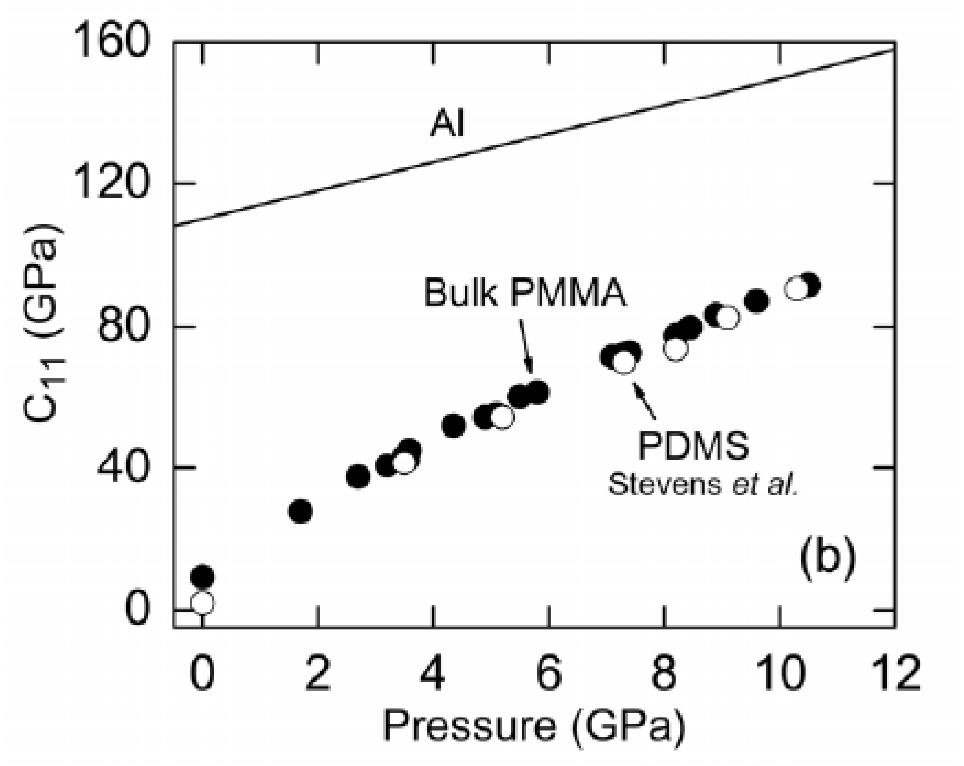


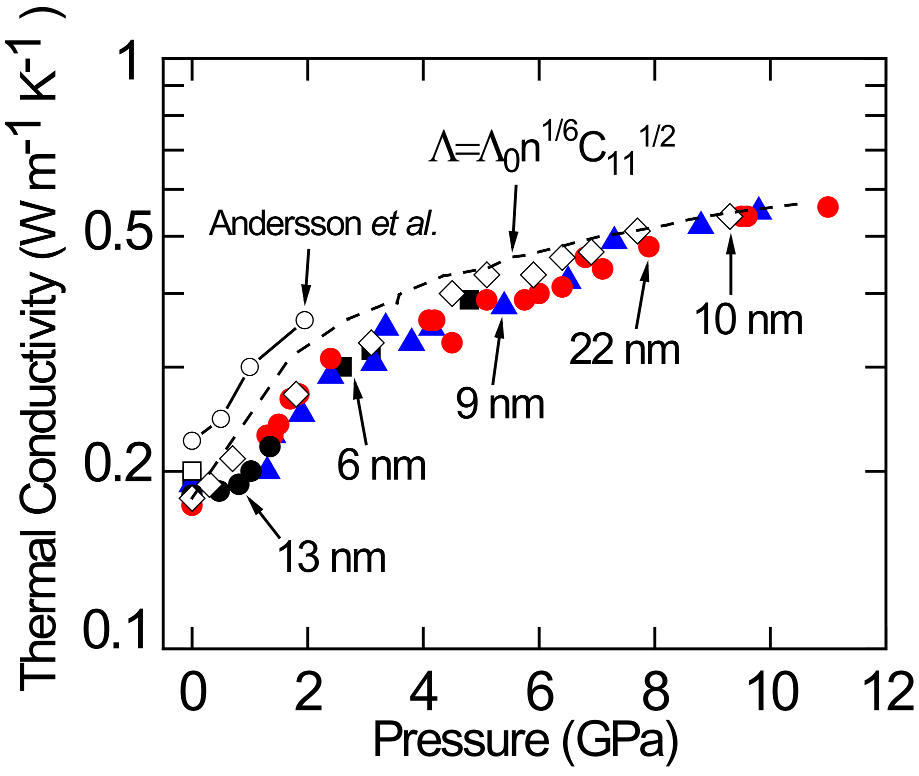
Wang, *PRB* (2013)

Wang, *Macromolecules* (2013)

11 years ago: thermal conductivity and elastic constants of a glassy polymer, PMMA, in a SiC high pressure anvil cell

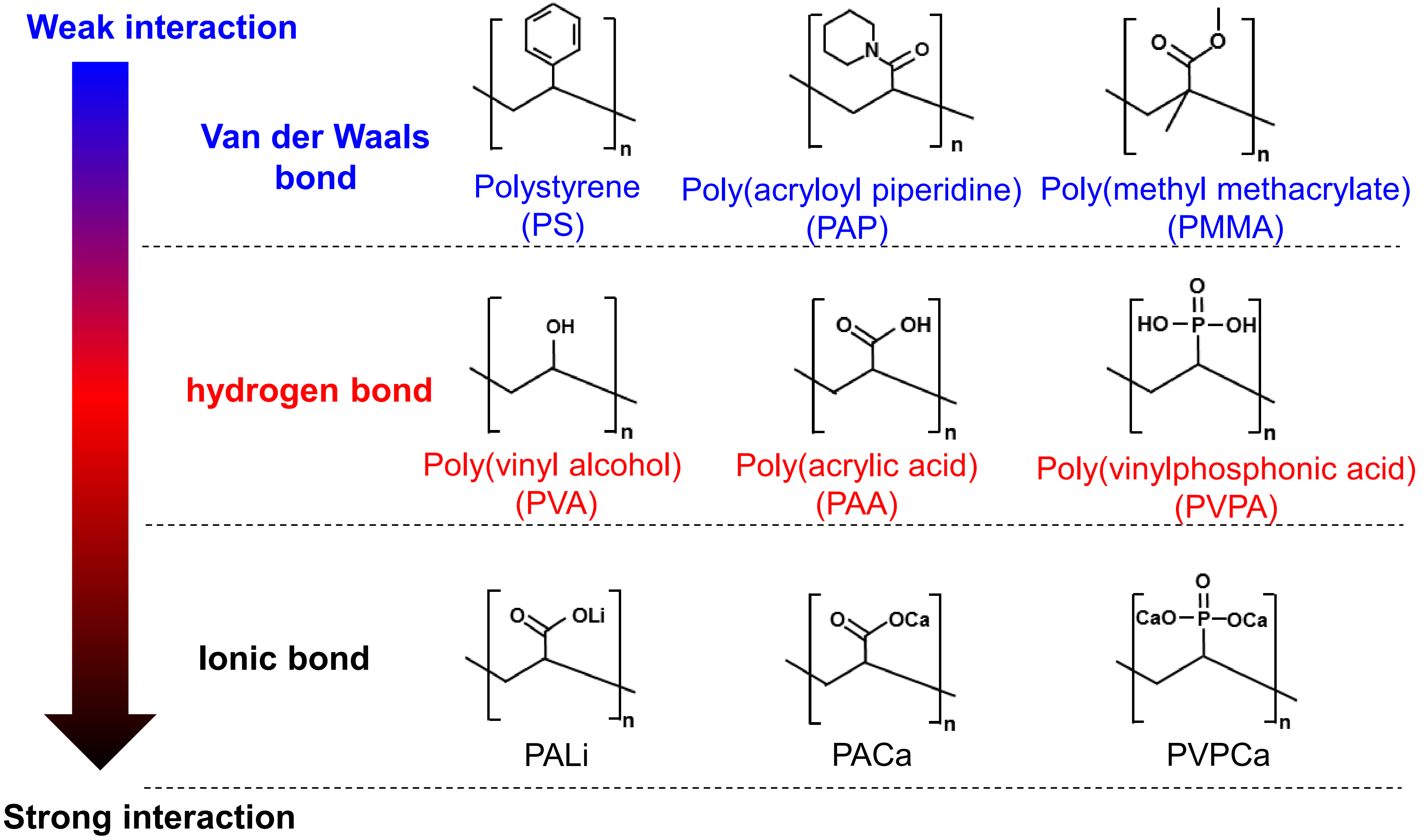
To double thermal conductivity requires a pressure of ≈5 GPA to increase the elastic modulus to C_{11}≈50 GPA





Hsieh et al, PRB (2011)

High throughput capabilities of TDTR allowed us to study many (27) molecular structures or compositions

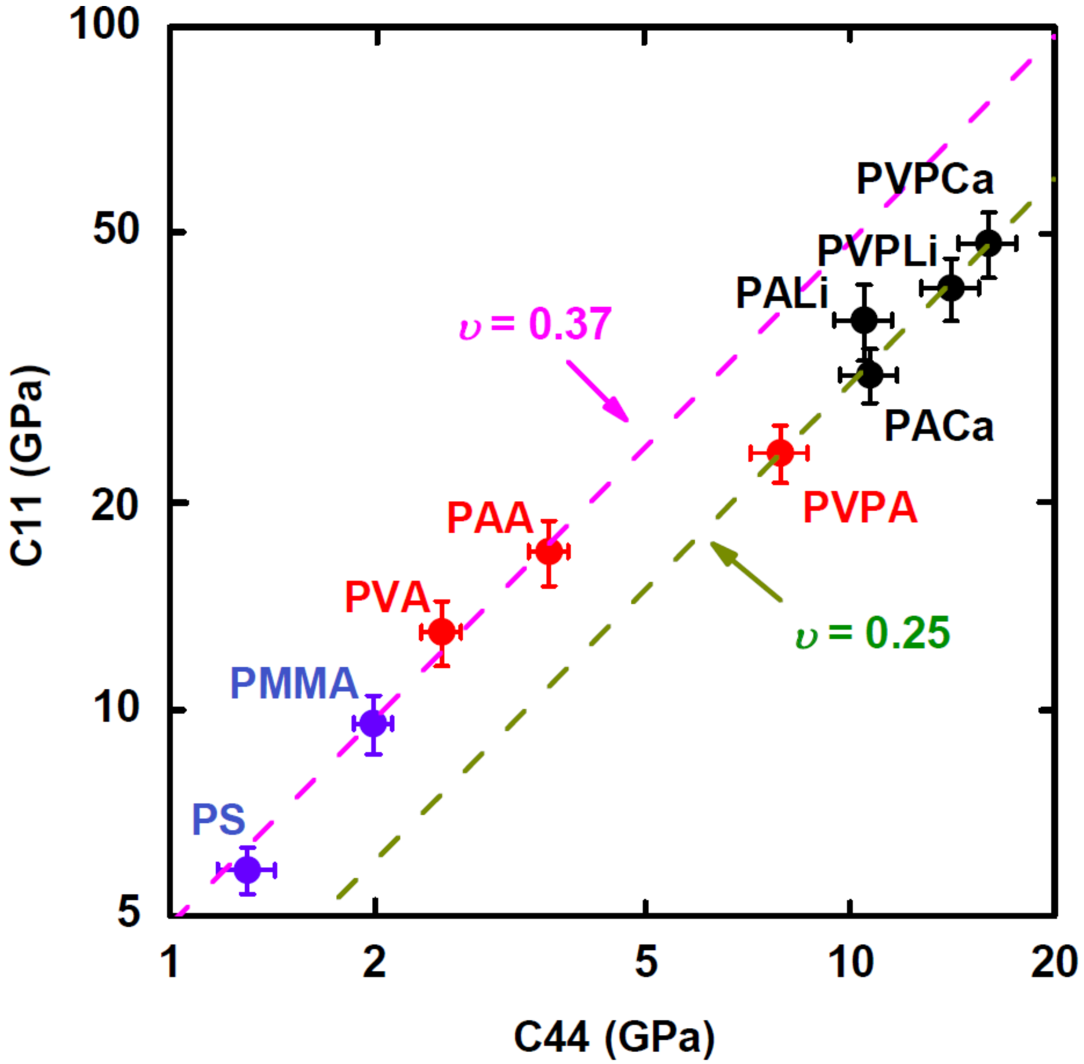


Xie *et al.*, Phys. Rev. B (2017)

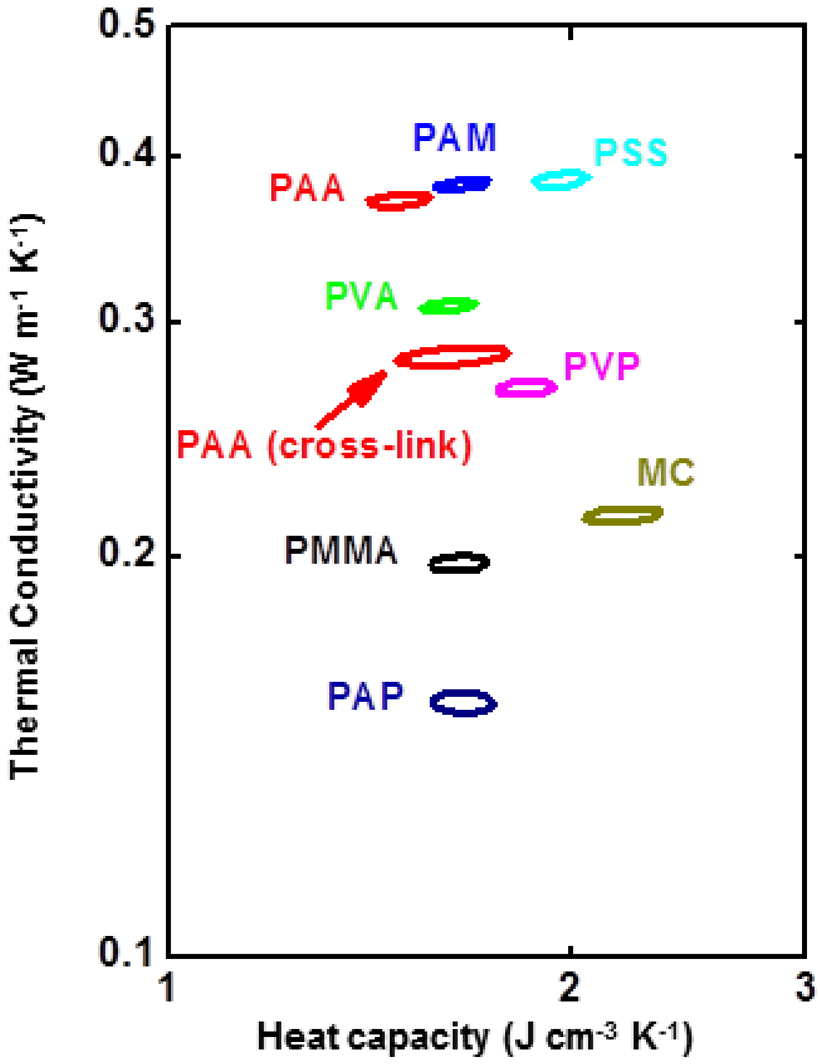
Elastic constants span an order of magnitude

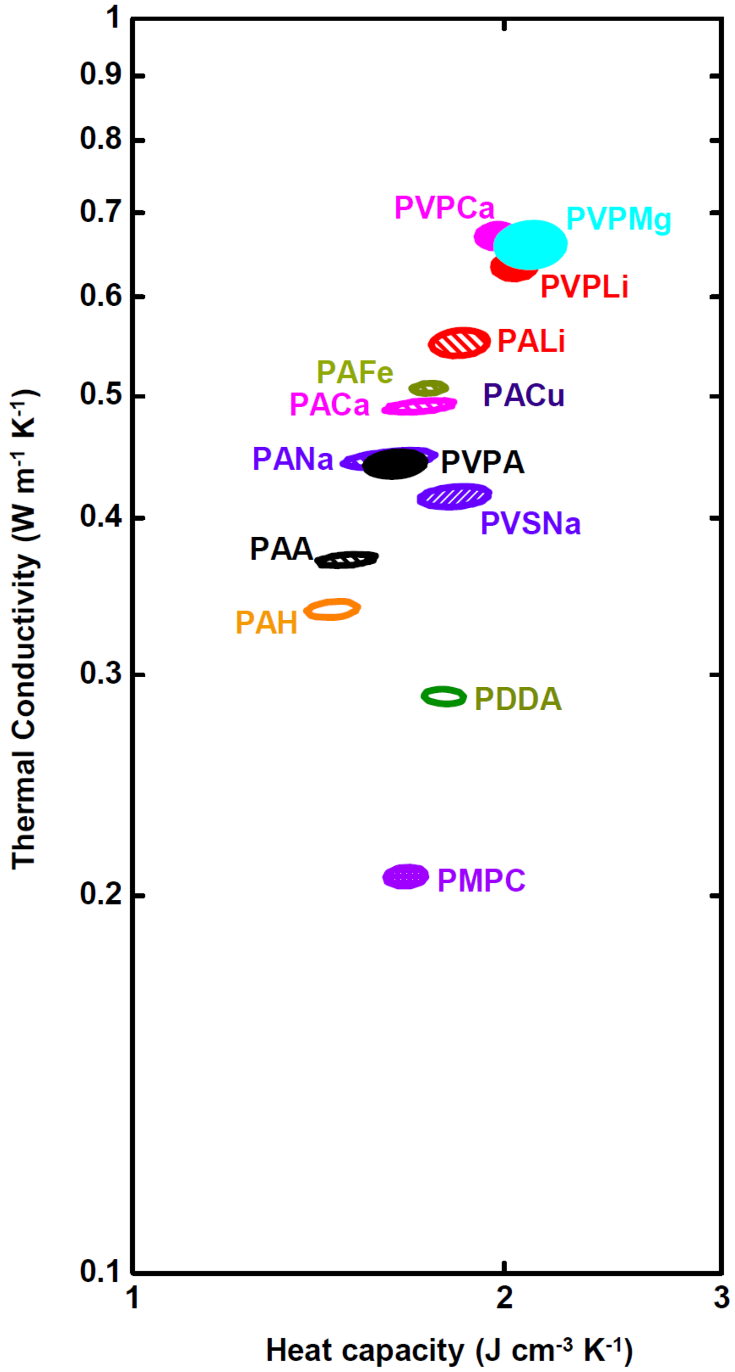
Poisson ratio ν

- 0.37 for polymers with small elastic constants.
- 0.25 for polymers with large elastic constants.



Thermal conductivities span a factor of 5

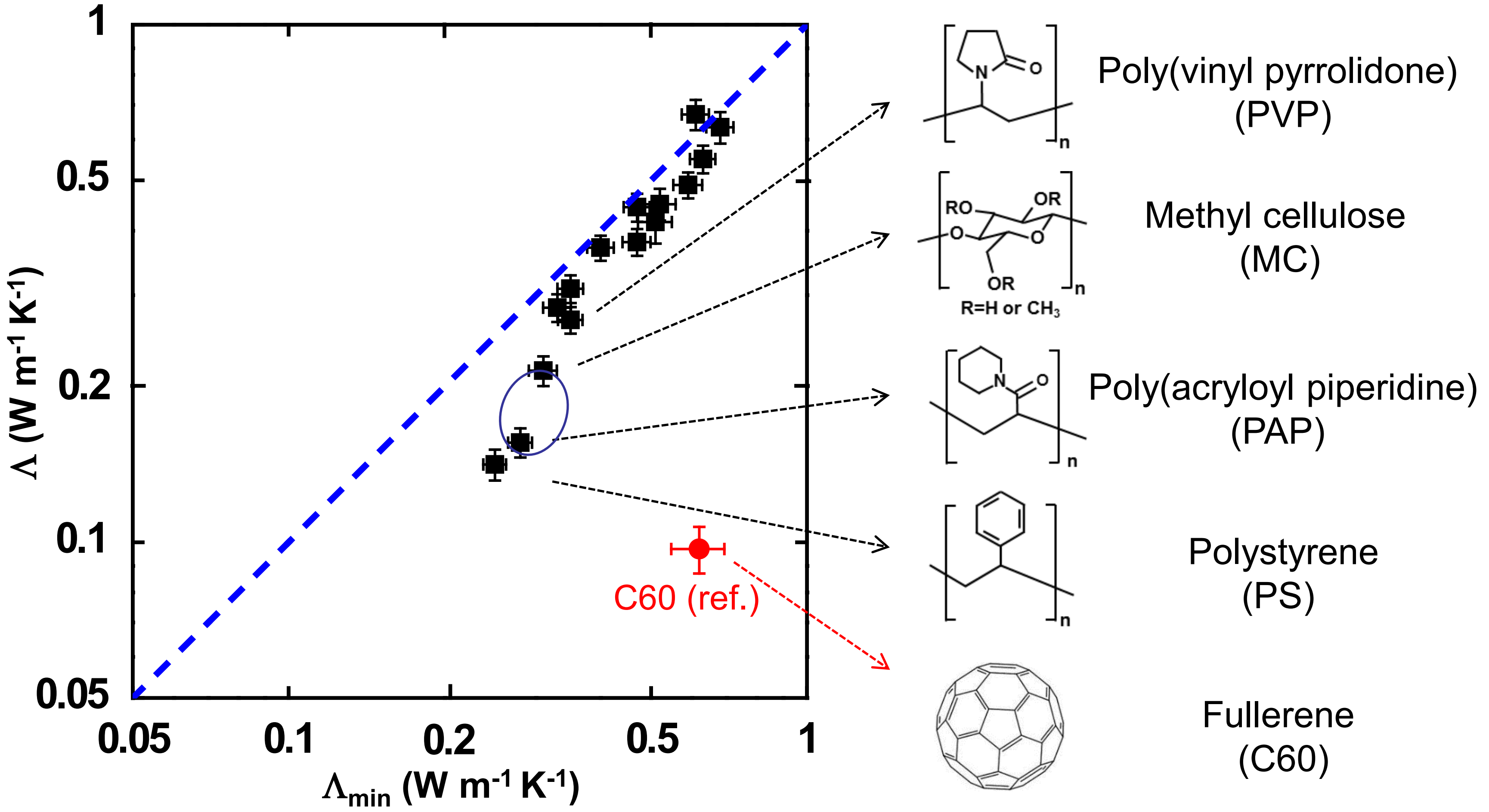




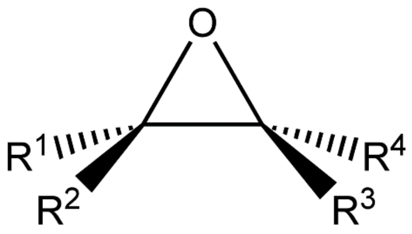
Xie *et al.*, Macromolecules (2016); PRB (2017)

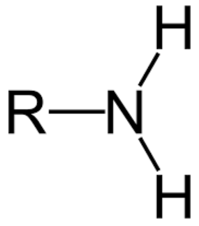
Compare to minimum thermal conductivity model by introducing a density of vibrational states $n_c = (2/3)(n - n_H)$

$$\Lambda_{\min} = \left(\frac{9\pi}{16}\right)^{1/3} k_B n_c^{2/3} \bar{V} \qquad \bar{V} = \frac{1}{3}\left(v_l + 2v_t\right)$$



Epoxies are thermosetting polymers built on the reaction between epoxide and amine functionalities.





10 G$ global annual market.

Wide range of chemical structures.

Conventional wisdom is that the thermal conductivity is 0.2 W/(m-K).

Our motivation: explore a large number of formulations and search for routes to high and low thermal conductivity within this class of economically important and easily processed polymers.

Need high throughput measurements of thermal conductivity, heat capacity, sound velocities, and density

In our previous work, we studied 100 nm thick films of polymers prepared by spin coating.

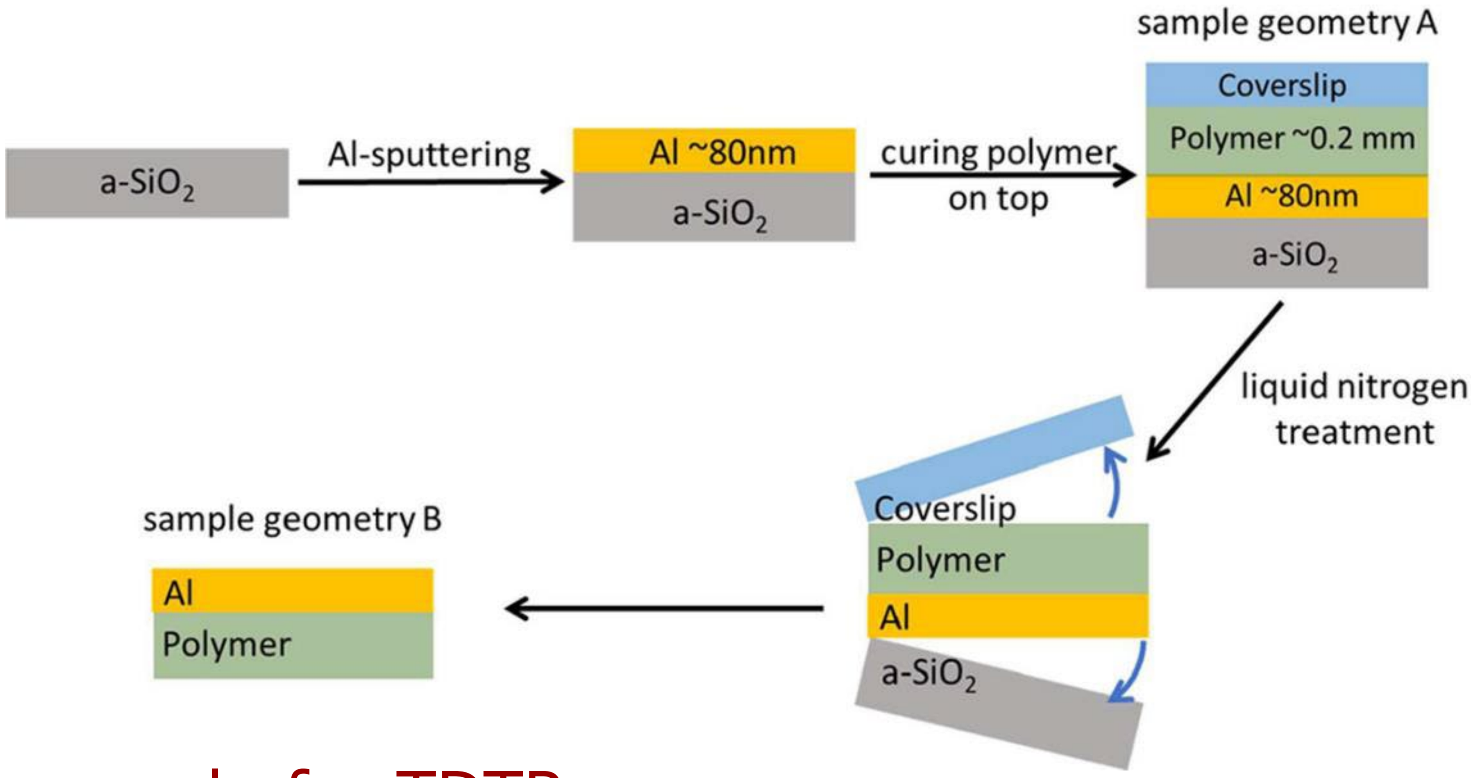
Need to be able to handle a wider variety of sample geometries.

TDTR of bulk, low thermal conductivity samples can only provide the effusivity of near surface region of the sample.

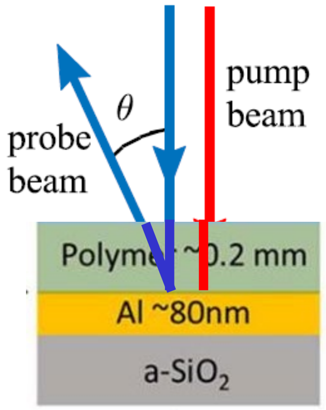
New approach of “Frequency domain probe beam deflection” that measures the thermal diffusivity of bulk transparent materials on lengths scales on the order of 10 microns.

Essentially a mirage effect method. Use gradients in the index of refraction to probe the temperature field in a transparent material.

Prepare bulk polymer samples on a-SiO_2 substrates that are precoated with Al. Separate from substrate for TDTR measurements.



sample for FD-PBD



sample for TDTR

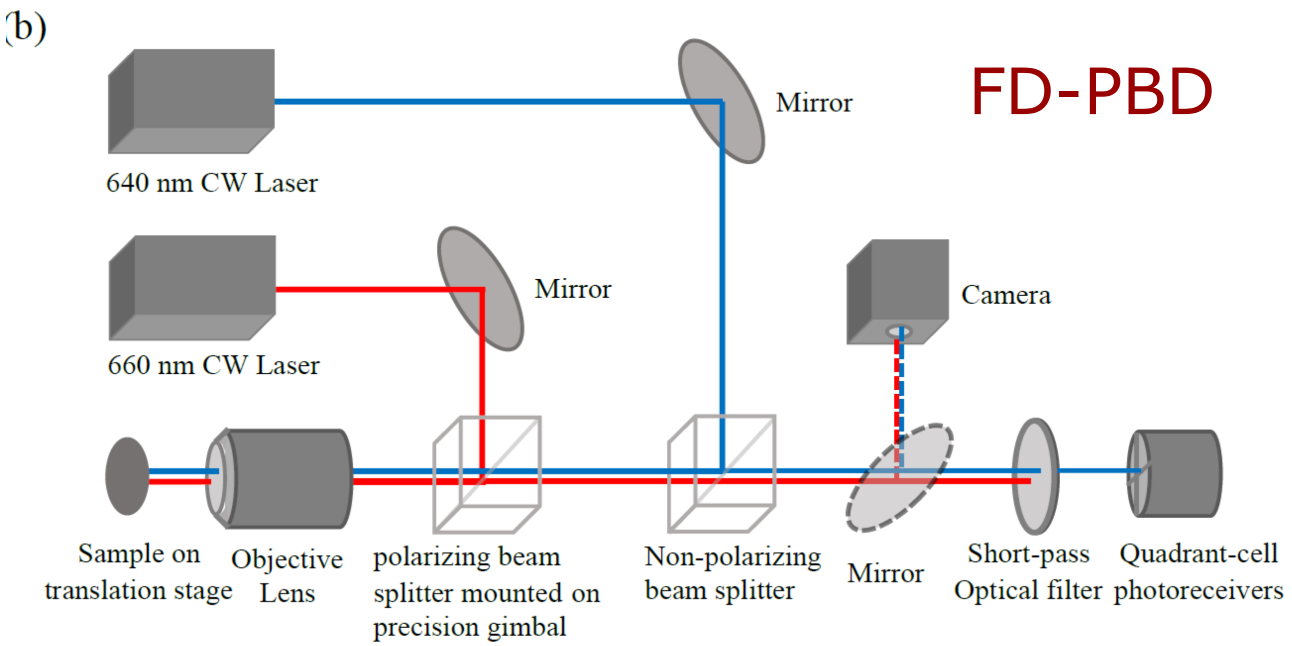
Lv et al. *ACS Applied Polymer Materials*, 2021a

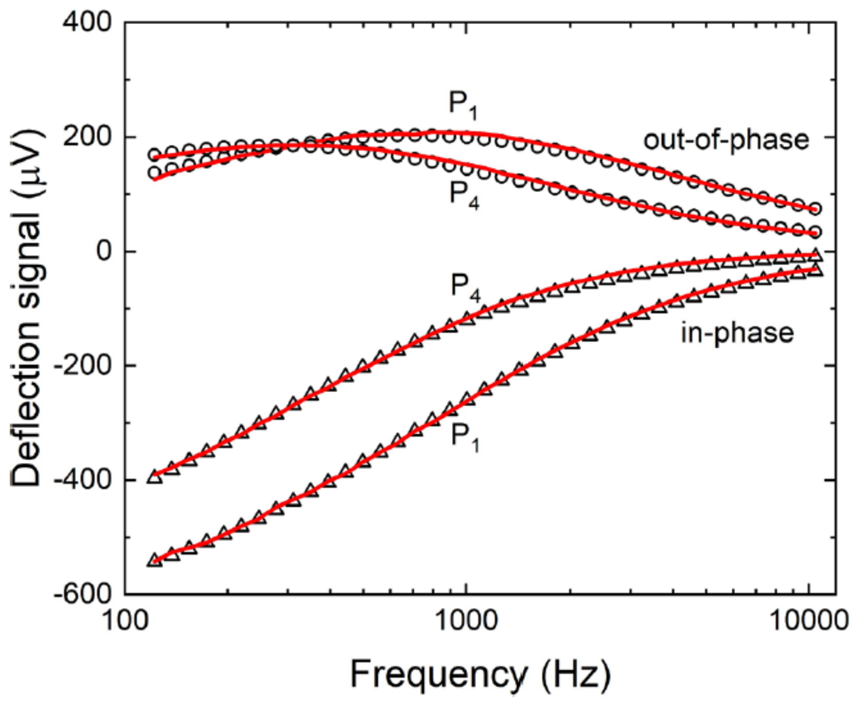
Combine frequency-domain probe beam deflection (FD-PBD), TDTR, and picosecond interferometry

FD-PBD measures thermal diffusivity.

TDTR measures thermal effusivity.

Picosecond interferometry measures C_{11}. (Index of refraction by ellipsometry and mass density measured by buoyancy.)

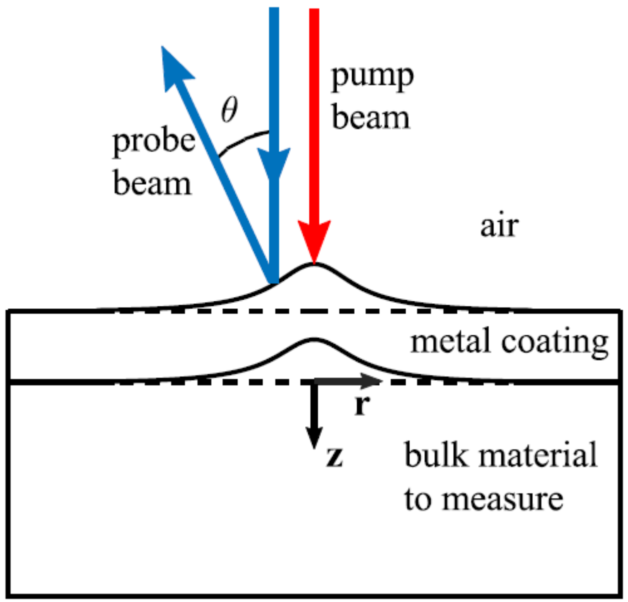


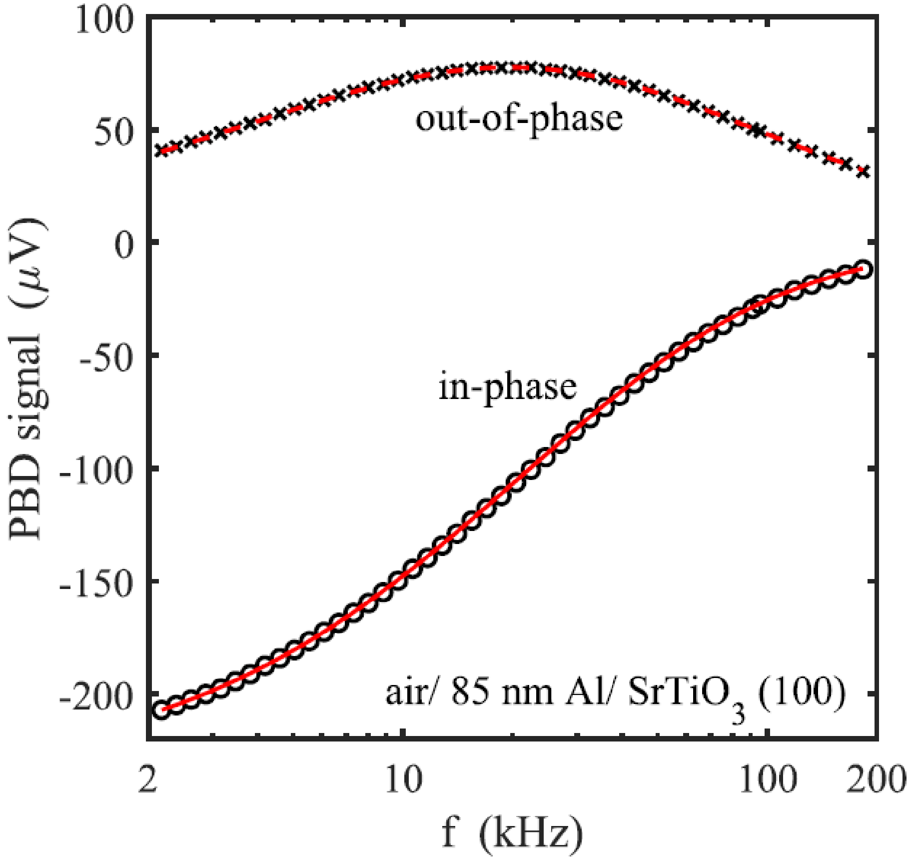


Lv et al. *ACS Applied Polymer Materials*, 2021a

Digression: recent advance in thermal diffusivity measurements by "front-side" frequency-domain probe beam deflection (fs-FD-PBD)

Beam deflection is created by the surface displacement generated by thermal expansion. Data collected by "front-side" FD-PBD has a similar appearance, signal-to-noise, and sensitivities as "back-side" FD-PBD.





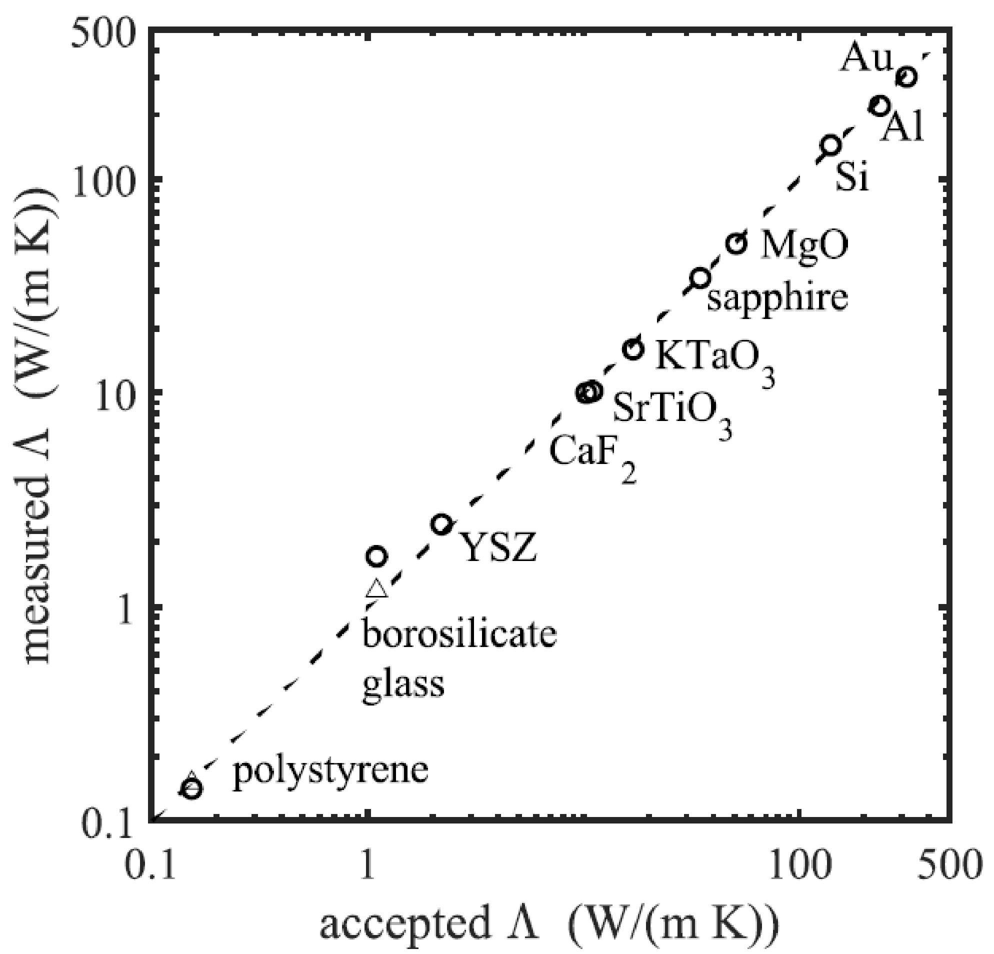
Sun et al. *submitted, arXiv:2209.08239*

Digression: recent advance in thermal diffusivity measurements by "front-side" frequency-domain probe beam deflection (fs-FD-PBD)

We only recently figured out how to solve the equations that describe the strain field that is generated by the temperature field in an anisotropic, multilayer sample (elastic constant, thermal conductivity, thermal expansion tensors)

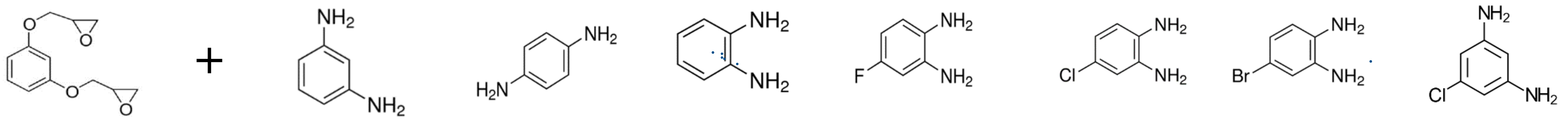
For isotropic materials, the result is insensitive to the values of the elastic constants.

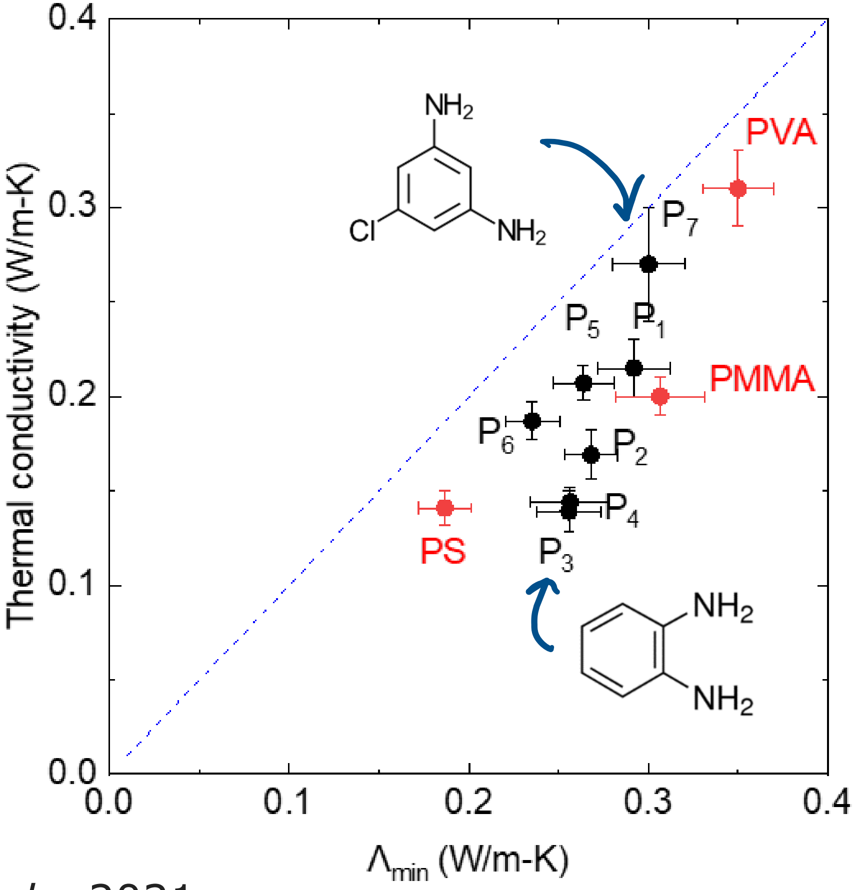
Less sensitive to surface roughness than thermoreflectance methods.



Sun et al. *submitted, arXiv:2209.08239*

On the order of 100 formulations of thermosetting epoxies studied to-date
Ia. Systematic study of phenylenediamine hardeners.

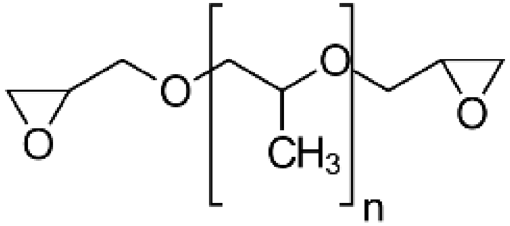




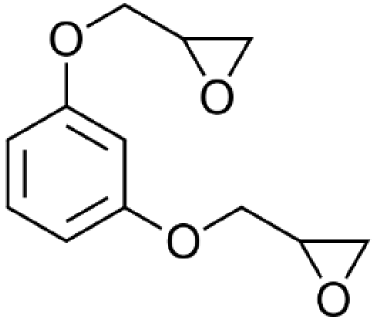
Lv et al. *ACS Applied Polymer Materials*, 2021a

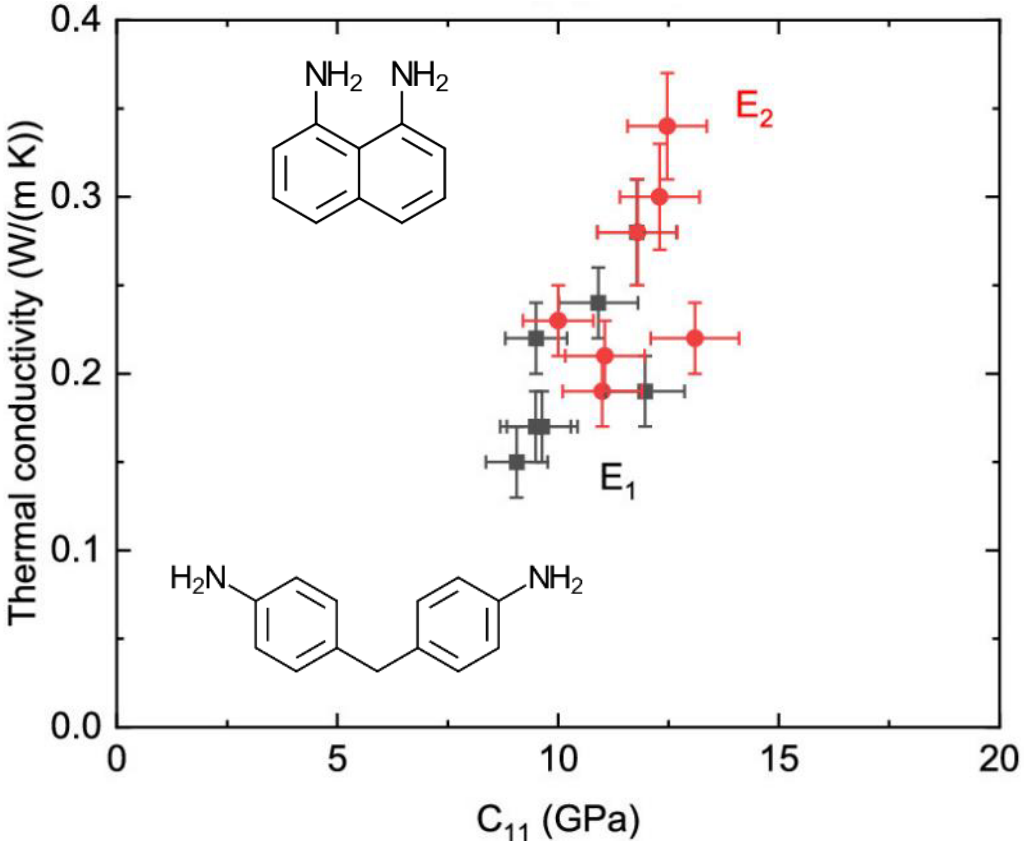
Ib. Comparison of aliphatic and aromatic monomers

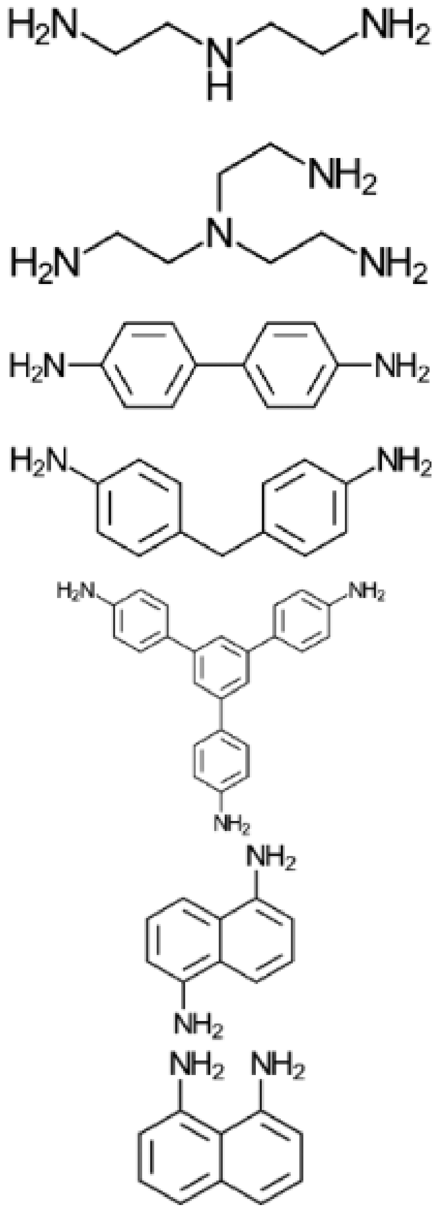
E_1



E_2

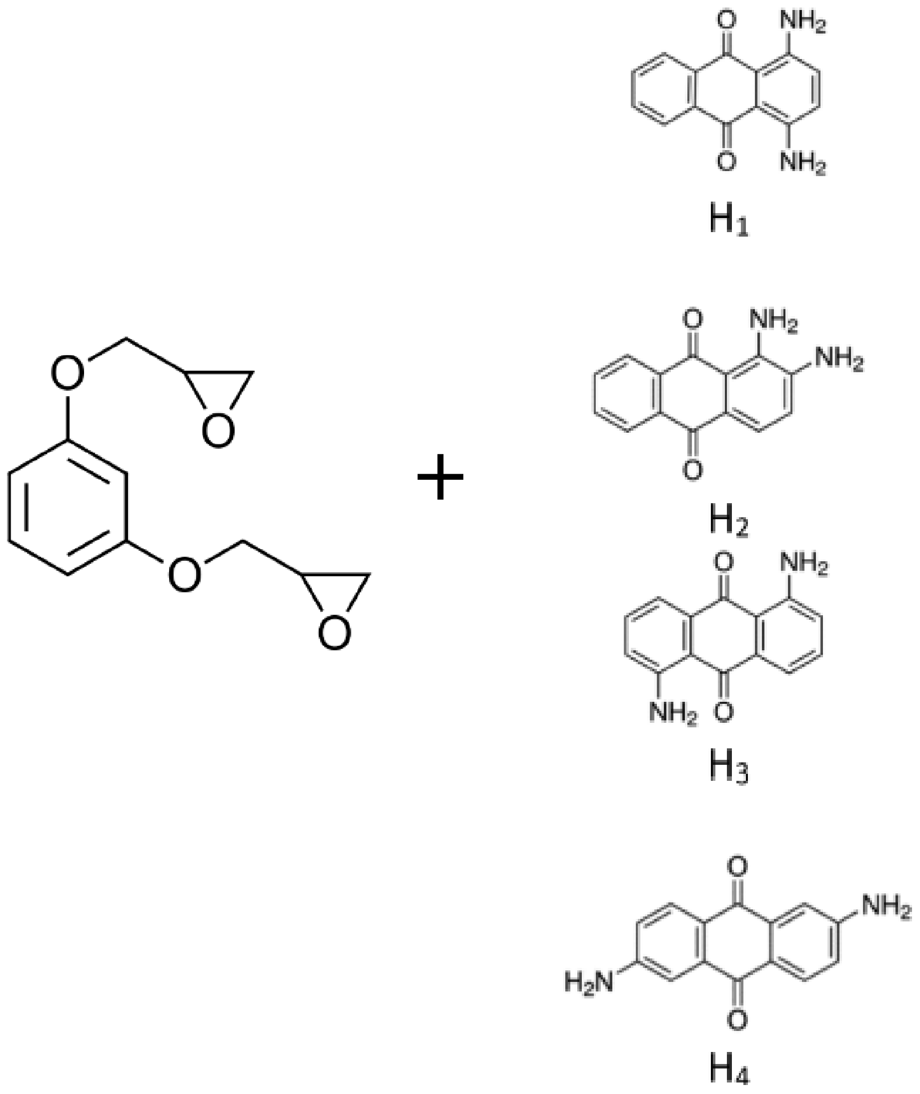




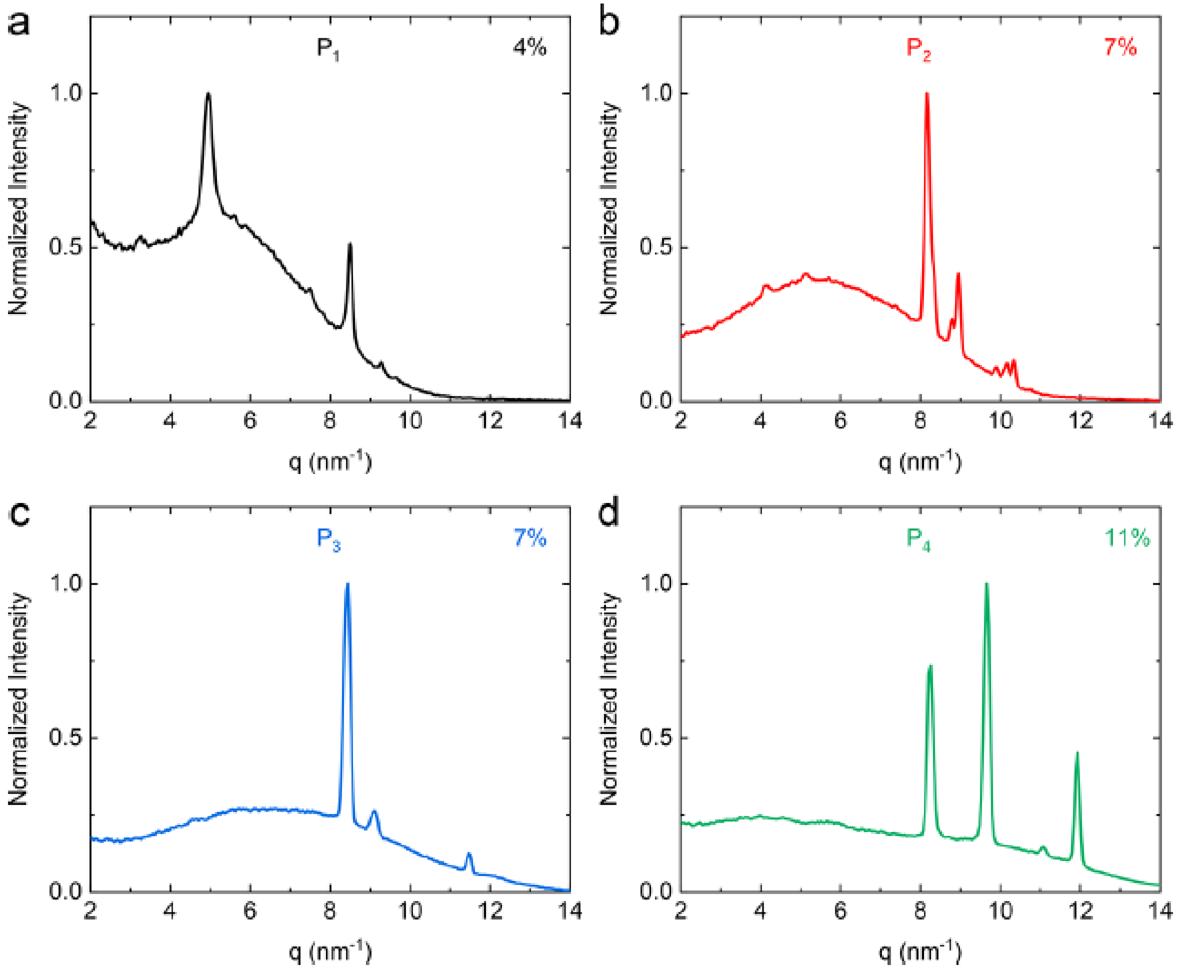


Lv et al. *ACS Applied Polymer Materials*, 2021b

Ic. If naphthalene-based diamine hardeners are good maybe anthraquinone-based hardeners are better?



Semicrystalline by x-ray diffraction



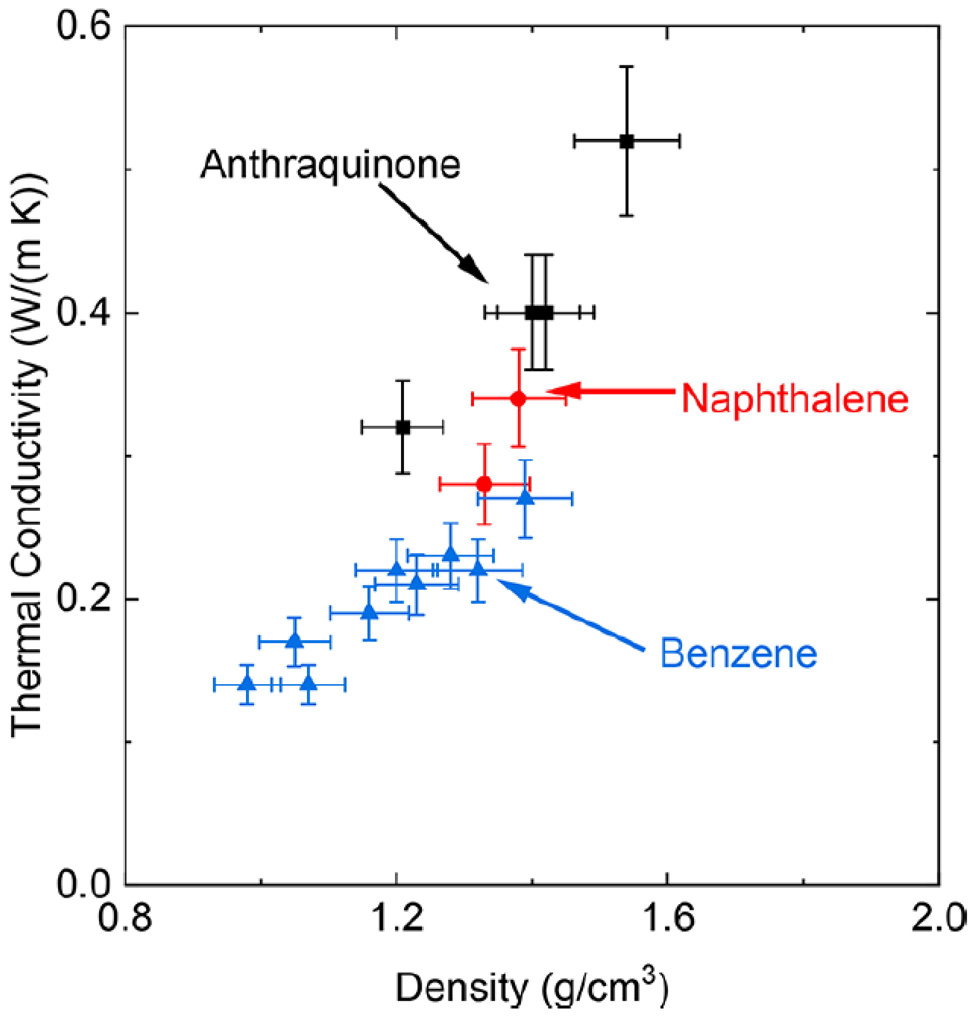
Lv et al. *ACS Applied Polymer Materials*, 2021c

I. Compare the trends in epoxies using density as the “descriptor”

Density (molecular packing) seems to be a good base-line descriptor for thermal conductivity of epoxy thermosets.

Highest densities are semicrystalline. Is crystallinity critical for producing higher thermal conductivity or does crystallinity simply provide a route for more densely packed molecules?

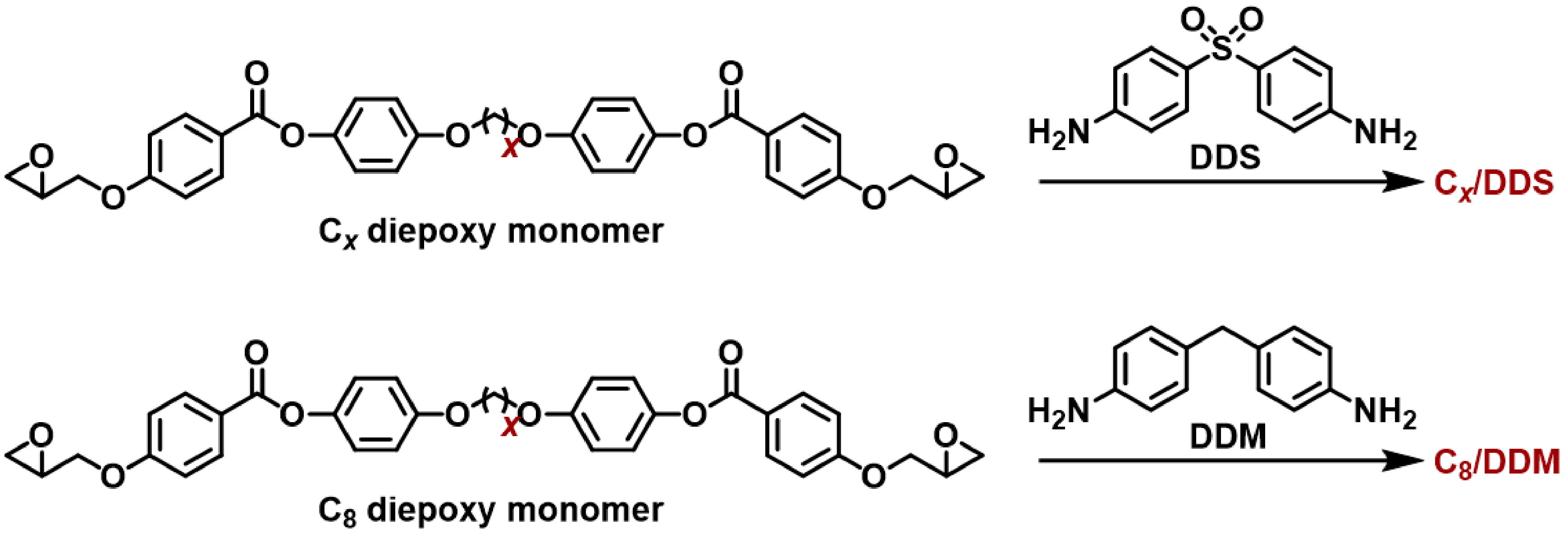
At the low end, can we decrease density further and produce ultralow thermal conductivity polymers?



Lv et al. *ACS Applied Polymer Materials*, 2021c

II. Giant odd-even effects in the thermal conductivity of liquid crystalline epoxy networks

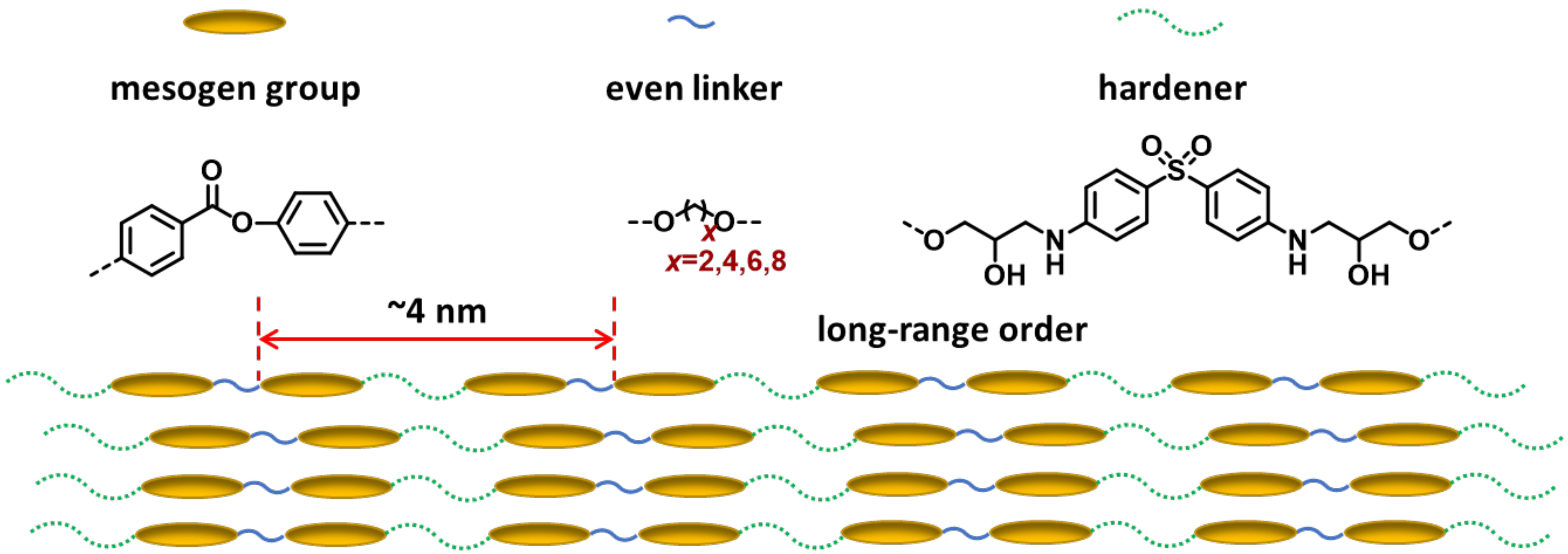
Systematically change the linker length of a twin-mesogen diepoxide monomer and form network with DDS or DDM hardeners



Lv et al. PNAS, in press.

II. Odd-even effects in liquid crystalline epoxy networks

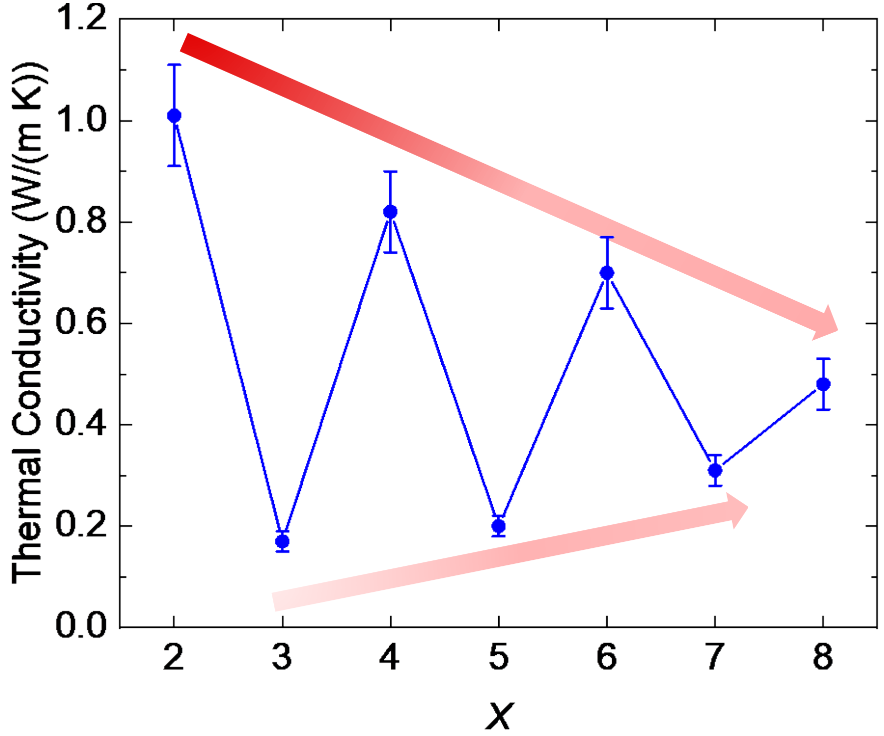
We find liquid crystalline long range order in x-ray diffraction and optical microscopy for even (x=2,4,6,8) linker lengths

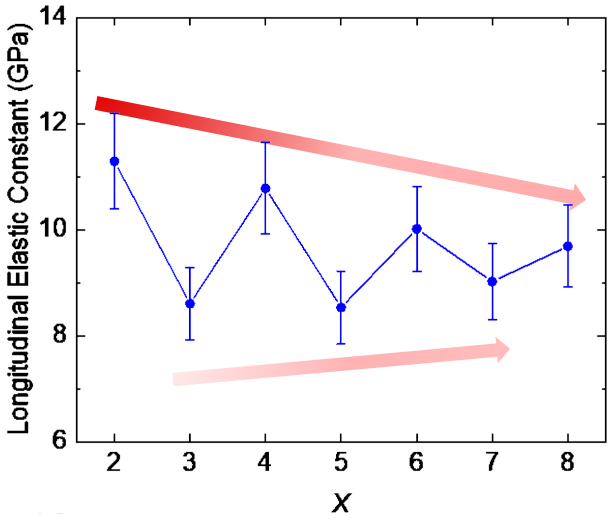


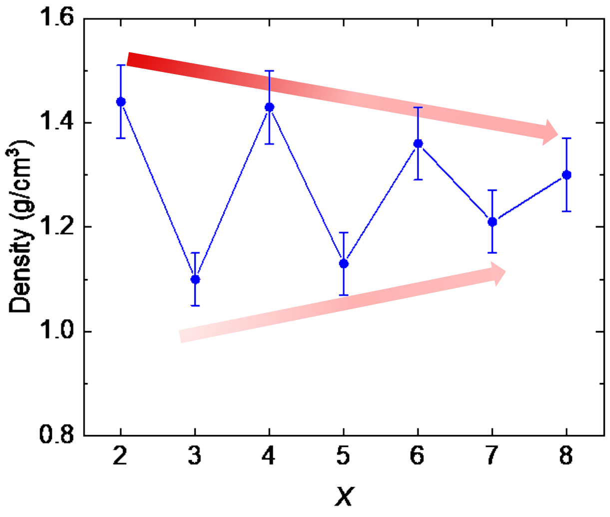
Lv et al. PNAS, in press.

II. Odd-even effects in liquid crystalline epoxy networks

Density, elastic constants and thermal conductivity. 1 W/(m-K) is the highest isotropic epoxy polymer thermal conductivity that we have measured. A change from x=2 to x=3 (one carbon atom) changes the thermal conductivity by a factor of 5







Lv et al. PNAS, in press.

Final topic: Thermally functional materials

- Passive function

  Thermal regulator: abrupt increase in thermal conductivity with increasing temperature.

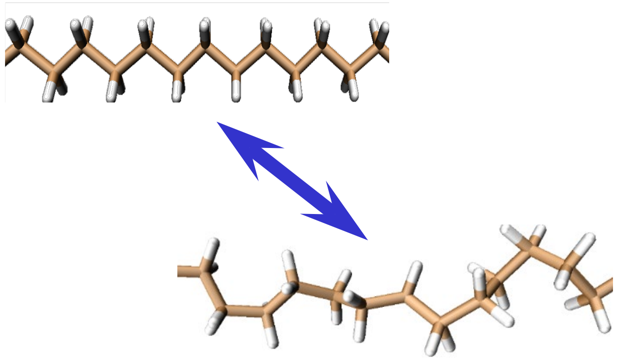
  Combine materials with positive and negative changes in thermal conductivity to form effective thermal rectifiers.

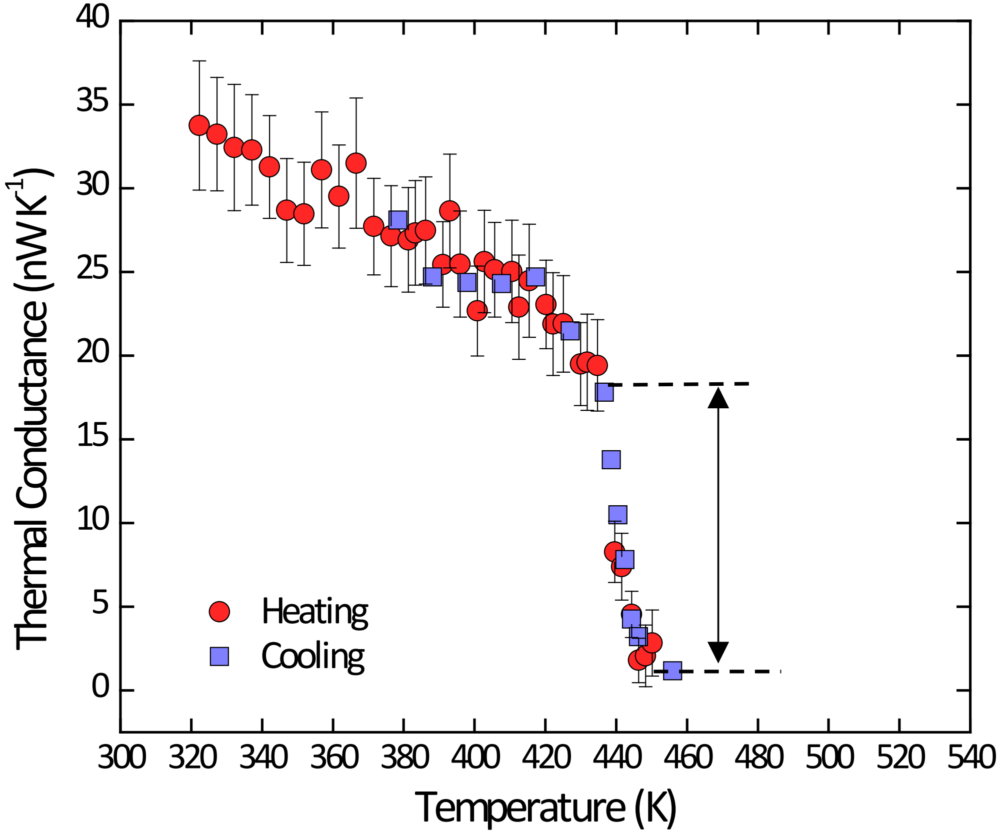
- Active function

  Thermal switch: thermal conductivity changes with application of external field or stimulus.

Abrupt x10 reversible drop in thermal conductivity of crystalline polyethylene at an order disorder transition.

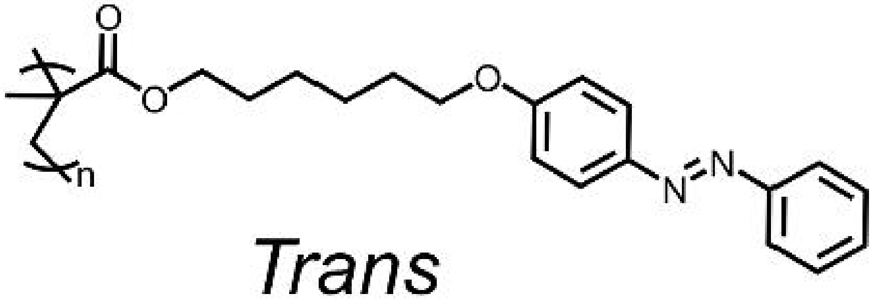
Shrestha, Shen (CMU) and co-workers *Science Advances* (2019)

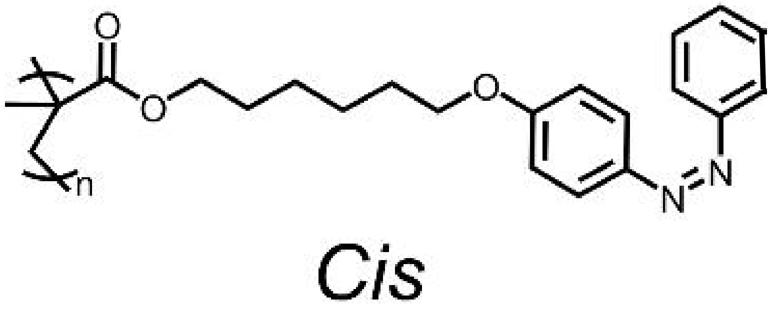




Light-activated isomerization (azo-polymer)

- UV light converts *trans* to *cis* conformation
- Visible light (or thermal relaxation to equilibrium) converts *cis* to *trans*



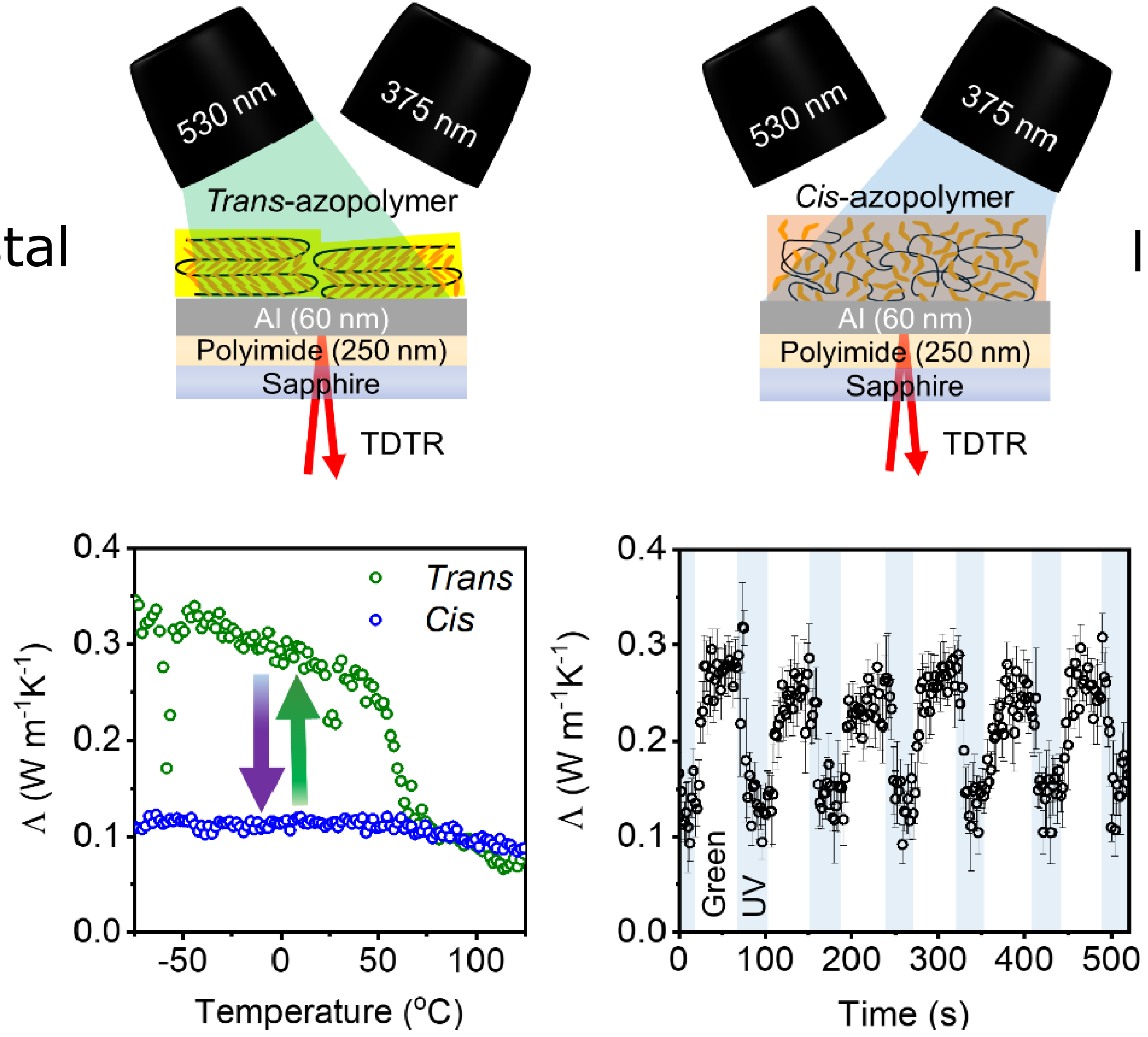


Shin, *PNAS* (2019)

see also work by Junko Morikawa’s group at Tokyo Tech, APL 2015, where azo-dendrimers were used to switch conventional liquid-crystals

Light-activated isomerization (azo-polymer)

crystal



liquid

Shin, *PNAS* (2019)

Concluding comments

Efficient methods for measuring thermal conductivity, heat capacity, density, and GHz frequency elastic constants of polymers.

The phase space of commercially available molecular structures is large but sometimes we need synthesis to systematically explore structure/property relationships. Synthesis is the rate-limiting step.

Can we exceed 1 W/(m-K) in isotropic, easily processed polymers?

Can we go below 0.14 W/(m-K)?

Can we find materials with switchable thermal conductivity with high contrast?