# New Synthesis Techniques on DVB and RF

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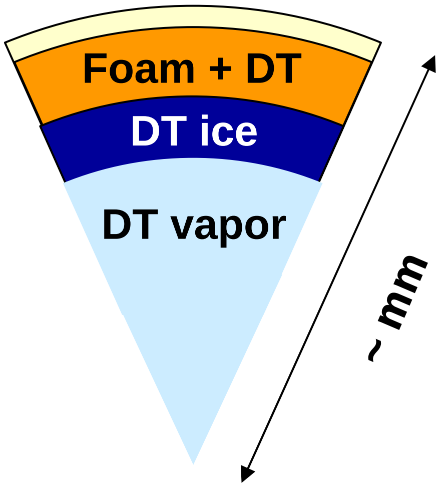
# The HAPL shell specifications are still challenging

- Out of round
- Wall uniformity
- Gas tight
- Smooth surface
  - < 50nm RMS
- Low cost
  - ¢ per target



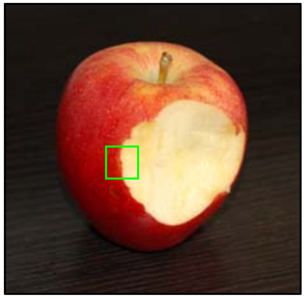

**Our efforts are focused on simplifying the shell production process and creating a smooth outer surface for coating deposition**

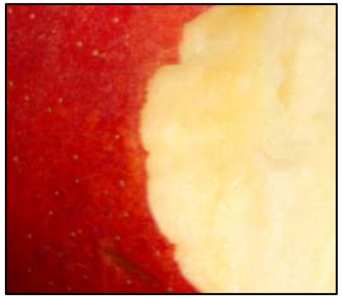
# We chose to address weaknesses of both of the major foam systems

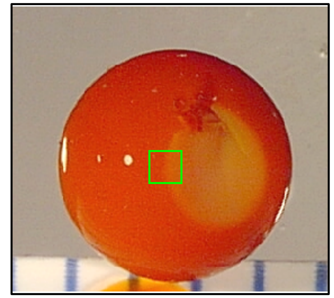
- **DVB**
  - Contains only C and H
  - Better wall uniformity and sphericity
  - Much easier to work with
  - Stronger than RF
  - Surface is rougher than RF
    - Surround the DVB capsule with a smooth skin

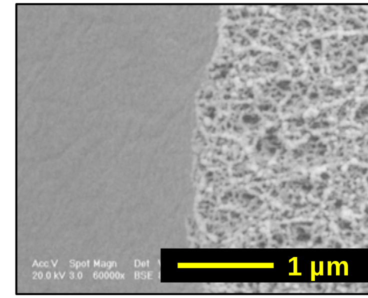
- **RF**
  - Smoother outer surface
  - Flexible synthesis enabling smooth skin
  - Recent advances in wall uniformity
  - Supercritical drying step makes them quite expensive to produce
    - Alter synthesis to allow air-drying without structural collapse

# We would like to emulate the RF "skin" technique on DVB



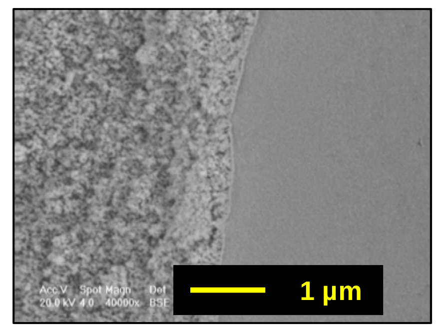







**we previously reported a technique that optimizes phase transfer RF synthesis* to produce a self-assembled smooth, submicron skin**

**We synthesized skinned RF shells using different acid species**

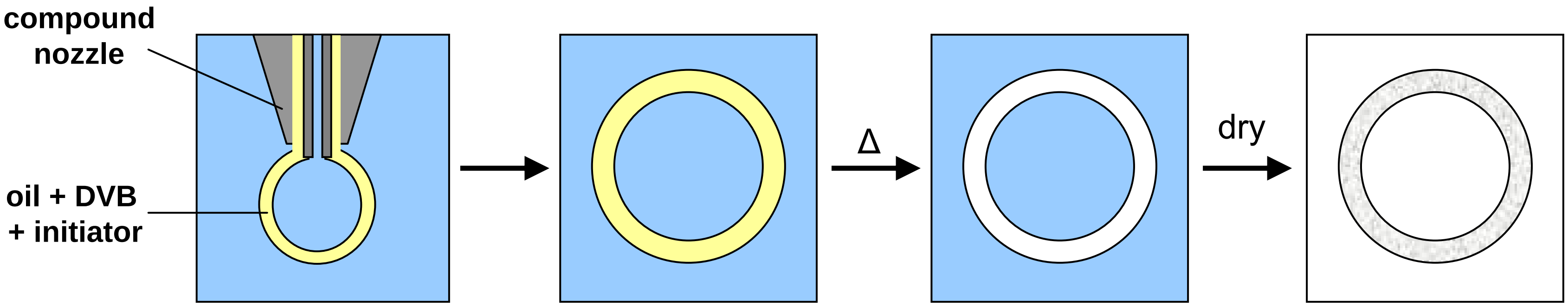



**RF shell synthesized by phase transfer of propanoic acid**

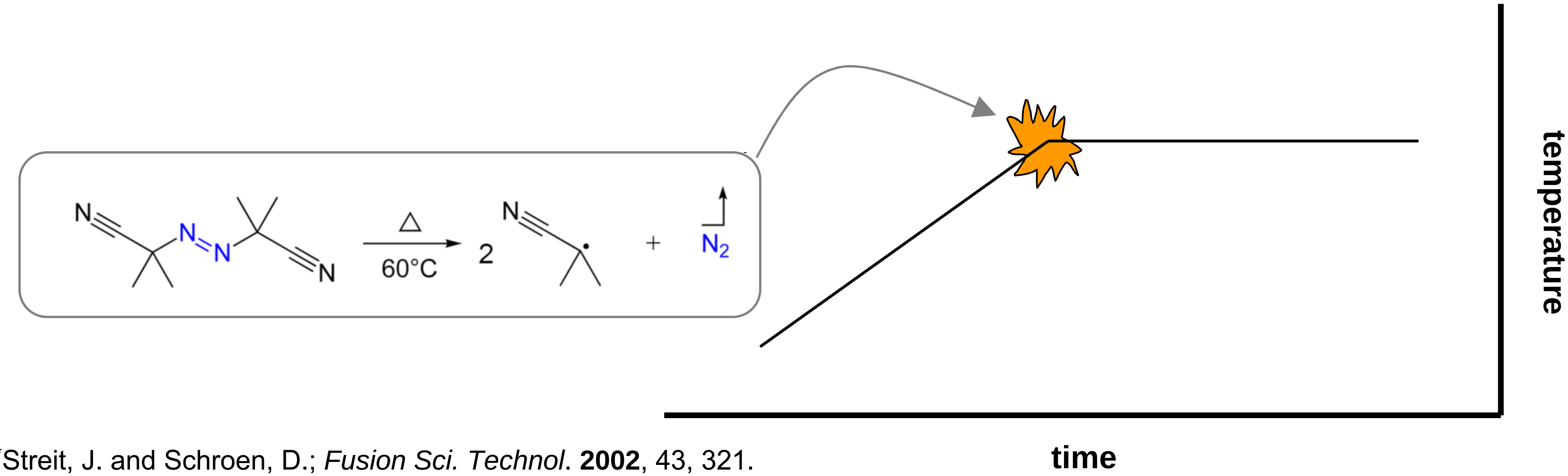
**Skin on DVB may eliminate surface roughness problems and result in the production of a gas permeation barrier on the shell**

*Ito, F., Nagai, K., Nakai, M., and Norimatsu, T.; *Macromol. Chem. Phys*. **2005**, 206, 2171.

# Basic DVB shell synthesis* is straightforward

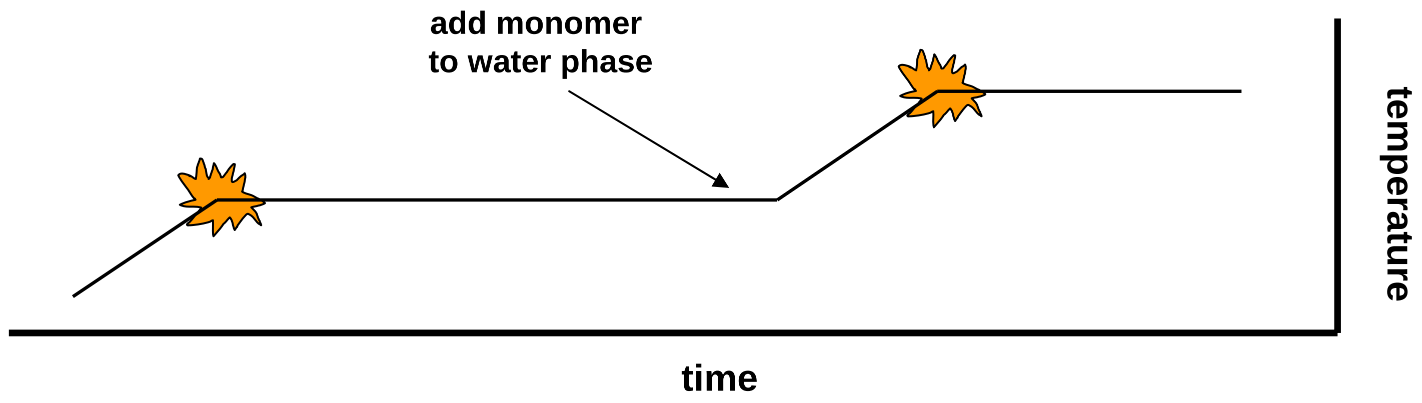



**The reactivity of the DVB system is thermally triggered. At a known temperature, a flurry of radicals is released within the oil phase.**

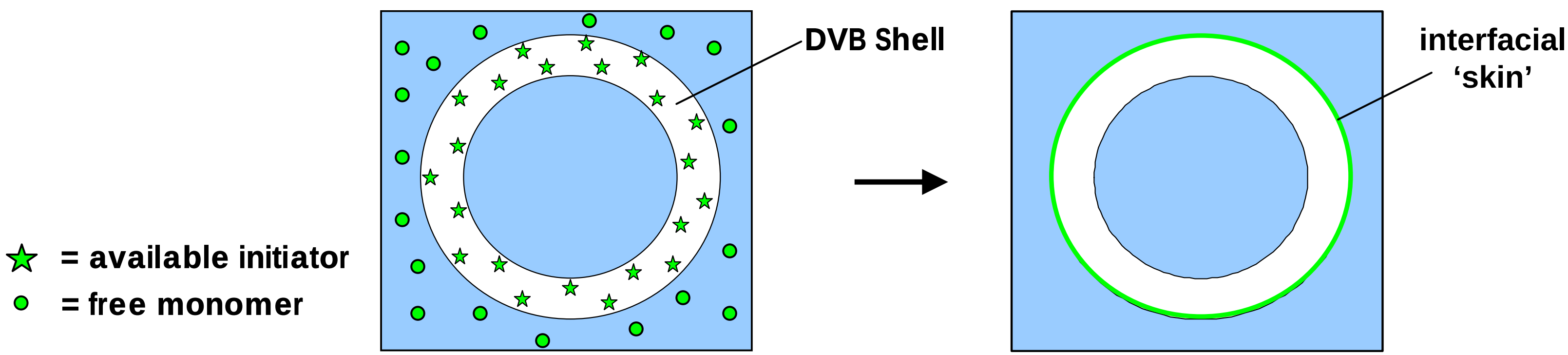



*Streit, J. and Schroen, D.; *Fusion Sci. Technol*. **2002**, 43, 321.

# We exploited dual thermal initiation* to produce DVB with 'skin'

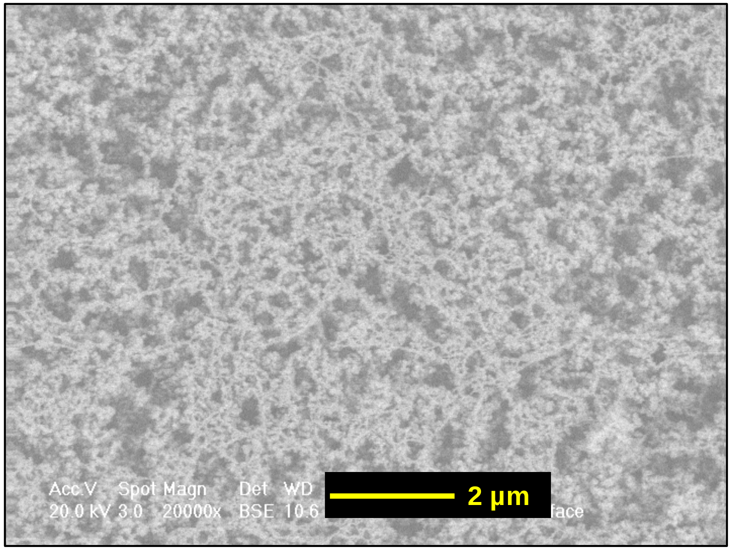



**Knowing how and when initiators trigger, we introduced a water soluble monomer into the external phase, hoping that radicals (or even propagating chains) would start polymerization events at the phase interface as the DVB gelled.**

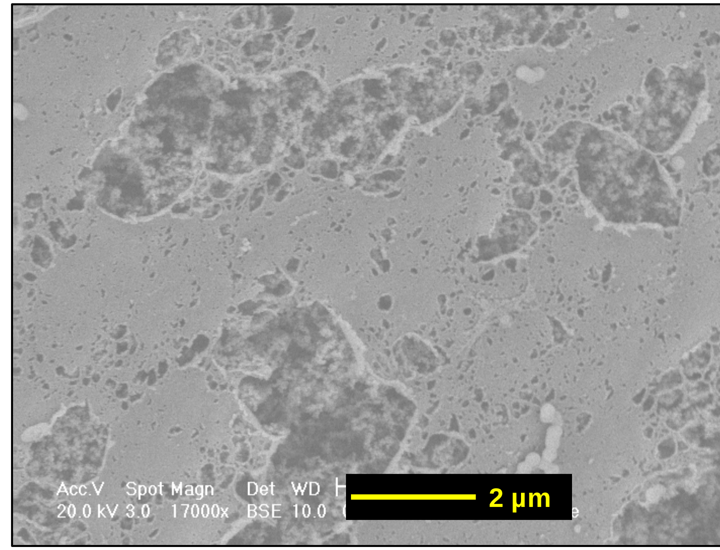



*Paguio, R. R., et al.; *J. Appl. Polym. Sci.* **2006**, 101, 2523.

# Our first experiment showed formation of a skin




outer surface of DVB shell

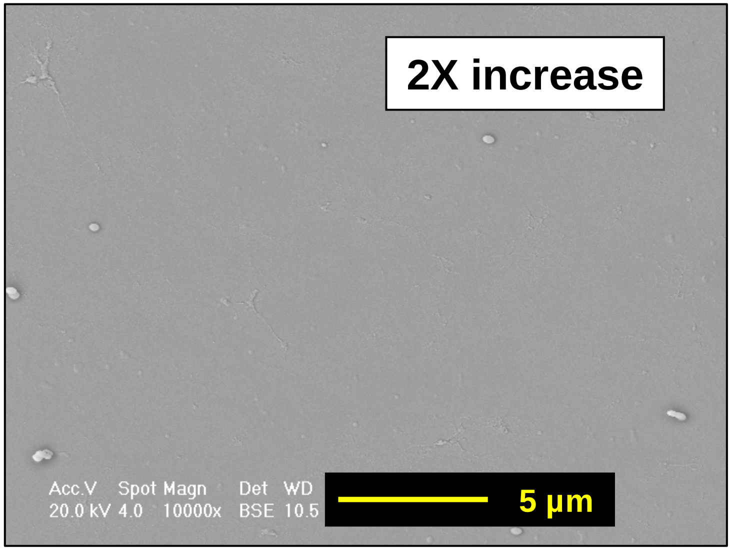


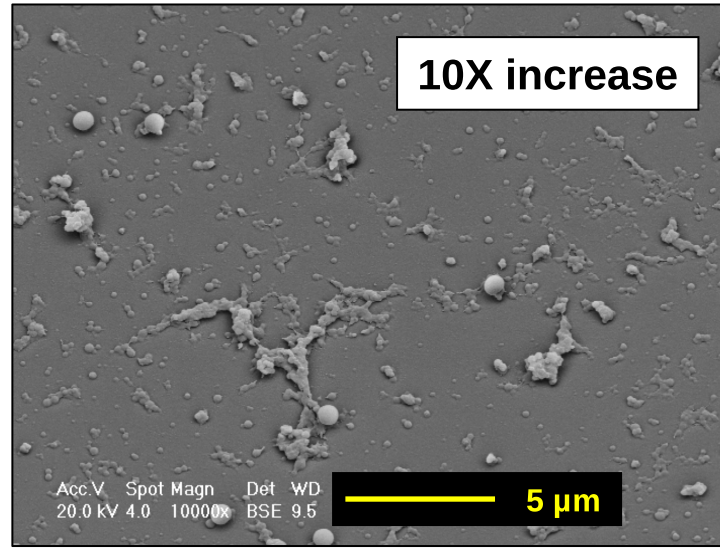

outer surface of DVB shell with ‘skin’

- **Our first experiment created a DVB shell with a thin, morphologically distinct skin that partially covered the shell**
- **We followed up this exciting result by attempting to synthesize thicker and copolymerized skins on DVB**

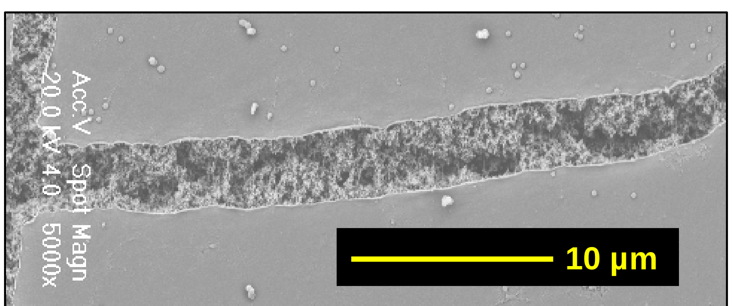
# The second DVB skin experiment produced a continuous skin

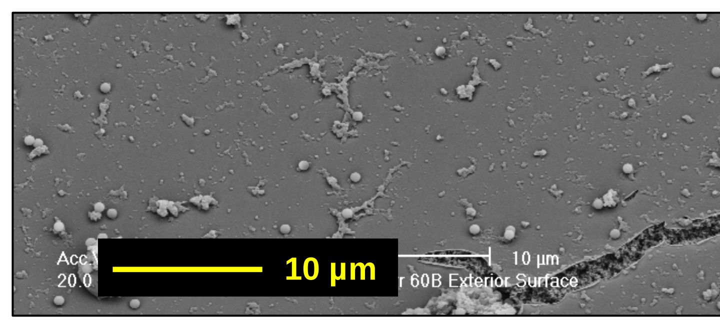
**In our second experiment we increased the monomer concentration in the external phase**




**Simply increasing the monomer concentration resulted in a thin, continuous skin**



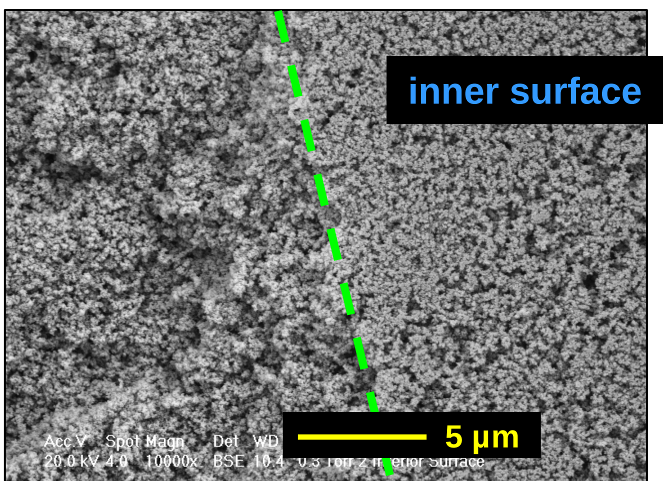



# With this technique, we discovered an interesting side effect

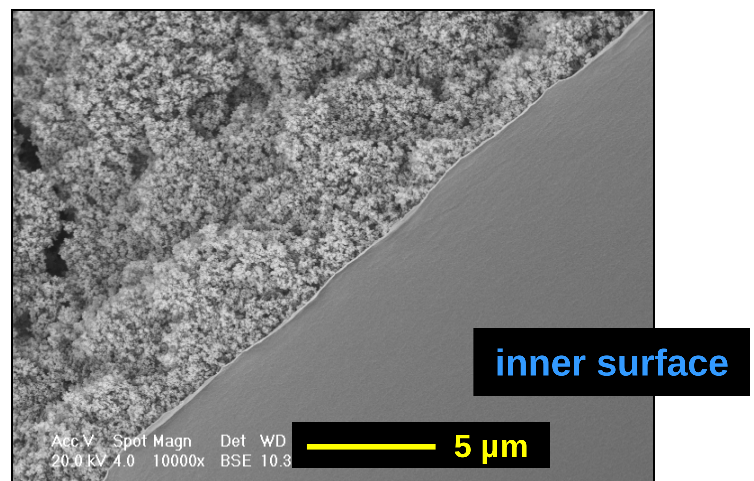
**In all of our experiments the inner surface of this 'skinned' DVB shell also has a skin.**

**We believe that we can eliminate this inner skin by slightly altering this technique**

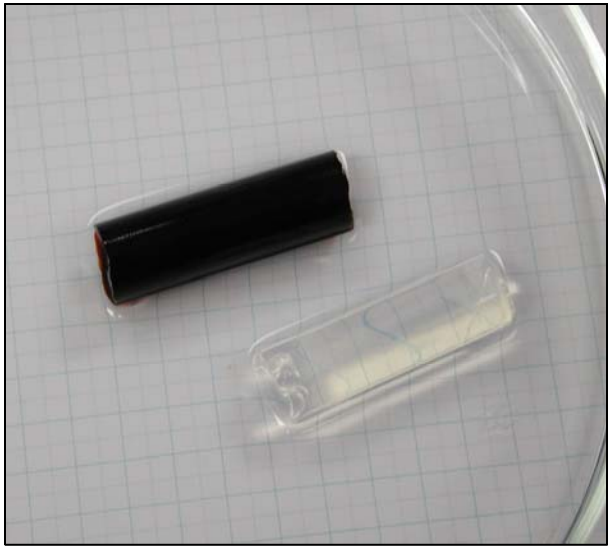

**standard synthesis**




**skin forming method**



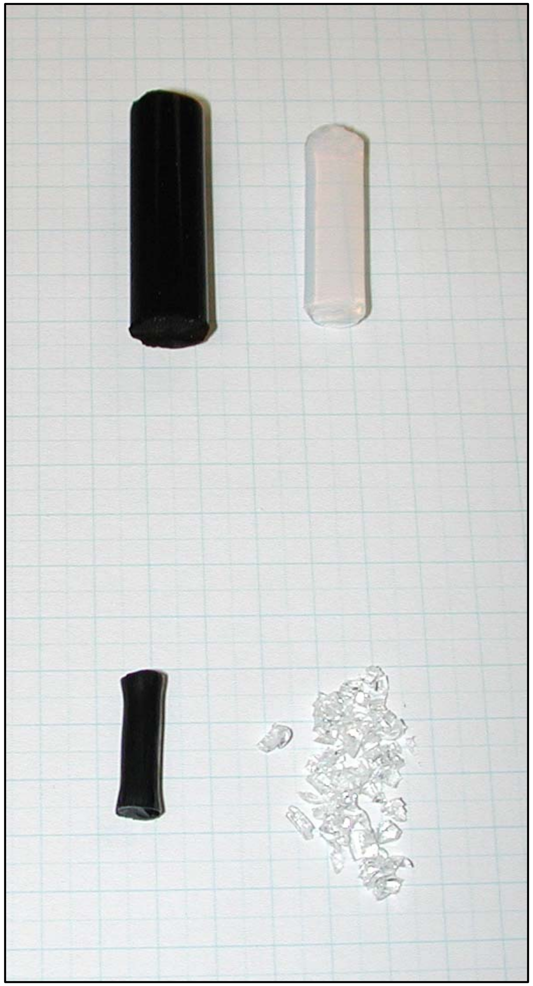
# We have also made progress toward an air-dried RF shell



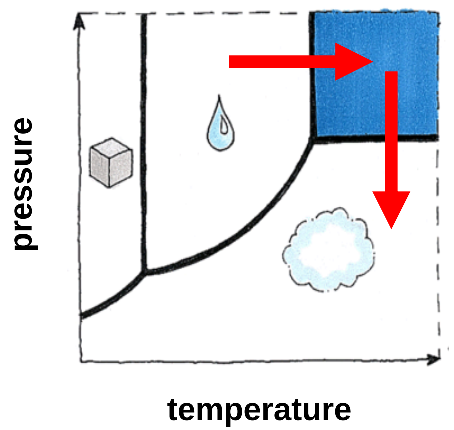
wet gels

critical point dry

air dry



# Air drying eliminates costly critical point drying step




- **Conventional RF must be critical point (CP) dried to preserve small pore structure**
- **CP drying process steps:**
  1) Exchange RF gel from water to IPA
  2) Exchange RF gel from IPA to liquid $CO_2$
  3) Increase pressure and temperature above critical point
  4) Controlled venting of $CO_2$

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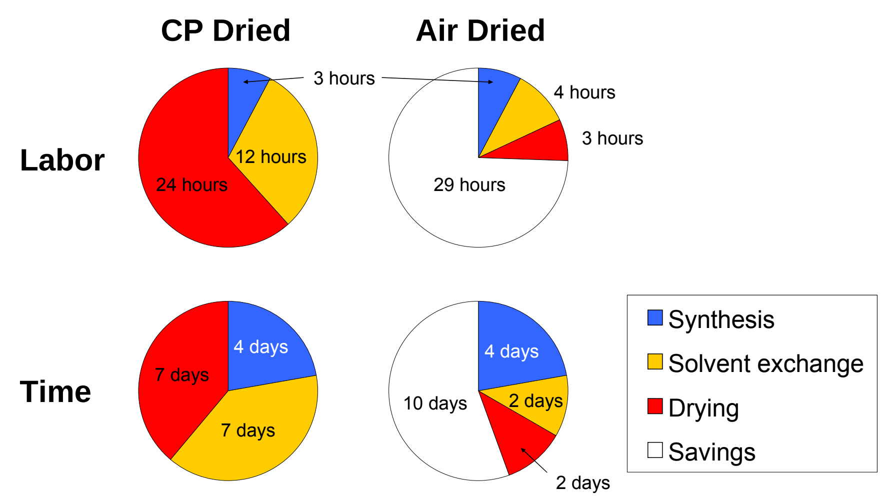
- **CP drying is both expensive and inherently a batch process**
- **Air-drying would reduce costs and streamline target manufacture**



# Precise synthetic control is required for air drying of RF

- We know what governs the collapse of the structures
- We have synthetic control over the pore radius
- We must balance capillary pressure with the structural strength of the aerogel

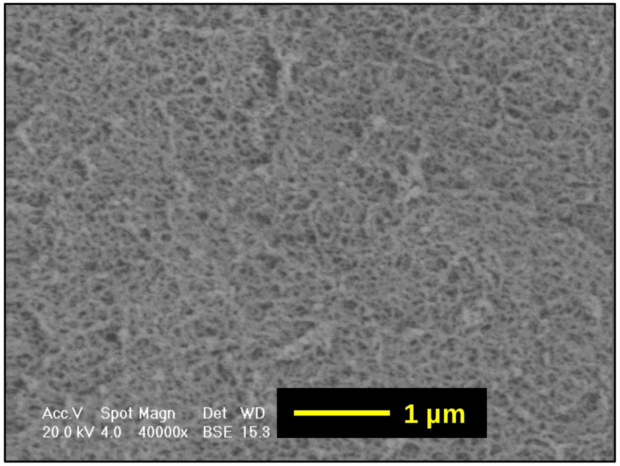
$$\Delta p = \frac{2\gamma \cos\theta}{r}$$

p =capillary pressure
$\gamma$ =surface tension
$\theta$=contact angle
r = pore radius

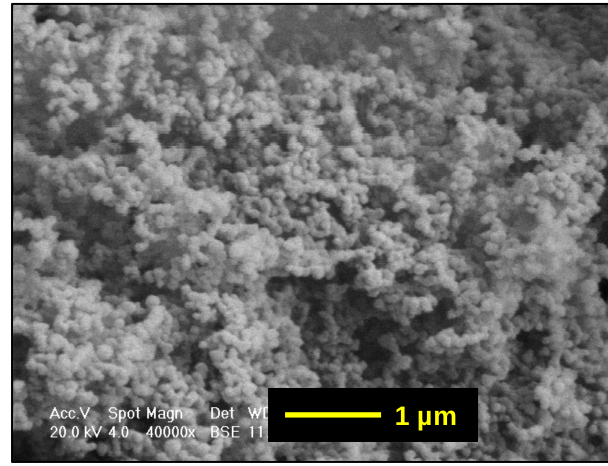
increasing pore size

As the pore size increases, the RF aerogel loses its optical transparency

# We have synthesized low density RF that can be air dried




**113 mg/cc RF as prepared for NRL's NIKE laser (CP dried)**




**100 mg/cc air-dried RF**

**113 mg/cc RF (CP dried)**

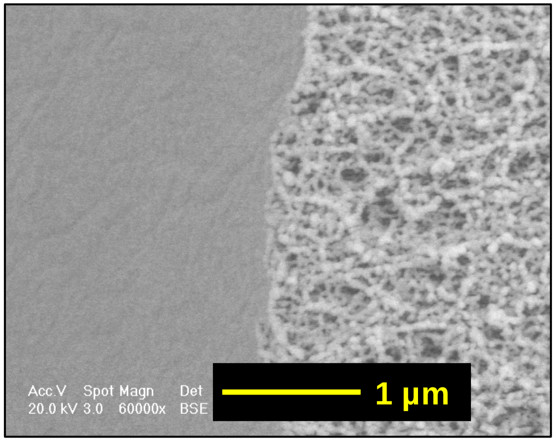
**95 mg/cc air-dried RF**

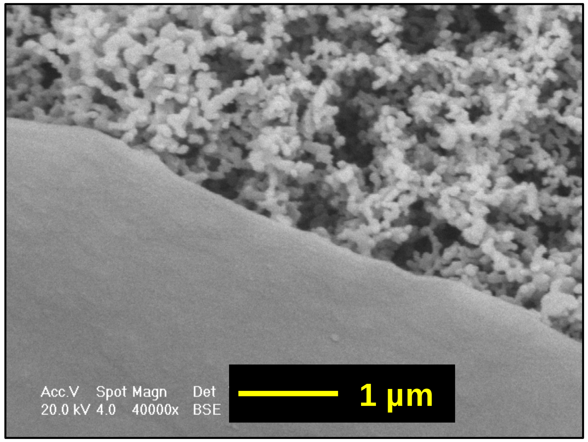
**Our next goal is to adapt this 'air-dried' synthesis to the mass production of shells**

# Our next challenge: increase pore size and retain the skin

- **The RF system has many parameters to optimize:**
  - gel time
  - acid species
  - acid concentration
  - theoretical density
  - heating cycle
  - R/C


**radically different RF beads arise from different experimental conditions**



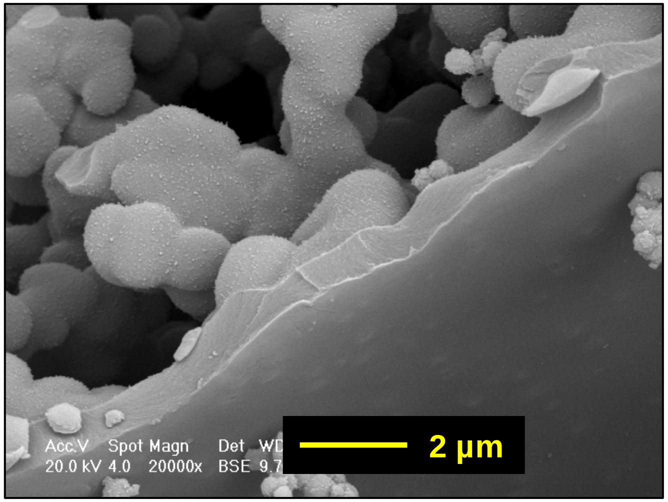

**Large pore RF with skin has been synthesized by the phase-transfer technique**

# We are making progress toward air-dried HAPL targets

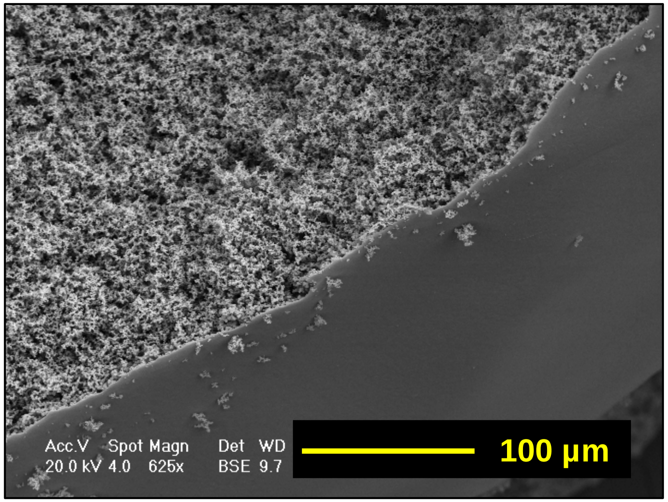
- After establishing our ability to vary pore size, we conducted a survey of experiments
- Recently in this survey we synthesized an RF sphere with a density of 103 mg/cc (above) after air drying
- This bead had the characteristic smooth, thin, and morphologically distinct skin seen in previous phase transfer work

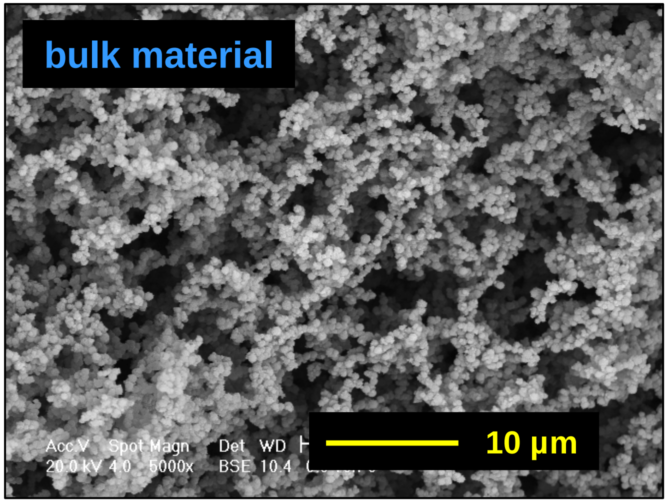
**We synthesized an air dried RF bead with skin at a density of 103 mg/cc**

# This air dried sample has the same morphology, only with much larger features




- **Retained features of phase transfer RF**
- **Characteristic skin (much thicker here)**
- **Homogenous aerogel structure**
- **Need additional characterization (roughness, etc.)**



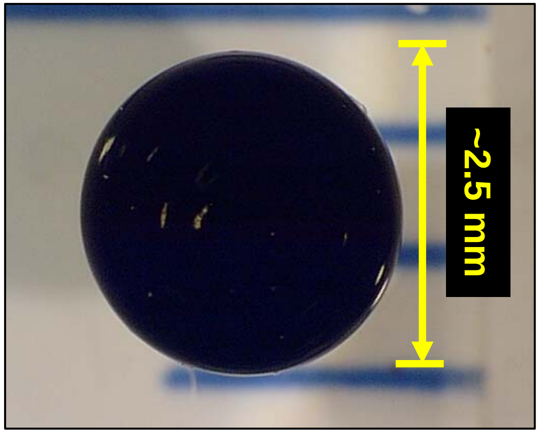
# This recent work may have important implications

- **DVB with Skin**
  - A DVB shell with a thin, smooth skin may allow us to apply a thin, gas tight coating that templates this now smooth surface

- **Air Dried RF**
  - We can air dry RF aerogel spheres
  - We have increased the pore size while keeping the smooth skin
  - We have learned how to make the RF skin much thicker

# Future Work

- **DVB**
  - Additional characterization
  - Fine tune synthesis to optimize the skin
  - Can we air-dry DVB?




CRF shell

- **Air dried RF with skin**
  - Refine parameters to reliably produce air dried RF with skin
  - Transfer synthesis techniques to shell production
  - Investigate gas retention properties of the skinned RF
  - Apply a coating to the dried shell and determine smoothness and gas permeation properties
  - Investigate conversion into CRF (higher buckle strength and burst pressure than DVB or RF)