

Multivariant Measurement
Methods Group

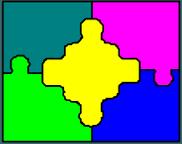
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Investigating Crystallization in Thin Films using High Throughput Methodologies *Isotactic Polystyrene*

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National Institute of Standards and Technology
Polymers Division

NIST Combinatorial Methods Center Kick-Off Meeting
January 2002



Semi-crystalline Polymer Thin Films

Industrial Motivation:

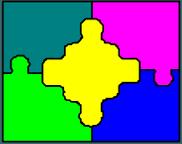
- Semicrystalline commodity materials (PP/PE, PLA, PC, PEG, ...)
- Effect control of mechanical and optical properties, conductivity and permeability

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

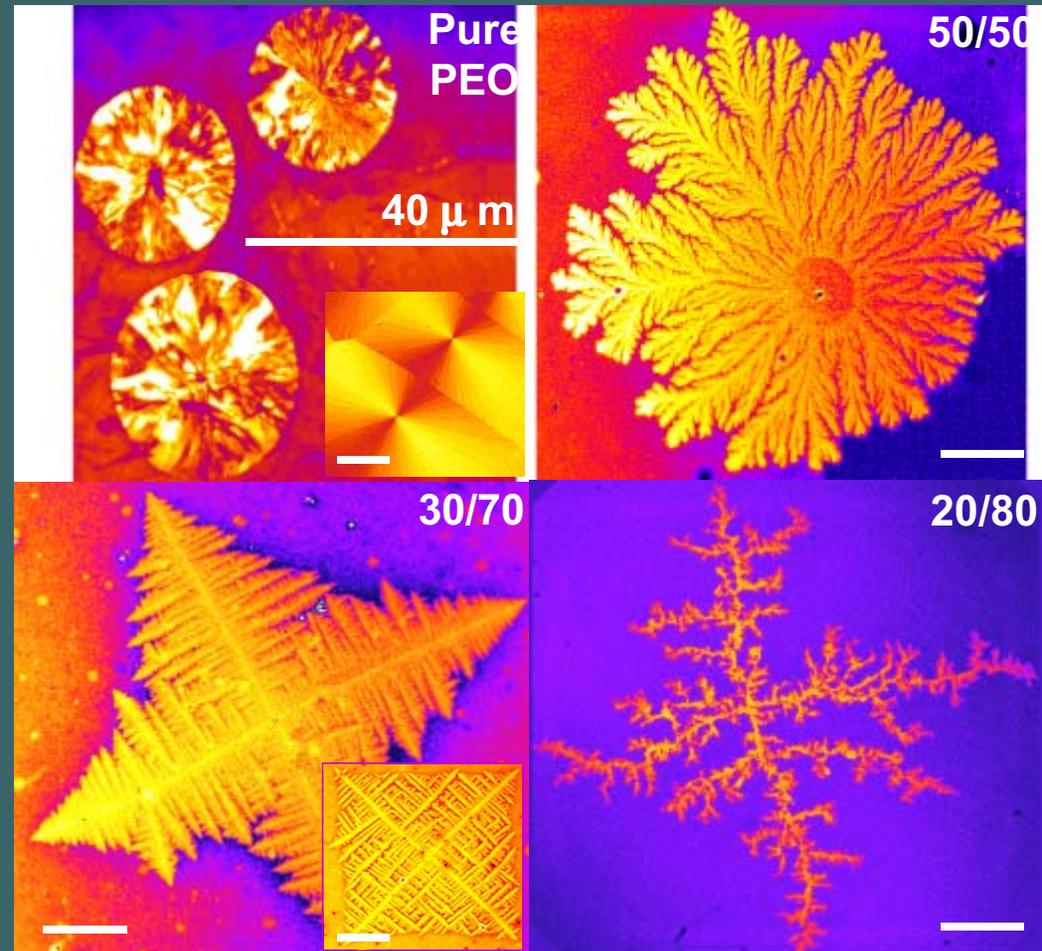


Amorphous / Semi-crystalline Polymer Blends

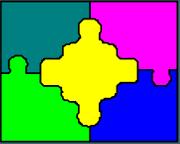
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PMMA/PEO Blends in Thin Films:

- Crystallization patterns tuned through polymer composition
- Competition with phase separation (below UCST) changes λ
- High F_{PMMA} leads to fractal dendrites (diffusion limited aggregation)

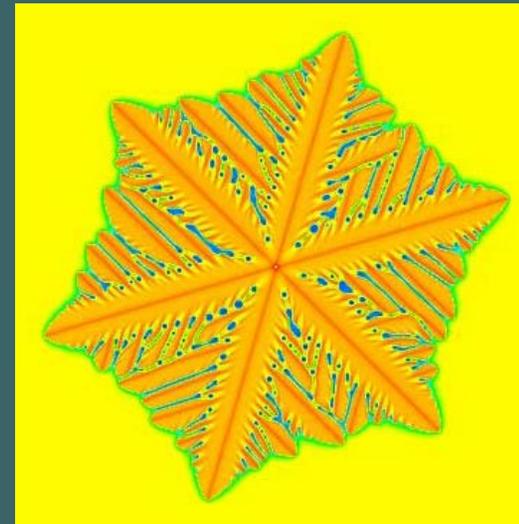


Ferreiro et al., *Phys. Rev. E*, submitted.



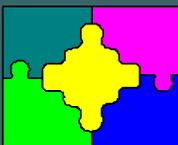
Modeling Morphologies

- Model simulations based on solidification in two-dimensional fluid mixtures (Cu-Ni alloys)
- Varying λ , seaweed and dendrite structures are obtained
- No spherulitic (elasticity) or fractal morphologies to date



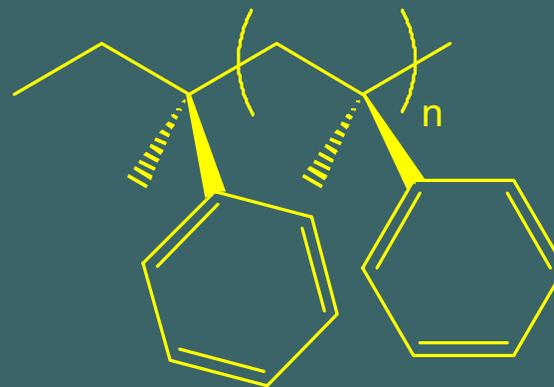
Phase-Field Simulated Hexagonal Dendrite (J. Warren)

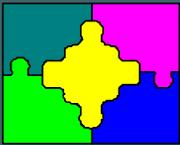
J. A. Warren and W. J. Boettinger, *Acta Metall. Mater.*, **1995**, 43, 689.



Why Isotactic Polystyrene (ipS)?

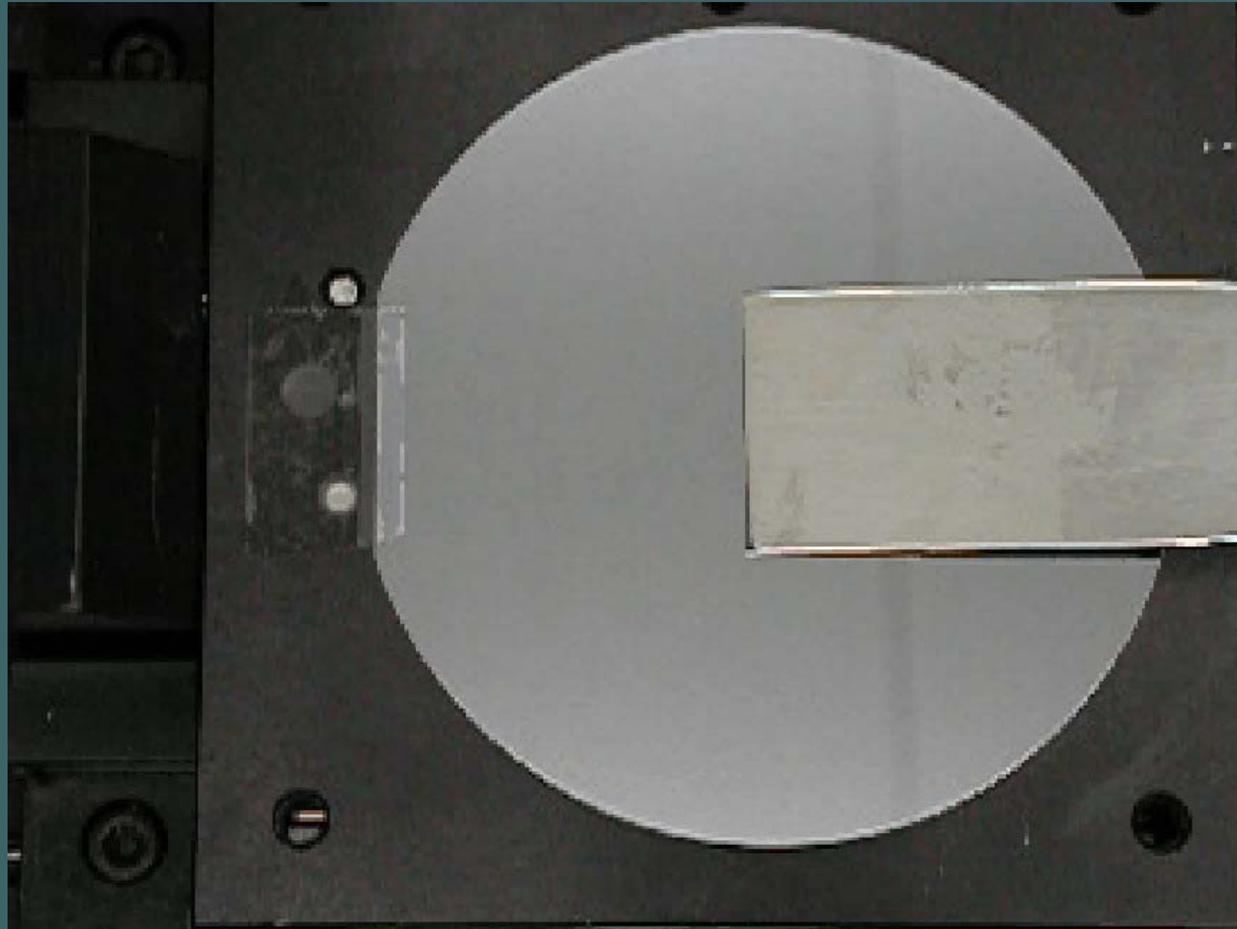
- Substantial literature on the crystallization of ipS in bulk and thin films
- ipS crystallizes slowly and on timescales measurable by “high-throughput” optical microscopy
- high T_g : Films quenched at room temperature
- Temperature stage spans T_g to near T_m (218 °C)

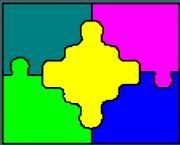




Flow Coating

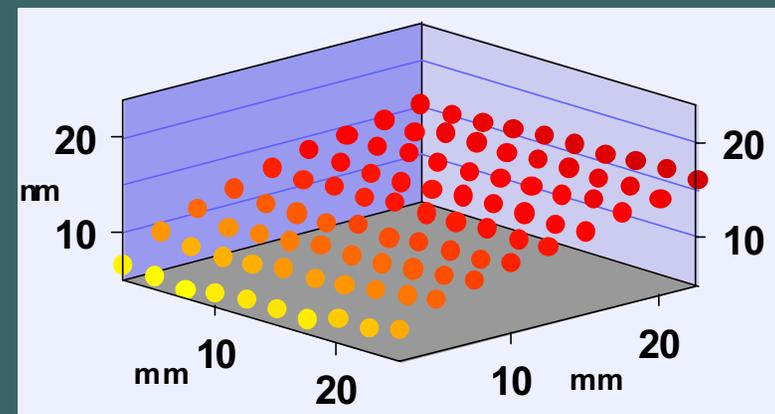
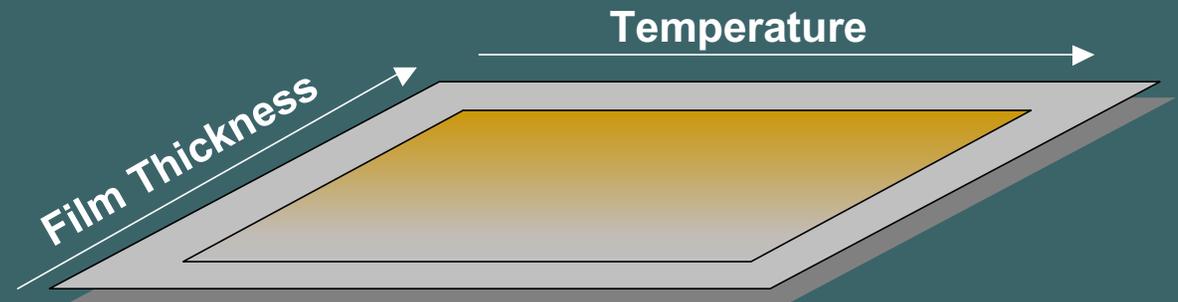
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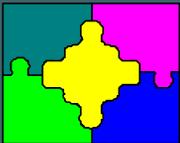




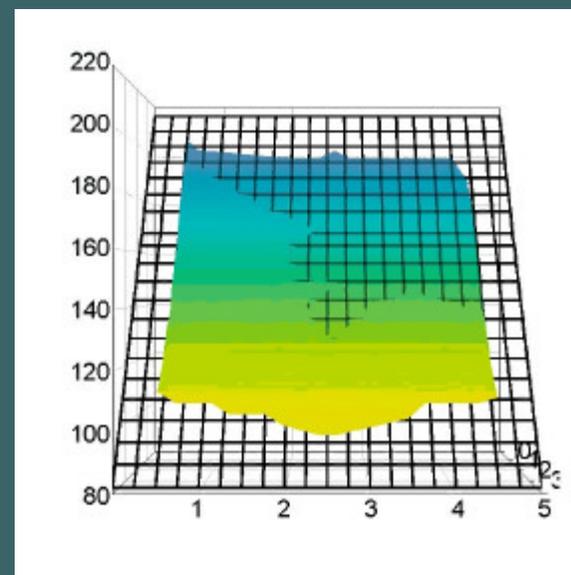
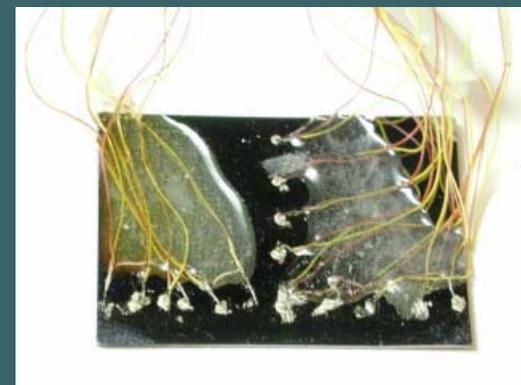
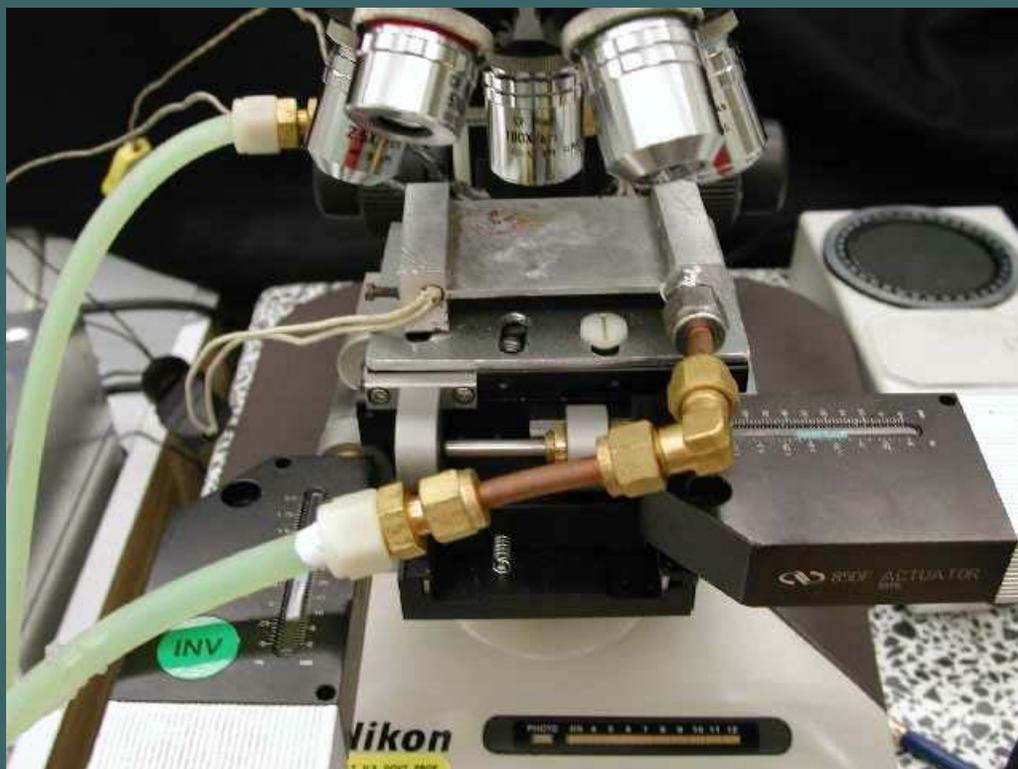
Combinatorial / High-throughput Polymer Crystallization

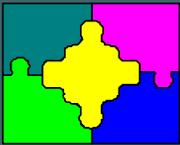
- Access to larger parameter space
- Faster
- Cheaper
- Potential to Investigate multiple parameters:
 - Under-cooling temperature
 - Film thickness
 - Nucleating agents
 - Surface energy gradients
 - Surface pattern gradients



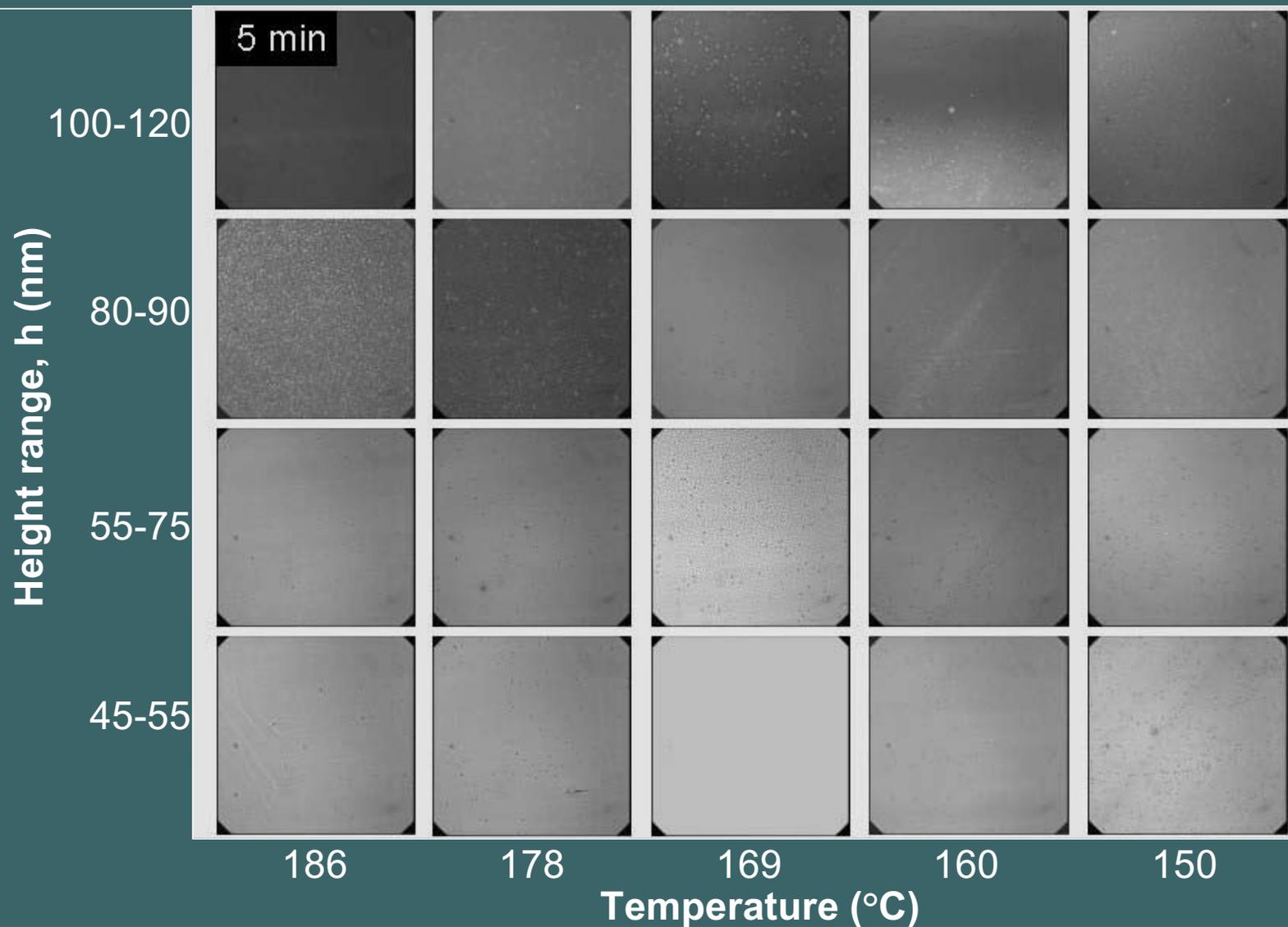


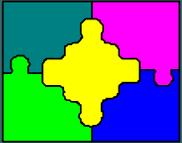
Temperature Gradient Stage





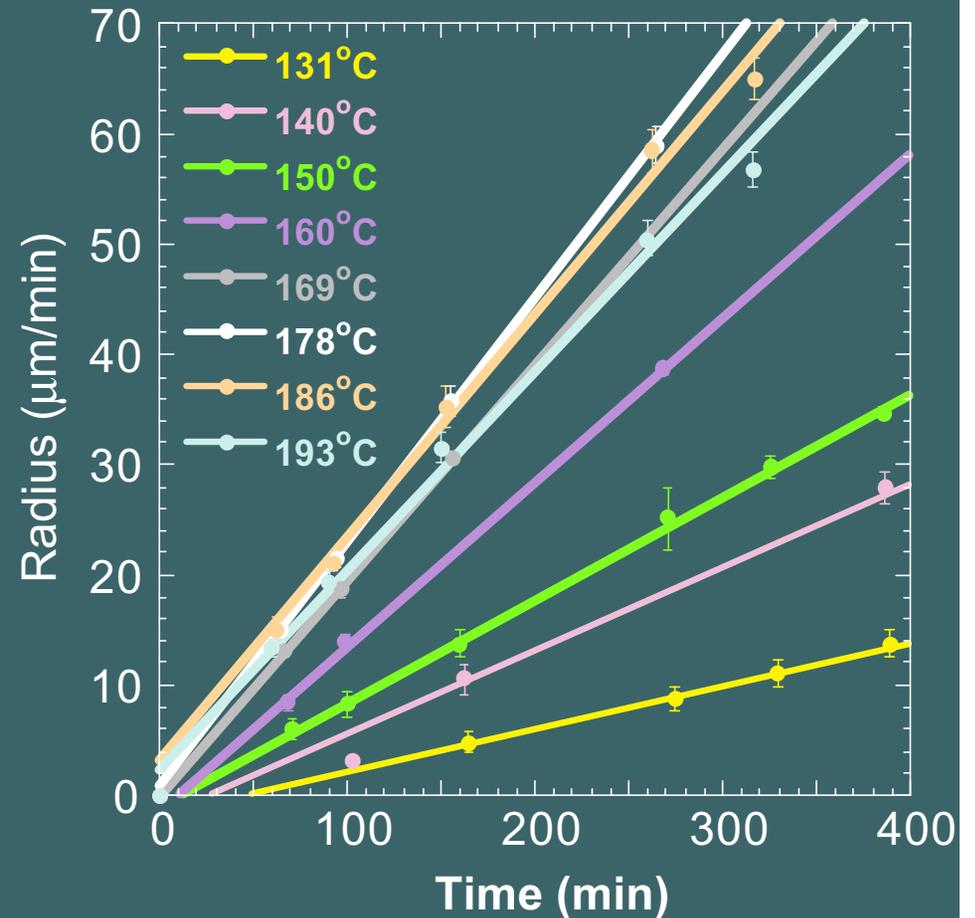
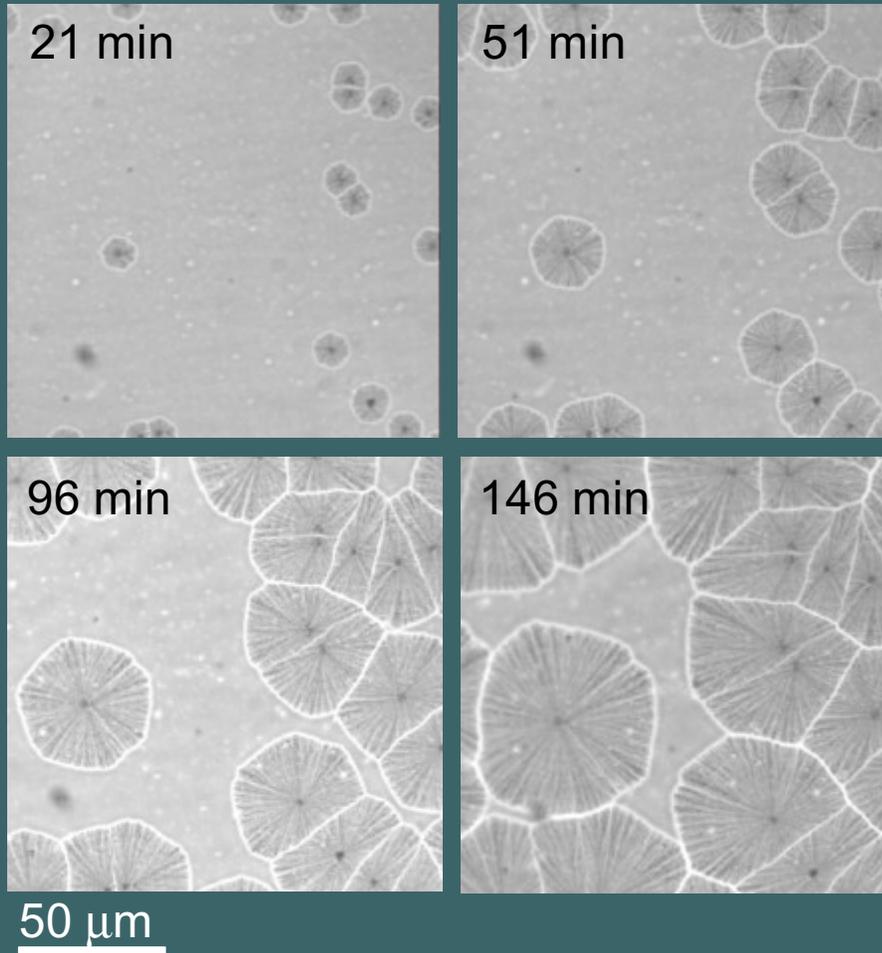
Optical Image Library

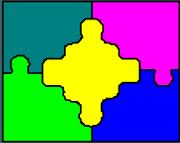




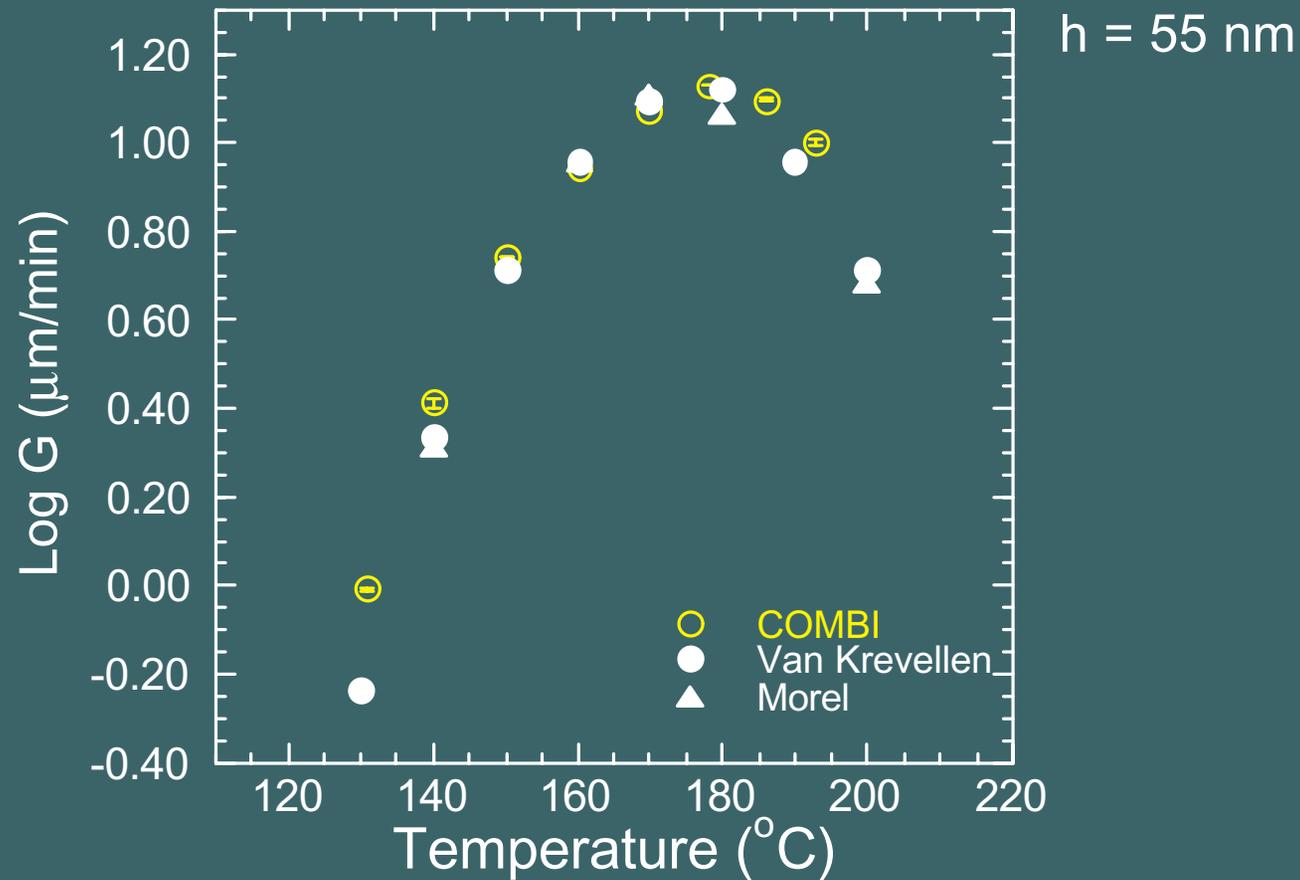
Effects of T on Growth Rates, G

T = 170°C; h = 45 nm

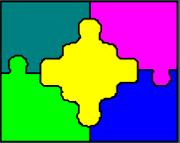




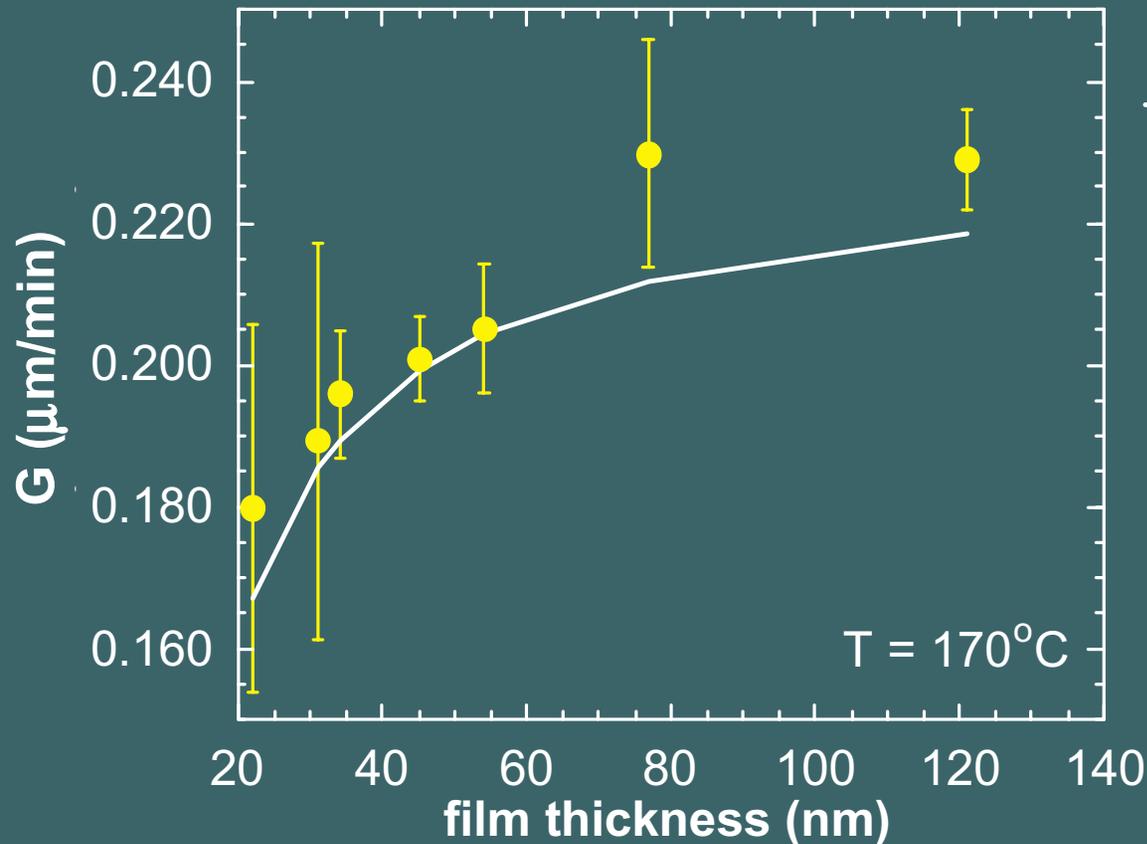
Effects of T on Growth Rates



J. Boon, *et al.*, *J. Poly. Sci. A-2*, **1968**, 6, 1791.



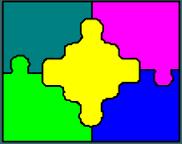
Effects of h on Growth Rates



Dependence of rate on
film thickness:

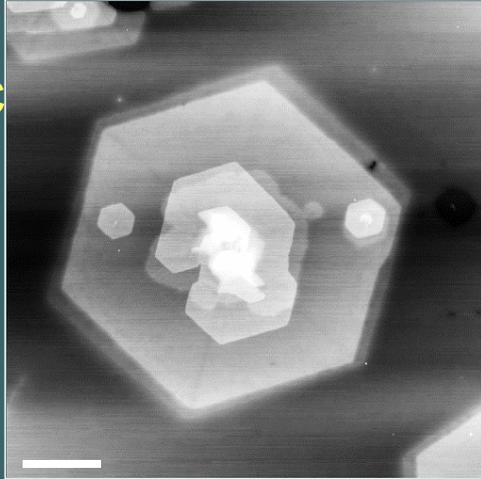
$$G(h) = G(\infty)(1-d/h)^*$$

*S. Sawamura, *et al.*, *J. Phys. Soc. Jpn.*, **1998**, 67, 3338.

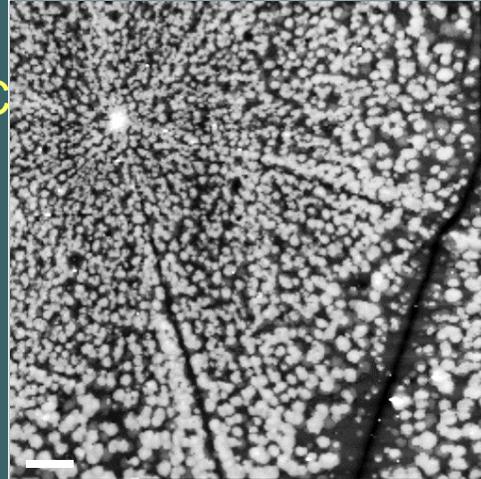


Effects of T on Structure ($h > 23$ nm)

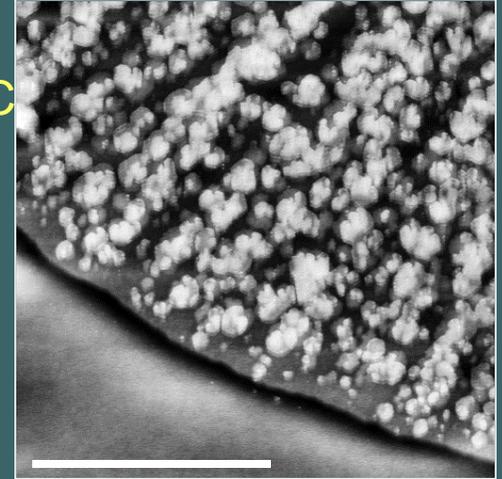
T =
202°C



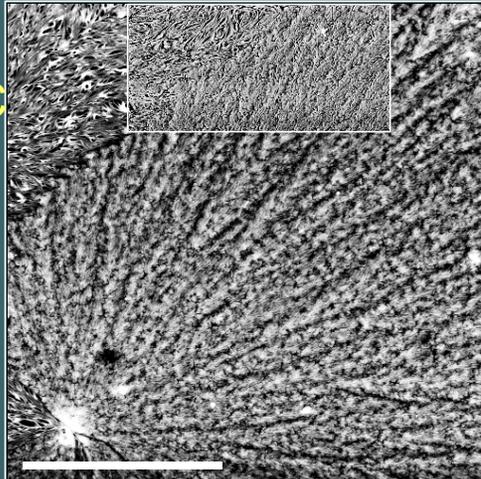
T =
193°C



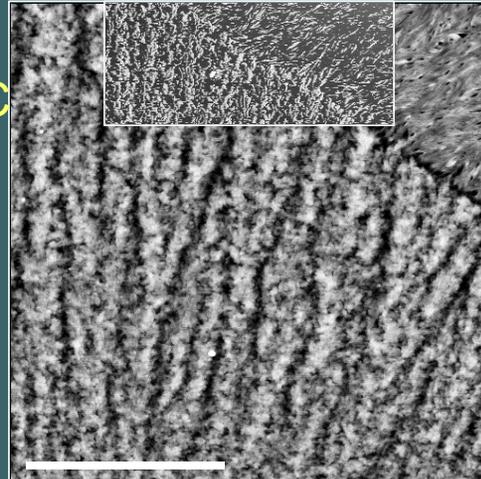
T =
169°C



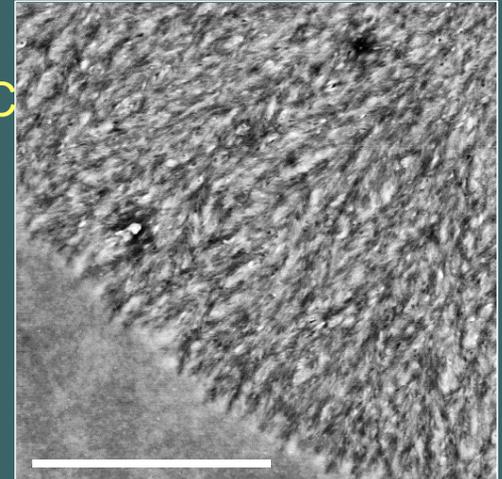
T =
160°C



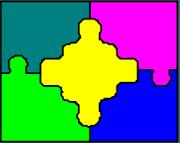
T =
150°C



T =
131°C

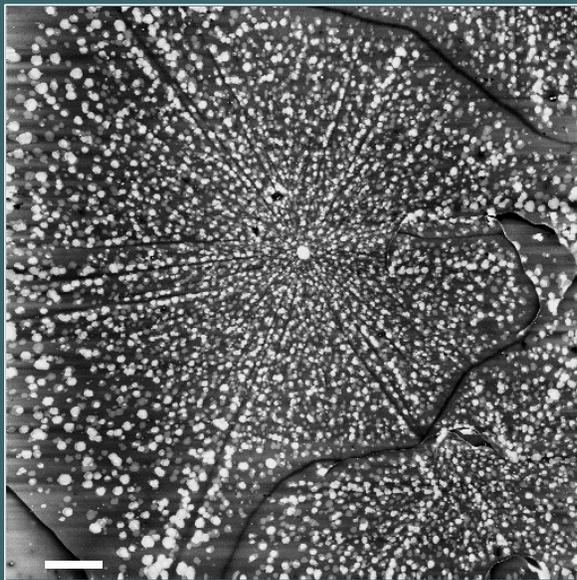


Scale Bars: 5 μ m

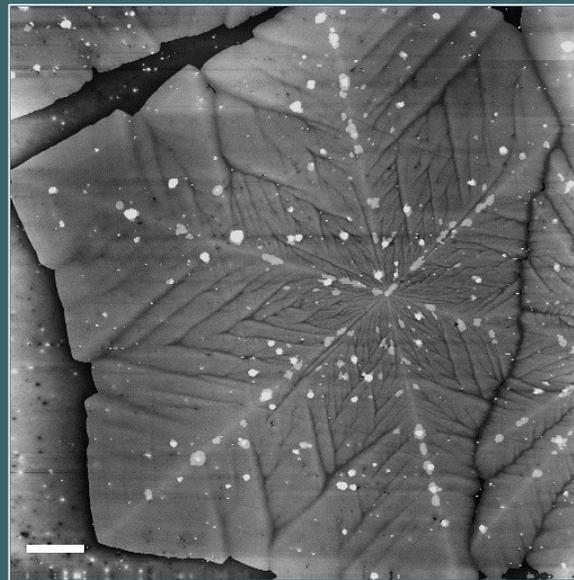


Effects of h on Structure

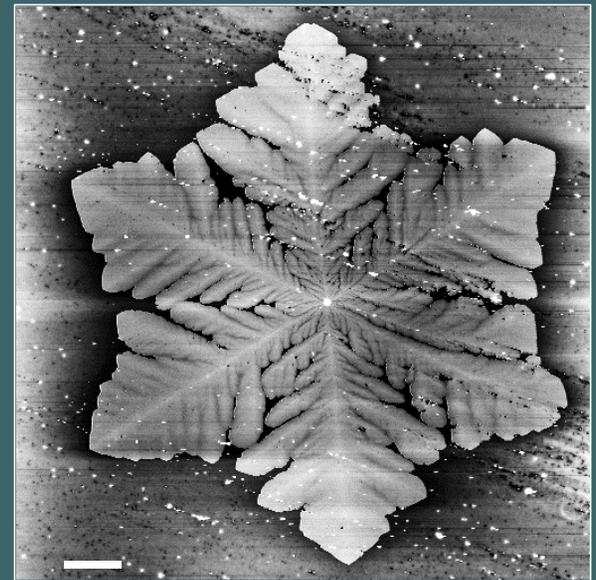
$T = 186^\circ\text{C}$
 $h = 24 \text{ nm}$



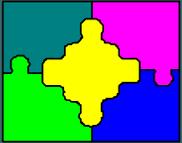
$T = 186^\circ\text{C}$
 $h = 19 \text{ nm}$



$T = 186^\circ\text{C}$
 $h = 15 \text{ nm}$

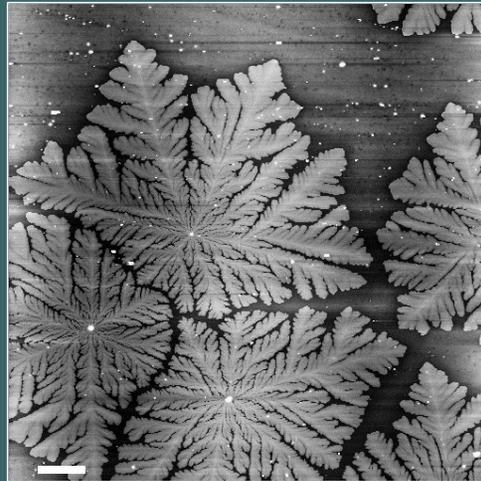


Scale Bars: $10 \mu\text{m}$

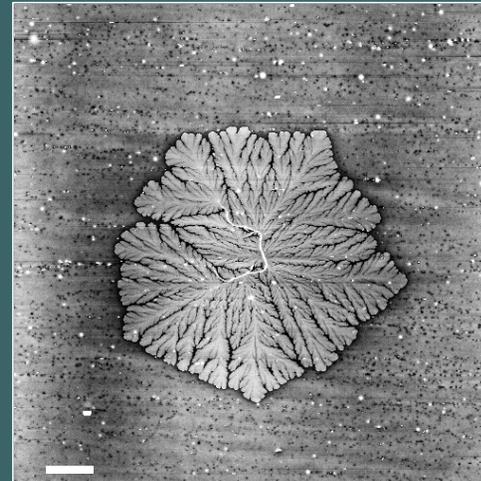


Effects of T on Dendritic Structures

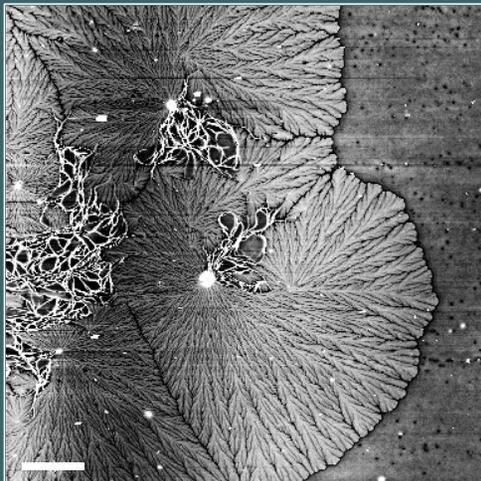
T =
169°C



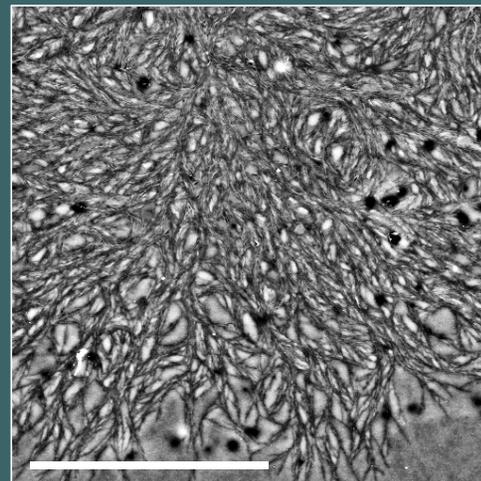
T =
160°C



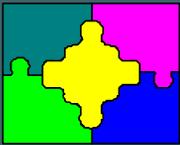
T =
150°C



T =
131°C

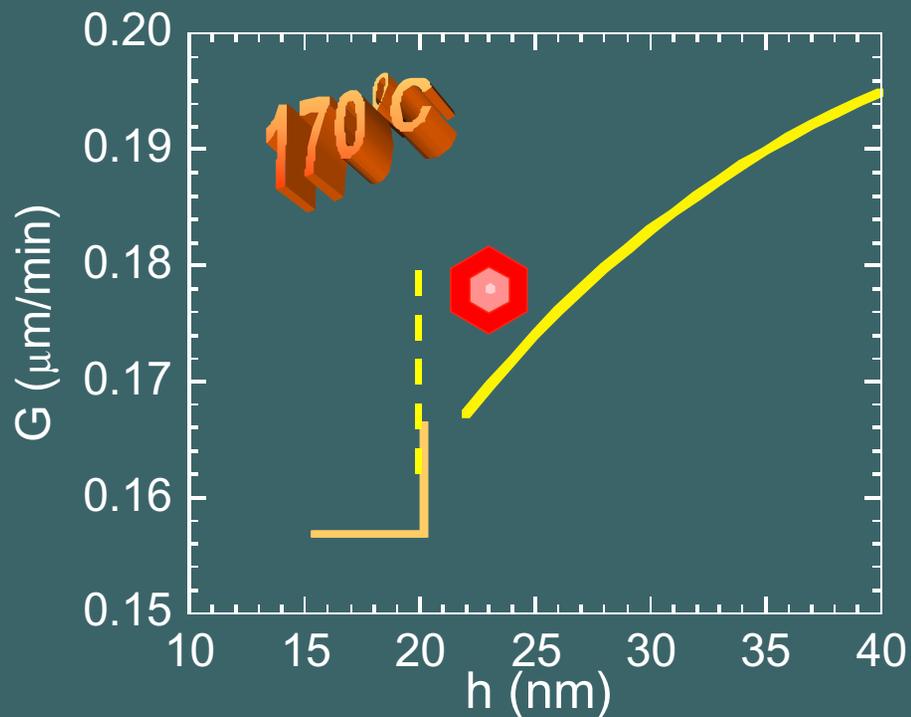


Scale Bars: 10 μm

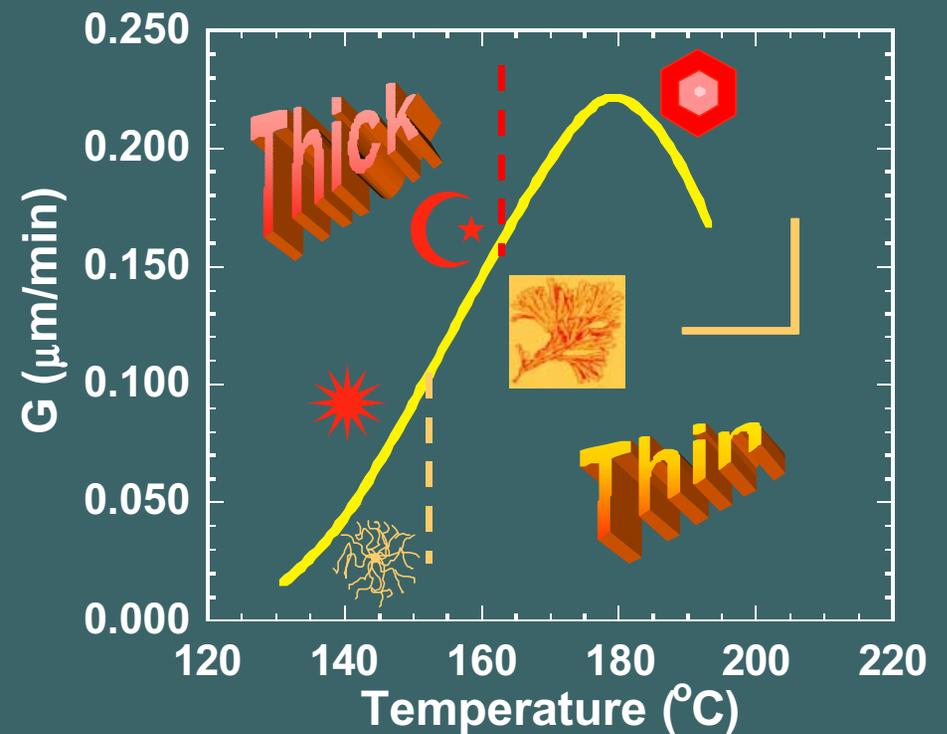


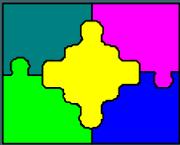
Structural Control Factors

Confinement Effect



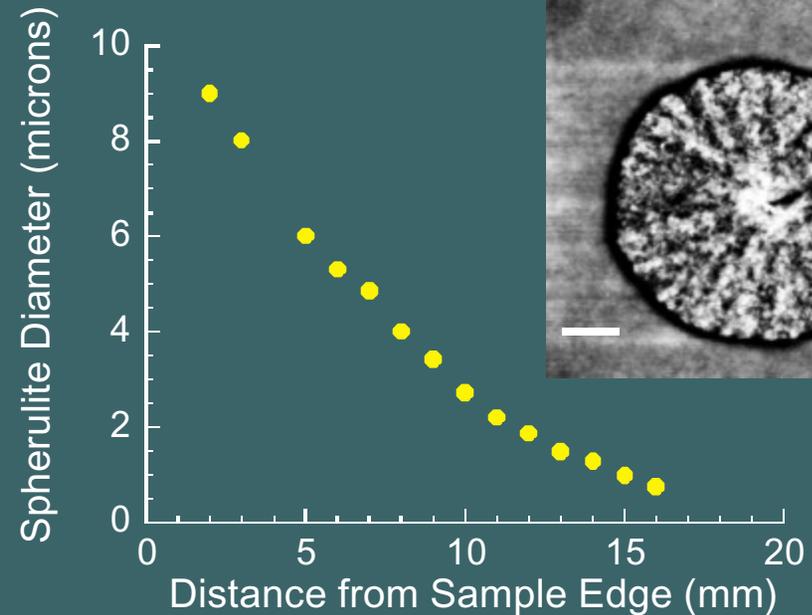
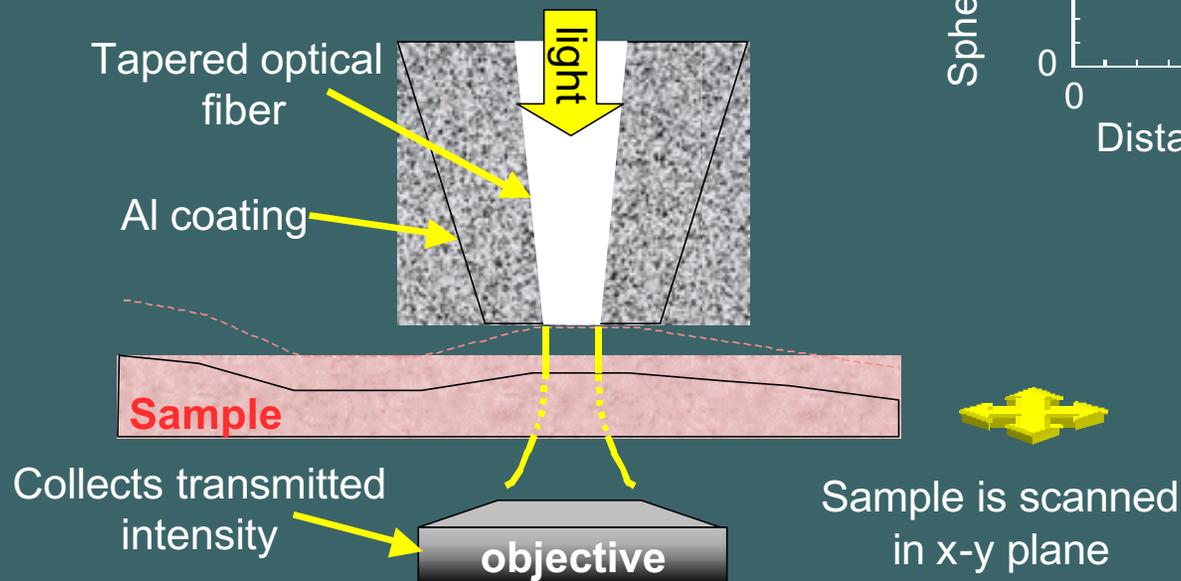
Viscoelastic Effect



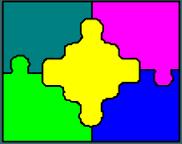


Focusing on Target Areas: NSOM

Samples prepared on a shallow temperature gradient for short times can contain a narrow range of size and structures.



In collaboration with:
L. Goldner and M. Fasolka
Optical Technology Division
NIST

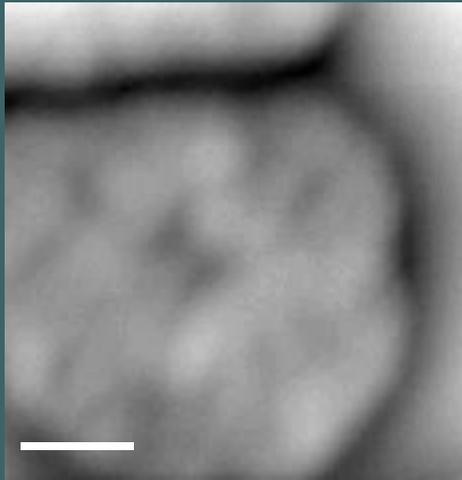


NSOM Polarimetry

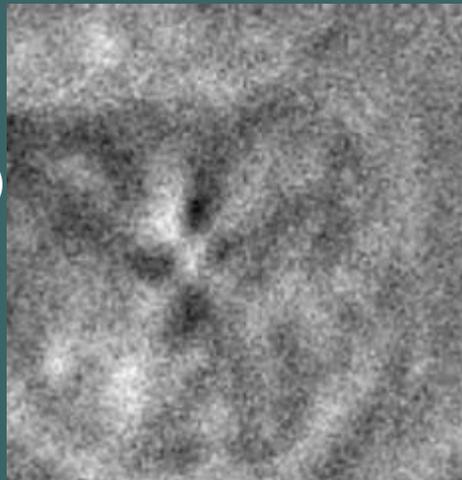
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L. Goldner and M. Faselka,
Optical Technology, NIST

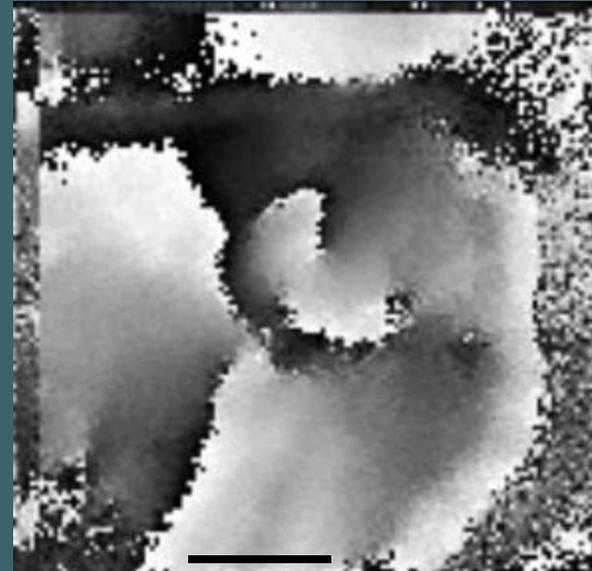
Topology
(from force
feedback)



Dichroism
(z-scale 0-4%)

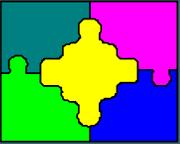


Angle of Birefringence (z-scale 0-180°)



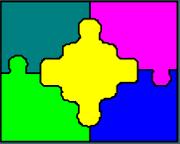
- NSOM polarimetry may provide insight into more complex optical activity for multiple crystal structures

Scale bars: 1 μm



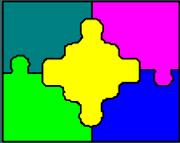
Conclusions

- Crystal growth rates of isotactic polystyrene as a function of h and T on continuous gradient films agree with literature. G passes through a maximum near 180°C and decreases with h below 80 nm.
- Morphological transitions with T and h are similar to a recent publication. As h approaches R_g , spherulites are replaced by hexagonal dendrites.
- First evidence of competition between surface tension anisotropy and viscoelastic effects in crystallization.



Future Directions

- New measurement techniques
 - Mechanical and optical properties of semi-crystalline films
 - Kinetics in faster crystallizing films
 - Access to continuous parameter space on film
 - Structural probes during crystal formation
- Development of new informatics techniques (image analysis)
- Extension to polymers, blends and parameters of interest
 - iPP, PEG, PLA
 - Nucleating agents, surface energy or pattern gradients



Acknowledgments

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Amit Sehgal
Alfred Crosby

\$\$
National Research Council