Combinatorial Methodology using Gradient Polymer Coatings: From Data to Information to Knowledge

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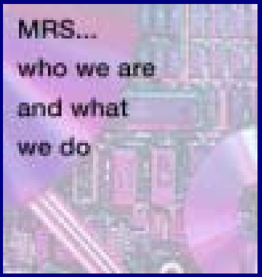
National Institute of Standards and Technology

Technology Administration, U.S. Department of Commerce

Leadership Role

Symposium Organization



- Materials Research Society, Fall 2001
  (E. Amis, Organizer, E. Amis & A. Karim, Symposium Chairs)
- Gordon Conference
  Combinatorial & High Throughput Materials Science
  Jun 30-Jul 5, Kimball Union Academy
  (Combinatorial Chemistry, Jul 7-12, Queen's College)
- New Technology Forum, ANTEC 2002, SPE
  May 5-9, San Francisco, CA

Gordon Research Conferences

Invited Articles

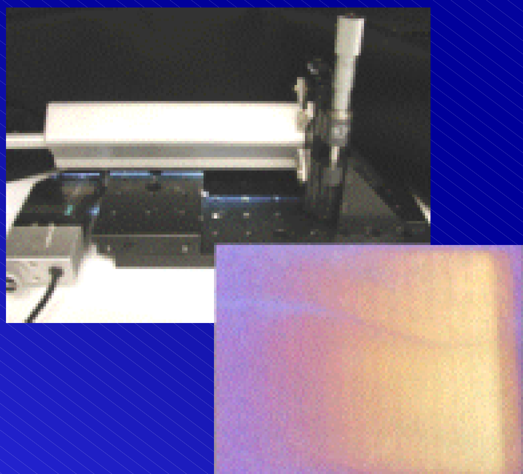
- Special focus issue "Combinatorial and High-throughput Methods for Materials Science, April 2002, Bulletin of Materials Research Society
- Book Chapter "Experimental Design for Combinatorial and High-Throughput Materials Development", Edt. James W. Cawse, GE Plastics, Pub. John Wiley
- Kirk-Othmer Review Article
- "Combinatorial Methods in Polymer Science" for the Encyclopedia of Polymer Science and Technology Review Article, Pub. John Wiley
- ACS Book "Combinatorial Approaches to Materials Development" chapter "Combinatorial Polymer Science: Synthesis and Characterization", Dec 2001.

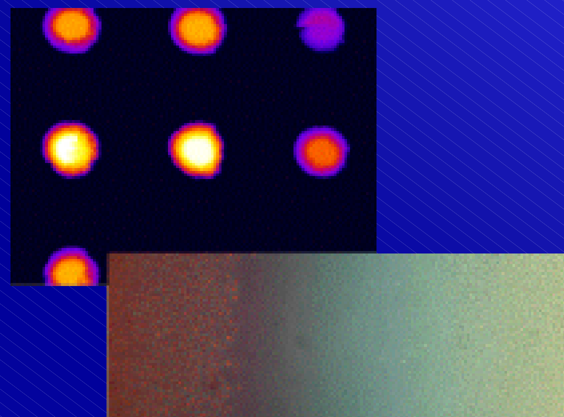
Combinatorial Methods at NIST brochure (NISTIR 6730)

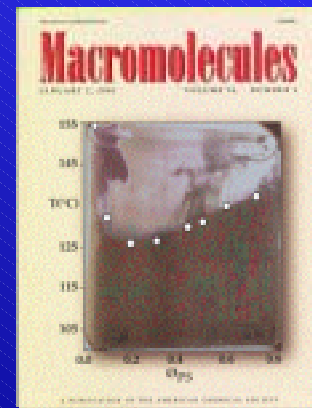
NIST Combinatorial Methods CenterJuly10, 2001 Meeting Proceedings (CD-NISTIR 6804)

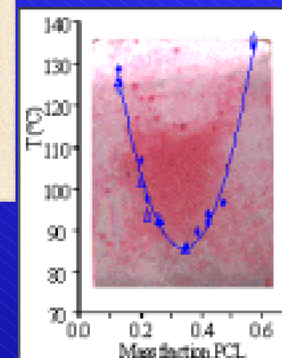
~ 20 Publications on Combi research to date

Scientific & Technical Accomplishments









Library Design
- Film thickness
- Composition gradients
- Optical microscopy
- Contact angle microscopy
- Micro-contact area lens
- Surface energy gradients
- UV cross-linking gradients

Custom Analysis Programs
- Lab view instrument control
- NIH Image analysis
- IDL program
- Matlab program
- Lispix
- Igor

Validation, Knowledge Discovery
- Binary phase diagram
- Polymer wettability
- ***Block copolymer ordering***
- ***Polymer crystallization***
- Polymer adhesion
- Biocompatibility

Block Copolymer Film Ordering Properties

- Motivation

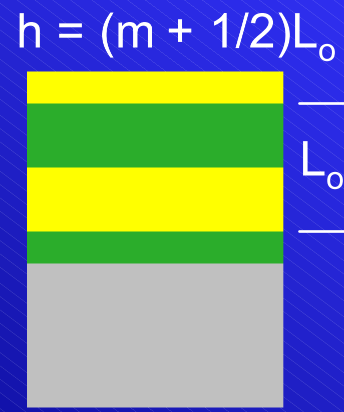
  Unique properties of block copolymers allow their use as adhesives, emulsifying agents, compatibilizers, etc.

- Establish validity of applying combinatorial methods

- Investigate the location and nature of morphological transitions not previously observed for **h, c_{sub}, Mw**

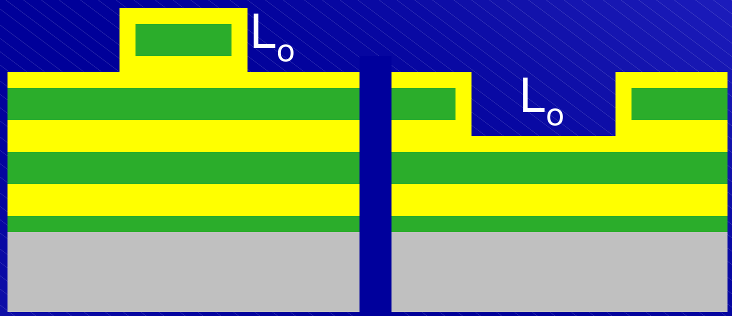
Data -> Information -> knowledge discovery

Thin Film Diblock Copolymer Morphology



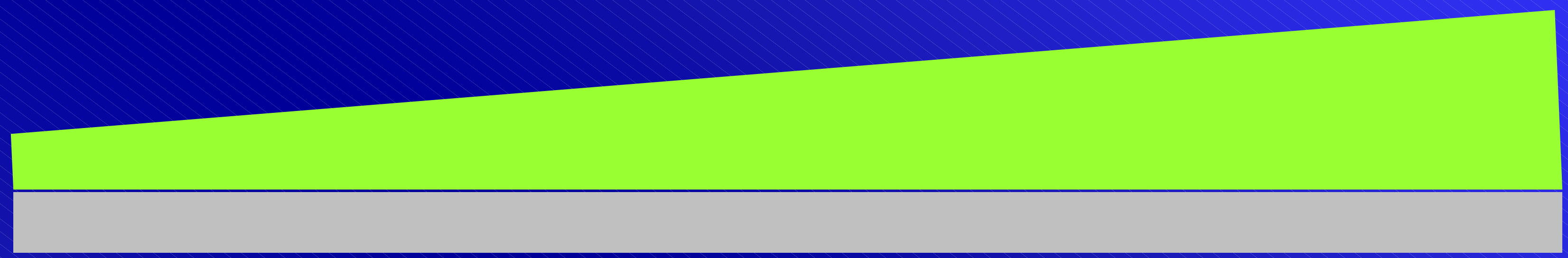
Surface interactions induces formation of lamellae parallel to the substrate and air interfaces

Smooth films form for total film thickness h = mL_o or (m + 1/2)L_o depending on the relative block/interface energetics.

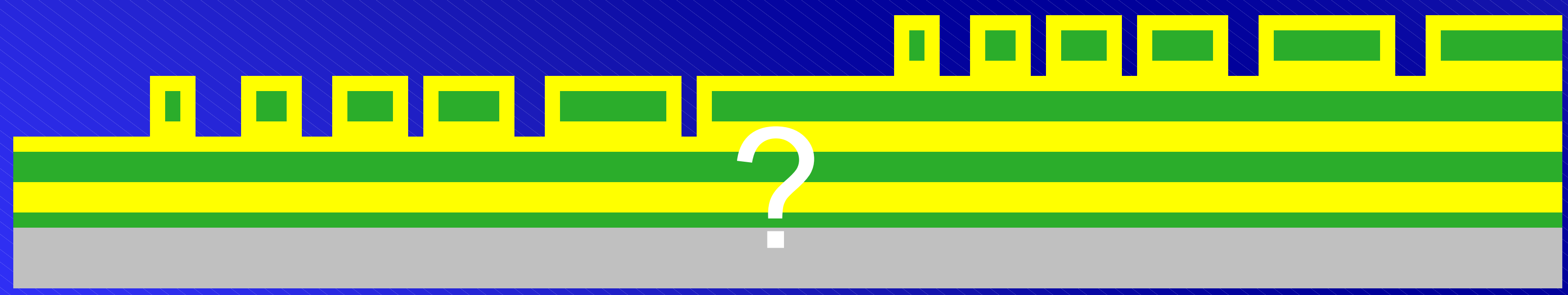


For films deviating from this height, islands or holes of height L_o are formed on the surface of the thin film

Effect of Film Thickness

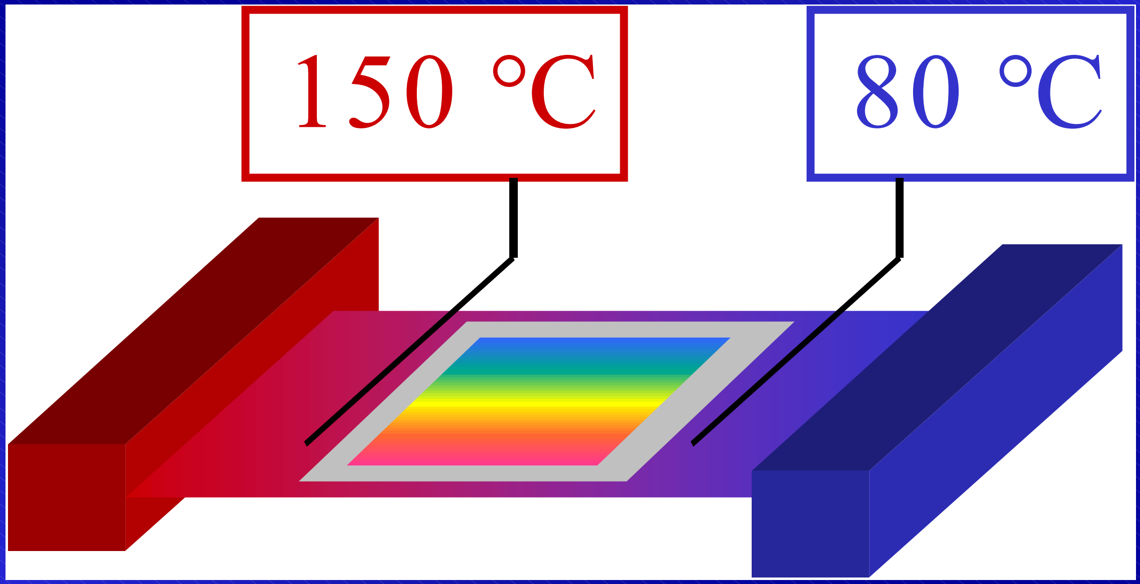


Anneal sample above its glass transition temperature to allow ordering



Film Processing

Investigate formation of surface patterns as a function of variable (h, Mw, c_{sub})

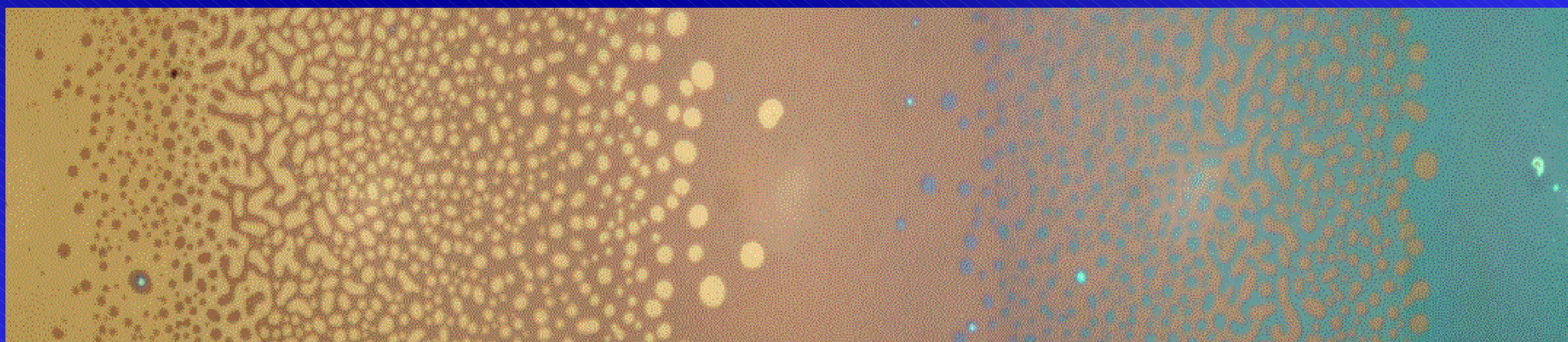


Position "variable" gradient orthogonal to processing temperature gradient DT

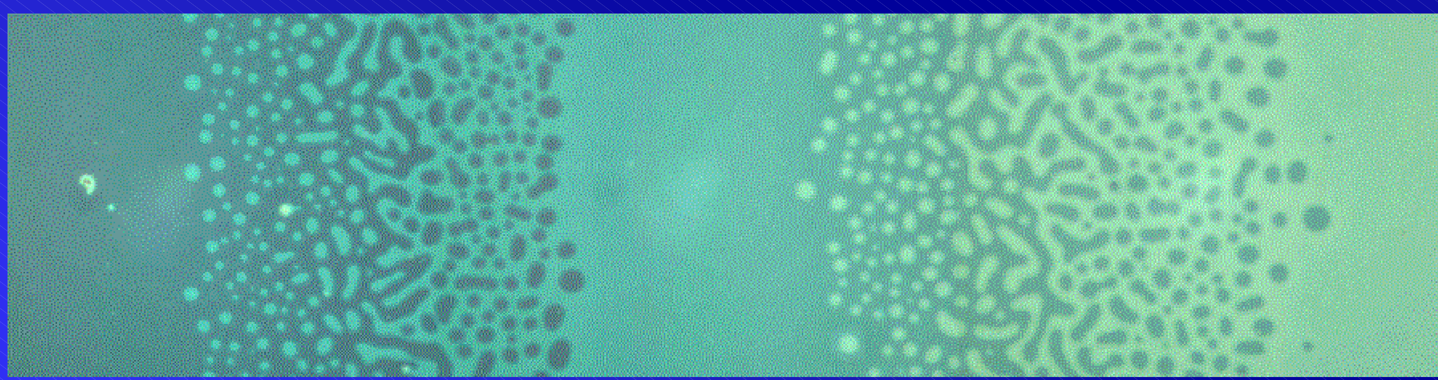
Thickness Gradient Morphology

Optical Micrographs of 26k PS-b-PMMA, annealed 6 h

45 nm 63 nm 81 nm



smooth islands holes smooth islands holes smooth

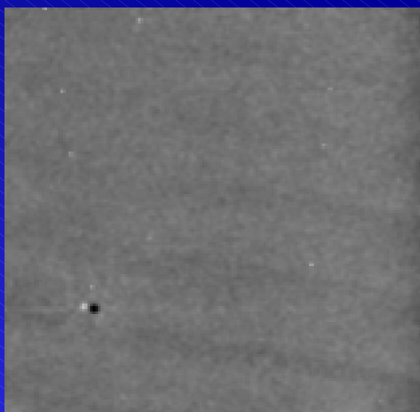
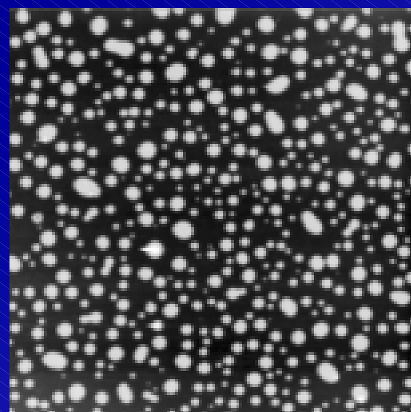
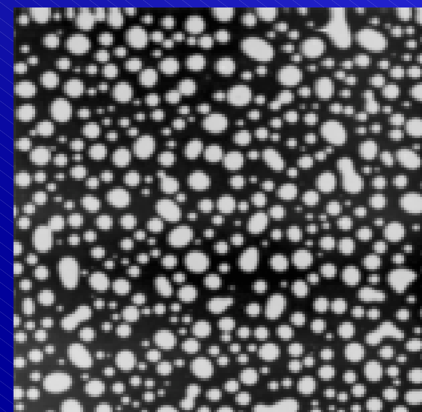
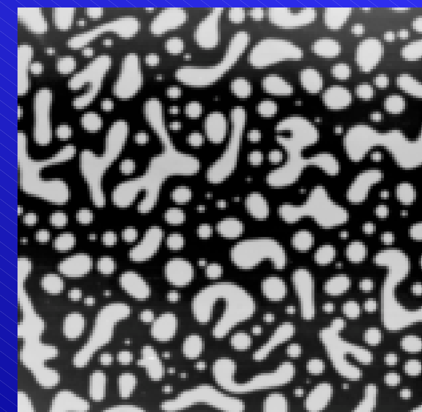


50 mm

81 nm 99 nm 117 nm

Thickness Gradient Morphology

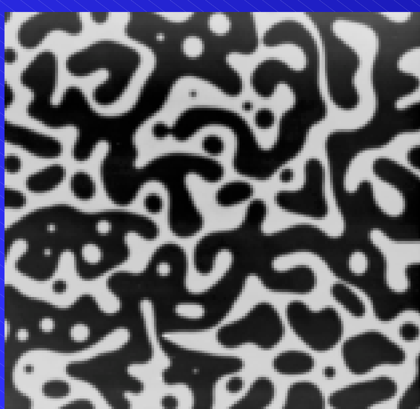
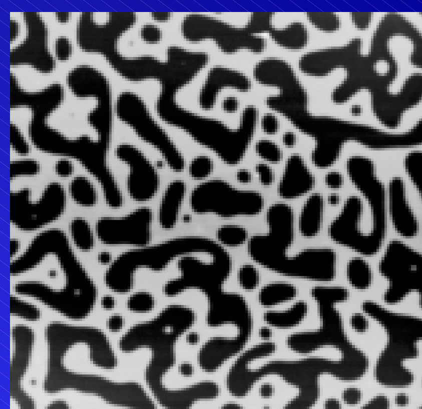
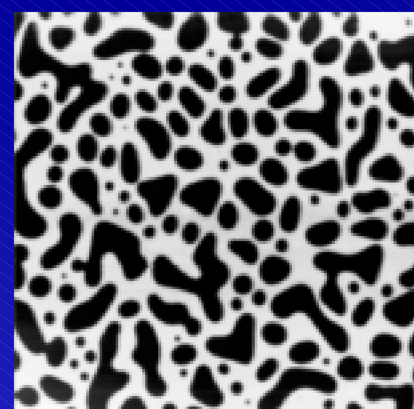
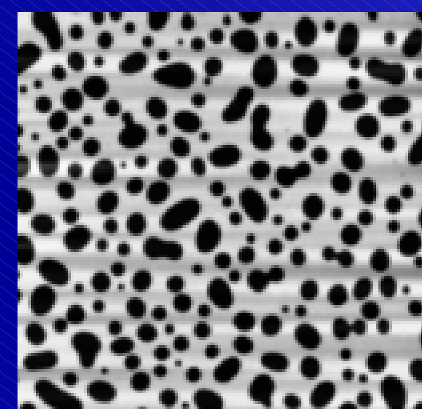
AFM micrographs of 51k PS-b-PMMA, annealed 6 h

smooth

10 mm

islands

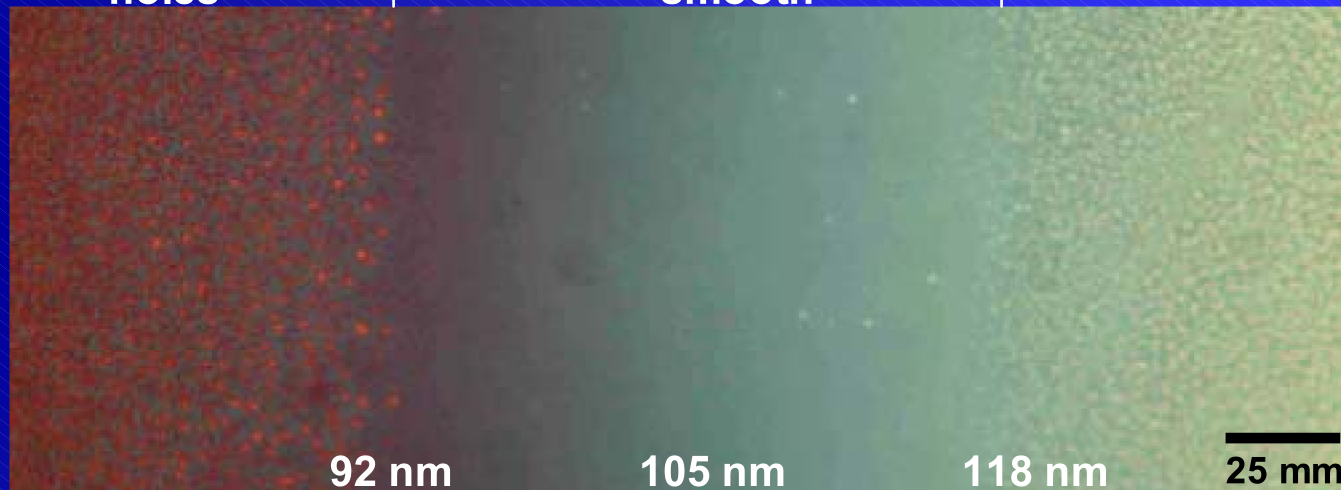





“bicontinuous”

holes

Thickness Gradient Smooth Region

Optical micrograph of 104k PS-b-PMMA



Dh = change in film thickness across the smooth region

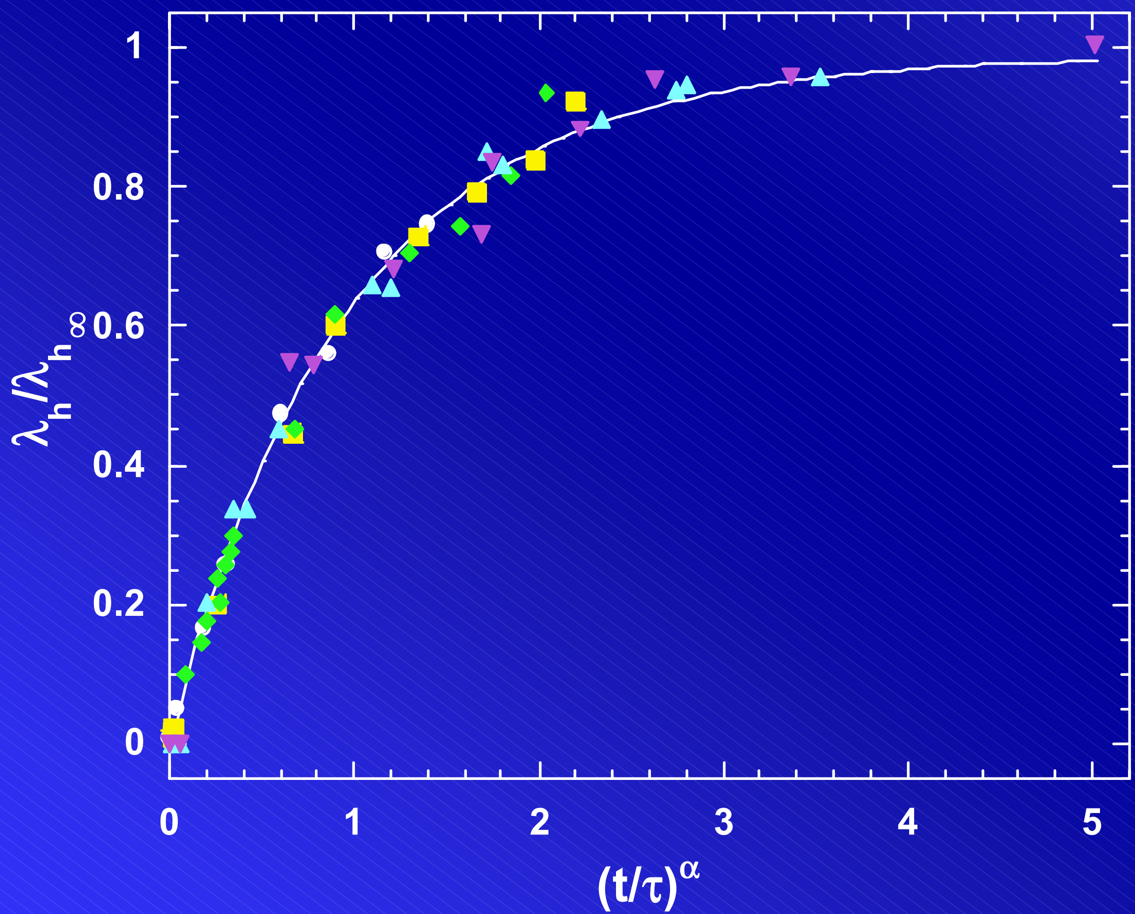
M_w (kg/mol)	Δh (nm)	$\Delta h/L_o$
26	4.1 ± 1.4	0.23 ± 0.07
50	8.4 ± 1.0	0.28 ± 0.03
104	11.6 ± 1.6	0.28 ± 0.03

Dh is symmetric and nearly INVARIANT with respect to m and L_o

Interpreted as deformation in outer block copolymer lamella

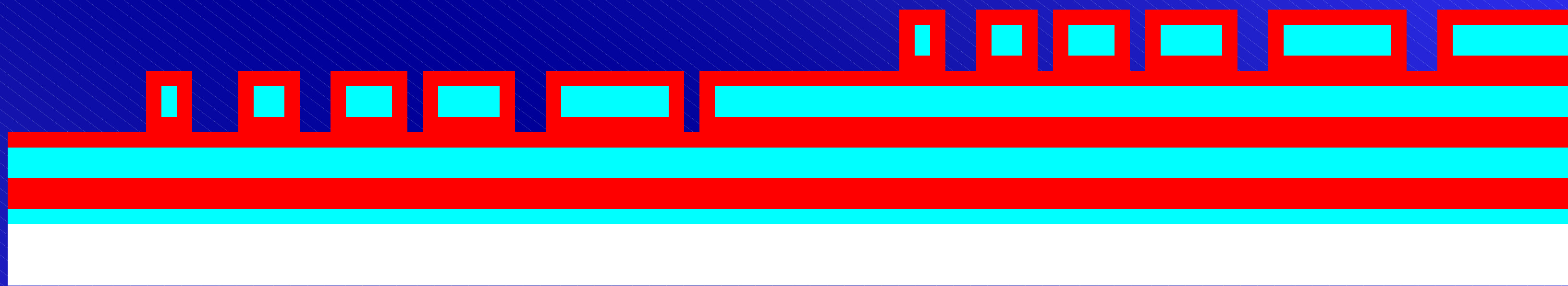
Pattern Kinetics Master Curve (h=53 nm)

$$\lambda_h = \lambda_{h,\infty}\{1 - \exp[-(t/\tau)^{\alpha}]\}$$



Tuning Surface Interactions (c_{sub}) to Control Ordering Morphology

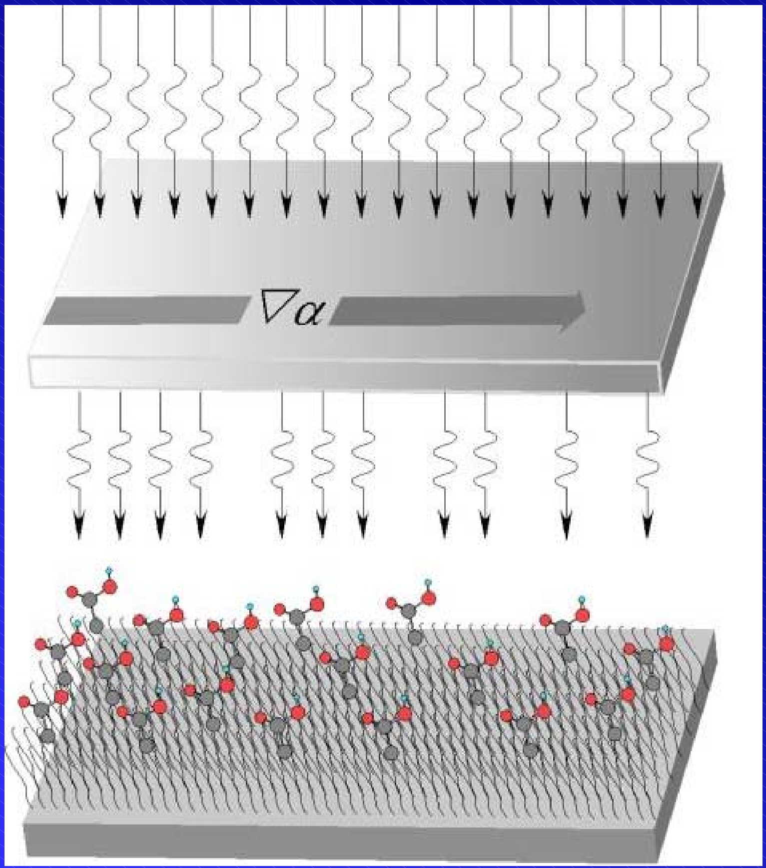
Cast a block copolymer film with a thickness gradient

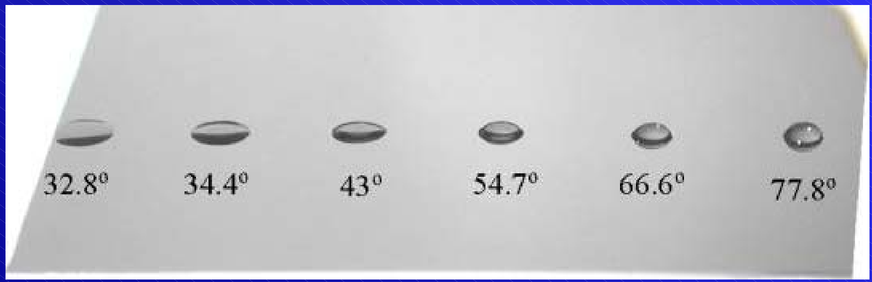


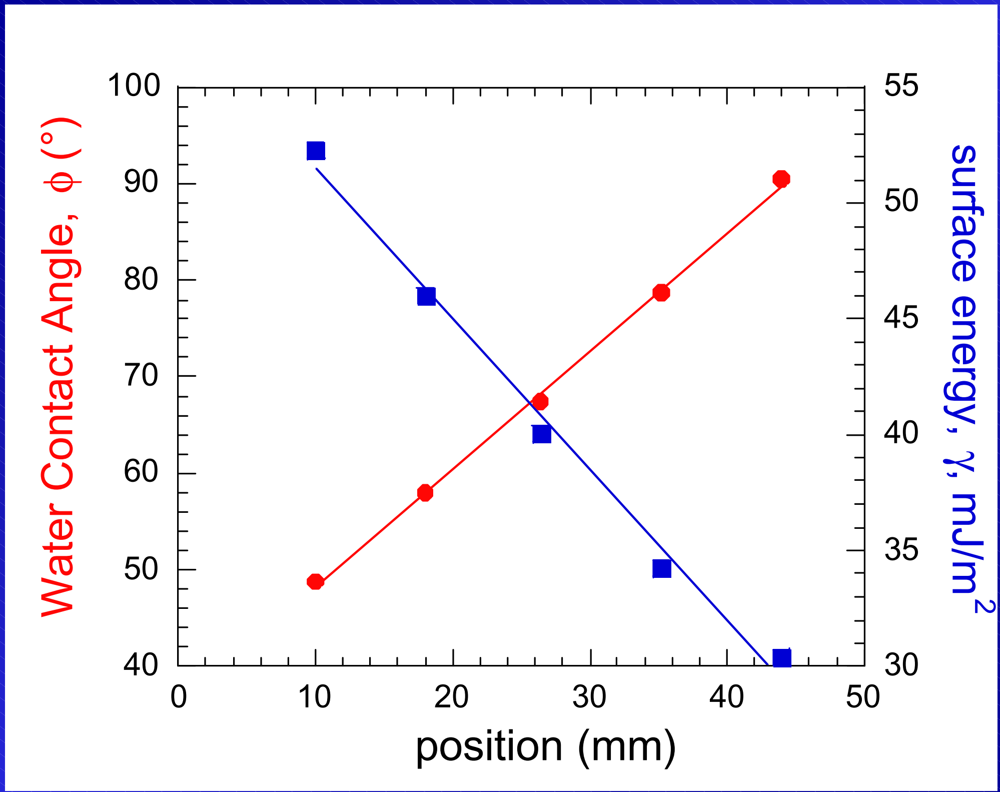
orthogonal to a substrate with a surface energy gradient

to create a two-dimensional thickness/surface energy block copolymer map

UV Surface Energy Gradients







Developed by Amit Seghal

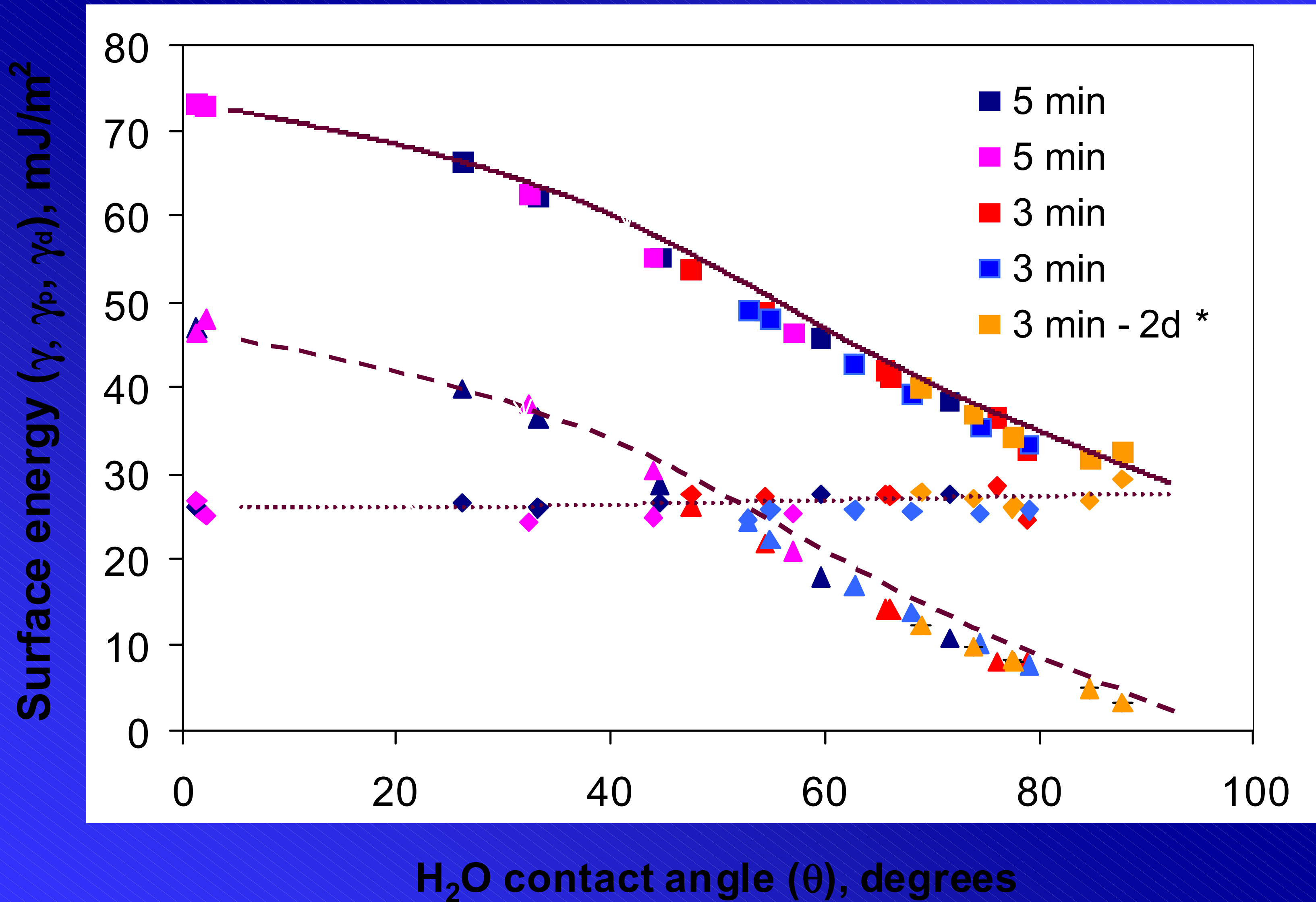
Combined Data on Surface Energies (including the polarity and dispersion components) for UVO treated octadecyldimethylchlorosilane monolayer.

Table of combined results for UVO treatments of 2, 4, 5 and 7 minutes.

UVO treatment (minutes)	H_2O contact angle measurements	CH_2I_2 contact angle measurements	Polarity component	Dispersion component	Surface energy value	Polarity
7	32.805	45.12	38.393	23.731	62.124	0.618
7	34.505	45.31	37.271	23.841	61.113	0.610
5	37.92	46.93	35.432	23.441	58.873	0.602
5	43.63	46.3	30.731	24.600	55.331	0.555
7	45.655	47.21	29.465	24.431	53.896	0.547
5	51.03	45.8	24.623	26.106	50.728	0.485
7	52.52	47.06	23.863	25.865	49.548	0.482
4	52.845	46.965	23.569	25.797	49.366	0.477
7	55.55	47.8	21.689	25.837	47.525	0.456
5	56.865	46.15	20.117	27.011	47.128	0.427
4	56.925	46.72	20.250	26.705	46.955	0.431
4	63.135	47.6	15.790	27.471	43.260	0.365
5	66.47	48.8	13.720	27.489	41.209	0.333
4	68.54	49.55	12.484	27.500	39.984	0.312
7	71.955	50.6	10.491	27.635	38.126	0.275
2	73.23	52.35	10.107	26.861	36.968	0.273
4	74.485	52.1	9.269	27.297	36.566	0.253
2	75.945	53	8.601	27.077	35.678	0.241
5	80.36	52.8	6.135	28.227	34.363	0.179
2	81.025	54.4	6.108	27.376	33.483	0.182
2	83.835	55.5	4.956	27.335	32.290	0.153
4	84.13	54.5	4.648	28.044	32.693	0.142
2	89.08	55.95	2.895	28.290	31.185	0.093
2	90.33	57.42	2.661	27.625	30.286	0.088

Surface energy - Polar (γ_p) and Dispersive (γ_d) components

Polymers
Materials Science and Engineering



2d* - 2 days later

NIST
National Institute of Standards and Technology

Thickness - (Surface Energy) Map

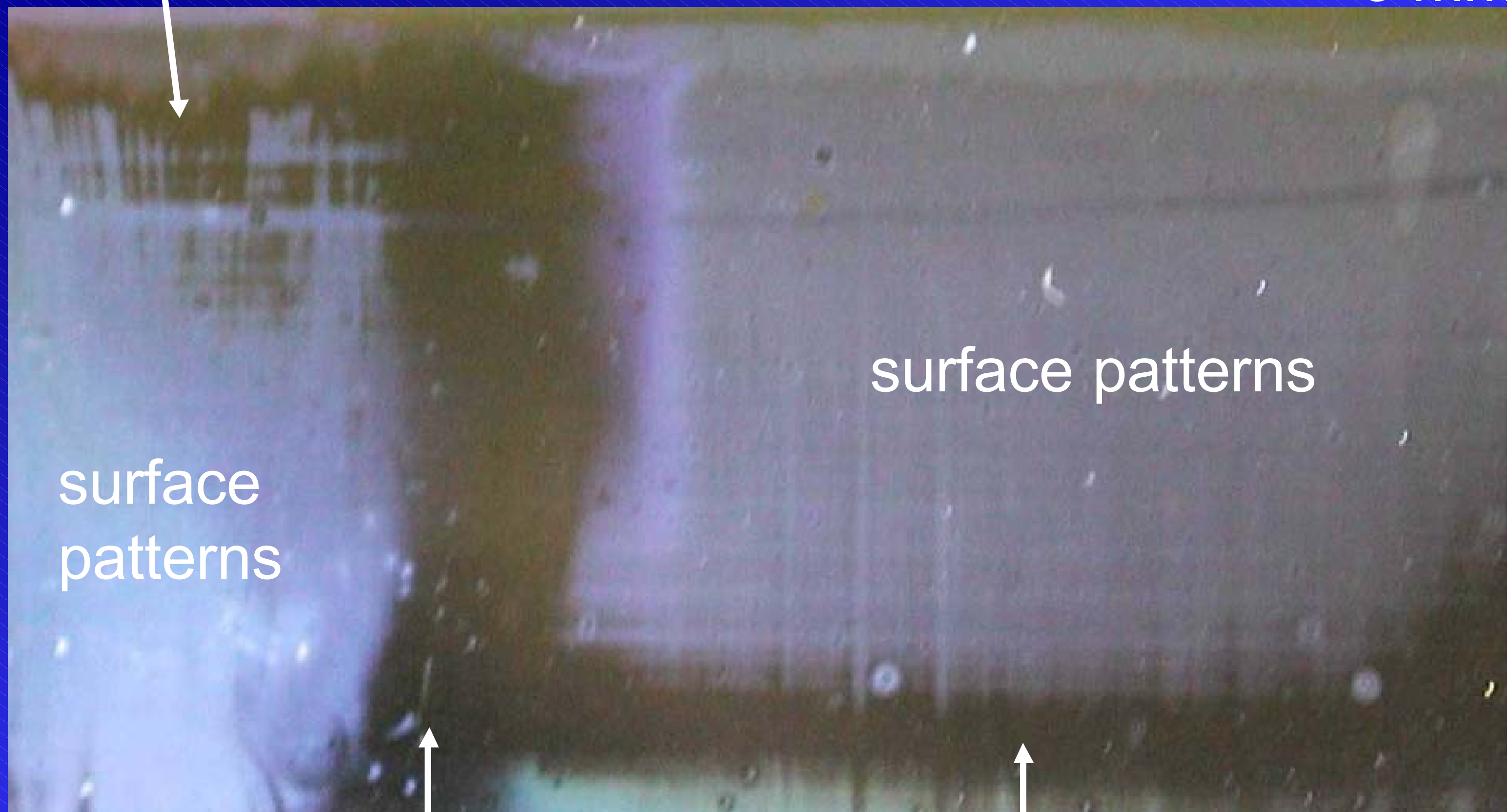
smooth, $h \sim 2.0\ L_o$

3 mm

~ 60 nm

h gradient

~ 80 nm



~ 52 mJ/m²

Surface Energy ~ c_{sub}

~32 mJ/m

smooth ~ 44 mJ/m²

smooth, $h \sim 2.5\ L_o$

Surface Pattern Morphology

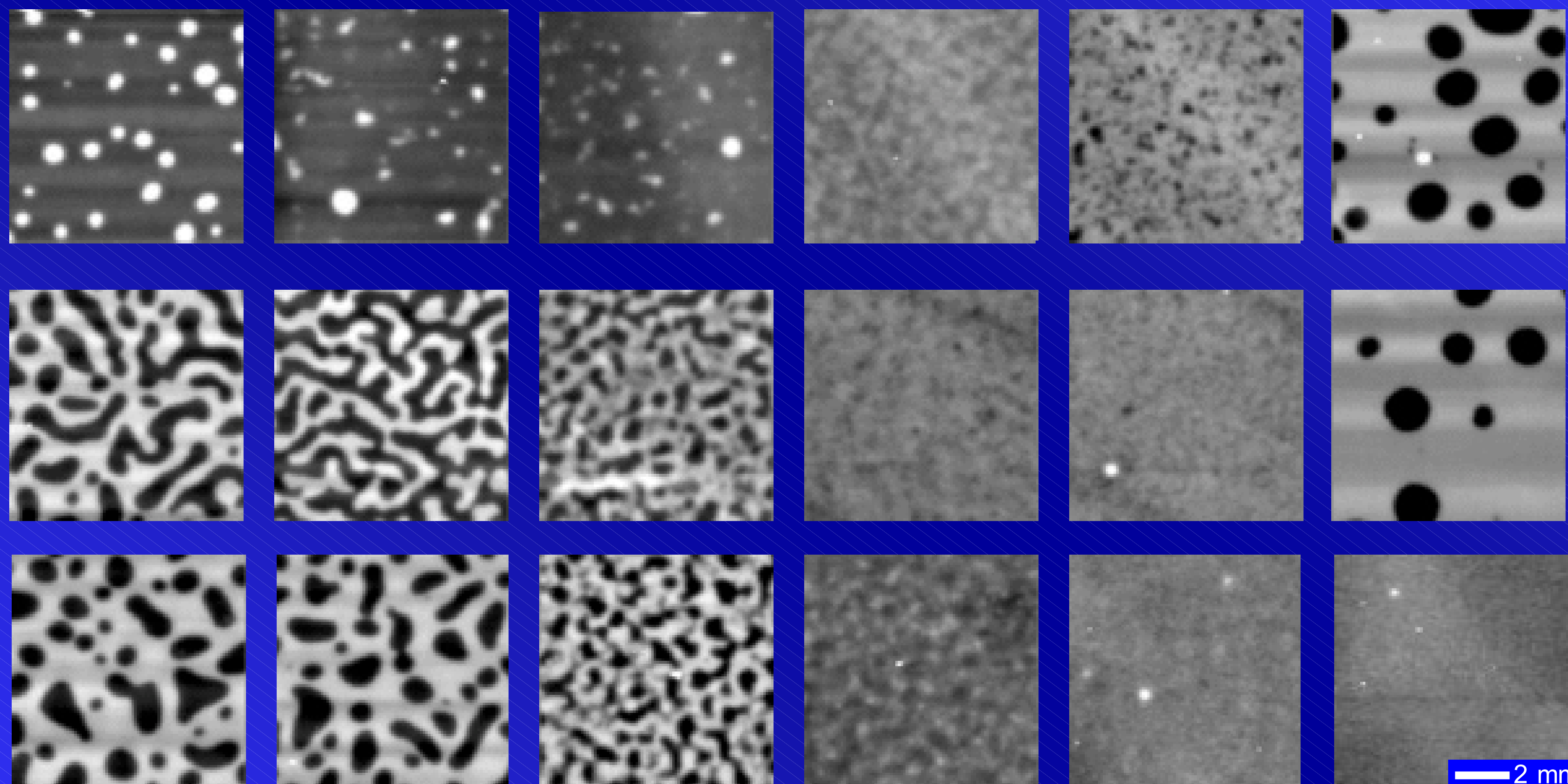
Change in morphology as surface energy increases

51k PS-*b*-PMMA

70 nm
~ 3.9 Lo

75 nm
~ 4.2 Lo

80 nm
~ 4.5 Lo



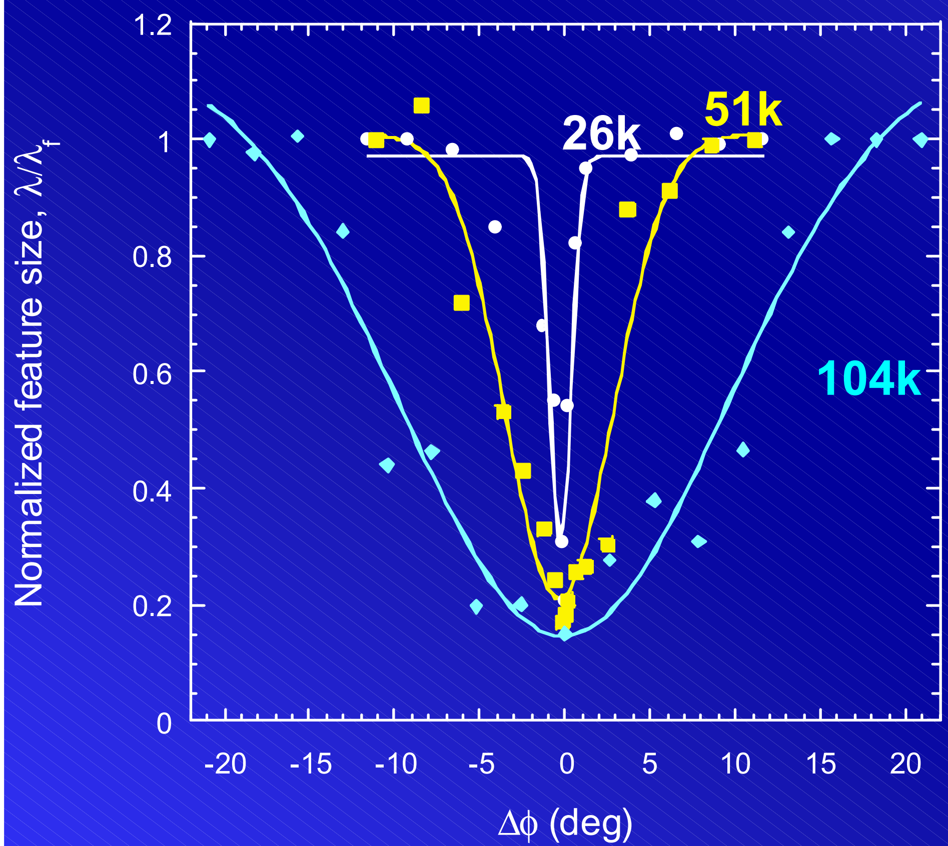
Symmetric
(PS at substrate)

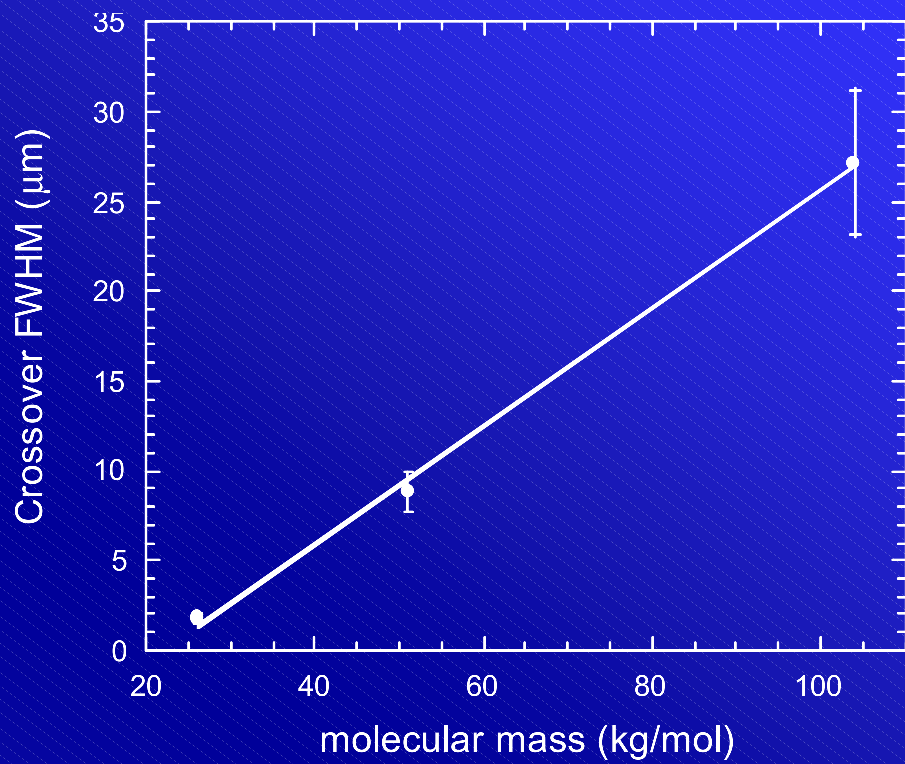
non-preferential

Asymmetric
(PMMA at substrate)

Increasing Surface Energy

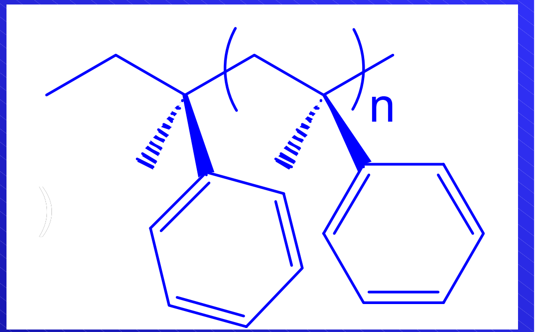
Effect of Molecular Mass on Crossover





Curves fit with gaussians:
FWHM: 26k ≈ 1.80°
51k ≈ 8.80°
104k ≈ 27.2°

Crystallization in Thin Films



Industrial Motivation:

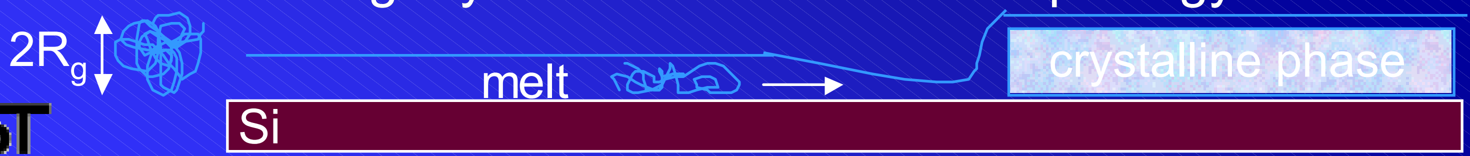
- Effect control of mechanical and optical properties,
- conductivity and permeability (PP/PE, PLA, PC, PEG)
- crystallization suppression?

Scientific Issues:

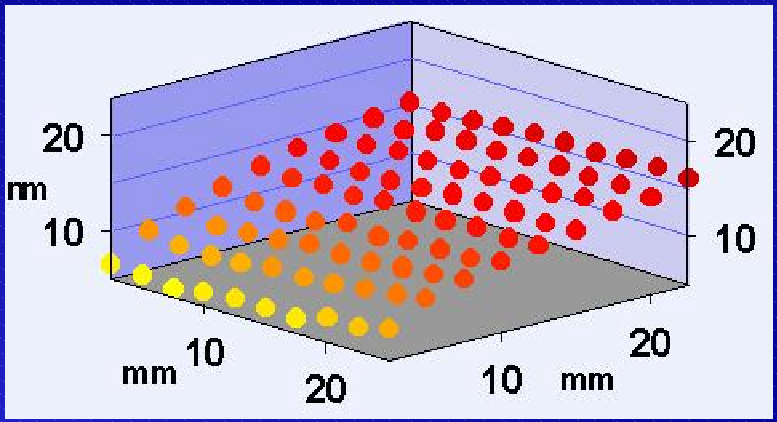
- Cooperativity in chain folding and diffusion, lamellar thickening, fractionation
- Molecular self-assembly
- Control of pattern formation → molecular architecture

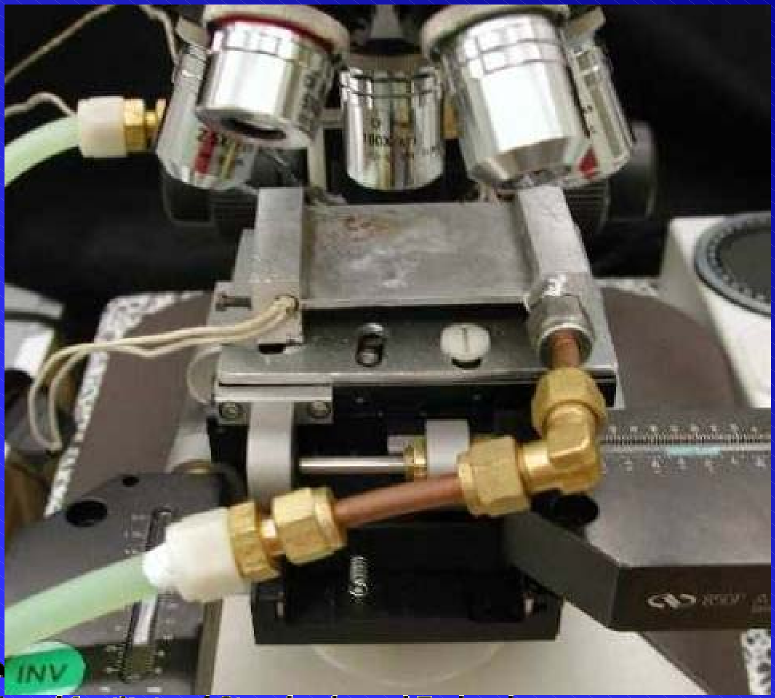
Objectives:

- Establish relevant length scales in model thin films for dominant forces influencing crystallization rate and morphology



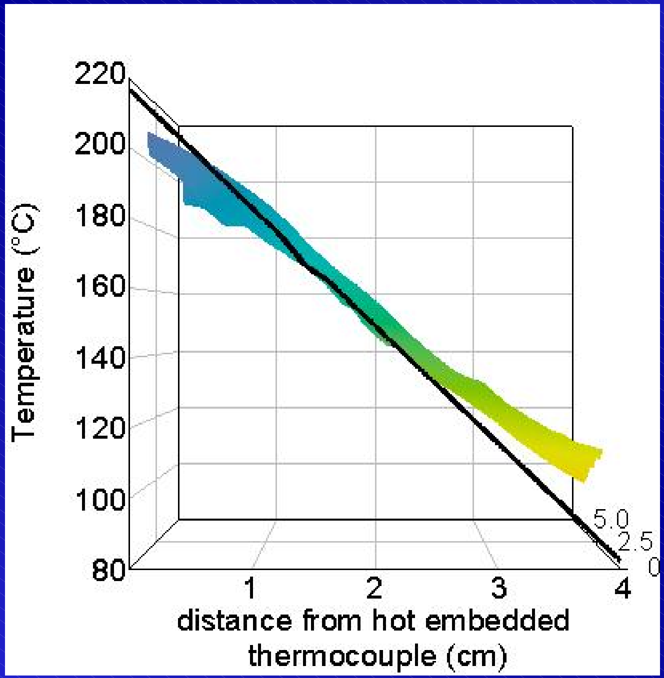
High Throughput Approach in Ultrathin Films



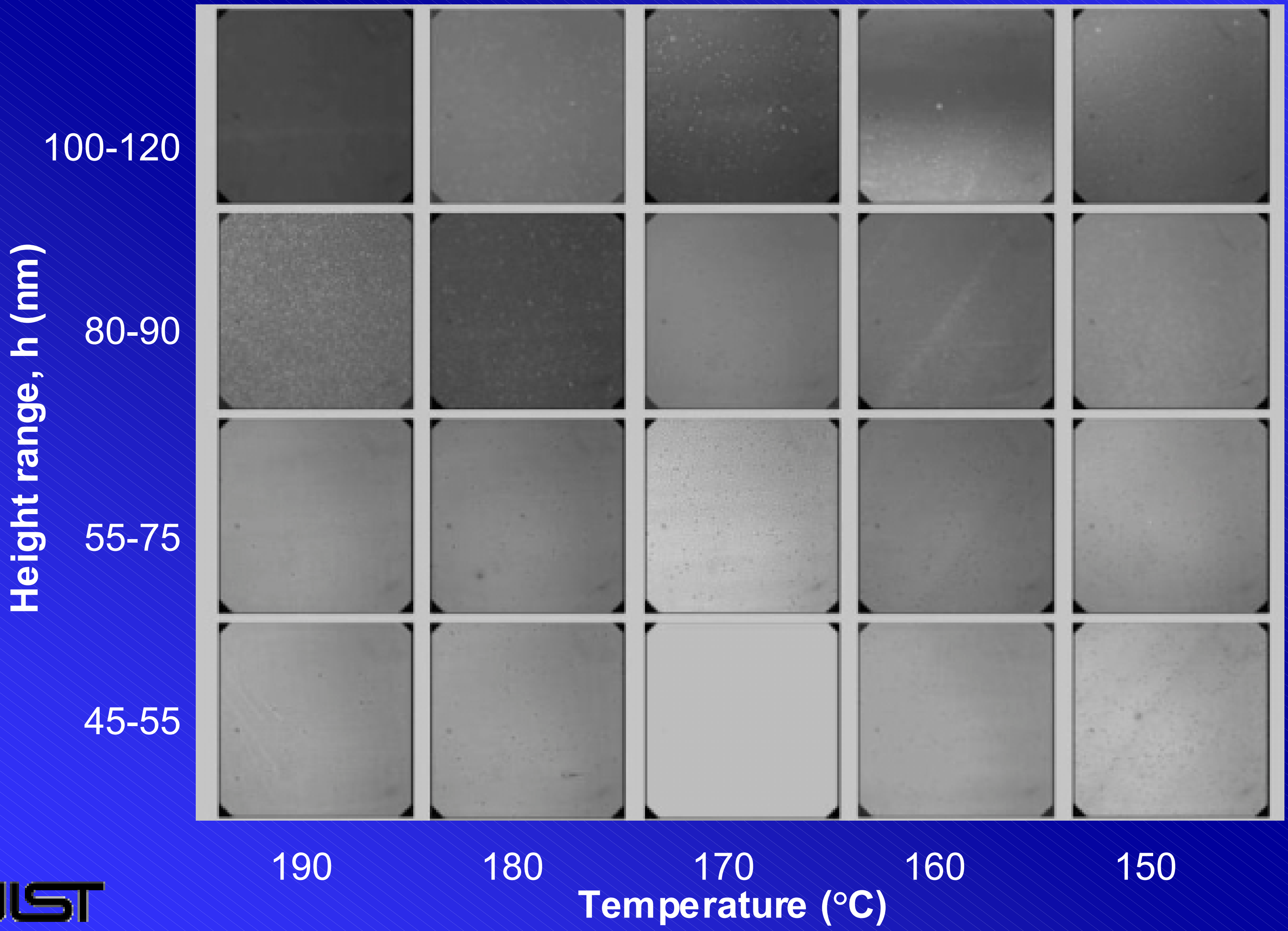


Potential to Investigate multiple parameters:

- Undercooling temperature
- Film thickness
- *Nucleating agents*
- Surface energy gradients

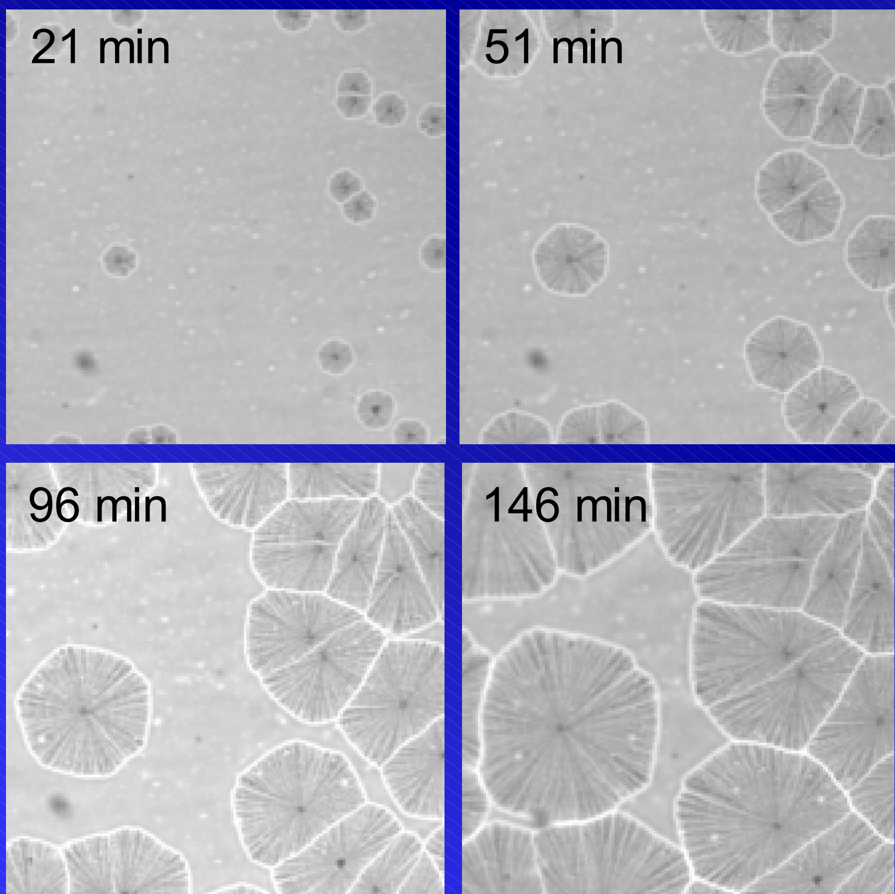


Crystallization Library Subset

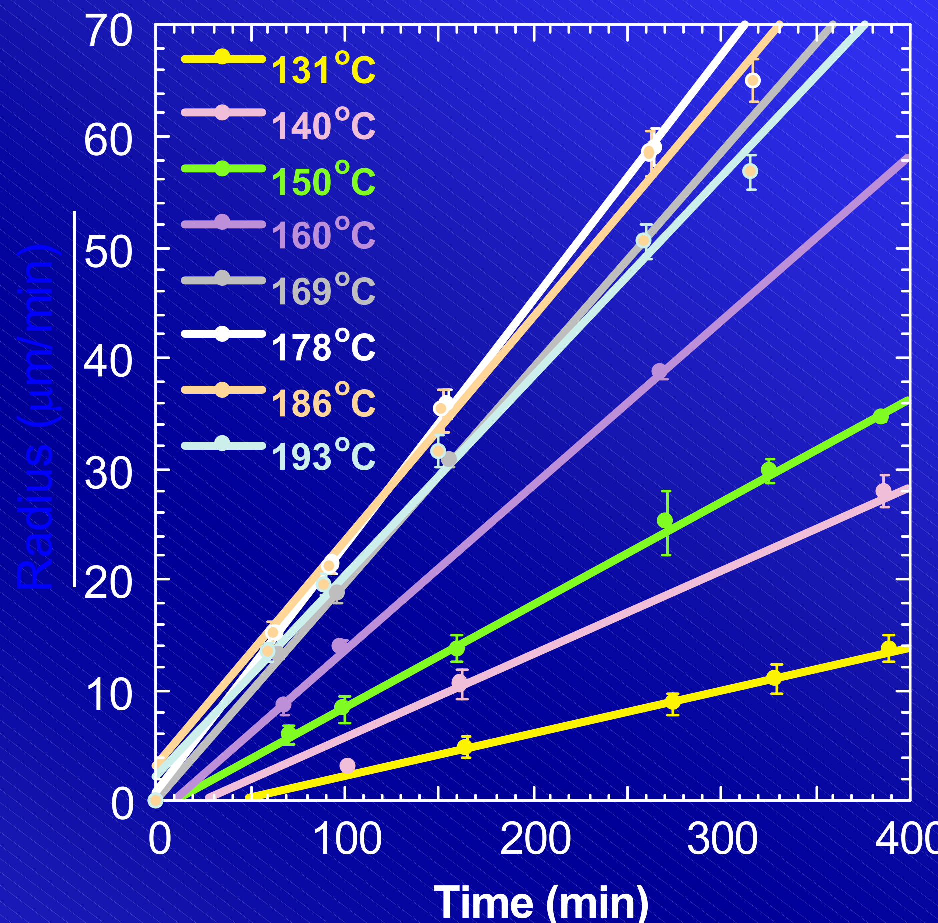


Effects of T on Growth Rates, G

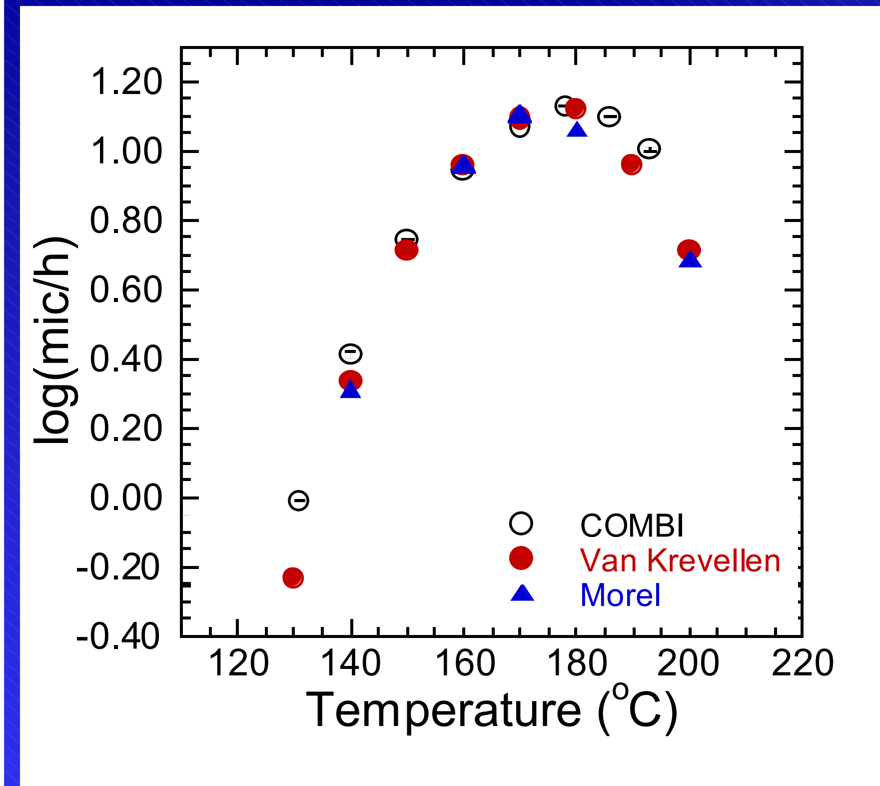
T = 170°C; h = 45 nm



50 µm

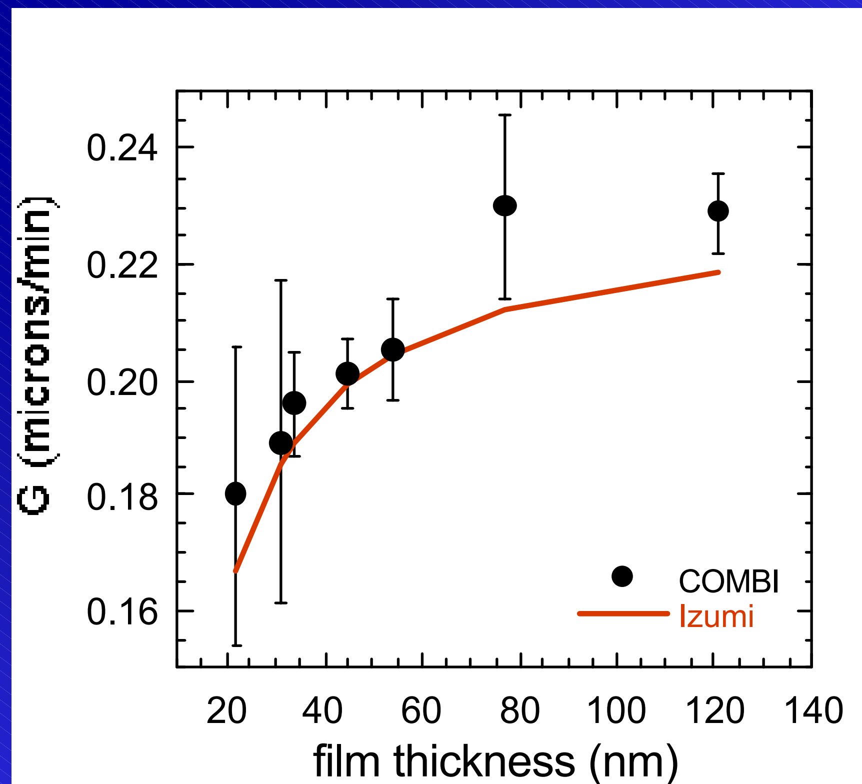


Crystallization Kinetics



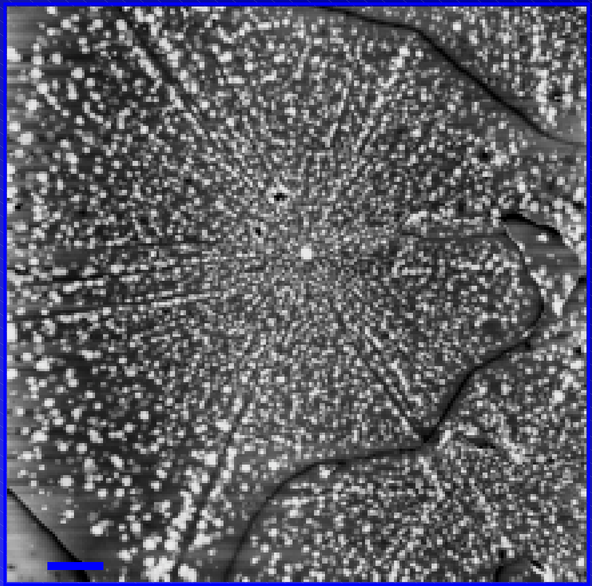
Viscoelastic effect:
As melt becomes more viscous, spherulites form and rates slow down.

Surface tension anisotropy:
Decrease in rate is observed in blends and thinning films.

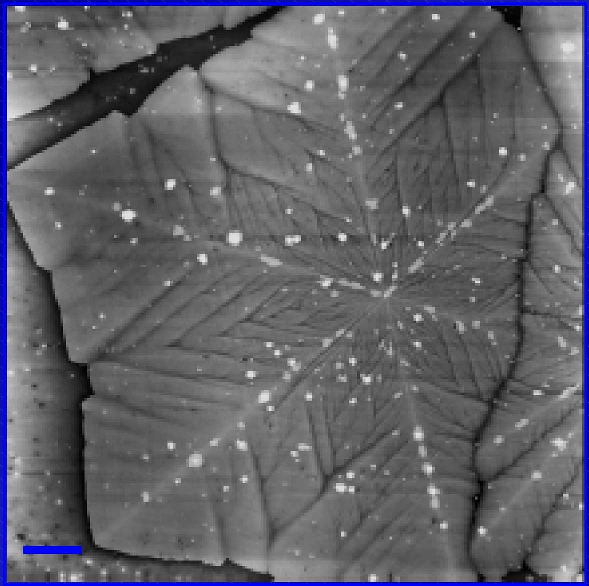


Effects of h on Structure (T=186 °C)

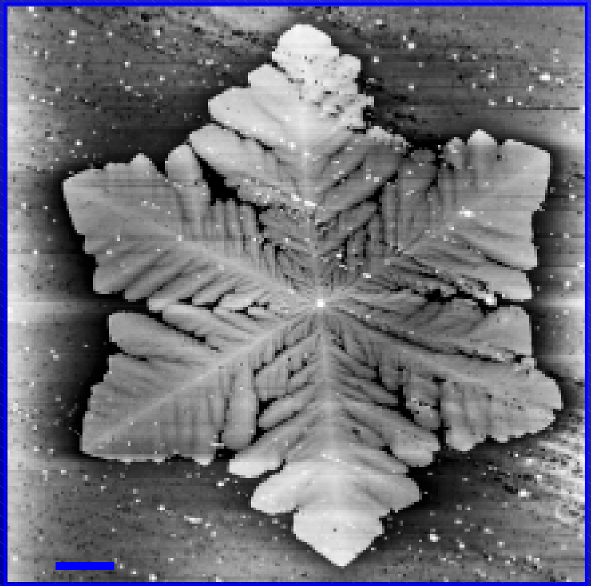
h = 24 nm



h = 19 nm



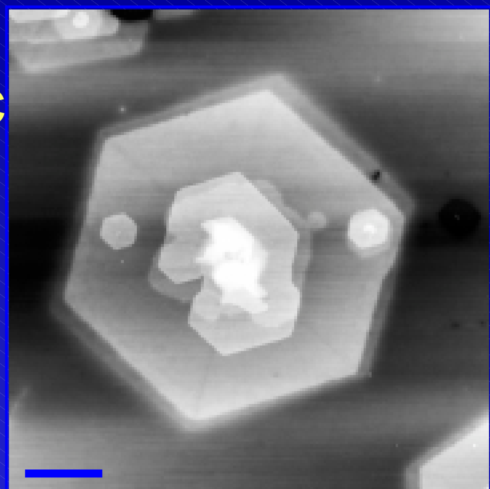
h = 15 nm



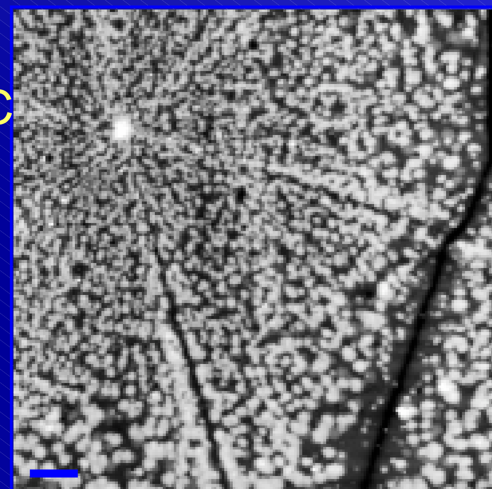
Scale Bars: 10 μm

Effects of T on Structure (h > 23 nm)

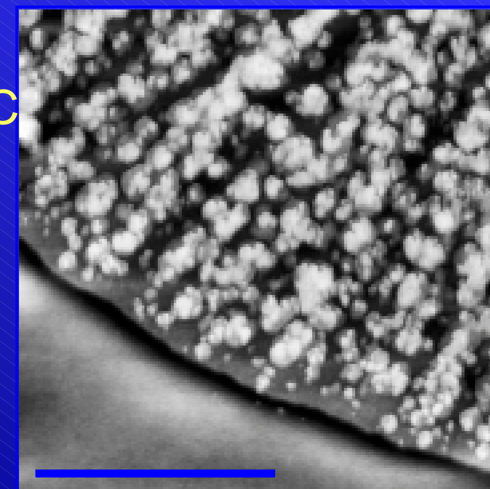
T = 202°C



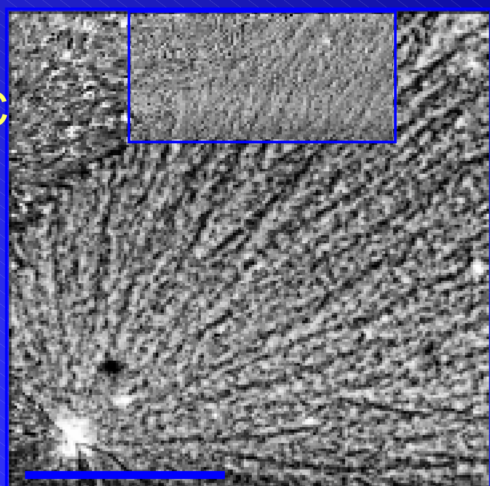
T = 193°C



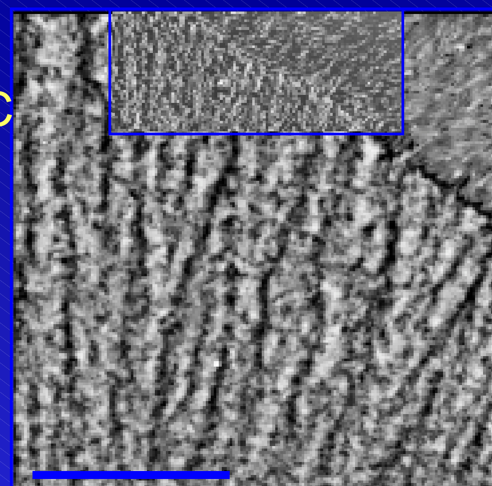
T = 169°C



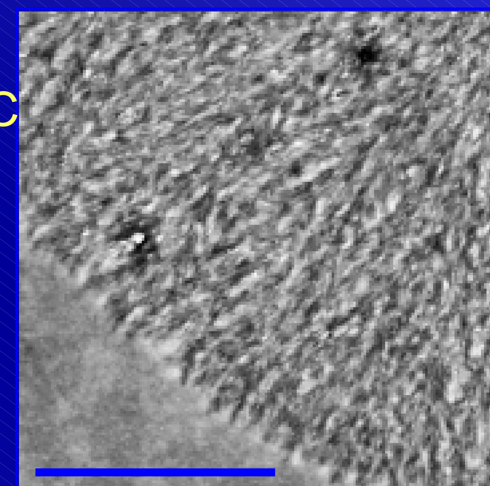
T = 160°C



T = 150°C



T = 131°C



Scale Bars: 5 μm

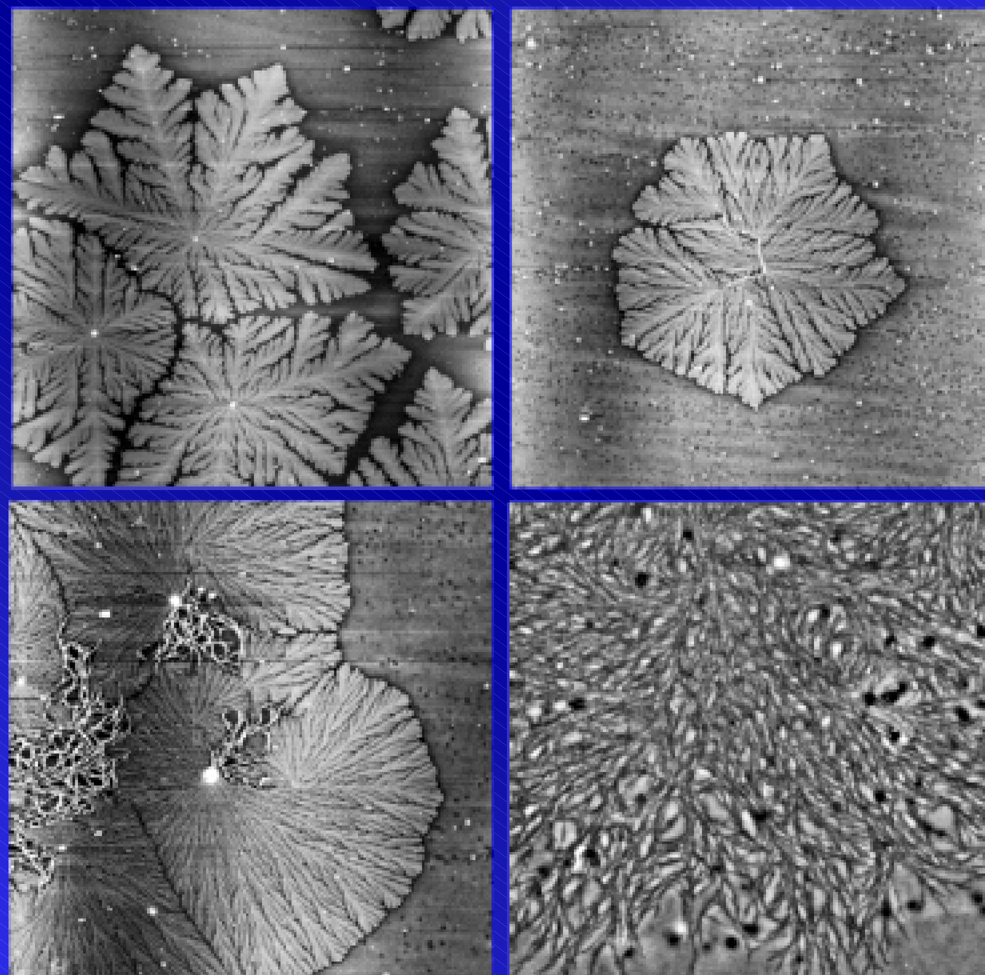
Effects of T on Dendritic Structures (h < 23 nm)

T = 169°C

T = 160°C

T = 150°C

T = 131°C



Scale Bars: 10 μm

Conclusions

- **Combinatorial techniques applied to study of block copolymer morphology and thin film crystallization**
- **Gradient energy surfaces promising as "self-reporting" library for characterizing interactions in multicomponent polymeric systems (e.g. block copolymer)**

Data -> Information -> knowledge discovery