High-throughput preparation of specimens for TEM

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Motivation

Transmission Electron Microscopy (TEM)

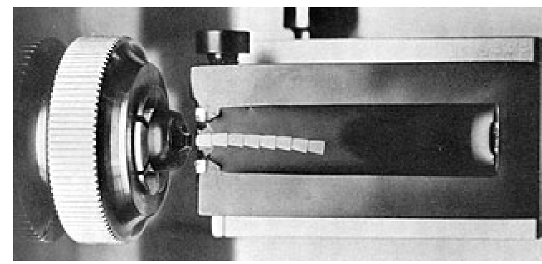
- A primary tool for nanomaterials analysis
- Applicable to a wide range of materials
  - Polymers, metals, ceramics, composites
- Near atomic resolution
- Well understood contrast mechanisms
- Reliable instrumentation

Motivation

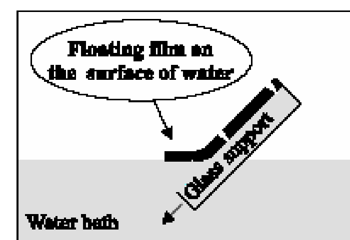
Preparation of TEM specimens is difficult and time consuming

Polymeric specimens must be less than ≈ 100 nm thick

- Bulk Specimens
  - Cryogenic ultramicrotomy
  - Slow, one at a time



- Film specimens
  - Sacrificial substrate: float, etch
  - Transparent substrates (SiN)
  - Annealing is a problem
  - No choice of substrate material



Goal

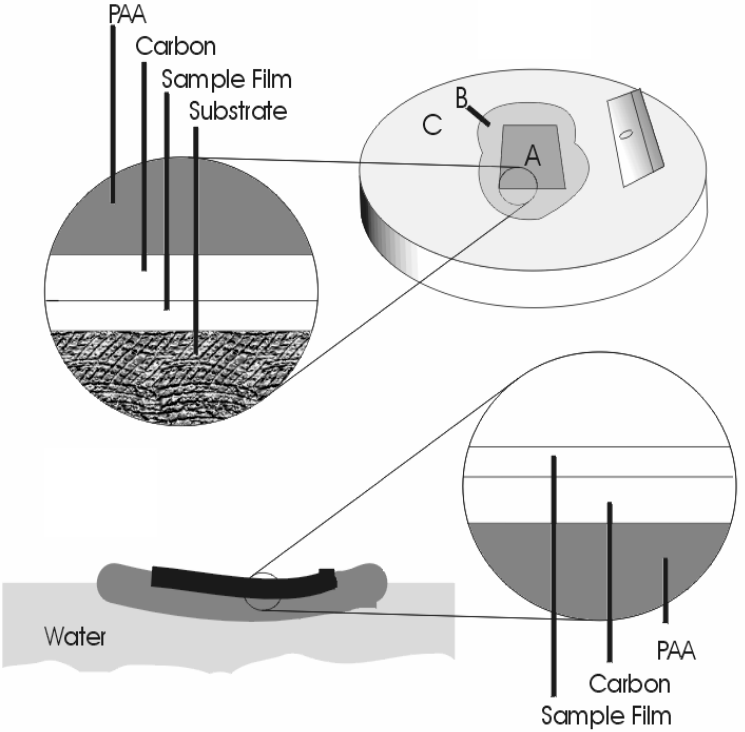
A high-throughput method for preparing polymer TEM specimens:

- Thin films
- Use with combinatorial libraries
- Parallel preparation of many specimens
- Flexible
- Amenable to automation

Peel Off Technique

- Originally developed for TEM “detachment replicas”
- Adapted to remove thin films from a substrate

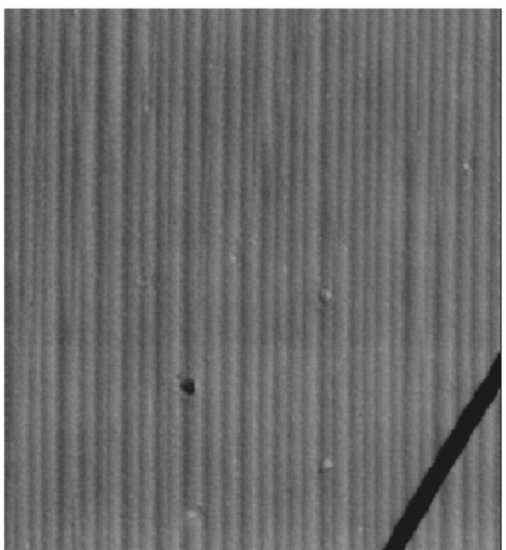
1. Deposit film specimen on substrate
2. Coat film with 10 nm evaporated carbon
3. Pour 25 wt% polyacrylic acid (PAA) solution over specimen
4. Dry PAA layer
5. Peel or “pop” PAA/carbon/specimen from substrate: Razor lift or LN_2 quench
6. Float multilayer on water pool to dissolve PAA
7. Retrieve specimen with TEM grid
8. Voila!



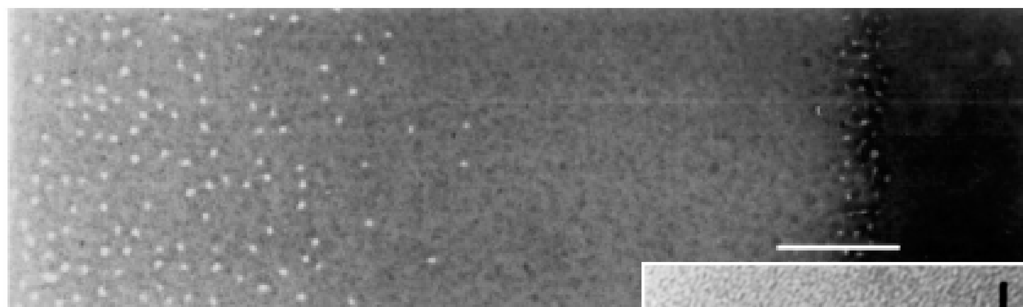
P. H. Geil, in *Polymer Single Crystals* (Wiley Interscience, New York, 1963).
M. J. Fasolka, et al., Physical Review Letters, 79, 3018 (1997).

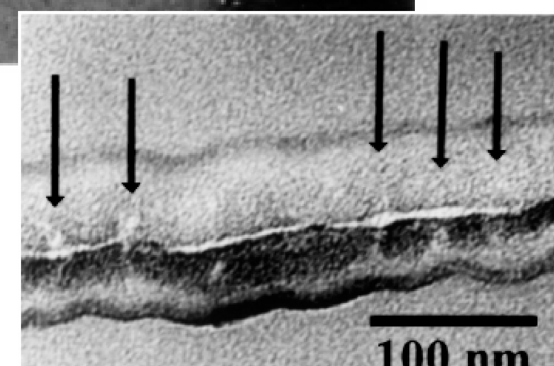
Viability and Advantages of Peel Method

- Films remain intact
- Enables analysis of "buried" film surface
- Enables cross-sectional analysis
- Carbon film adds stability to beam-damaged materials



AFM of bottom surface of BC film peeled from corrugated substrate



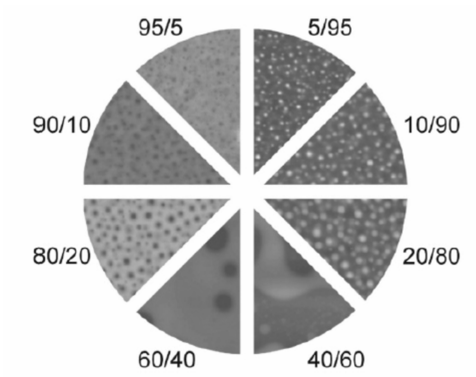


Plan and cross-sectional TEM micrographs of peeled BC films

M. J. Fasolka, et al., Physical Review Letters, 79, 3018 (1997).

Strategy for Hi-Throughput Peel Method

1) Fabrication of combinatorial thin film library

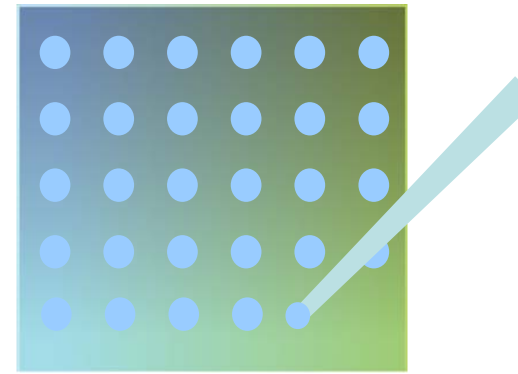


Sector Spin Coating*

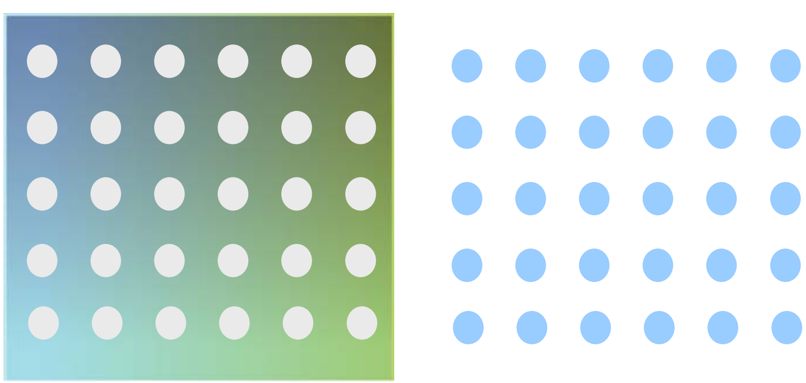
NCMC Film Methods

Carbon Coat →

2) Deposit array of PAA droplets

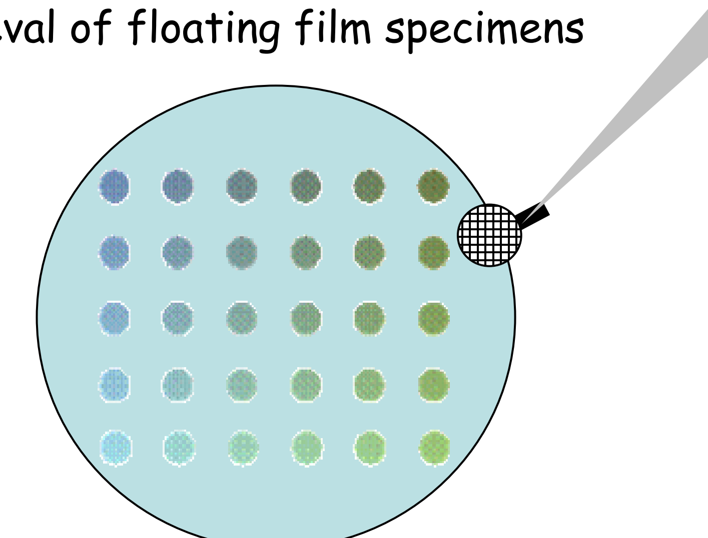


3) Simultaneous removal of droplet/film specimens



Dissolve PAA →

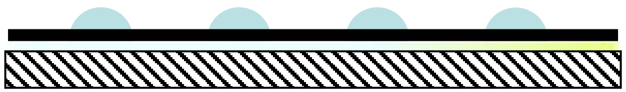
4) Retrieval of floating film specimens

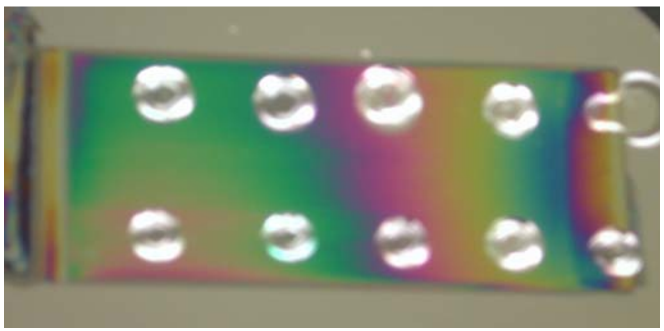


*de Gans et al, J. COMBI CHEM 7 (6): 952-957 2005

Demonstration of specimen removal

PAA droplets on polystyrene film thickness gradient library on Si

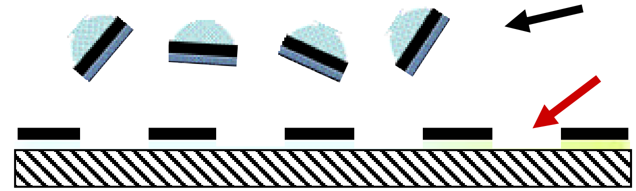


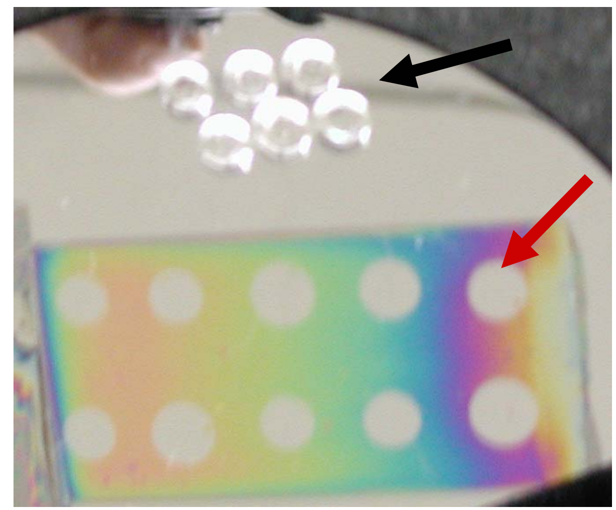


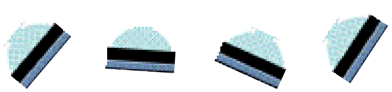
Immersion in pool of LN_2

Droplets "pop" from substrate

PAA/Film specimens harvested from LN_2







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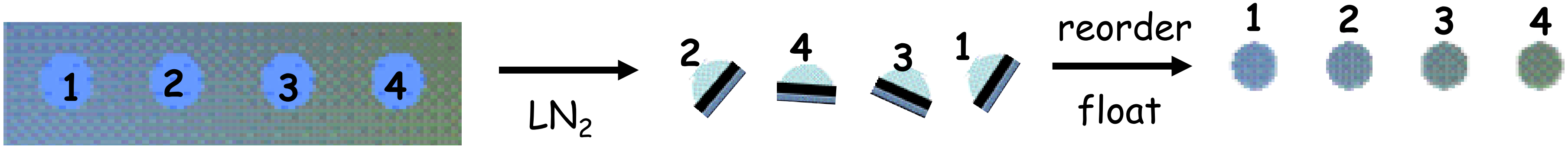
Simultaneous specimen removal via LN_2 works…

…but how do we "register" the harvested specimens in library order?

Library registry strategies

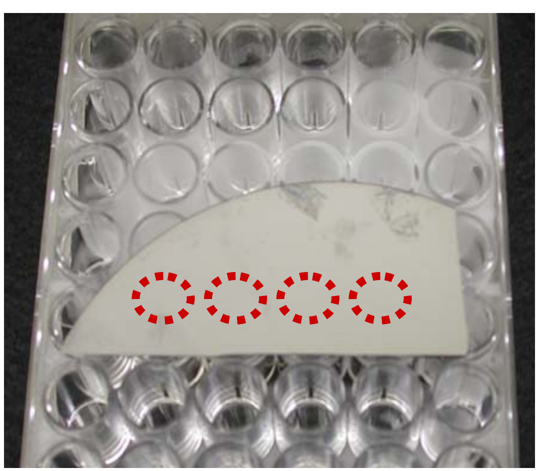
1) Pre-labeling of PAA droplets followed by library reconstruction

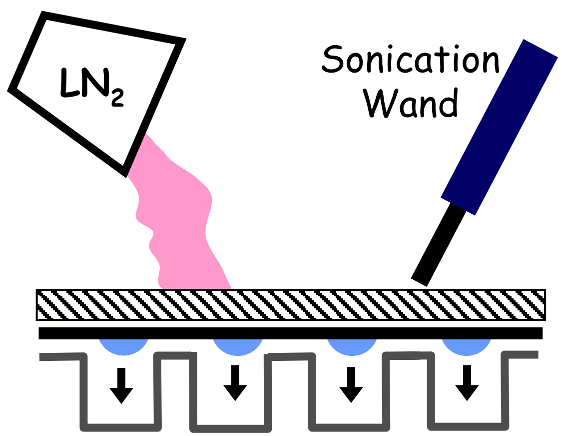
- Emboss soft PAA droplets with numbers
- Color PAA with gradient of soluble dies



2) Droplet removal into individual wells

- Spacing of droplets matches well spacing
- Wells filled with water for PAA dissolution



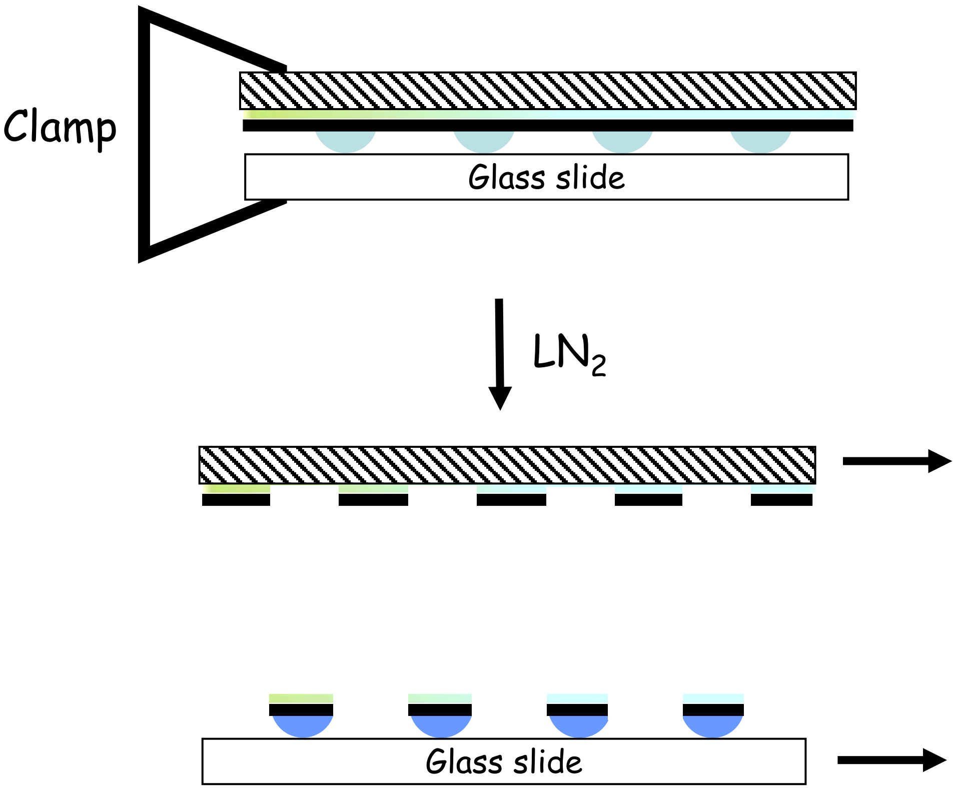


Process	Droplets removed (of 4)
LN_2	0-1
LN_2, sonication	1-2
Sonication, LN_2, Sonication	2+

Library Registration Strategies

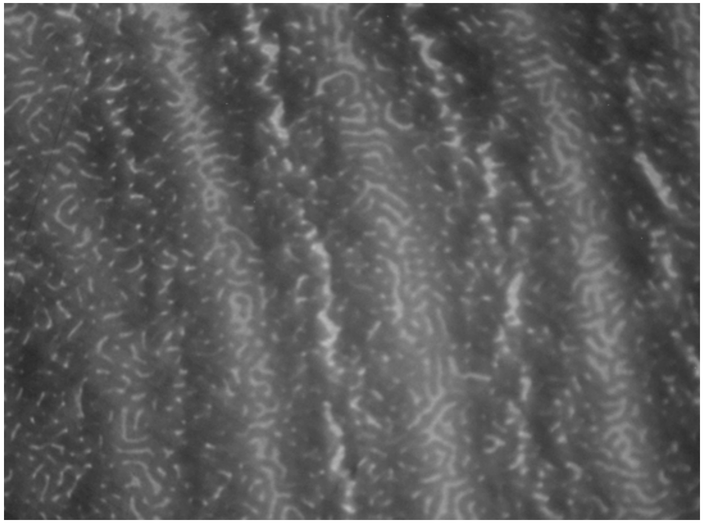
3) Transfer of droplets to another subsrate

- Example: damp glass slide that adheres to PAA



Demonstration: 100% film removal with registry

Summary and Future Work



TEM of poly(styrene-b-isoprene) block copolymer film harvested from PAA droplet
Thanks to Dr. Brian Berry

Summary:

Demonstrated a strategy for HT preparation of TEM specimens

- Adapted "peel off" method for thin films
  - Samples viable for TEM
  - Amenable to combi libraries
  - Parallel processing
- Evaluated strategies for maintaining registry of library specimens

Future Work:

- Optimize registry methods
- Determine sensitivity to annealing, adhesion, film thickness, specimen type

Focus Project Proposed at NCMC-6

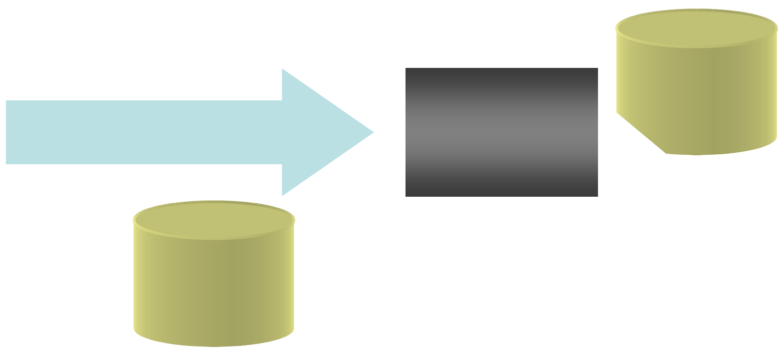
High-Throughput Facing of Bulk Polymer Specimens

Goal:

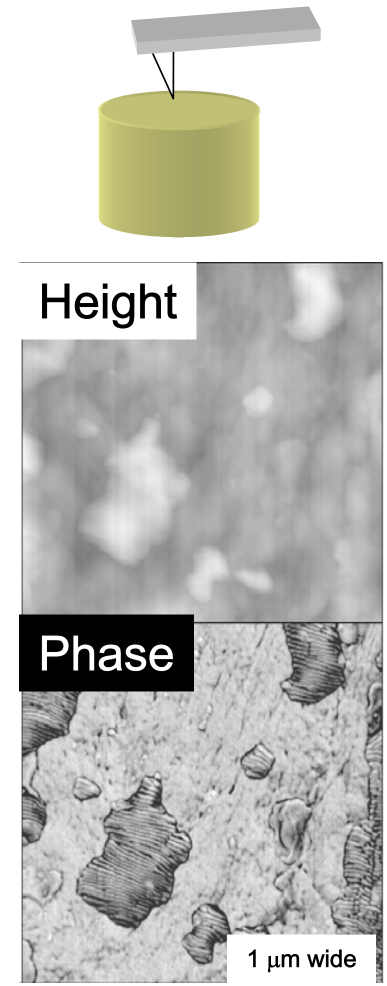
- Method for simultaneous *cryogenic fracture facing* of multiple bulk polymer specimens for surface analysis such as AFM and SEM

Experimental Design

- Cryogenic fracture suggests a facing route amenable to multiple sample processing



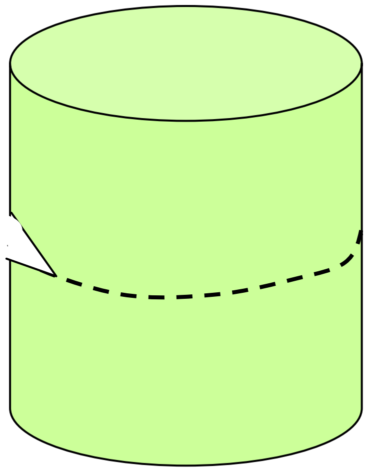
1. A notched bulk specimen is chilled in LN_2
2. A swift blow to the specimen creates a smooth fracture face amenable to SPM, SEM etc.



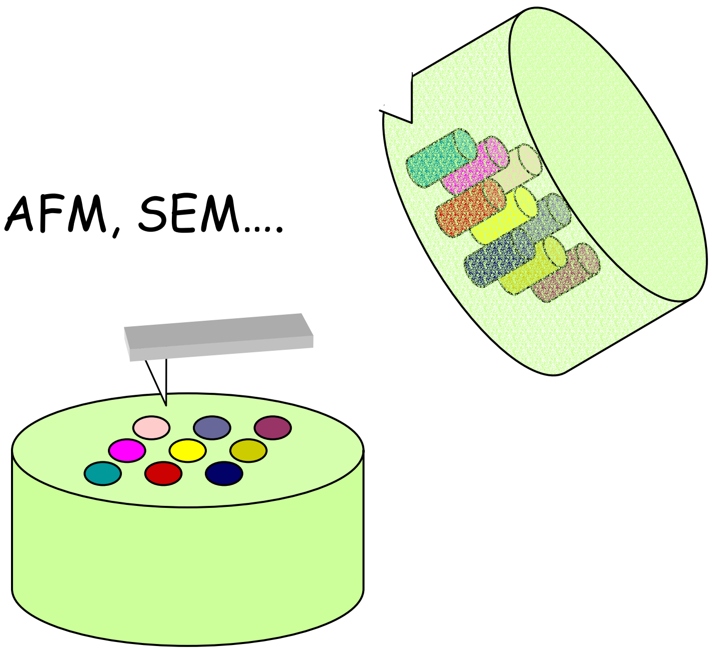
AFM of PS PEO Blend - cryofractured

Parallel CryoFracture Technique

By embedding an array of bulk specimens in a notched epoxy matrix, multiple specimen facing could be achieved



Array of 9 different polymer specimens embedded in an notched epoxy capsule



Cryogenic fracture of the epoxy capsule results in facing of the embedded array.

Challenges and Milestones

Challenges to be met:

- Fracture of multiple epoxy-embedded samples not yet demonstrated (single samples have been)
- Multiple sample embedding scheme and capsule design
- Cooling protocol for wide range of specimen T_Gs
- Fracture device (Charpy impact tester?)

Deliverables for Focus Project:

- Demonstration of multiple sample fracture
- Embedding protocol and capsule design
- Cooling Protocol
- Demonstration study
- Fracture device/protocol

Impact Areas and Contact Info

- **Impact areas:**
  - Extruded products
  - Polymer Blends
  - Composites and Filled Systems
  - Nanostructured Materials

- **Contact for further discussion:**

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