SAND2011-5572C

Thermal conductance behavior of self-assembled lamellar block copolymer thin films

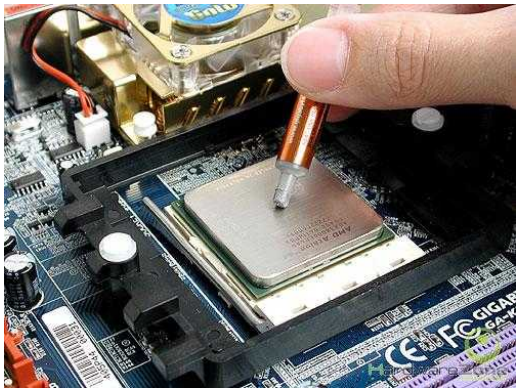
Matthew C. George, Mark A. Rodriguez, Michael S. Kent, Patrick E. Hopkins

A portion of this work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

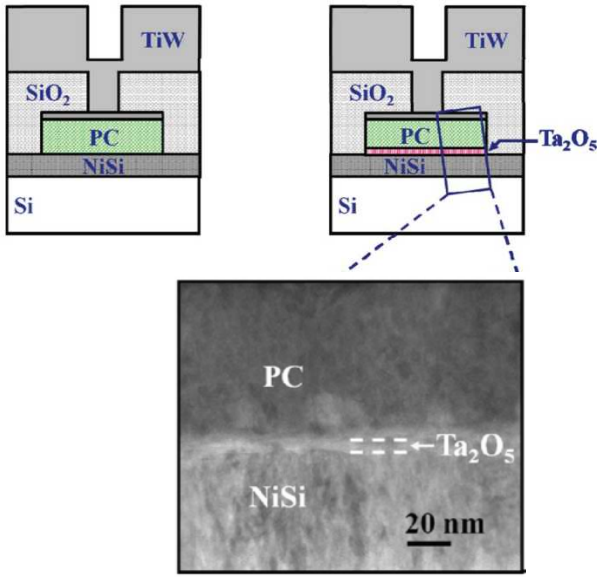
Towards nano-scale control of thermal transport

Importance:

- Integrated circuit thermal management
  - encapsulants for electronic packaging
  - thermal interface materials
  - transition to 3D stacked chip and optical interconnects
- Efficiency of switching in phase change memories
- Thermoelectrics (low-dimensional systems, multiphase nanocomposites)

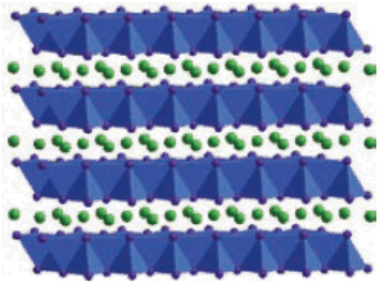


PC-RAM with low *k* inner-layer



J. Vac. Sci. Technol. B, **29**, pp. 032207 (2011);

Decoupling electron and phonon transport in thermoelectrics



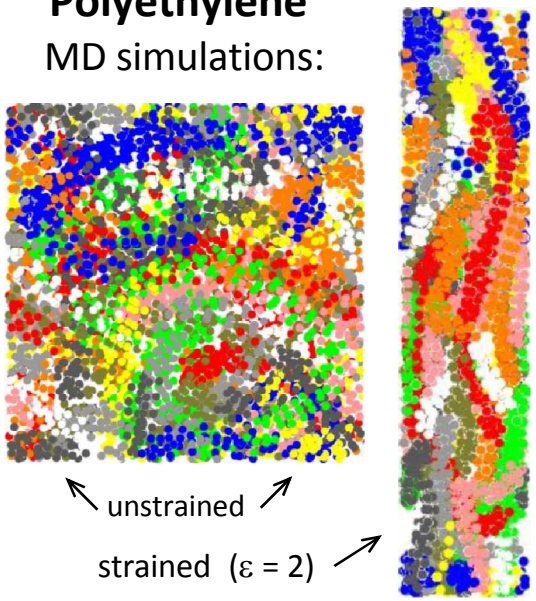
Layered structures of ordered polyhedra separated by disordered cations for electron-crystal / phonon-glass structures.

Nature Materials, **7**, pp.105-14 (2008)

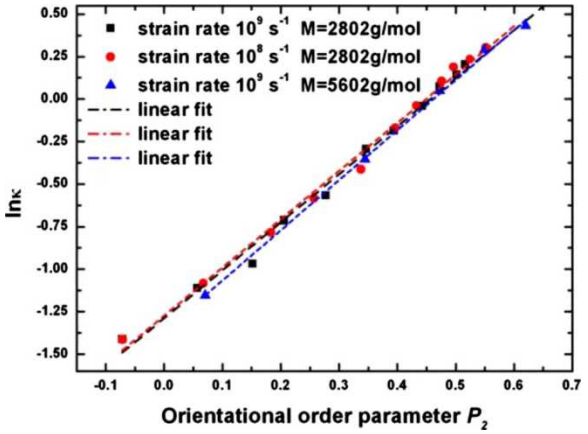
Tuning thermal conductivity of polymers via chain alignment

Polyethylene

MD simulations:



>5-fold increase in κ



Phys. Rev. B, **81**, pp.174122 (2010)

Polyethylene

Ultradrawn micro and nano-fibers: 120- to 300-fold increase in in κ

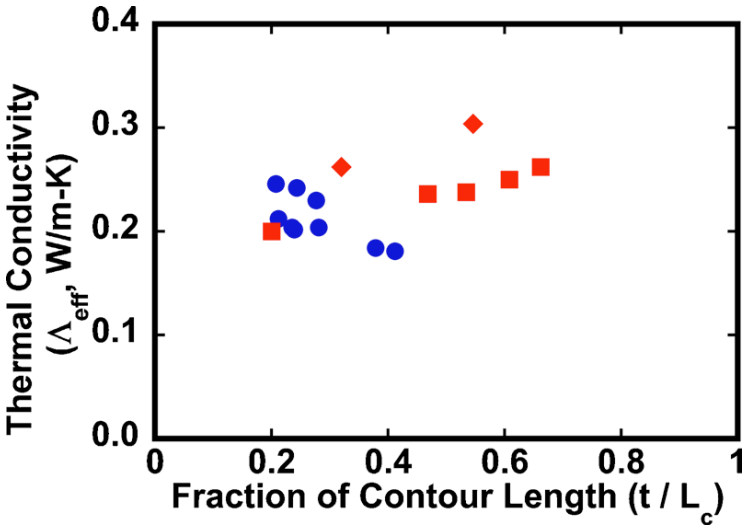
J. Polymer Sci. Pt. B, **37**, pp.3359–67 (1999) and *Nature Nanotech.,* **5**, pp.251-55 (2010)

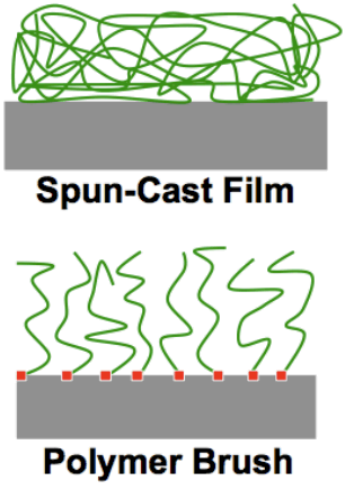
Theoretical predictions of κ for individual polyethylene chain: 350 W/(m·K) or even divergent

Nature Nanotech., **5**, pp.251-55 (2010) and *Phys. Rev. B,* **79**, pp.144305 (2009)

Poly(methyl methacrylate)

Up to 50% increase in κ for PMMA fibers with draw ratio of 4.
Only modest increase in κ for polymer brush samples.



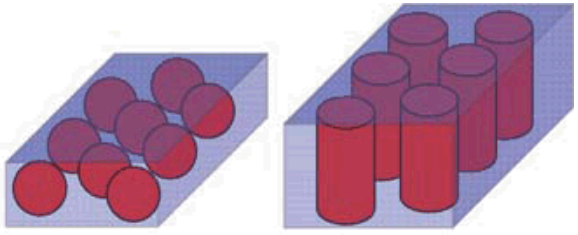


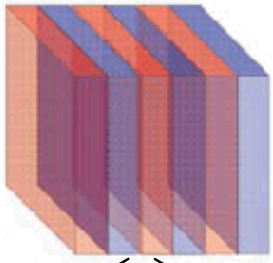
App. Physics Lett., **97**, pp. 011908 (2010)

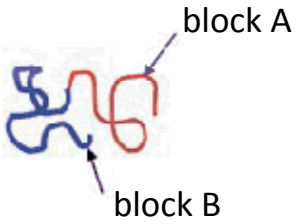
Self-Assembly of Block Copolymers

<u>diblock copolymer:</u> two immiscible polymer blocks covalently bonded together

- periodicity depends on polymer molecule length
- morphology depends on the volume fraction of each block
- equilibrium phases include periodic structures composed of lamellae, cylinders, spheres, and gyroids
- our block copolymer choice: symmetric polystyrene-b-PMMA

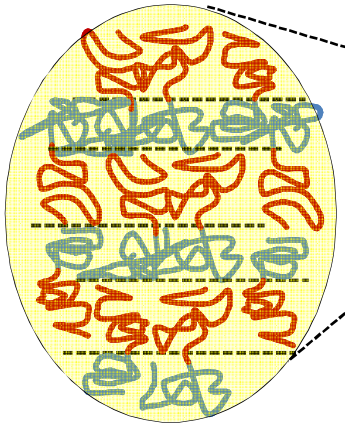


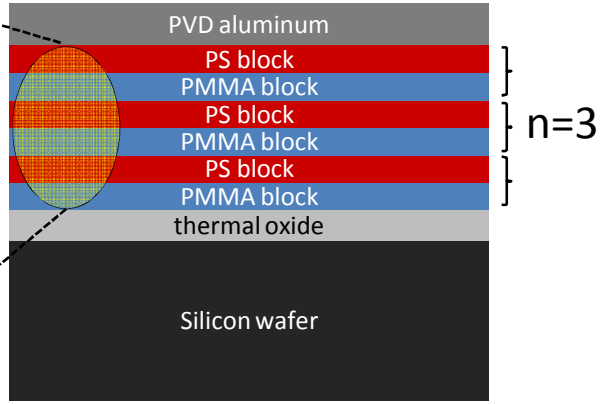


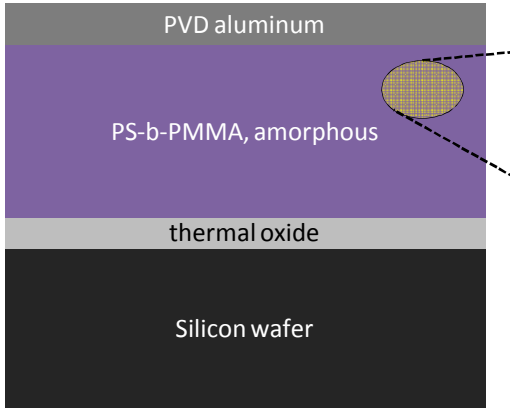


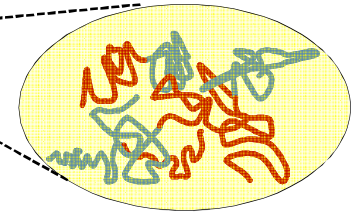
Mat. Res. Soc. Bull., **33**, pp. 838 (2008)

L_o (lamellar period)



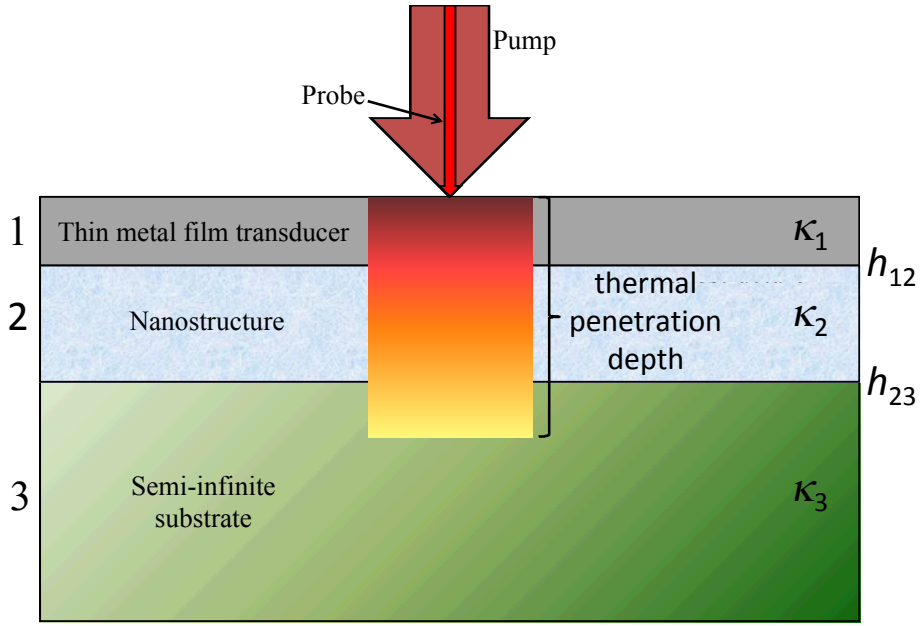


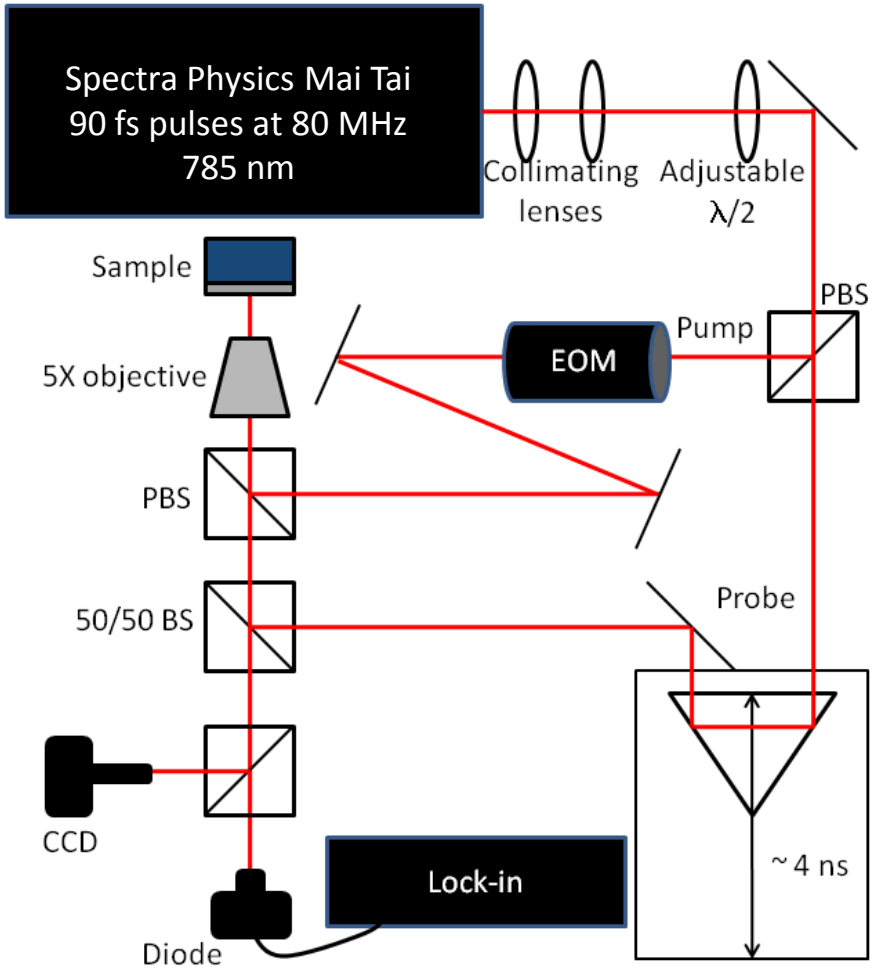




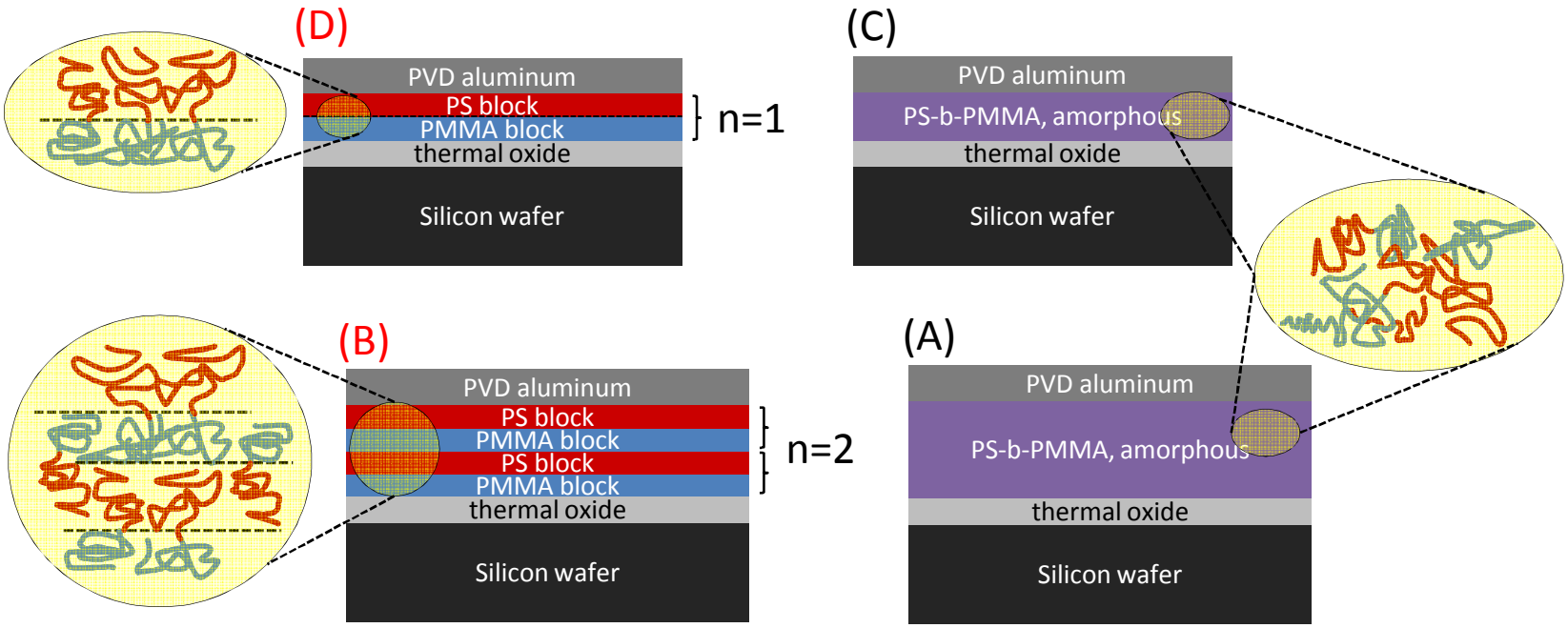
Time-domain thermoreflectance (TDTR)

- Can measure thermal conductivity of thin films (κ) and thermal boundary conductance between films (h)
- Nanometer axial spatial resolution (~10's of nm)
- Femtosecond to nanosecond temporal resolution
- Noncontact





Film properties for initial study



Sample number	thickness* [nm]	expected # of periods (n)	expected lamellar period	M_n of each block [g/mol]	spin-coating speed [rpm]	spin-coating conc. [wt. %]	spin-coat solvent	anneal hold Temp. [°C}	anneal hold time [hr]
A	55	disordered	--	18k	4250	1.5	toluene	n/a	n/a
B	55	2	27.5	18k	4250	1.5	toluene	230	16
C	26	disordered	--	18k	4250b	0.75	toluene	n/a	n/a
D	26	1	26	18k	4250b	0.75	toluene	230	16

* from single wavelength ellipsometry

If the annealed samples (B and D) have good lamellar ordering, they should have the following layered structural form: Silicon//*31.4 nm thick* thermal oxide {//13.75 *nm thick* poly(methyl methacrylate)//*13.75 nm thick* poly(styrene)}$_n$ //air

Thermal conductivity of disordered and self-assembled lamellar PS-b-PMMA films vs. thin homopolymer films / polymer brushes.

Bulk thermal conductivity for individual homopolymers = 0.17 and 0.20 $Wm^{-1}K^{-1}$ for PS and PMMA

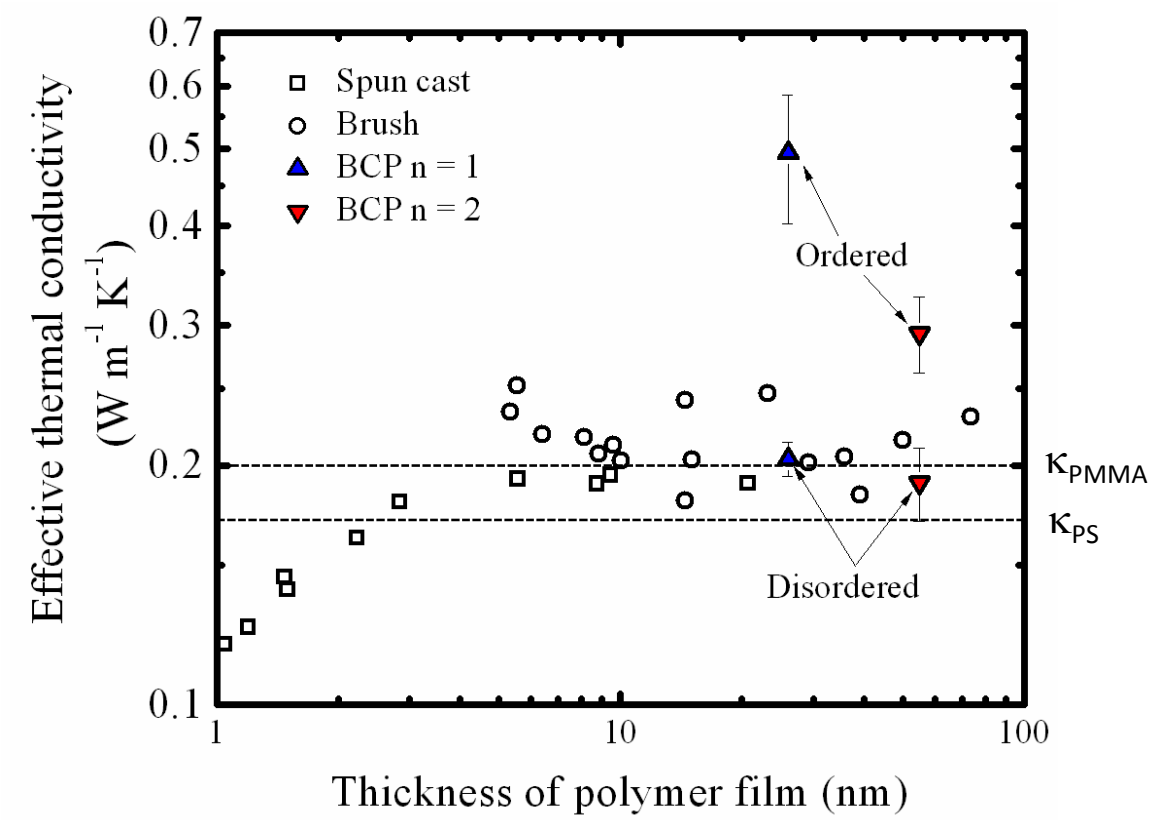
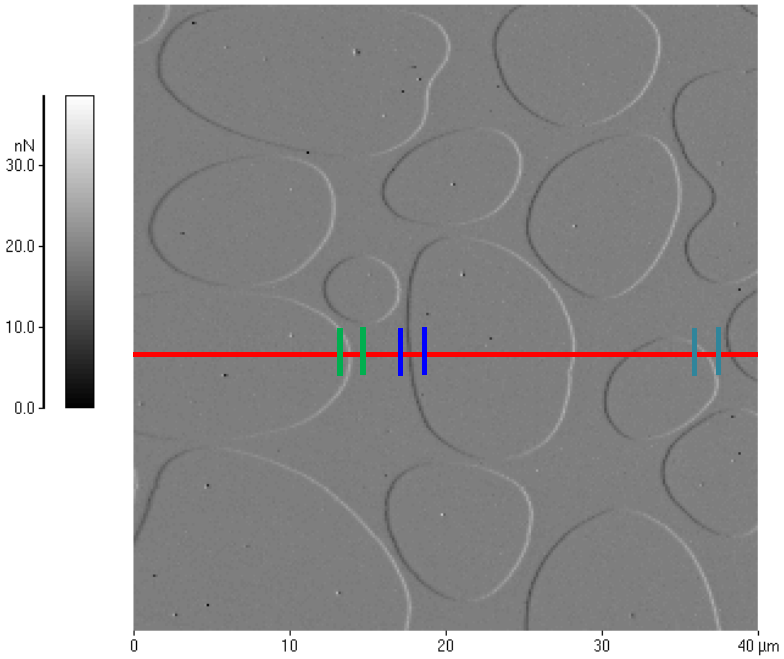


Figure 2 Thermal conductivity of our block copolymer (bcp) films compared to that of spun-cast PMMA films and polymer brushes†. The ordered films exhibit a higher thermal conductivity than the disordered films, spun-cast films, and brushes.

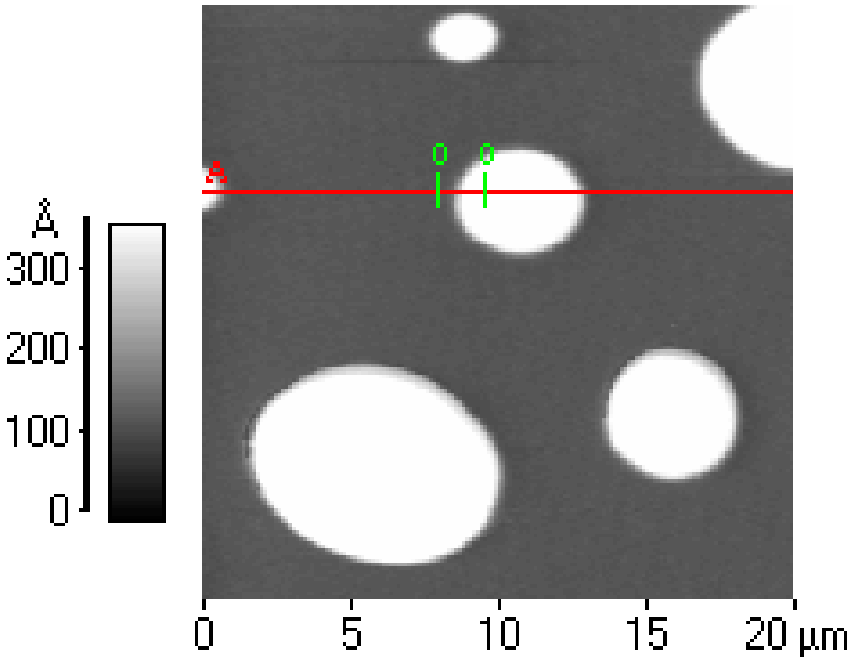
† *Appl. Phys. Lett.*, **97**, pp.011908 (2010).

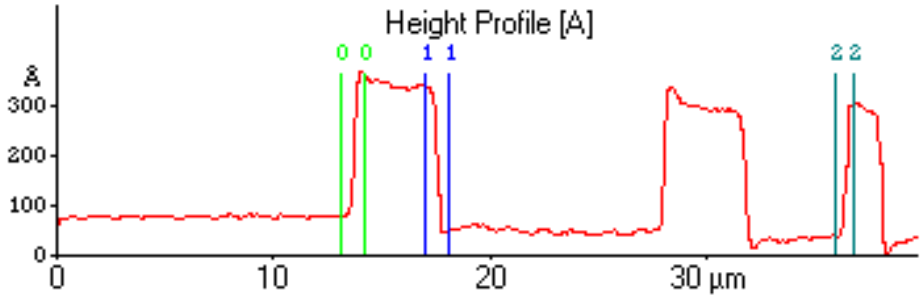
AFM: annealed films with n = integer have terraced structure

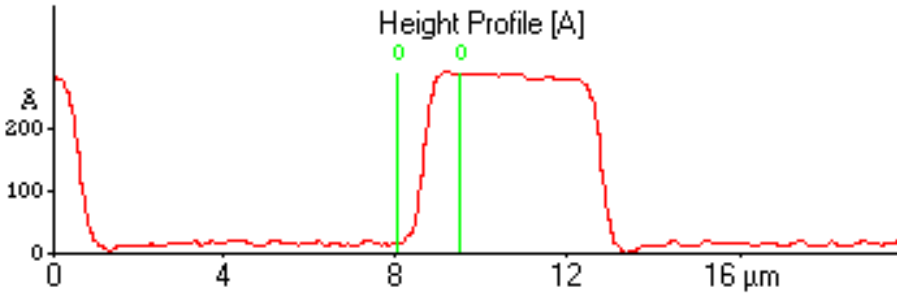
AFM Error Signal image, n = 1



AFM Topography image, n = 3







Step heights: 28.2nm 28.4nm 27.2nm 27.7nm

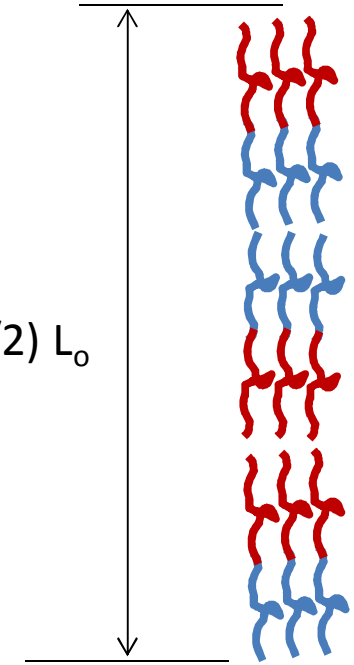
Surface Segregation Drives terracing

t_i = *initial film thickness*

t_i = n L_o

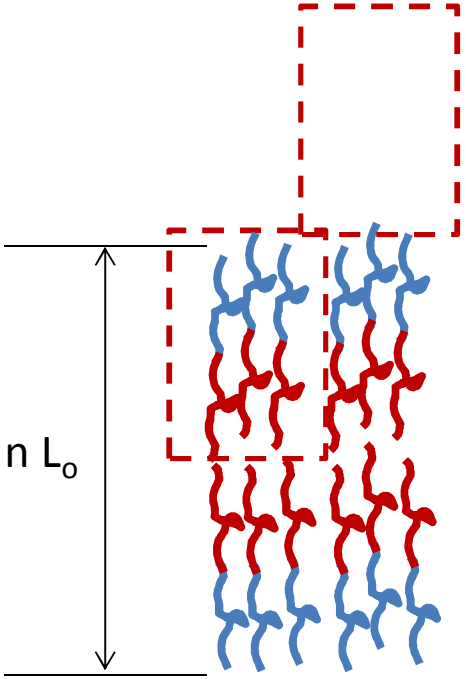
symmetric wetting

t_i = (n+1/2) L_o

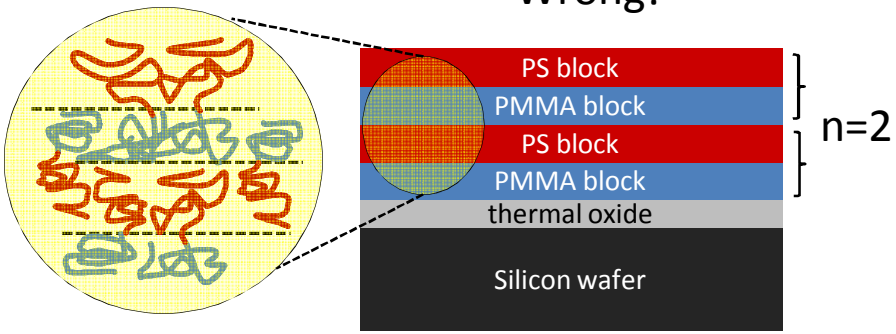


asymmetric wetting

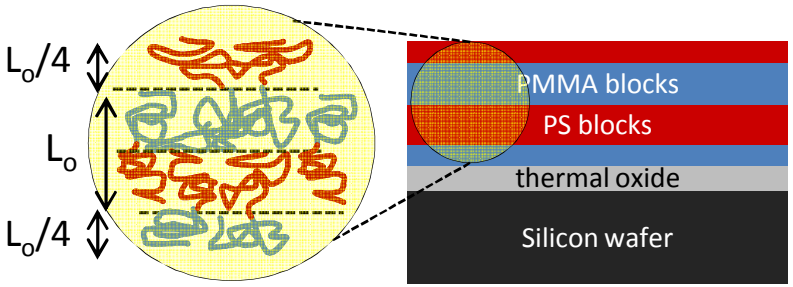
t_i = n L_o



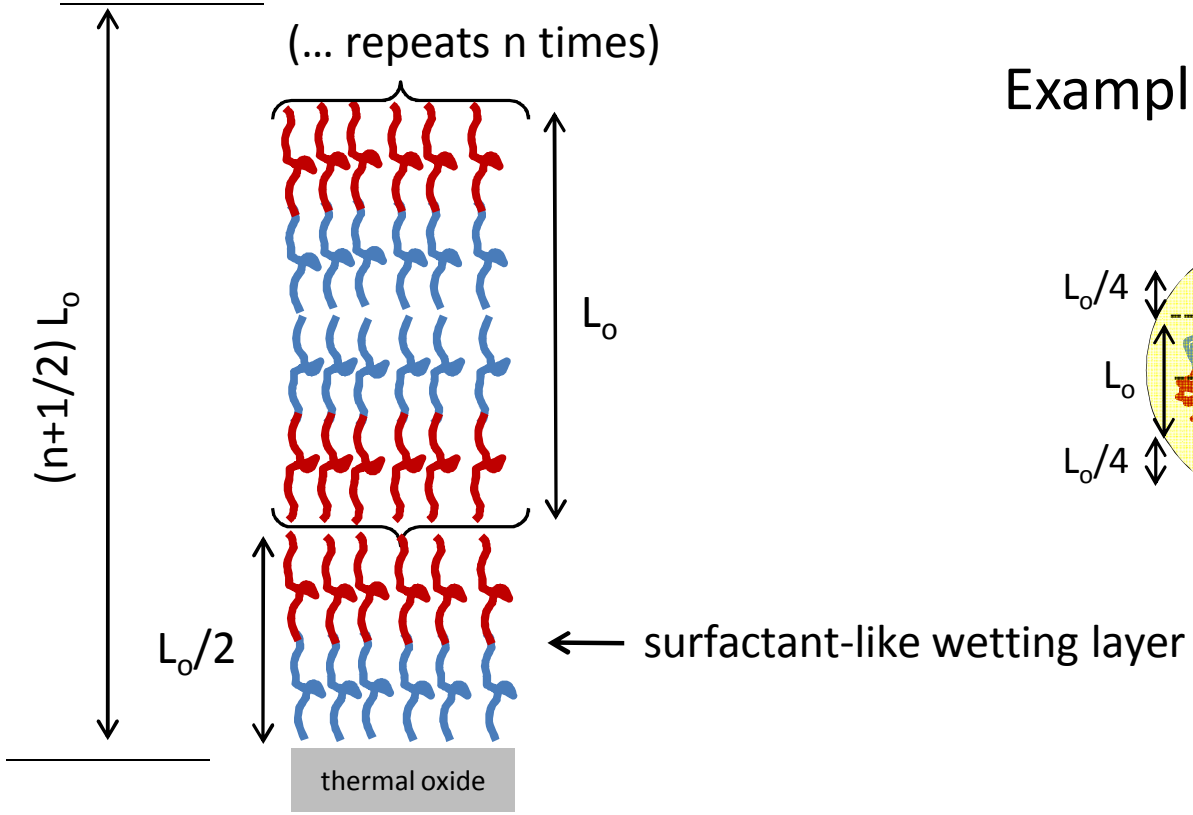
Wrong!



correct (n = 1.5)

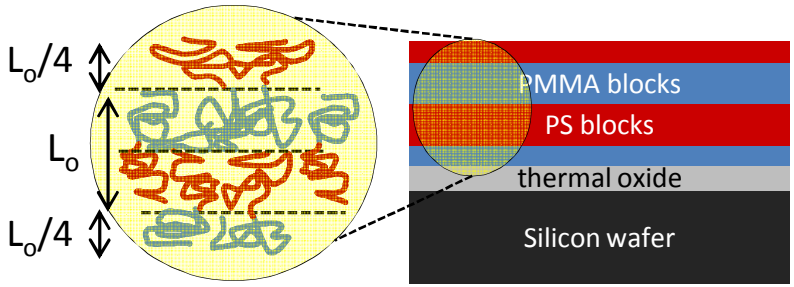


Block copolymer asymmetric wetting condition



Example cases:

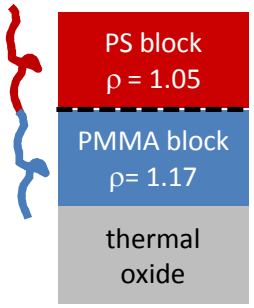
(n = 1.5)

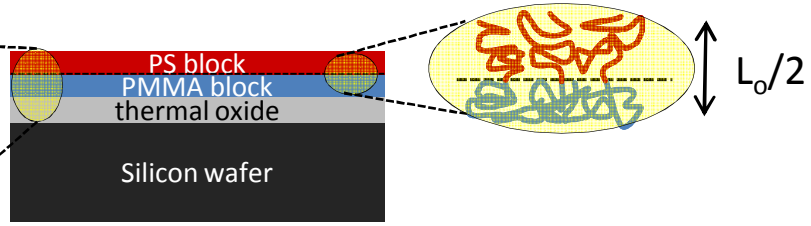


(n = 0.5)

Legend:

chain alignment near the block interface

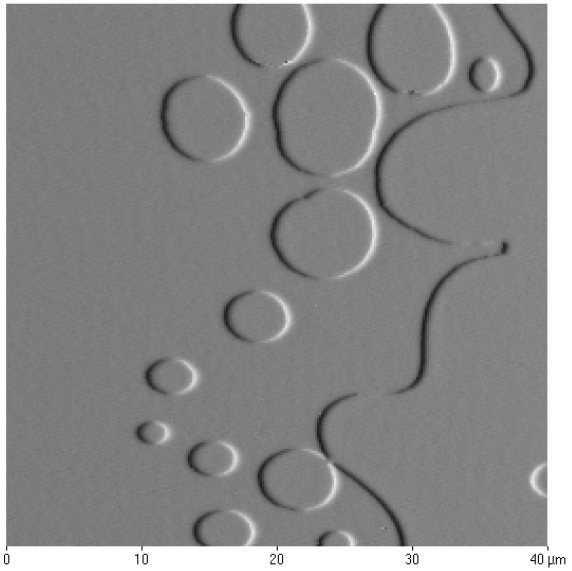




$L_o \approx 27.5$nm

Modified sample preparation

n = 8.5 (AFM Error Signal)



target thickness: $t_i = (n+1/2)\ L_o$

1.6% off target thickness for n = 8.5 still gave terracing. Missing ~35% of top layer

Must be within ~2nm of target thickness to prevent terracing on top layer.

Toluene too volatile for accurate spin-coating.

- Use PGMEA as PS-b-PMMA spin-coating solvent for more precise control of thickness
- Anneal under milder temperature (~36 hrs at 200°C instead of 16 hours at 230°C)
- Check all samples, annealed (layered) and un-annealed (amorphous) under AFM to verify uniform film coverage

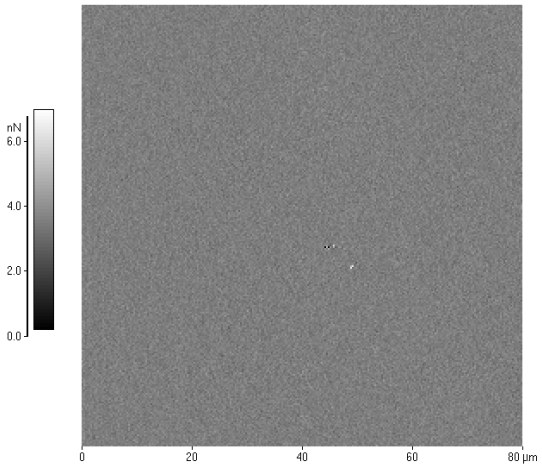
Sample description

	thickness* [nm]	st dev. [nm]	expected # of periods (**n**)	expected lamellar period thickness [nm]
→	201.75	2.44	7.5	26.9
	183.30	0.61	6.5	28.2
	160.45	0.11	5.5	29.2
	129.01	0.68	4.5	28.7
	99.08	1.21	3.5	28.3
→	71.44	2.47	2.5	28.6
→	41.84	0.16	1.5	27.9
	15.28	0.05	0.5 (++)	30.6
	14.69	0.04	0.5 (+)	29.4
→	14.06	0.06	0.5	28.1
	13.10	0.06	0.5 (-)	26.2

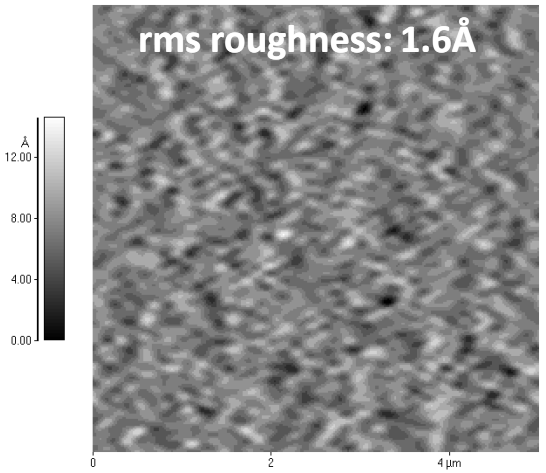
* from single wavelength ellipsometry

Typical AFM results

n = 1.5, annealed

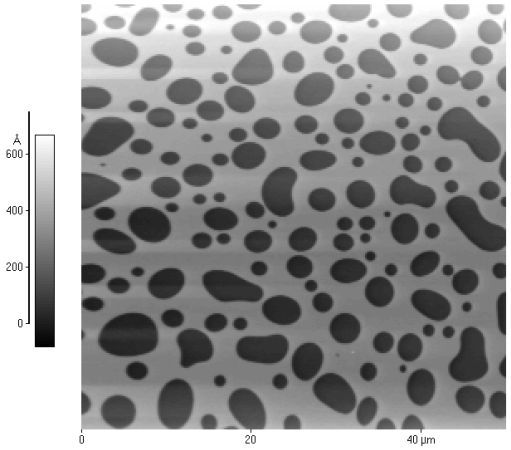


80 µm



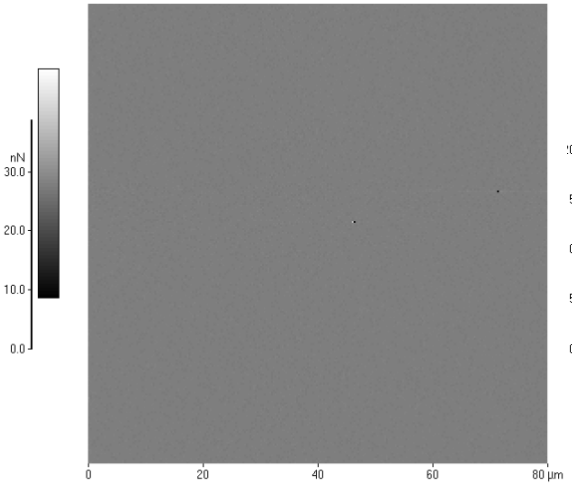
5 µm

n = 1.5, annealed
(extreme edge of wafer chip)

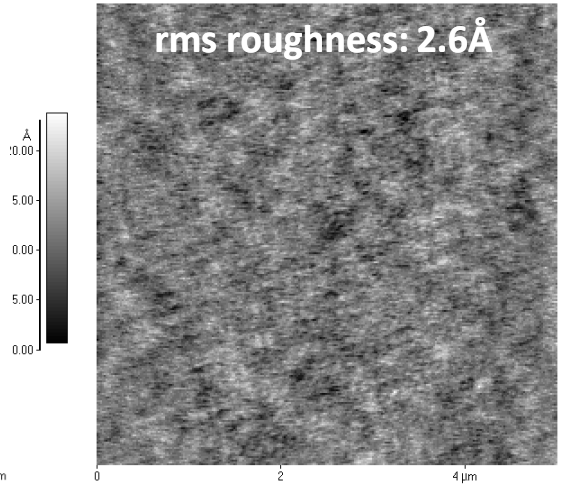


50 µm

n = 6.5, annealed

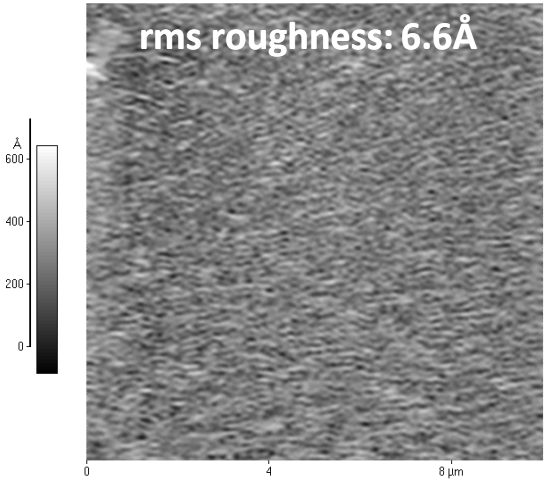


80 µm



5 µm

(as spun-cast)

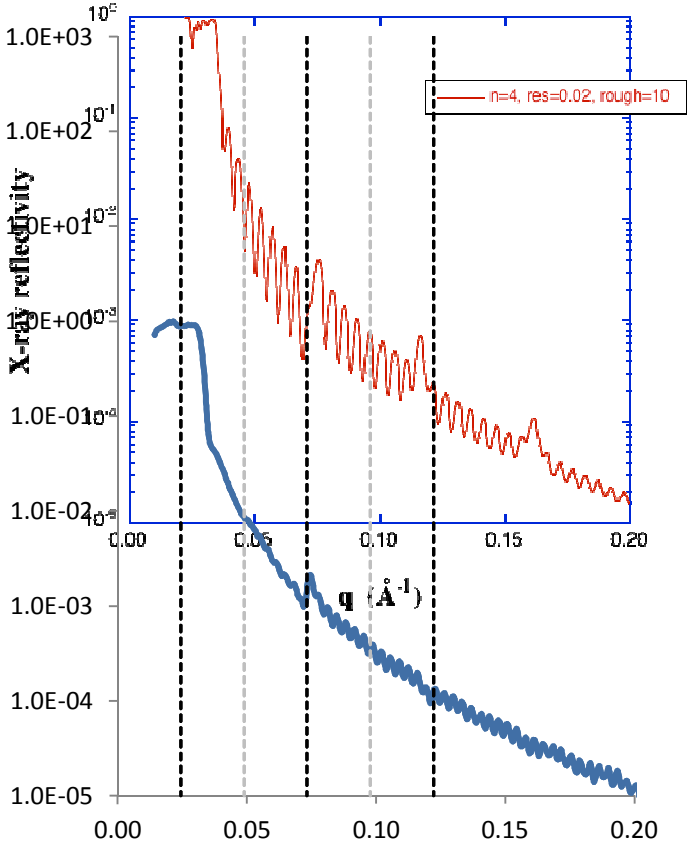


10 µm

Typical X-ray reflectivity results

Modeled Reflectivity

n = 4.5, annealed

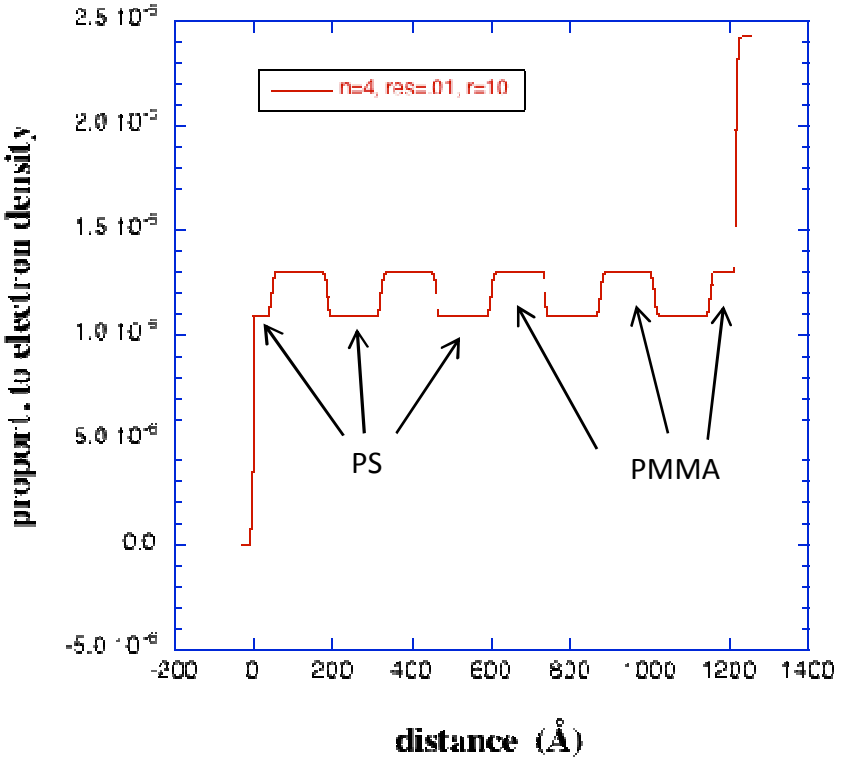


n = 6.5, annealed

Experimental Reflectivity

Structural Model

n = 4.5, annealed



NEW TDTR DATA FROM Patrick Hopkins

Conclusions

Acknowledgements

University of Wisconsin/IBM
Chi-Chun Liu

A portion of this work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

END

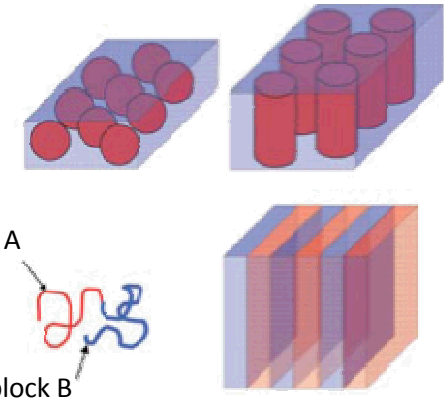
EXTRA SLIDES

Thermal conductance behavior of self-assembled lamellar block copolymer thin films

Matthew George[1], Patrick Hopkins[1], Mark Rodriguez[1]

1.

Example block copolymer phases:

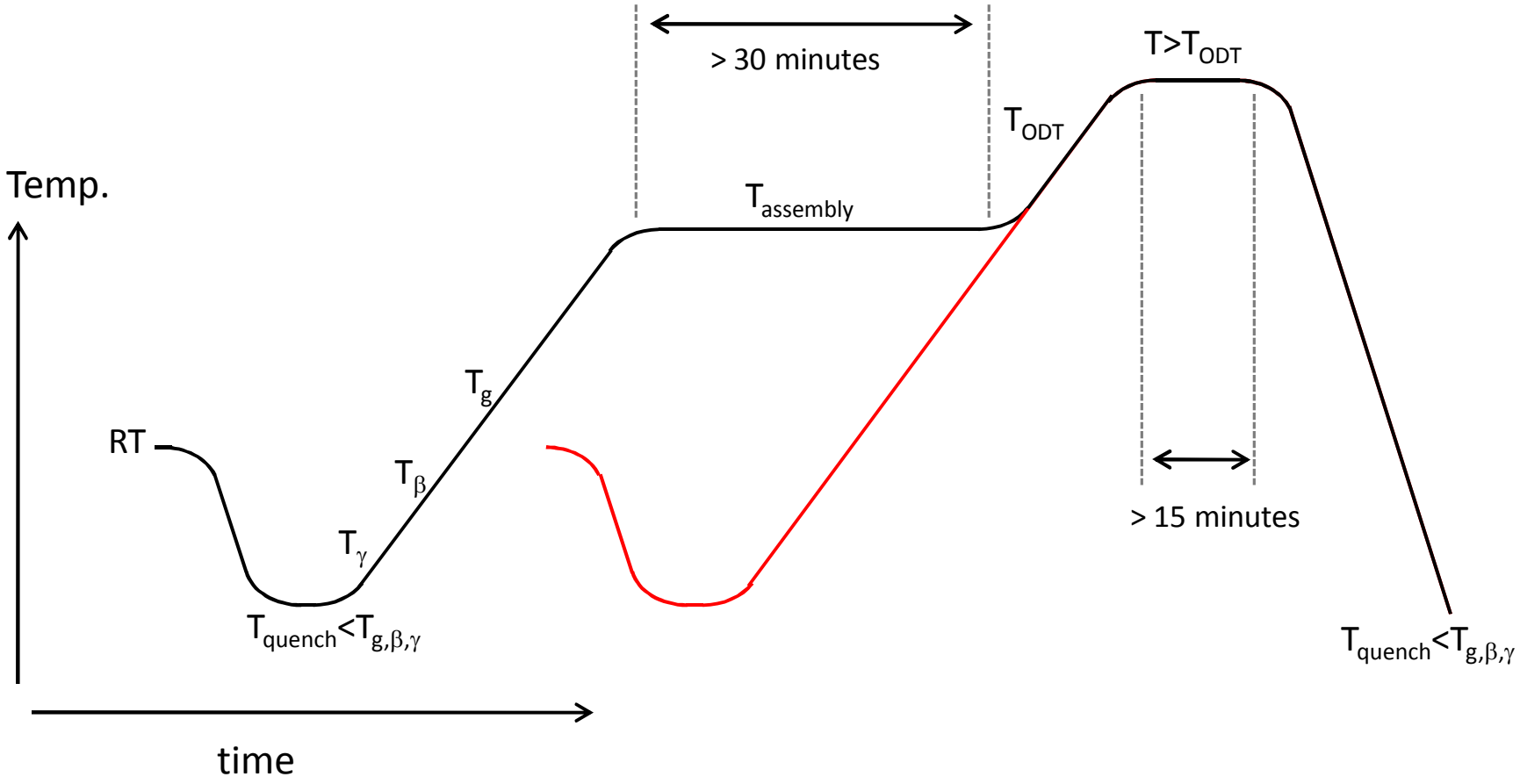


Ross *et al*., MRSB 33 838 (2008)

Start with diblock copolymer (polystyrene-b-PMMA**) and compare lamellar vs. disordered phase**

A portion of this work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

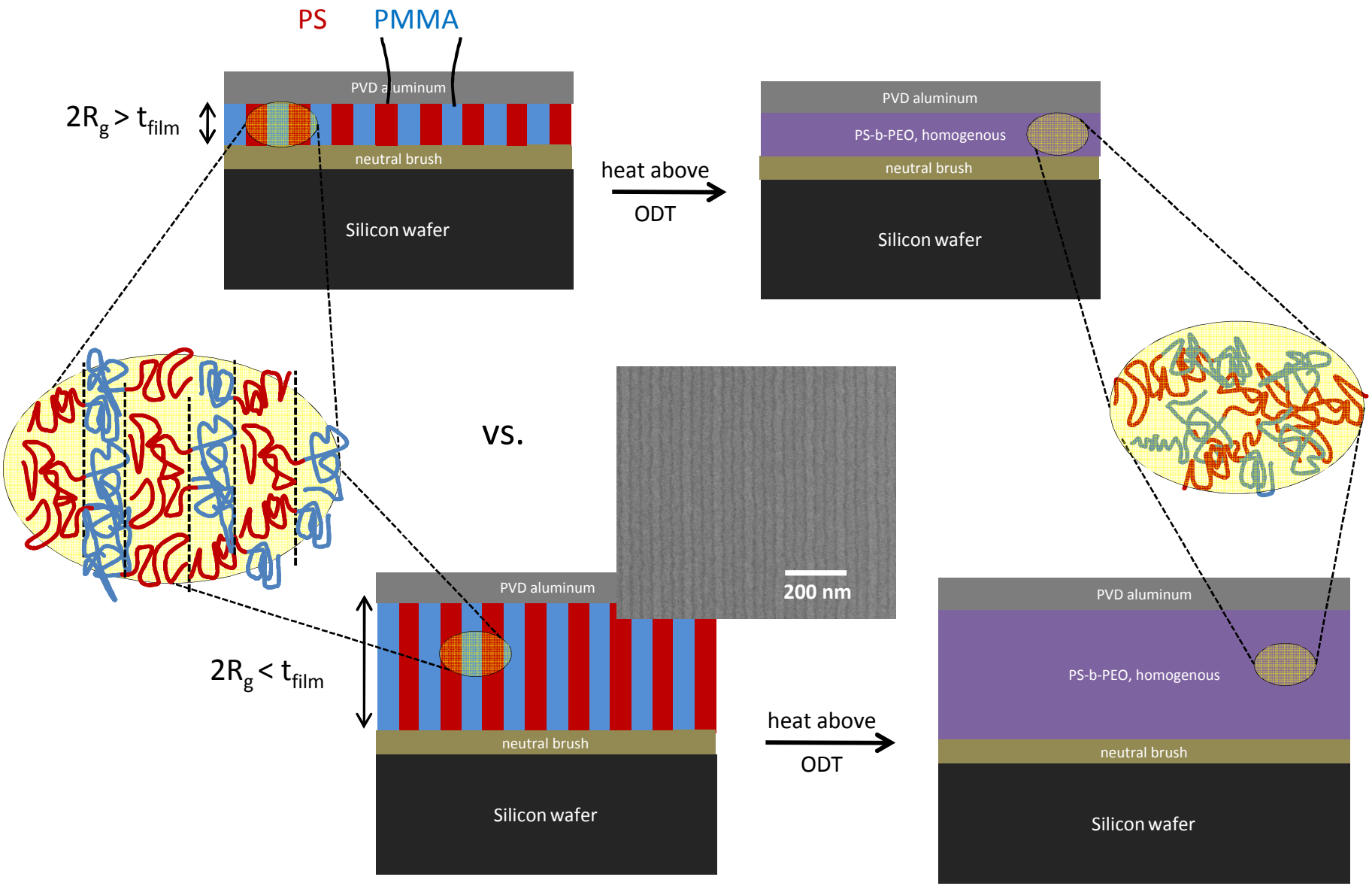
Proposed Anneal Schedule for in-situ thermoreflectance study



Black ⇒ un-annealed sample
Red ⇒ previously annealed (assembled) sample

Material	T_{quench}	T_γ	T_β	T_g	$T_{assembly}$	T_{ODT}
Polystyrene (PS)		?	~360-370K	~380K	n/a	n/a
PMMA		?	~275K- 313K	~406K	n/a	n/a
18kPS-b-18kPMMA	< 173K				~473K	513-548K

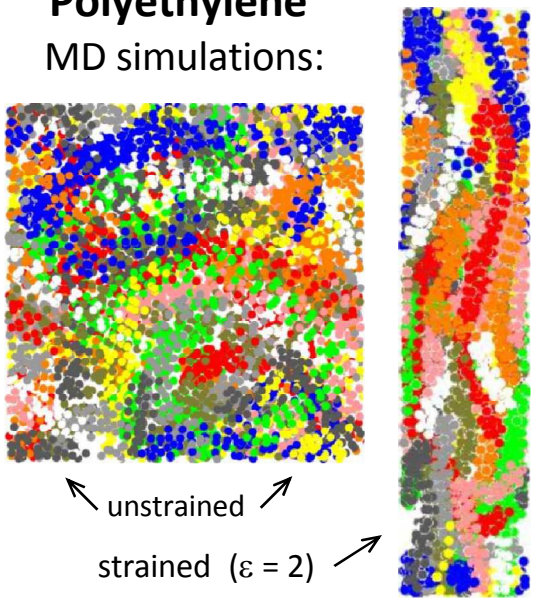
Can we measure in-plane thermal transport?



Tuning thermal conductivity of polymers via chain alignment

Polyethylene

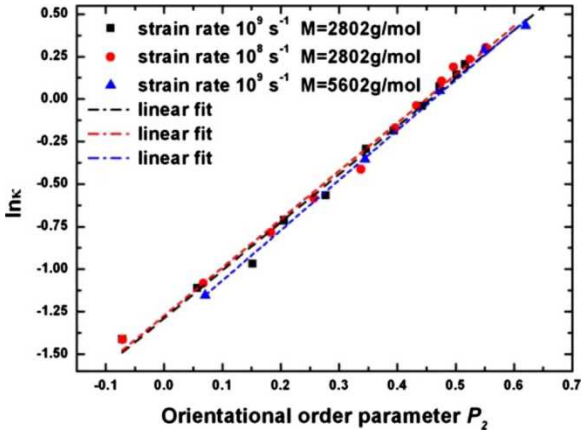
MD simulations:



unstrained

strained ($\varepsilon = 2$)

>5-fold increase in κ



Phys. Rev. B, **81**, pp.174122 (2010)

Polyethylene

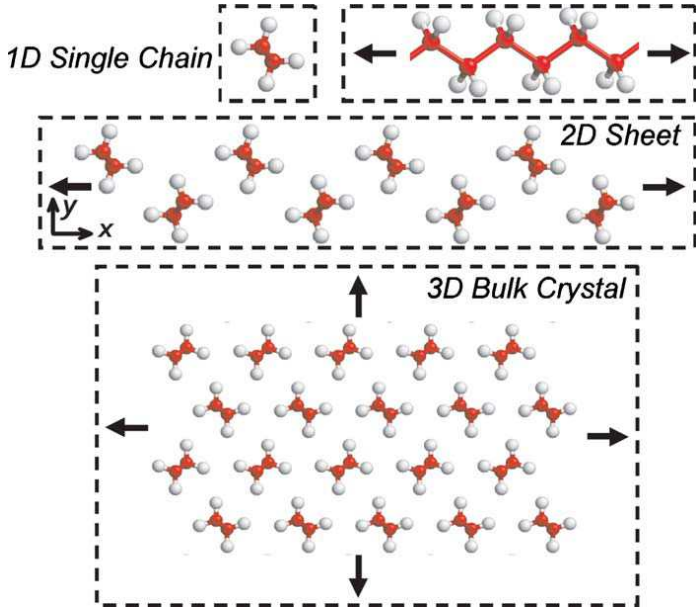
Ultradrawn micro and nano-fibers: 120- to 300-fold increase in in κ

J. Polymer Sci. Pt. B, **37**, pp.3359–67 (1999) and *Nature Nanotech.,* **5**, pp.251-55 (2010)

Theoretical predictions of κ for individual polyethylene chain: 350 W/(m·K) or even divergent

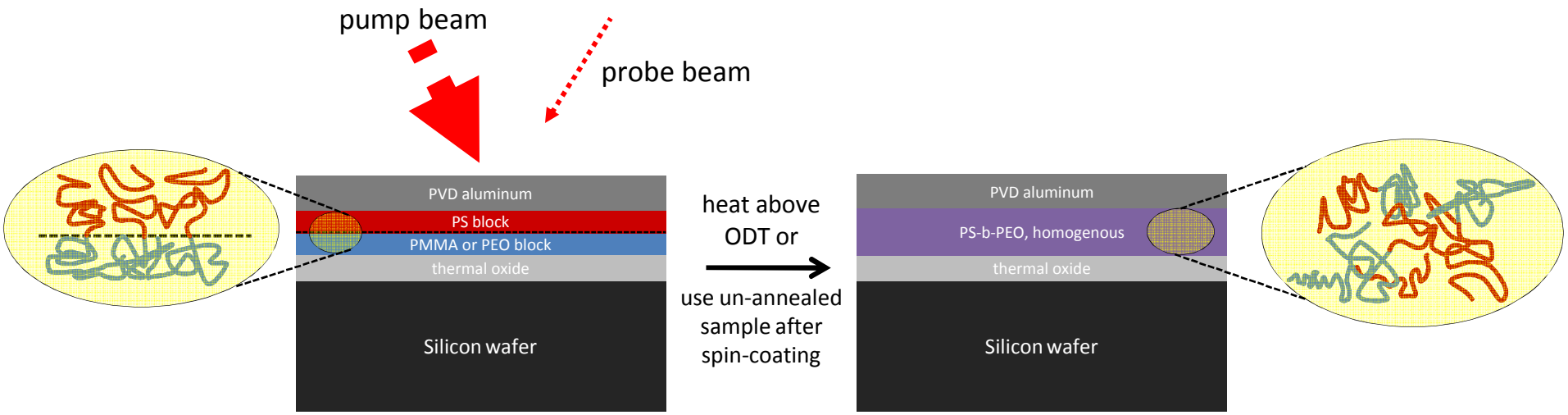
Nature Nanotech., **5**, pp.251-55 (2010) and *Phys. Rev. B,* **79**, pp.144305 (2009)

1D-to-3D transition of phonon heat conduction in polyethylene using molecular dynamics simulations

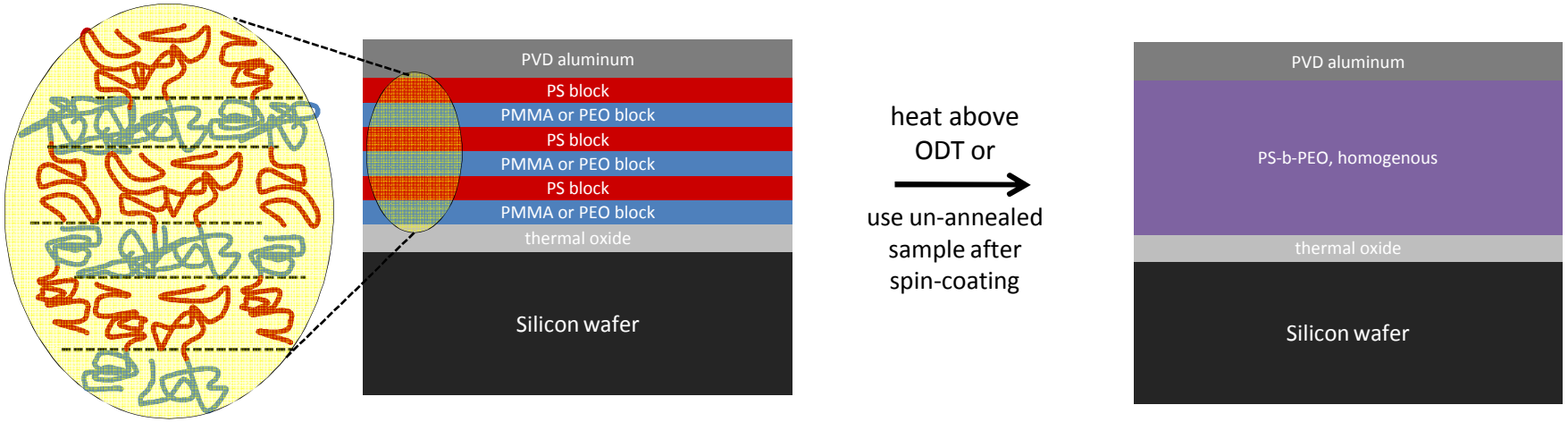


Phys. Rev. B **82**, pp.144308 (2010)

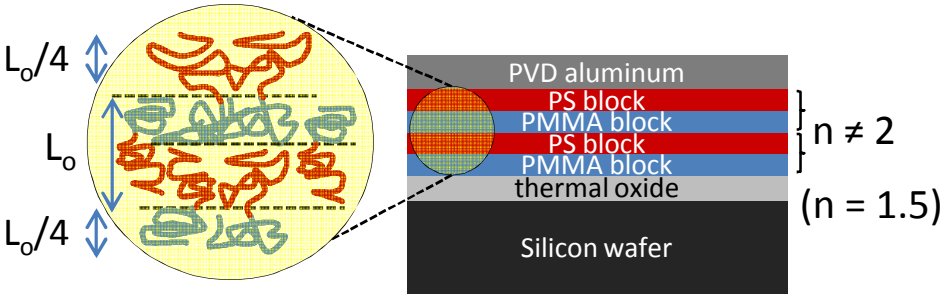
Schematic of ordered vs. disordered films

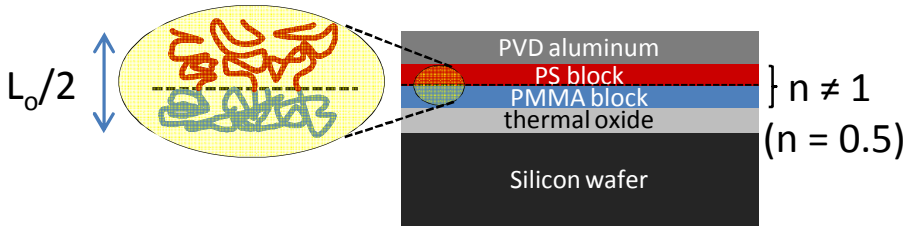


vs.

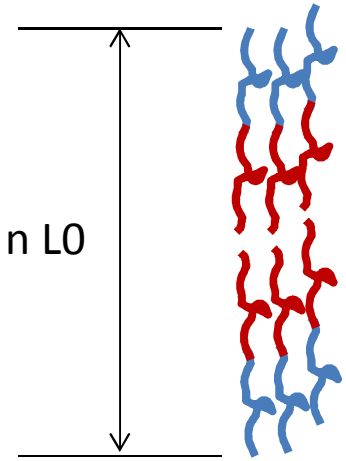


Surface Assembly Misunderstanding

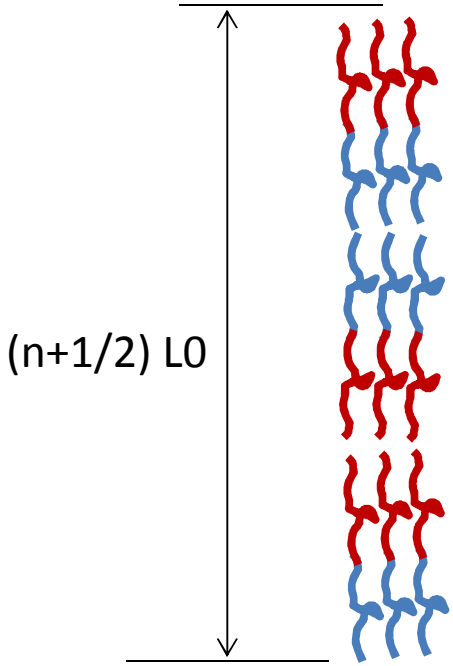




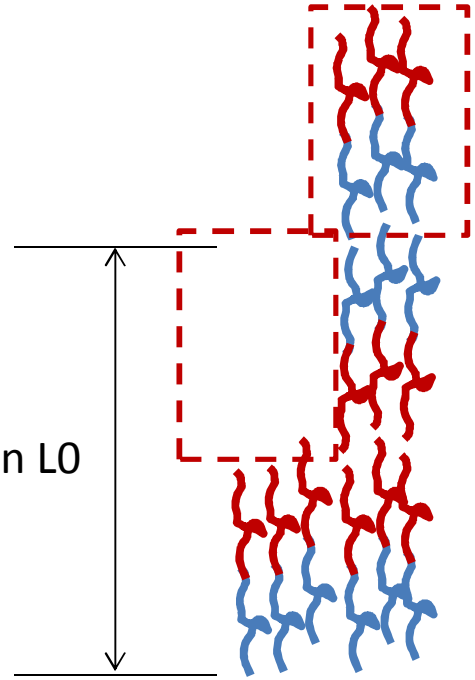
Symmetric wetting



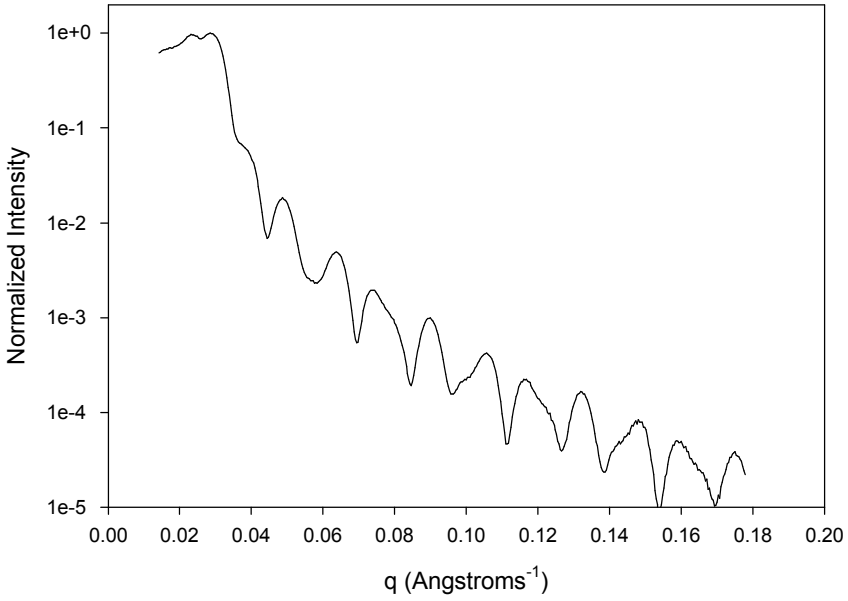
asymmetric wetting



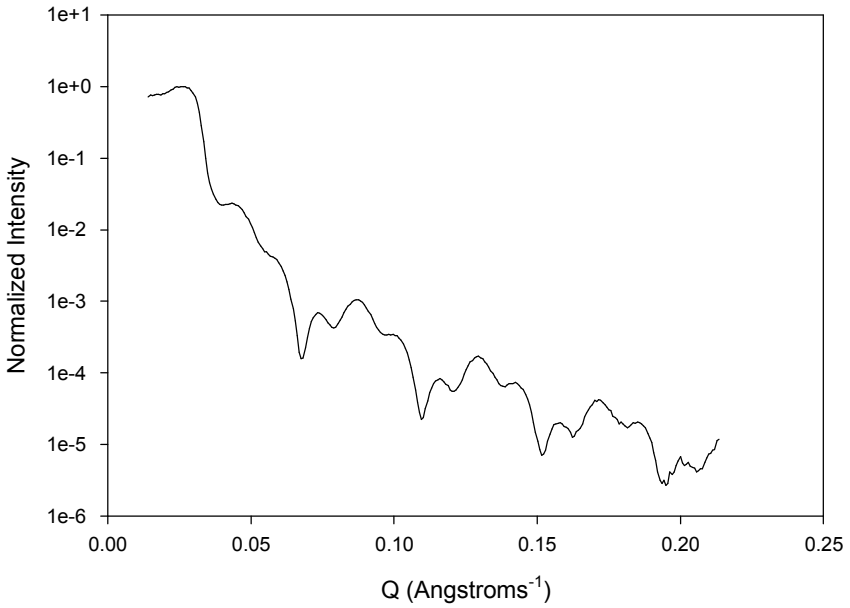
asymmetric wetting with initial film tihk of nL_0



Thermal transport in thin block copolymer films



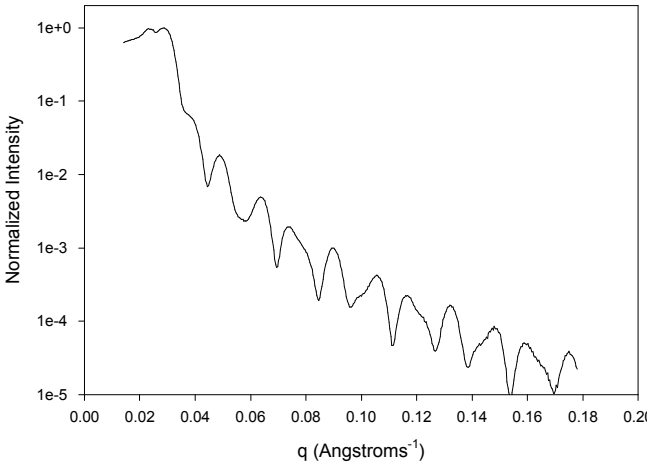
Film 2



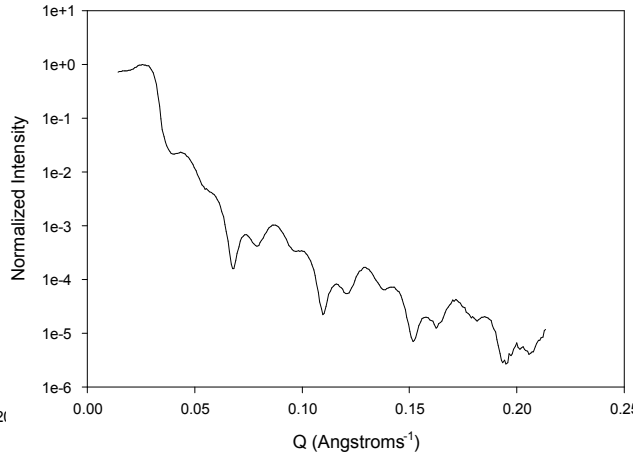
The density of PMMA is ~1.18 or 1.19, and PS is ~ 1.05

Sample number	thickness* [nm]	expected # of bilayers (n)	expected bilayer thickness (x + y)	M_n of each block [g/mol]	spin-coating speed [rpm]	spin-coating conc. [wt. %]	spin-coating solvent
1	55	2	27.5	18k	4250	1.5	toluene
2	25.5	1	25.5	18k	3750	0.75	toluene
3	60	3	20	10k	3375	1.5	toluene
4	56.5	3	19	10k	4500	1.5	toluene
5	22.5	1	22.5	10k	1250	0.5	toluene
6	21	1	21	10k	2000	0.5	toluene

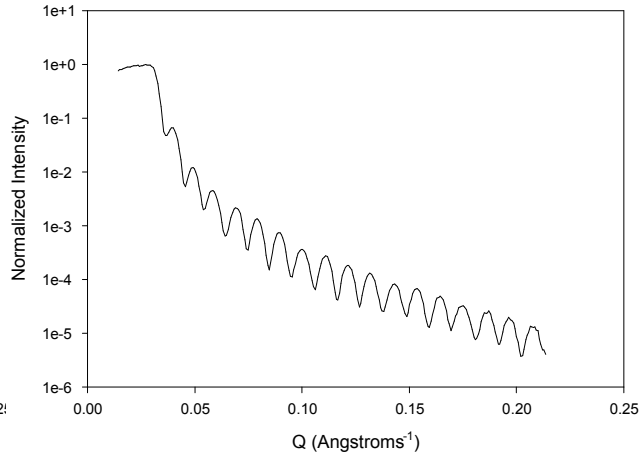
Thermal transport in thin block copolymer films



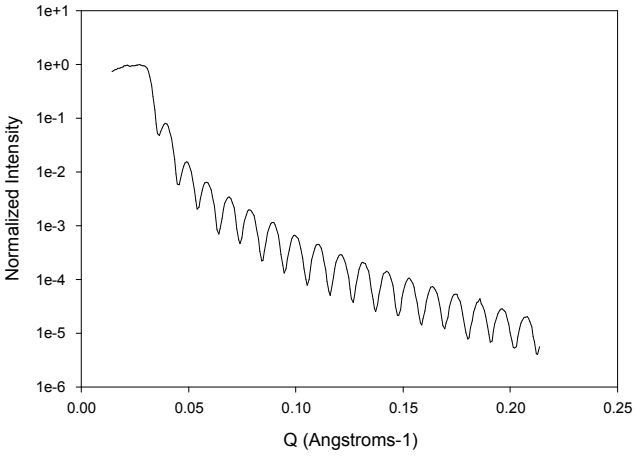
Film 2



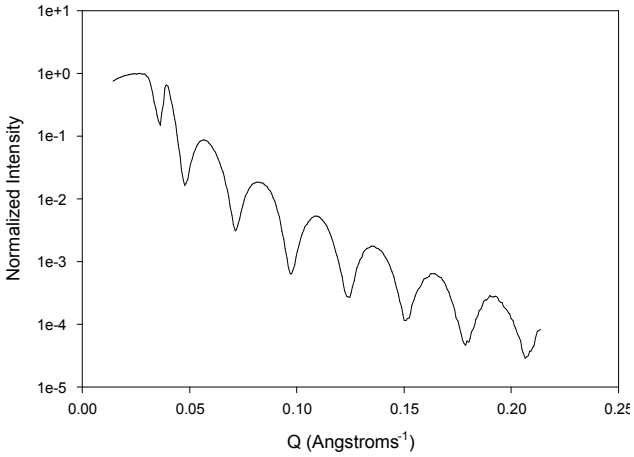
Film 3



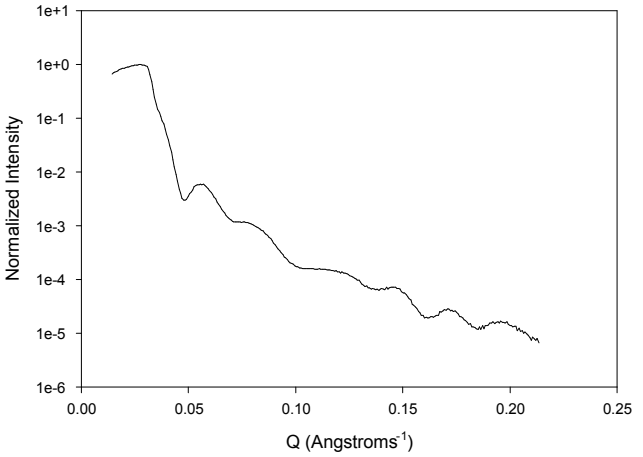
Film 4



Film 5

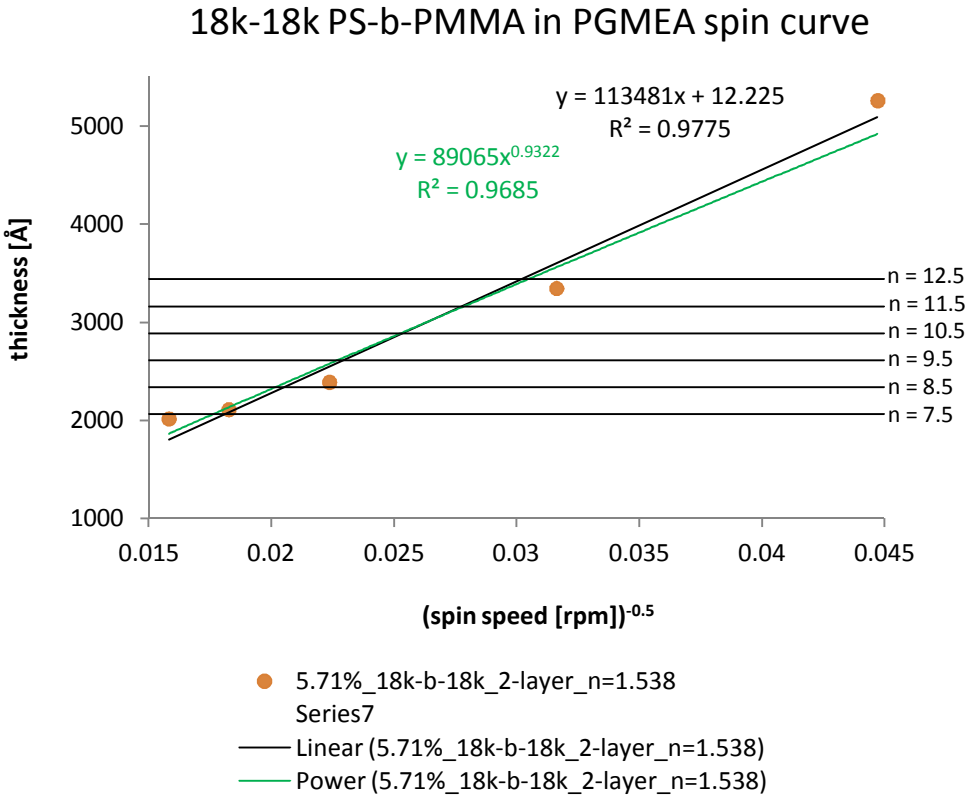


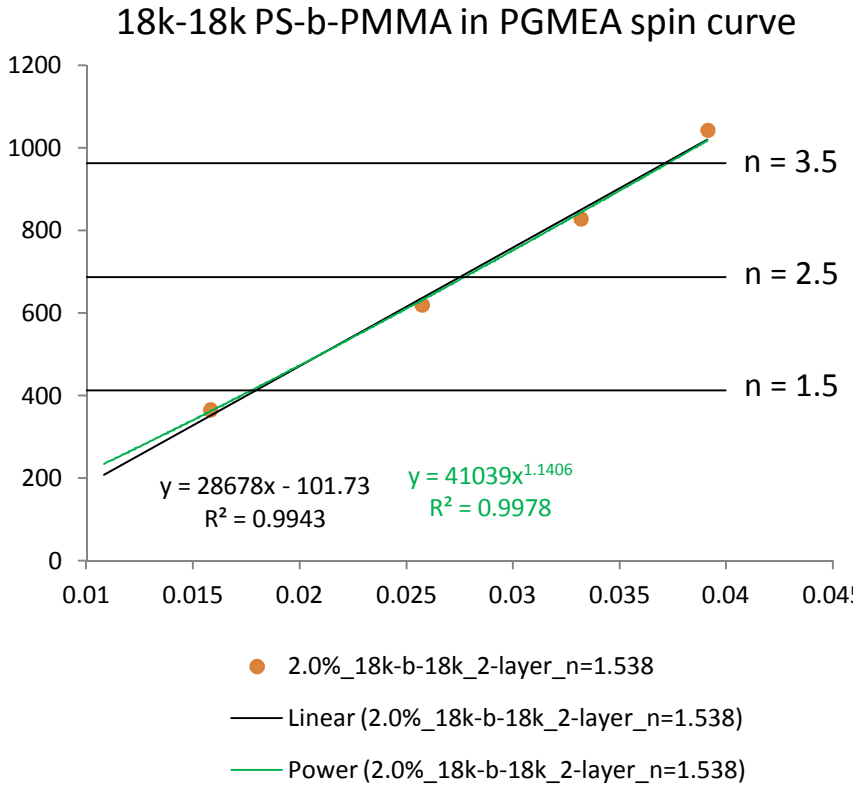
Film 6



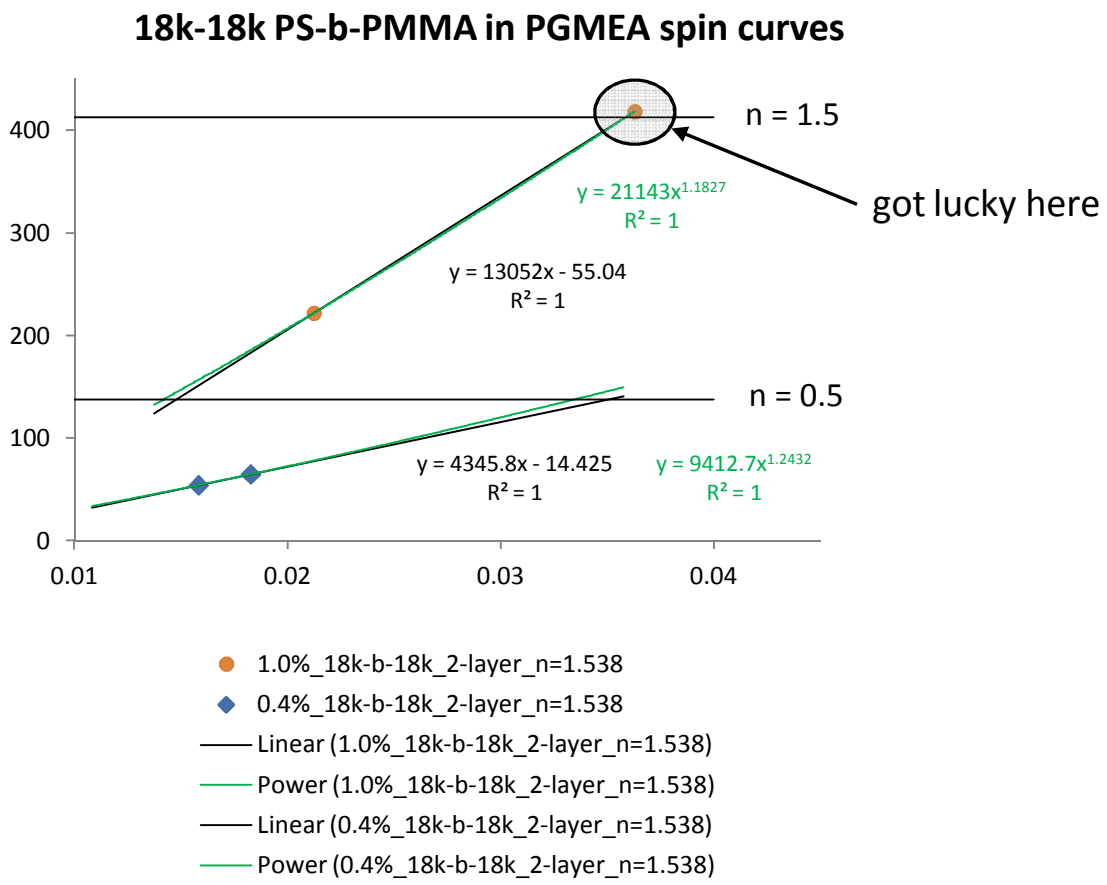
Better spin-coating solvent

Replacing toluene with PGMEA
(1-methoxy-2-propyl-acetate)





Dilute PGMEA spin curves



So far only two data points for each concentration (had four thermal oxide chips left)