NIST Combinatorial Methods Center

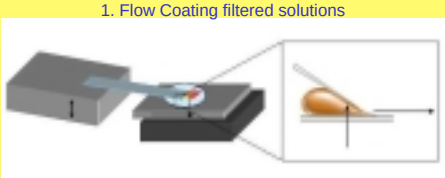
Mapping Isotactic Polystyrene Crystallization with High Throughput Methods

Introduction

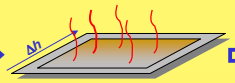
In the combinatorial methodology, experimental design begins with specification and development of a library encompassing a subset of parameter space. Crystallinity is a critical parameter affecting material properties of many polymers. In order to add this variable to the index of gradient libraries, it is necessary to verify that consistent, quantifiable libraries can be fabricated, measured and analyzed. To that end, we used isotactic polystyrene (ipS) to validate the use of high-throughput gradients to measure kinetics and morphology of polymer crystallization. Having accomplished that, it is possible to consider combining gradients in the crystalline nature of a film (including, morphology, degree of crystallinity, etc.) with existing techniques, such as blend composition, as well as incorporating them into new tests being developed in parallel, such as adhesive and mechanical properties.

Sample Preparation

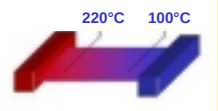
1. Flow Coating filtered solutions



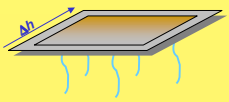
2. Drying thickness gradients



3. Crystallize on a gradient temperature OM stage

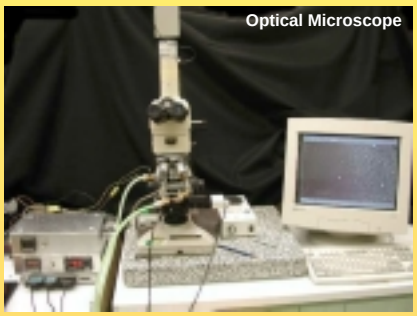


4. Quench to observe morphology (AFM)

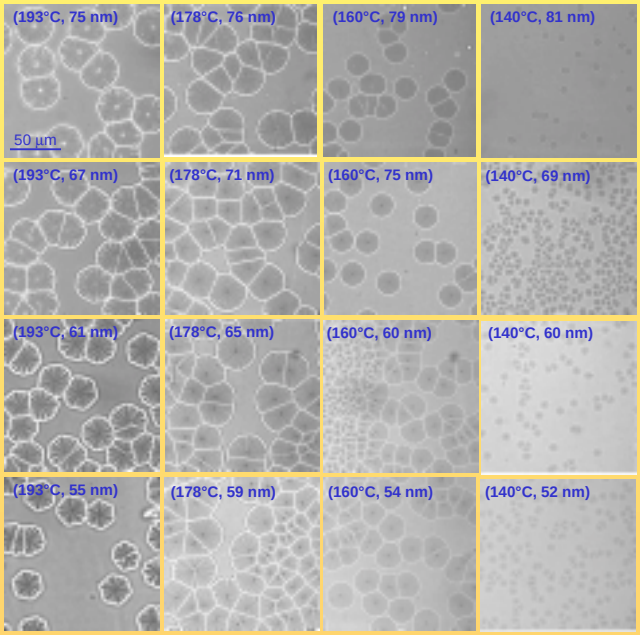


Thickness (*h*) contour maps are constructed using spot interferometry before and after step 2. Surface temperature (T_x) contour maps are constructed using thermocouple arrays mounted on silicon wafers prior to step 3. Linear steps in x and y stages during crystallization are later calibrated to real values of *h* and T_x using the contour maps.

Experimental Techniques

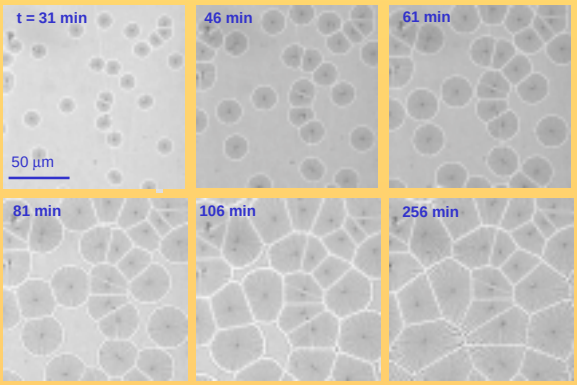


The films are oriented with the thickness gradient orthogonal to temperature on an optical microscope stage (left) and arrays of images at fixed positions are captured over time as the film crystallizes, producing a library of images representing (T_x, *h*, t).



A subset from an array of optical microscope images of ipS at t = 65 min and various (T_x, *h*)

Cross sections of the library show subregions of the ipS film crystallizing over time (below) or capture the different size and structure of crystallites at a given time depending on the temperature and film thickness represented in the image (right). Values of spherulite radius are averages of multiple measurements in each image.



Optical Microscope images of ipS crystallizing at T_x = 169°C, *h* = 60 nm

AFM of each subregion is captured in tapping mode using an automated x-y stage (below) in order to a.) elucidate structure in regions of the film for which we have kinetic data, and b.) probe regions of the film beyond the resolution of the optical microscope.

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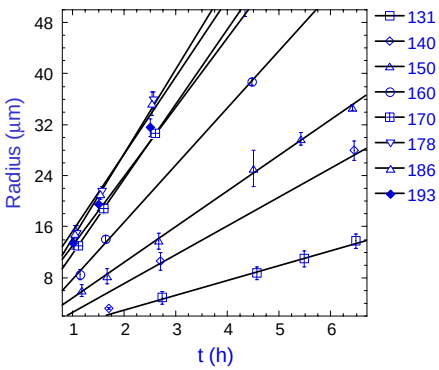
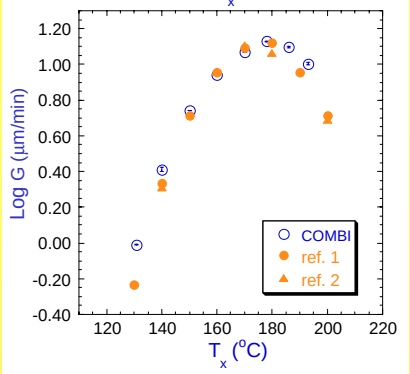
Growth Rate Dependence on T_x and *h*

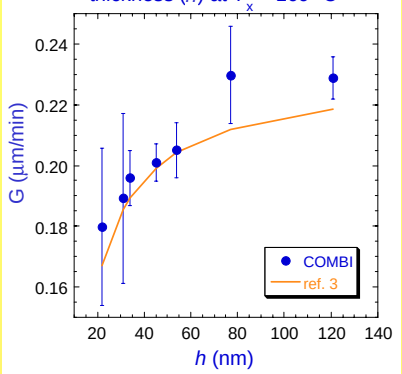
Spherulitic radius of ipS crystals as a funtion of time at various temperatures and *h* = 45 nm



Spherulitic growth rate (G) as a function of temperature (T_x) at *h* = 55 nm



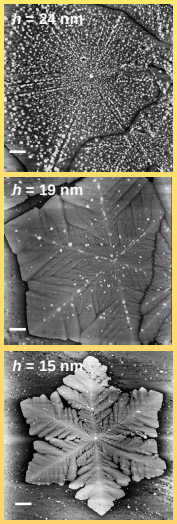
Growth rate (G) as a function of film thickness (*h*) at T_x = 169 °C



- Growth rates, G (slopes of lines plotted to left), from various subregions of the films are equivalent to rates measured previously in discrete films.
- Over the temperature range studied, competition between the decreasing rate of crystallization with decreasing diffusivity and the increase in rate at increased undercooling results in a maximum in G near 175 °C (center).
- Rates also slow as the films become thinner (*h* < 50 nm, right). This has been attributed to decreasing mobility in thin films (ref. 3). Residual solvent plasticizes the film at thicker *h* (> 80 nm).

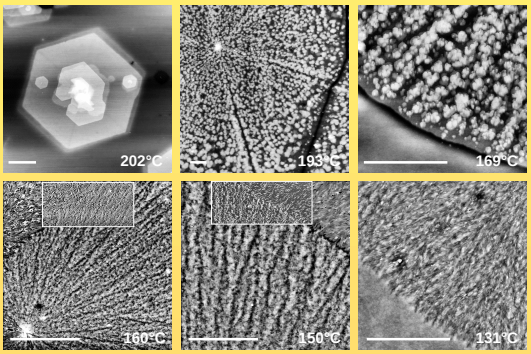
References:
1. J. Boon, G. Challa and D.W. Van Krevellen, "Crystallization Kinetics of Isotactic Polystyrene. 1. Spherulitic Growth Rate", *J. Poly. Sci. A-2*, **6**, 1791-1801, 1791.
2. D. Morel and D.T. Grubb. "Craze Behavior in Isotactic Polystyrene: 1. Craze-Spherulite Interaction", *Polym.*, **25**, 417-429, 1984.
3. S. Sawamura, *et al.*, "Growth Rate of Isotactic Polystyrene Crystals in Thin Films", *J. Phys. Soc. Jpn.*, **67**, 3338-3344, 1998.

Morphology



Topography of ipS crystals, T_x = 193°C (scale bars: 10 µm)

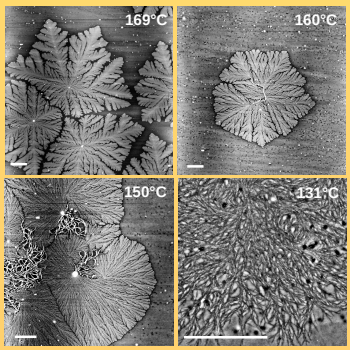
- T_x ~ 200 °C: ipS crystals grow as hexagonal plates with terraced growth from both the nucleus and other points in the plates (screw dislocations; upper right).
- 193 °C > T_x > 170 °C: dislocations become more numerous and the hexagonal order radiating from the nucleation sites becomes obscured by dense overgrowth.
- This secondary nucleation is eventually responsible for the transition from the hexagonal to circular morphology.



Topography of ipS crystals grown at *h* > 30 nm for 5 h at various T_x (scale bars: 5 µm). Insets are phase images of the same region.

- In the thin region, where *h* < radius of gyration (R_g = 22 nm), the morphology of the crystals is observed to change substantially.
- Here it is reasonable to consider the films as quasi two-dimensional and changes in the crystallization morphology are expected from spatial confinement.
- AFM images taken at different points on the film along the 193 °C isotherm illustrate this transition (left).

- Near the same temperature at which the six-fold symmetry of the hexagonal plates gives way to circular structures, hexagonal dendrites are replaced by a randomly branched dendritic morphology.
- As T_x decreases in the ultra-thin region (lower right) there is progressive loss of symmetry about the nucleation centers.



Topography of ipS crystals, *h* < 18 nm (scale bars: 10 µm)

Summary

This high throughput method of investigating crystallization of polymers in thin films produces information previously requiring numerous films. In general, we find excellent agreement with previous results, validating the high throughput, combinatorial approach. The effects of film thickness and temperature on the growth rate and morphology of ipS were demonstrated across more than 80 % of the temperature range in which ipS crystallizes and a full range of film thickness was shown, within which rate changes and morphological transitions have been reported. Our next goal is to incorporate high throughput crystallization into other combinatorial methods to understand the impact of the degree and type of crystallinity in a given polymer on material properties such as toughness.

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Mapping Toughness of Isotactic Polystyrene in Thin Films: Craze Growth

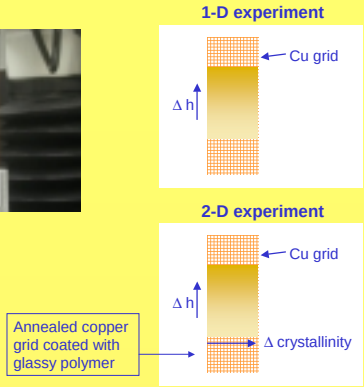
Scientific Issues

- Toughness of polymer related to craze formation
- Heterogeneities in processing of thin films may play role in craze formation and fracture properties
- Decades of research history on crazing

The Copper Grid Test*:

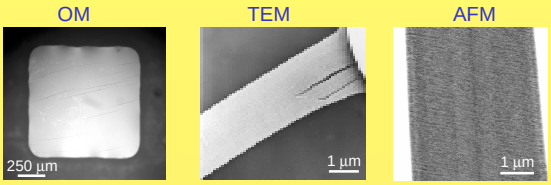
- Isolate crazes in thin films
- Statistical population of equally strained cells in one sample (for 1D gradient)
- Copper plastically deforms to "lock-in" applied strain
- Use microscopy to analyze craze and fracture microstructures

*B. D. Lauterwasser and E.J. Kramer. "Microscopic mechanisms and mechanics of craze growth and fracture", *Phil. Mag. A*, **39**, *4*, 469-495, 1979.

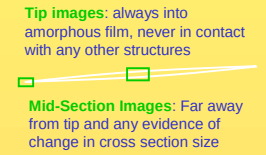


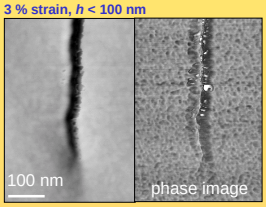
Sample Preparation and Experimental Techniques

1. Films are flow-coated on UV-treated glass with a gradient in film thickness (20 nm < *h* < 120 nm).
2. Film is cut along thickness gradient and floated off on water. One strip is transferred to silicon and the other to the copper grid (annealed, dipped in polystyrene).
3. The polymer strip on silicon is used to measure the thickness gradient.
4. The film on the copper grid is briefly exposed to solvent vapor to allow the film to relax and adhere to the grid bars.
5. Strain is applied to the copper grid and film and craze structure at the tip and mid-section is analyzed using various microscopes (right).

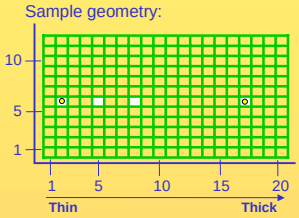


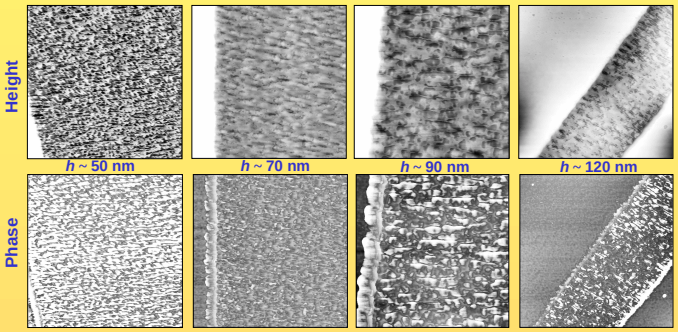
Morphology from AFM





Craze tip region showing perforation at the tip in "thick" region of gradient films of ipS.



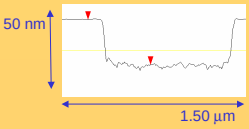


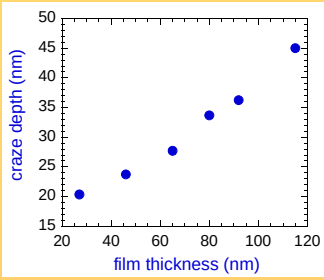
Mid-section of typical crazes in different thickness films illustrate variations in craze microstructure

- Previous work established that fibril thickness varies inversely with *h*.
- Our results (above, right) show an increase in lateral resolution of craze microstructure with decreasing *h*.
- We are not observing fibril microstructures, but other strain-induced ordering, z.B. crystallization.

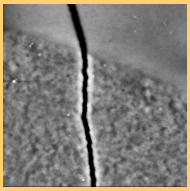
Quantifying Craze Depth

- Using AFM to quantify craze depth across 100 nm range in one film demonstrates the power of combi.
- Preliminary data suggests an increasing assymetry in stress state with decreasing *h*.
- No evidence of craze growth suppression with changing mobility in ultrathin region.
- Craze depth should plateau upon extending the *h*-range in both directions.





Post-strain Crystallization



Future Directions

- Imaging the underside of the craze structure to look for a stress state assymetry
- Comparing microstructure of crazes in atactic and isotactic polystyrene
- Developing 2-D gradients
- Quantifying roughness in craze microstructure

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