GENERAL ATOMICS
AND AFFILIATED COMPANIES

Fabrication of Overcoated Divinylbenzene (DVB) Shells

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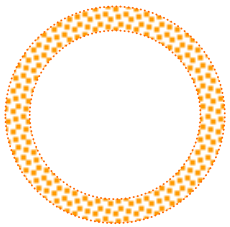
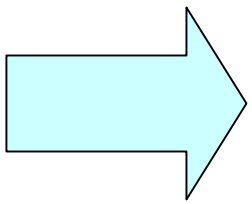
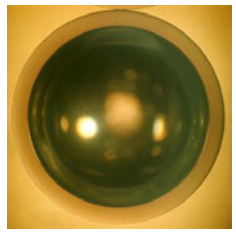
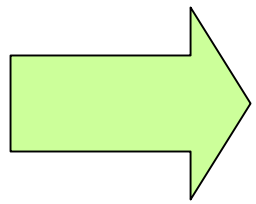
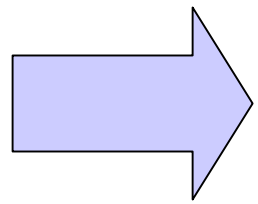
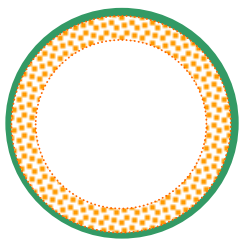
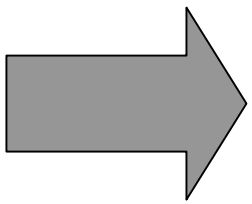
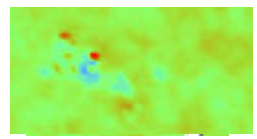
Task Goal

Target Design Specifications to support the High Average Power Laser Program

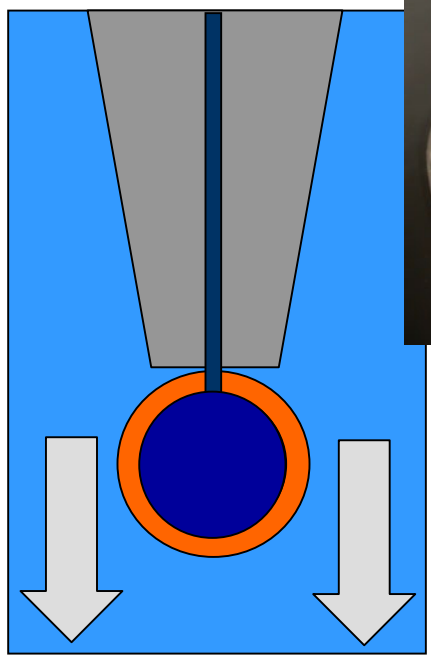
Specification	Comments
• CH Polymer • 1-3 Micron Cell Size • 20-120 mg/cc Density range	Met with Divinylbenzene Foam
4 mm Diameter / 300 µm Wall Thickness	Met through production using droplet generator
Shell Nonconcentricity < 1 %	Average batch NC about 3%. Shells characterized with NC < 2%.
1 – 5 µm Overcoat with RMS surface roughness of 20 – 50 nm	Overcoat thickness met using interfacial technique. Surface roughness within range of interest for patch scans. Shrinkage has remained a problem. PVP, PVP with GDP, and M-F, ED being investigated.

Current Production Flow

1. Gelation 	2. Exchange to Benzyl Salicylate 	3. Characterize 	4. Exchange to IPA 	5. Exchange to Diethyl Phthalate 
6. Overcoat Applied 	7. Exchange to IPA 	8. Supercritical Drying 	9. Characterize Overcoat 	10. Dried, Overcoated Shell Completed

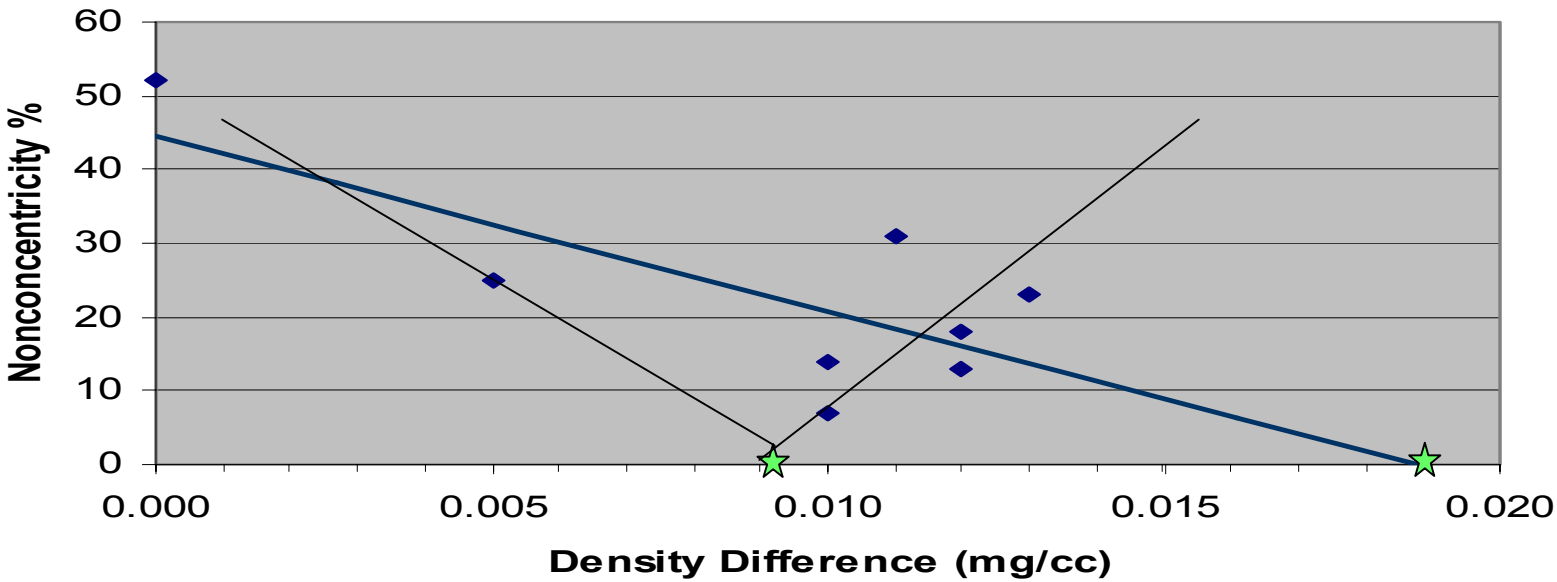
Formation Of Shells Using Droplet Generator

- **Inner Water Phase (W1):**
  - D_2O / H_2O Blend
  - Syringe Pump
  - Flows through needle
- **Organic Phase (O):**
  - Dibutyl Phthalate, DVB, AIBN
  - Syringe pump
  - Flows through second orifice
- **Stripping Phase (W2):**
  - 0.05 % PAA in H_2O
  - Gear Pump
  - Flows around second orifice



Nonconcentricity and Density Matching

The effects of density matching on NC, which was the original focus for NC reduction, has not proven to have a significant effect within the range of study. It still may prove to be important to achieve NC < 1%.



Nonconcentricity and Gelation Time

Batch	PAA %	Gelation Time	NC%
64A	0.05	Standard	15
64B	0.05	Longer	10
64C	0.1	Standard	10
66B	0.1	Longer	5

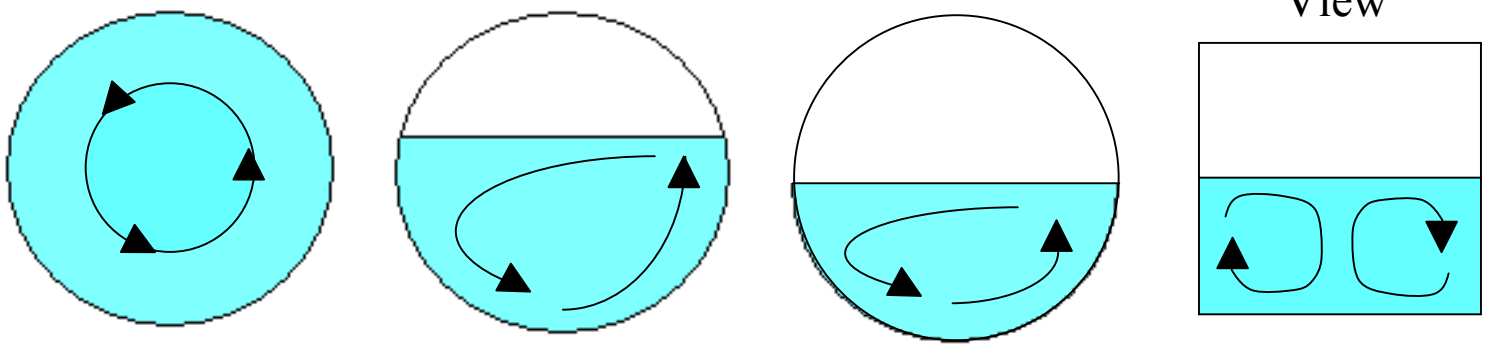
Temperature was lowered to adjust gelationtime from ½ to 1 hour with a corresponding density adjustment. Longer gelation times appear to reduce NC.

Nonconcentricity and Agitation

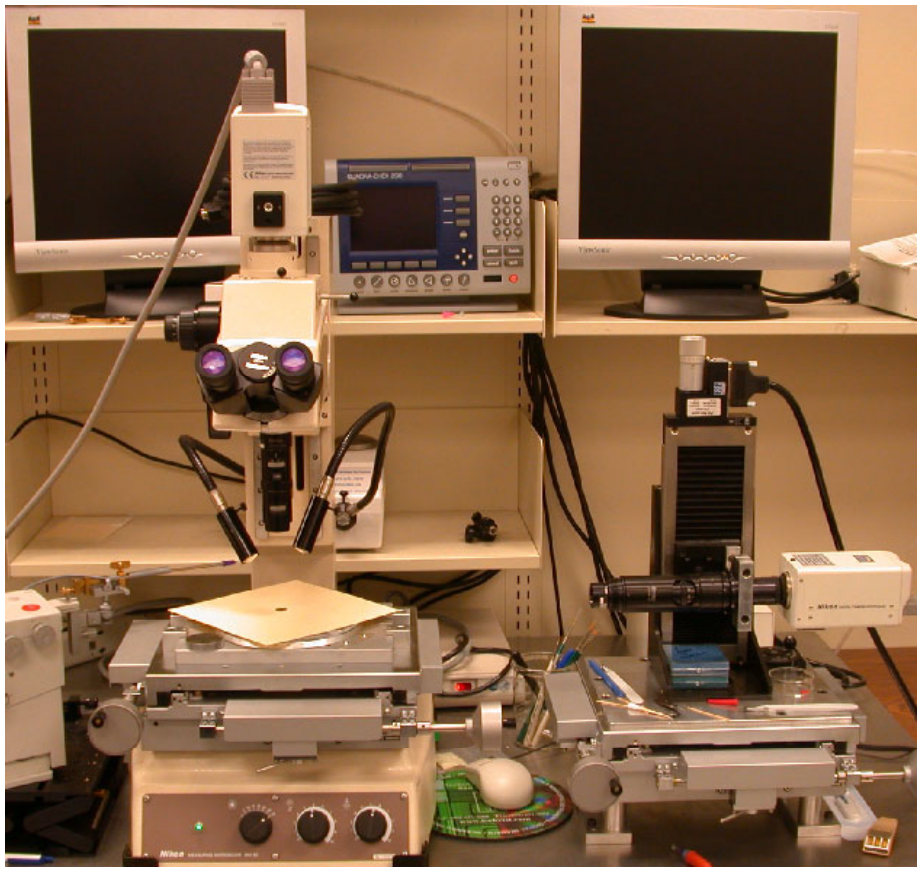
Three different flask configurations have been used with very different results.

Flask Configuration	Full, Angled	2/3 Full, Angled	1/2 Full, Horizontal
NC % (Four Best batches)	15	4	3
	21	5	3
	41	5	3
	46	6	4

Flow Patterns

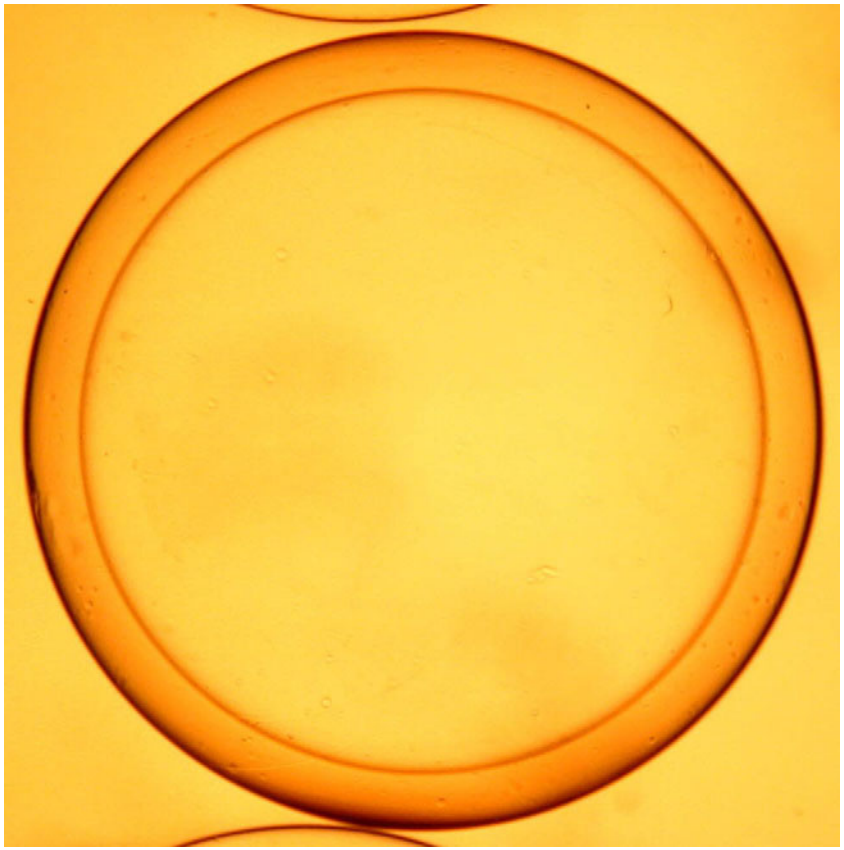


Shell Characterization



- Shells are exchanged into Benzyl Salycilate, an index matching solution, which results in a translucent shell wall. These shells are placed in an optical cell and two orthogonal images are collected.
- Shell images analyzed using Image Pro Plus Software.
- Data exported to Excel.

Shell Images: 2% Nonconcentricity, 100 mg/cc

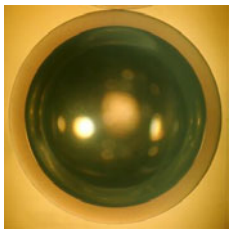
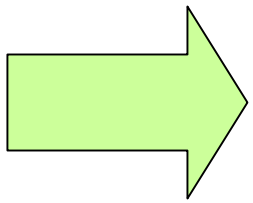
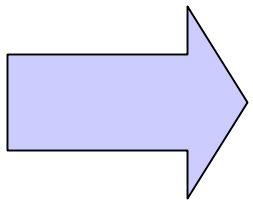
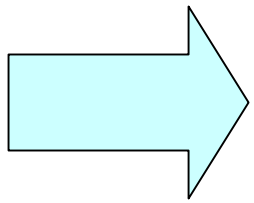
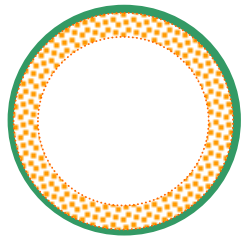


Top View

Side View

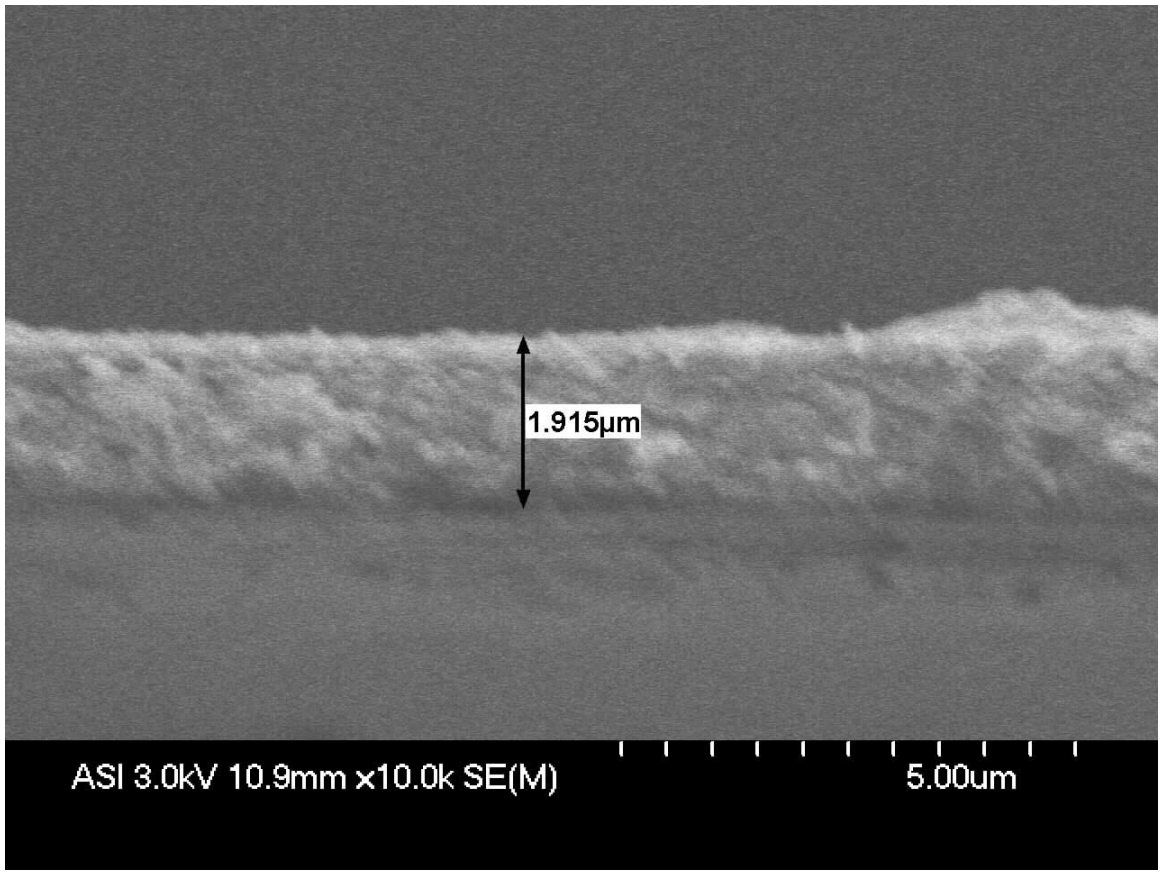
Note: Color variation is due to differing lighting conditions.

Overcoating

1. Characterized Shell	2. Exchange to IPA	3. Exchange to Diethyl Phthalate	4. Exchange to DEP & IPC; place in PVP solution	5. Overcoat Applied
				

- Desired thickness of the overcoat of 1-5 microns can be achieved
- Major problem arises with shrinkage during the drying process for thicknesses > 2 microns
- IPC = Isophthaloyl Dichloride, PVP = Poly(4-vinyl phenol)

Overcoat Profile



Approximately 1.9 micron thickness (10 minute reaction time)

PVP Surface Finish

Surface Statistics:

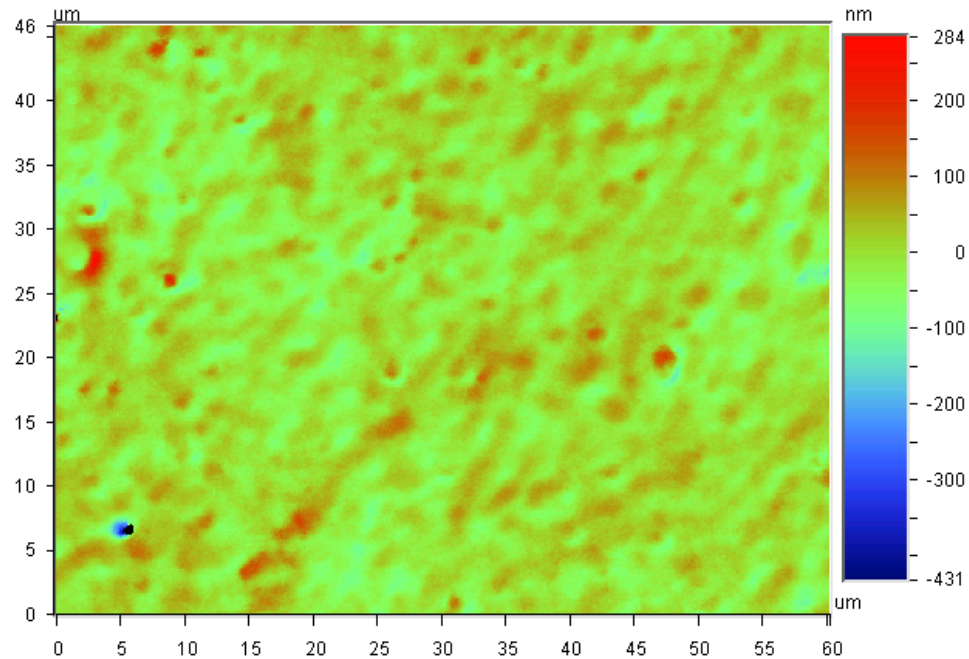
Ra: 26.04 nm
Rq: 33.91 nm
Rz: 395.69 nm
Rt: 714.97 nm

Set-up Parameters:

Size: 736 X 480
Sampling: 82.03 nm

Processed Options:

Terms Removed:
Curvature & Tilt
Filtering:
None



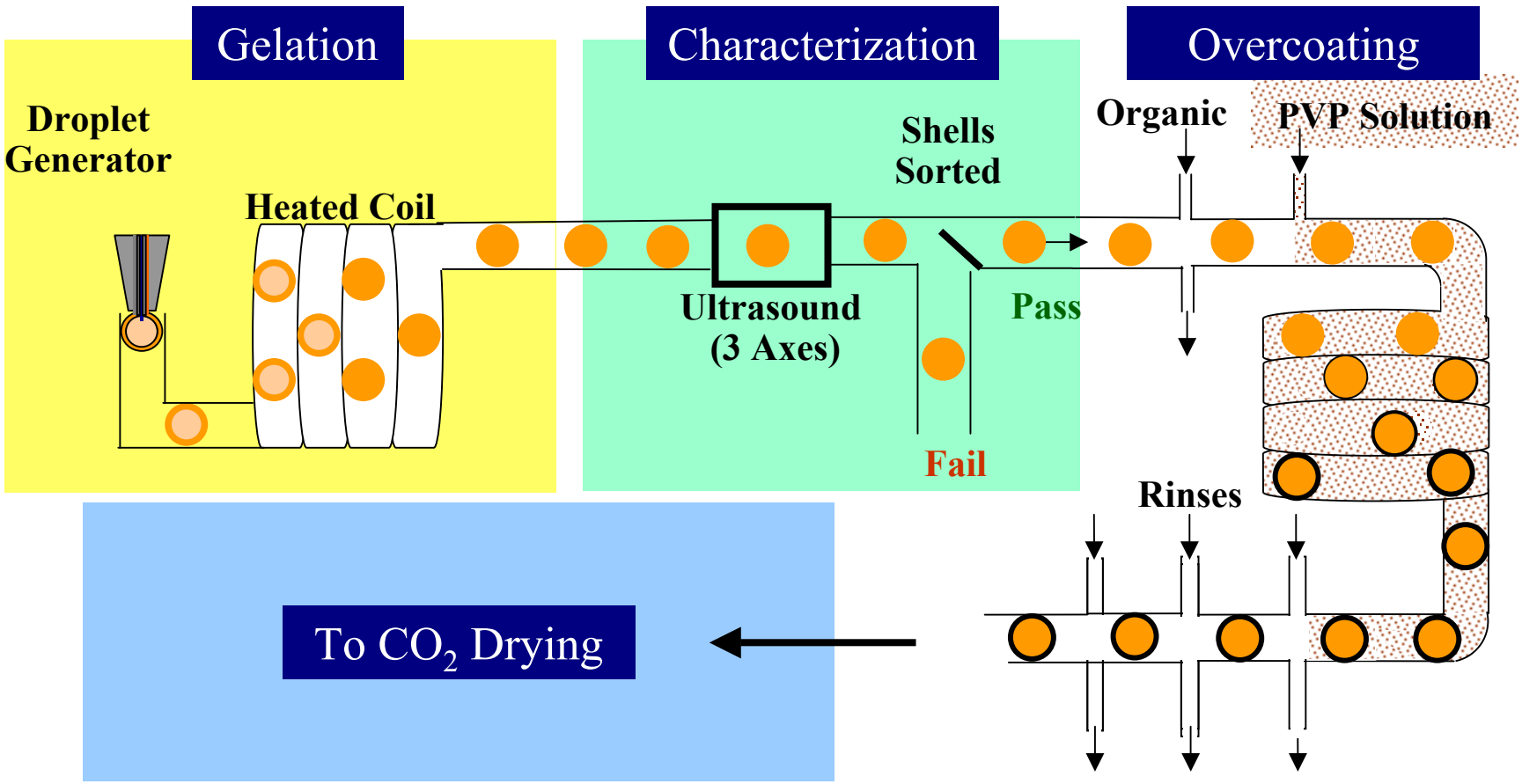
Interferometer surface roughness measurement of overcoat. PVP reacted for 30 minutes with DEP as solvent, RMS = 34 nm

- Dry yields were low for all PVP overcoat trials. The best surface finish achieved was for the reaction conditions above.

PVP Alternatives

- Ethylene diamine is being investigated as an overcoat
  - Ethylene diamine and diethylene triamine are the water soluble reactants.
  - Crosslink density can be controlled to control shrinkage.
  - Terephthaloyl dichloride is the oil soluble reactant; polymer forms at interface.
- Melamine-formaldehyde is also being investigated
  - Shells are place in an aqueous solution of a melamine-formaldehyde pre-condensate.
  - Melamine-formaldehyde condenses at oil interface over time with pH adjustment.
  - May be possible to apply without exchanges – there is no oil soluble reactant.

Proposed Flow-through Production



Summary

- Have met goals of:
  - CH Polymer
  - Cell Size
  - Density
  - Diameter & Wall Thickness
- Closing in on Nonconcentricity
  - Best individual shells have been < 2 %; need < 1 %
- Exploring overcoat chemistry options and combinations to fix yield problem due to breakage & shrinkage.