

# CELLULOSE NANOCRYSTAL AEROGELS

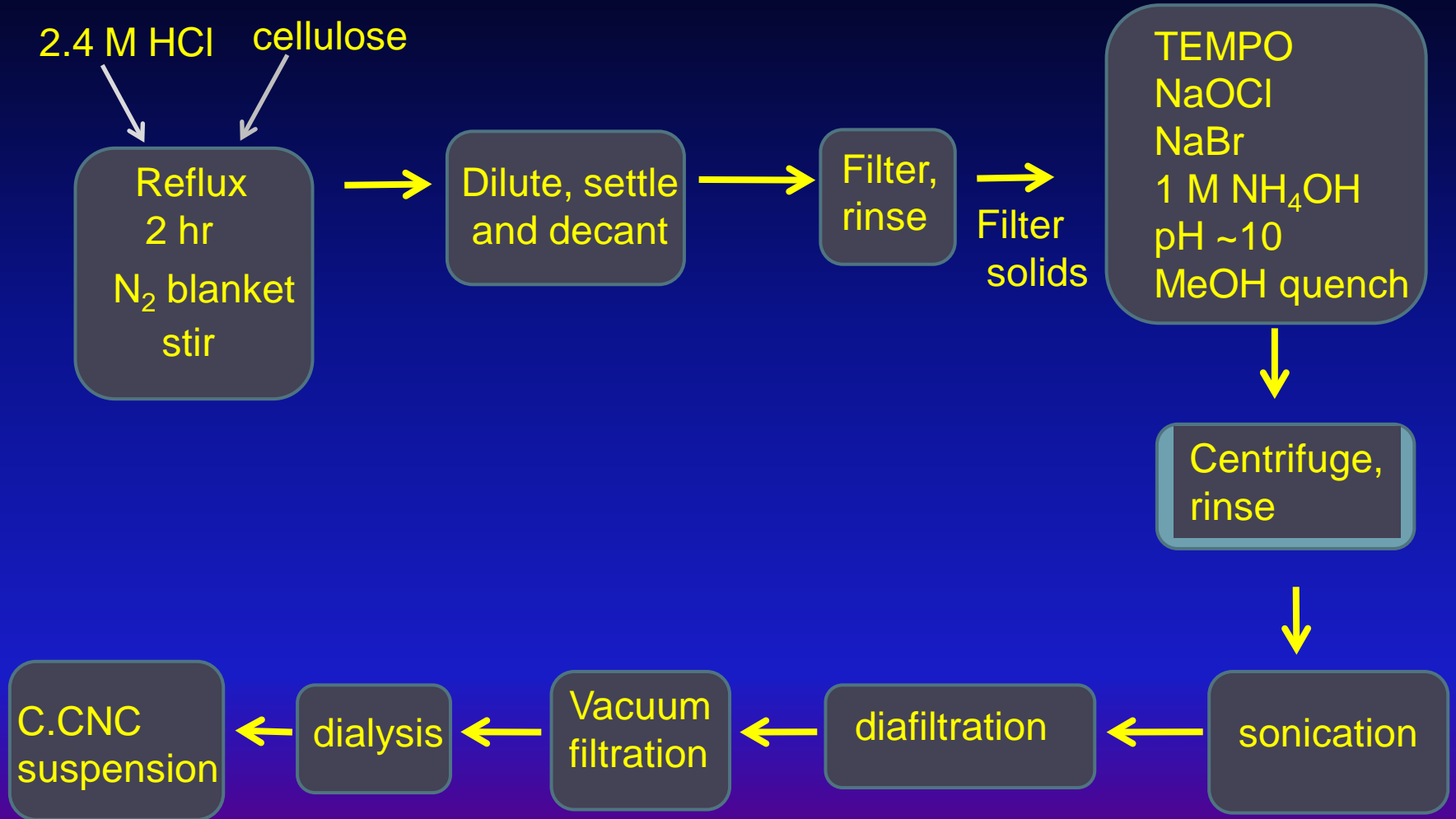
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PNNL

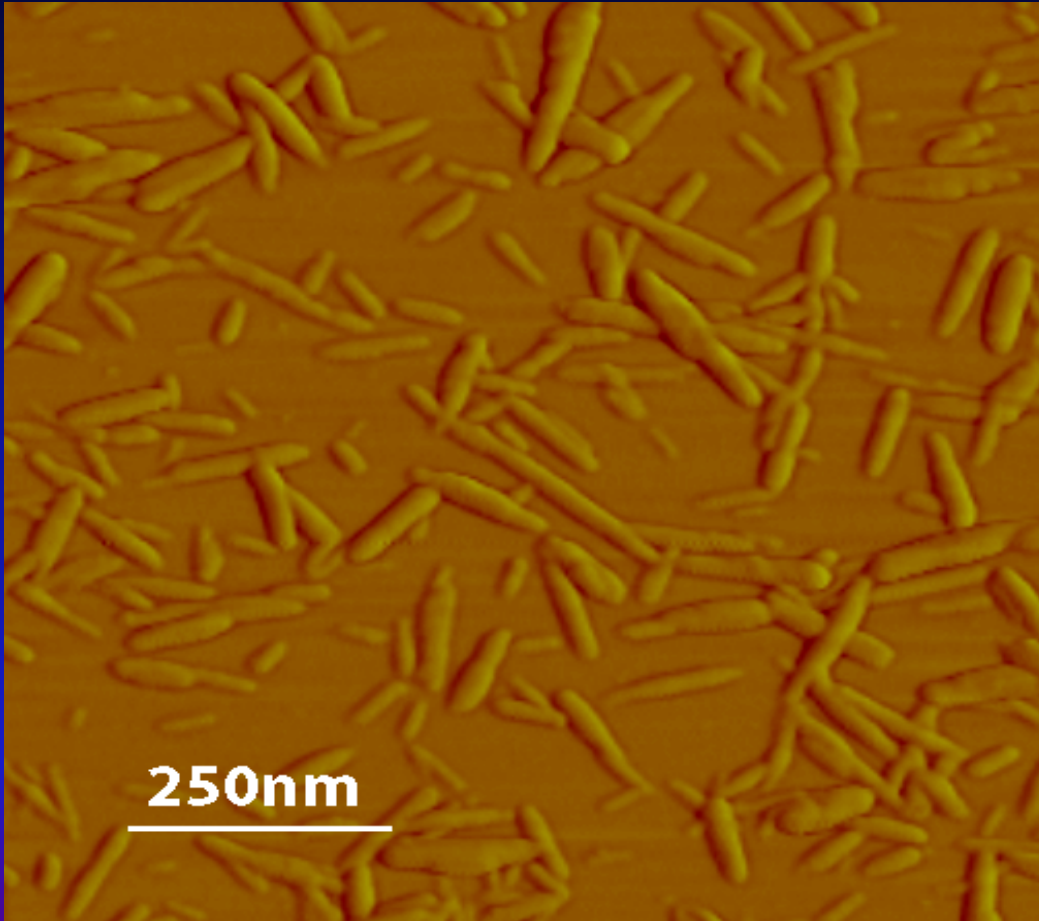
# Coming attractions:

- ⊙ Preparation of carboxylated cellulose nanocrystals (C.CNXLs)
- ⊙ Preparation of C.CNXL aerogels
- ⊙ Stability of aerogels
- ⊙ Ester formation
- ⊙ Evaluation
  - SEM
  - FTIR
  - XRD

# Carboxylated CNC prep



# Carboxylated CNCs

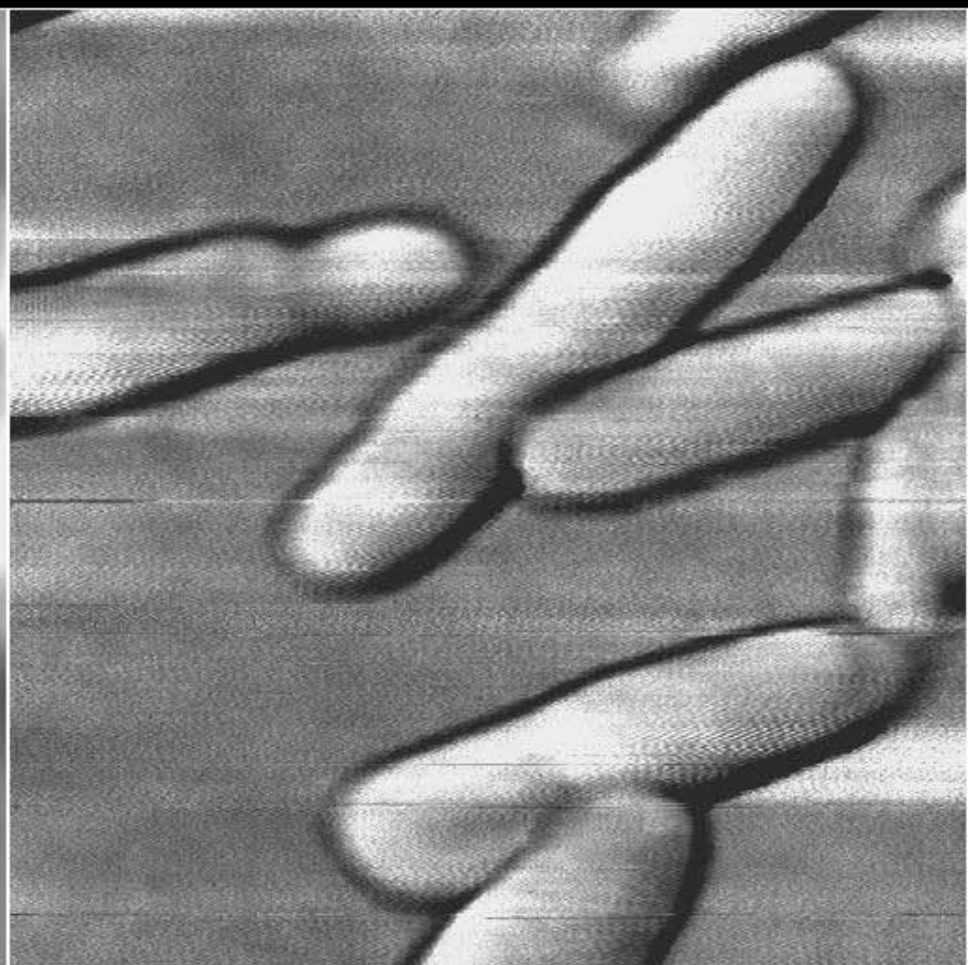


Typical size 7 X 140 nm  
1.4 mmol CO<sub>2</sub>H/g CNC  
~ 2.4 acid groups/nm<sup>2</sup>  
Zeta potential ~ -50  
Conductivity of 2%  
dispersion ~ 1 mS/cm



0 200 nm 0

Data type Height  
Z range 19.68 nm

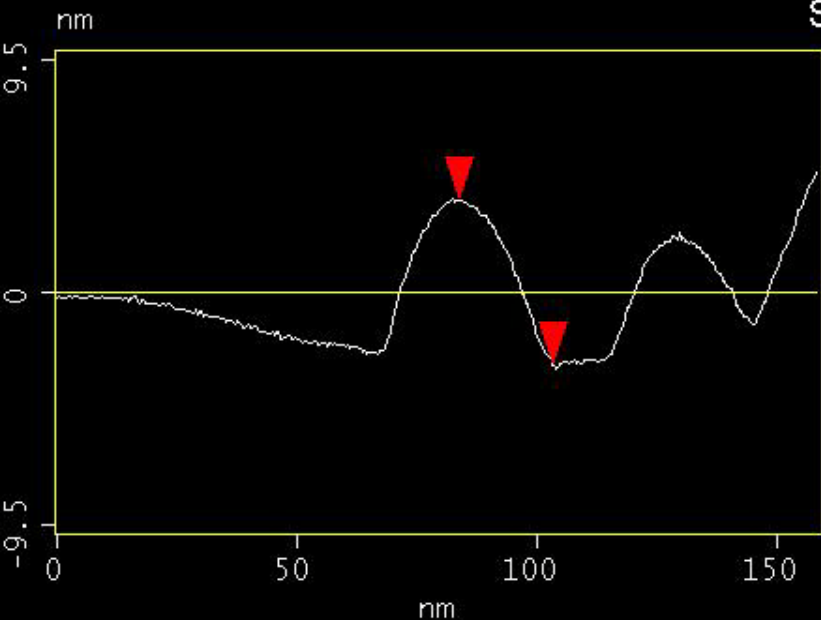


200 nm

Data type Phase  
Z range 28.11 °

js\_c-cnxl1sn200nm.000  
carboxylatd CNXL dried dispersion

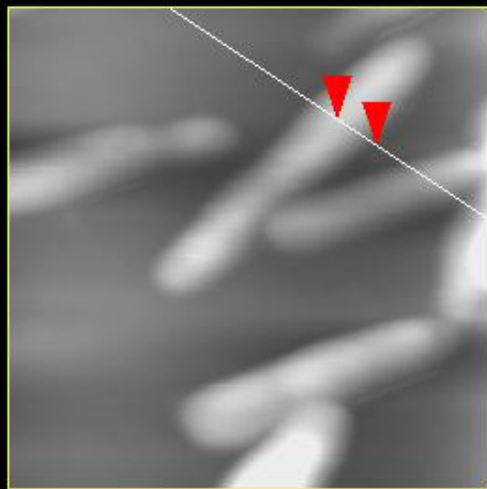
### Section Analysis



~ 7 nm

L	19.531 nm
RMS	2.249 nm
lc	DC
Ra(lc)	0.384 nm
Rmax	1.722 nm
Rz	0.802 nm
Rz Cnt	6
Radius	35.649 nm
Sigma	0.212 nm

### Spectrum

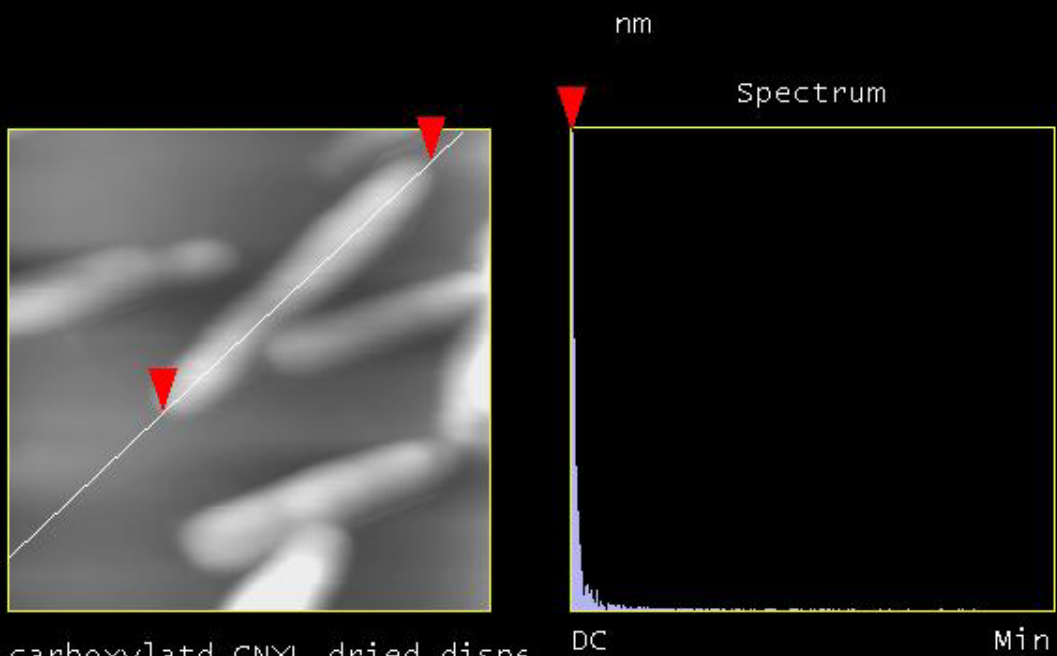


Surface distance	21.639 nm
Horiz distance(L)	19.531 nm
Vert distance	6.743 nm
Angle	19.046 °
Surface distance	
Horiz distance	
Vert distance	
Angle	
Surface distance	
Horiz distance	
Vert distance	
Angle	
Spectral period	DC
Spectral freq	0 Hz
Spectral RMS amp	0.0002 nm

carboxylatd CNXL dried dispe  
js\_c-cnxl1sn200nm.000



L	152.34 nm
RMS	0.877 nm
lc	DC
Ra(lc)	0.707 nm
Rmax	4.191 nm
Rz	3.724 nm
Rz Cnt	4
Radius	56.248 nm
Sigma	15.475 nm



Surface distance	157.28 nm
Horiz distance(L)	152.34 nm
Vert distance	1.192 nm
Angle	0.448 °
Surface distance	
Horiz distance	
Vert distance	
Angle	
Surface distance	
Horiz distance	
Vert distance	
Angle	
Spectral period	DC
Spectral freq	0 Hz
Spectral RMS amp	0.003 nm

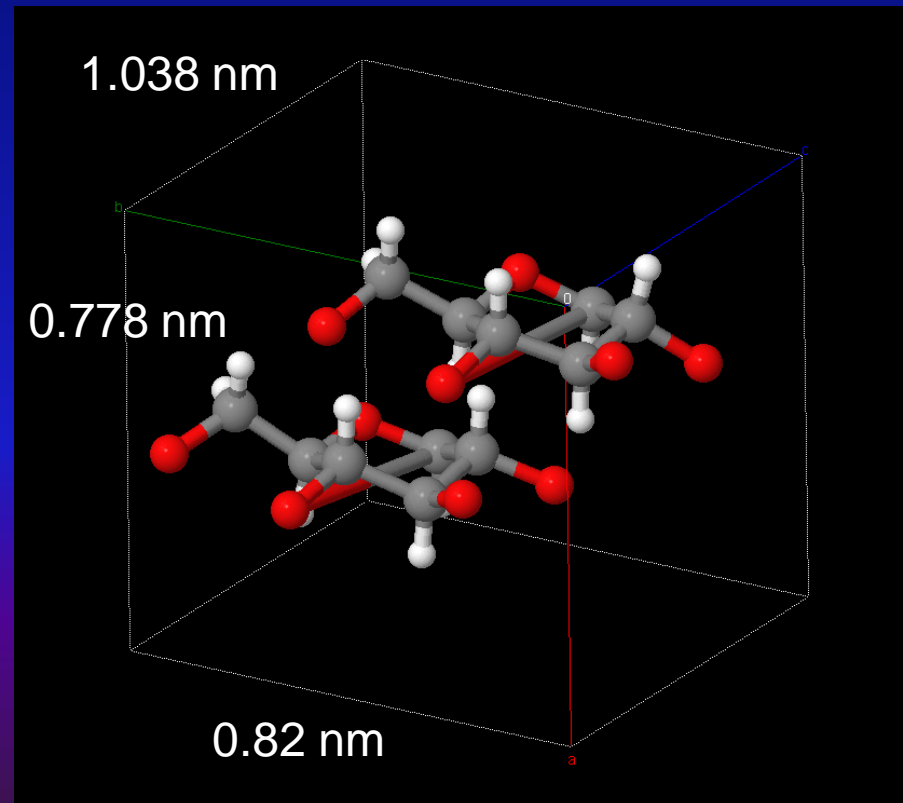
carboxylatd CNXL dried dispe  
js\_c-cnxl1sn200nm.000

# Surface charges

- 1 $\beta$  unit cell has a surface area of 3.32 nm<sup>2</sup> neglecting the longitudinal ends and contains two cellulose chains with a cellobiose repeat unit
- Thus 1.2 C6 groups/nm<sup>2</sup>

Not consistent with  
measured value of  
2.4 groups/nm<sup>2</sup>

Assumes a 7 X 7 nm crystal



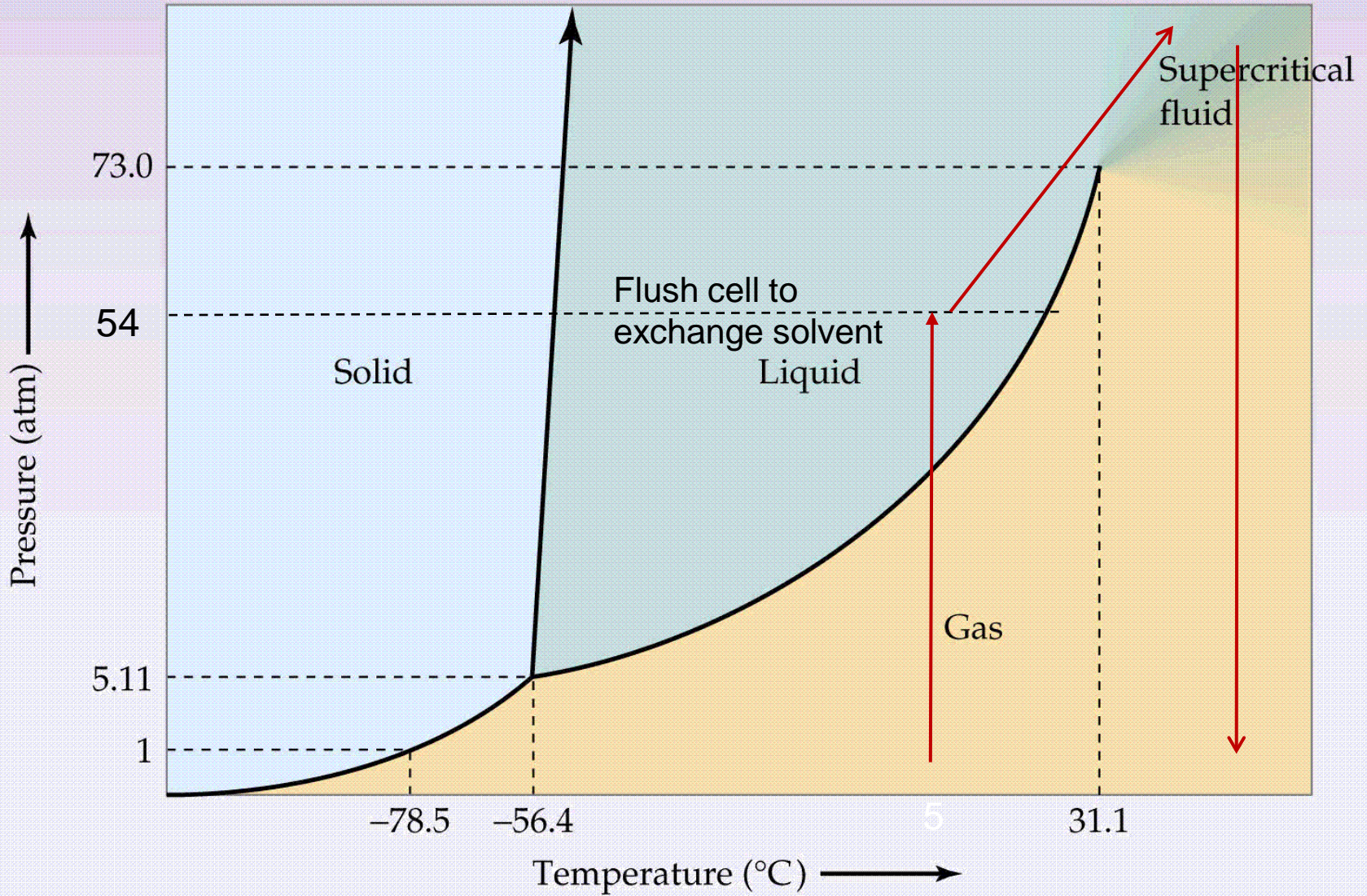


# CARBOXYLATED CNC AEROGELS

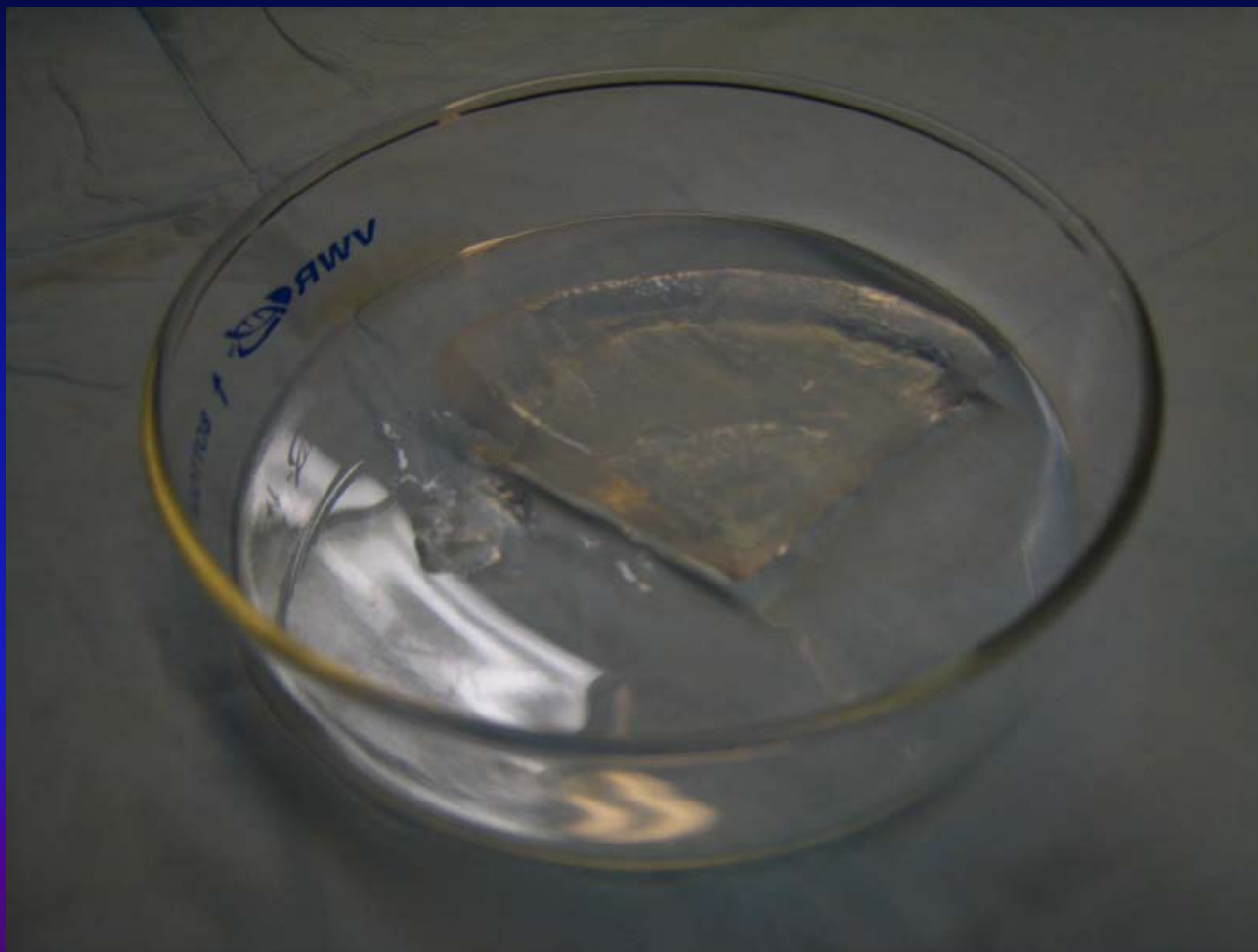
# Fabrication

- ⦿ Layer acetone over aqueous suspension of C.CNCs
- ⦿ Gel forms in < 1 day
- ⦿ Replace the acetone layer at least three times
- ⦿ Dry in supercritical dryer
- ⦿ Densities to  $30 \text{ mg/cm}^3$  have been achieved

# Supercritical drying

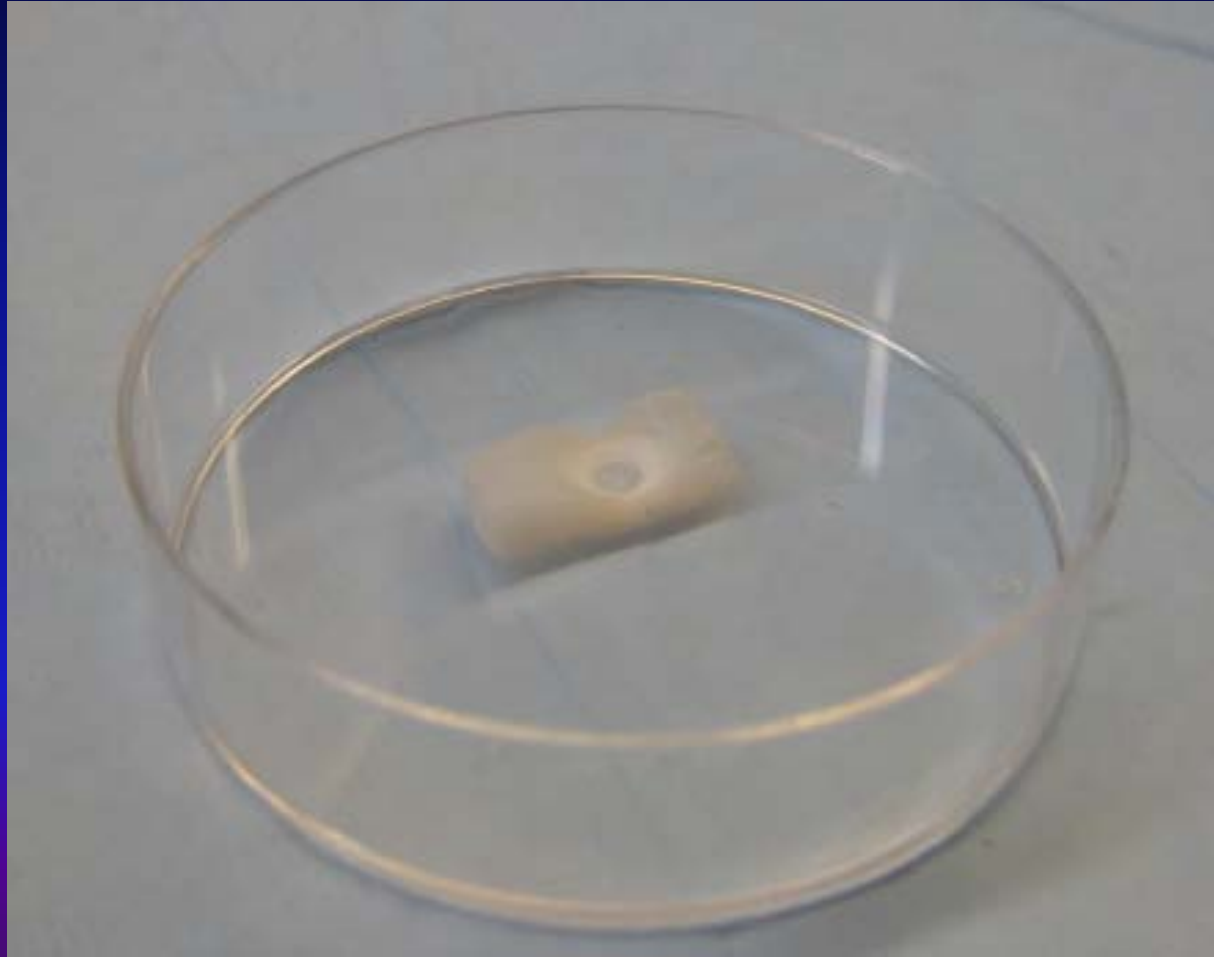


# C.CNC aerogels



ORGANOGELE/LYOGEL

# C.CNC aerogels



AEROGEL

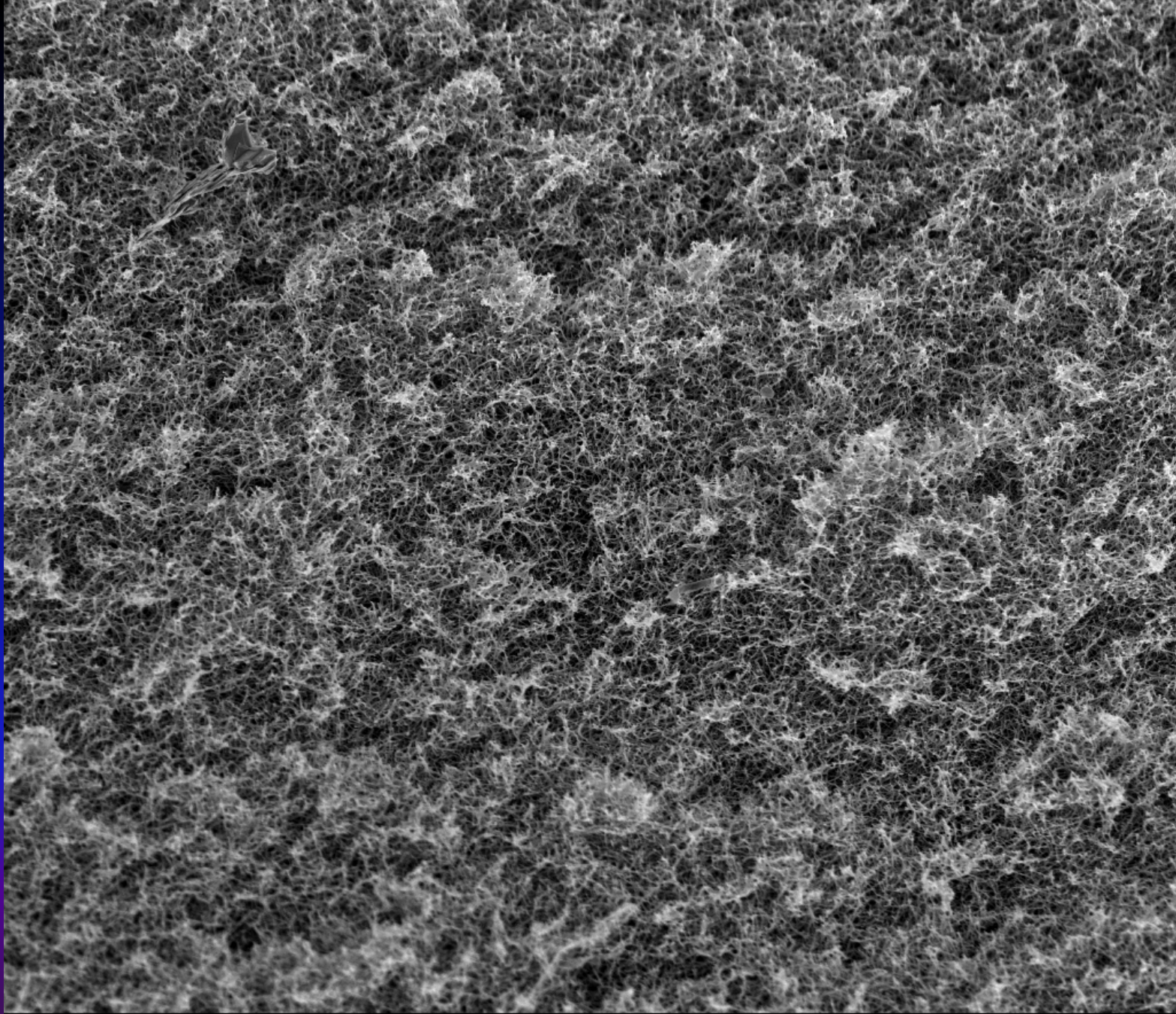
# C.CNC aerogels



REFLECTED LIGHT



TRANSMITTED LIGHT



10/24/2008

7:25:28 AM

det

TLD

HFW

25.6  $\mu\text{m}$

mag

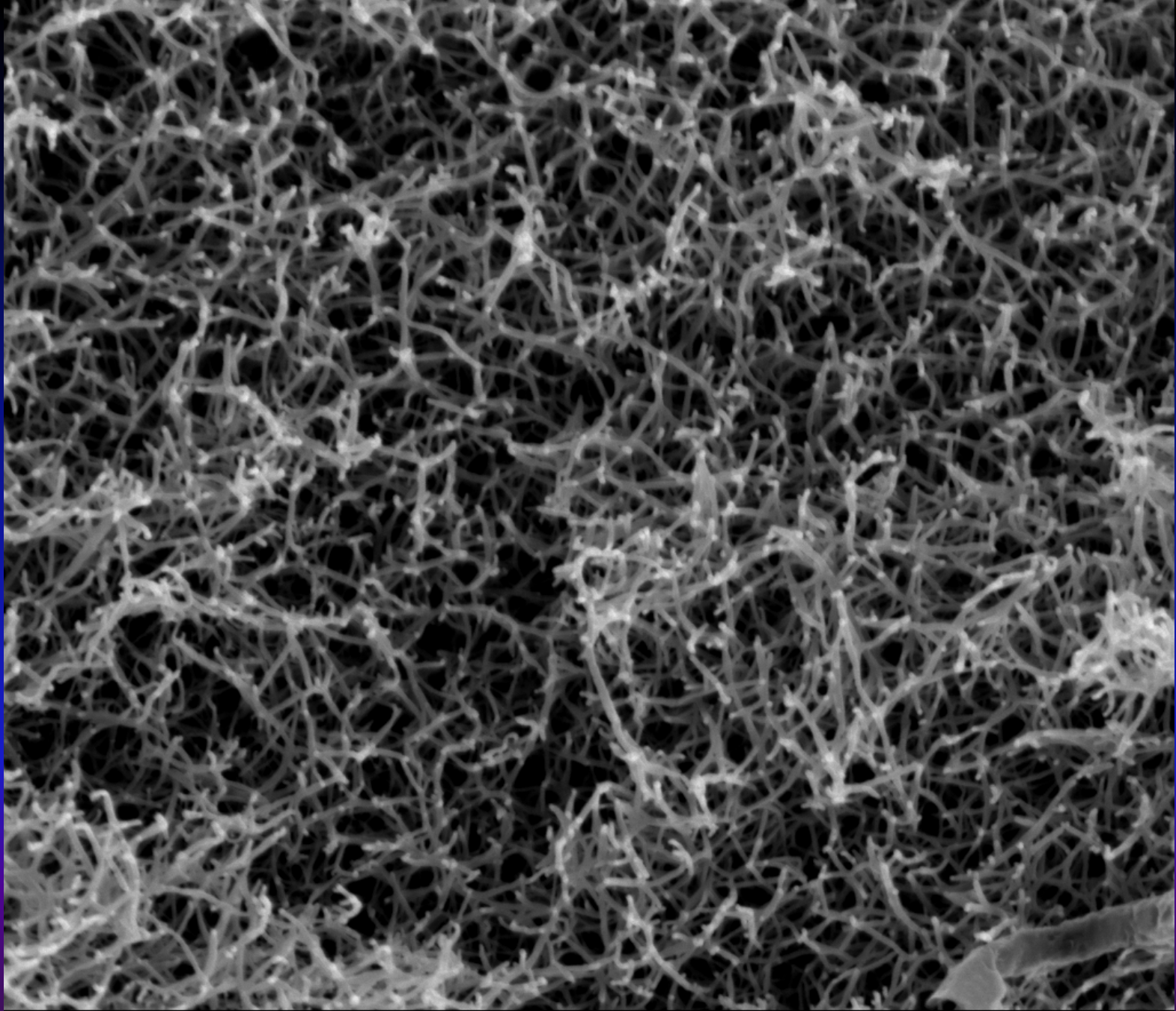
10 000 x

WD

4.0 mm

10  $\mu\text{m}$

Simonsen Sample



10/24/2008  
7:27:00 AM

det  
TLD

HFW  
5.12  $\mu\text{m}$

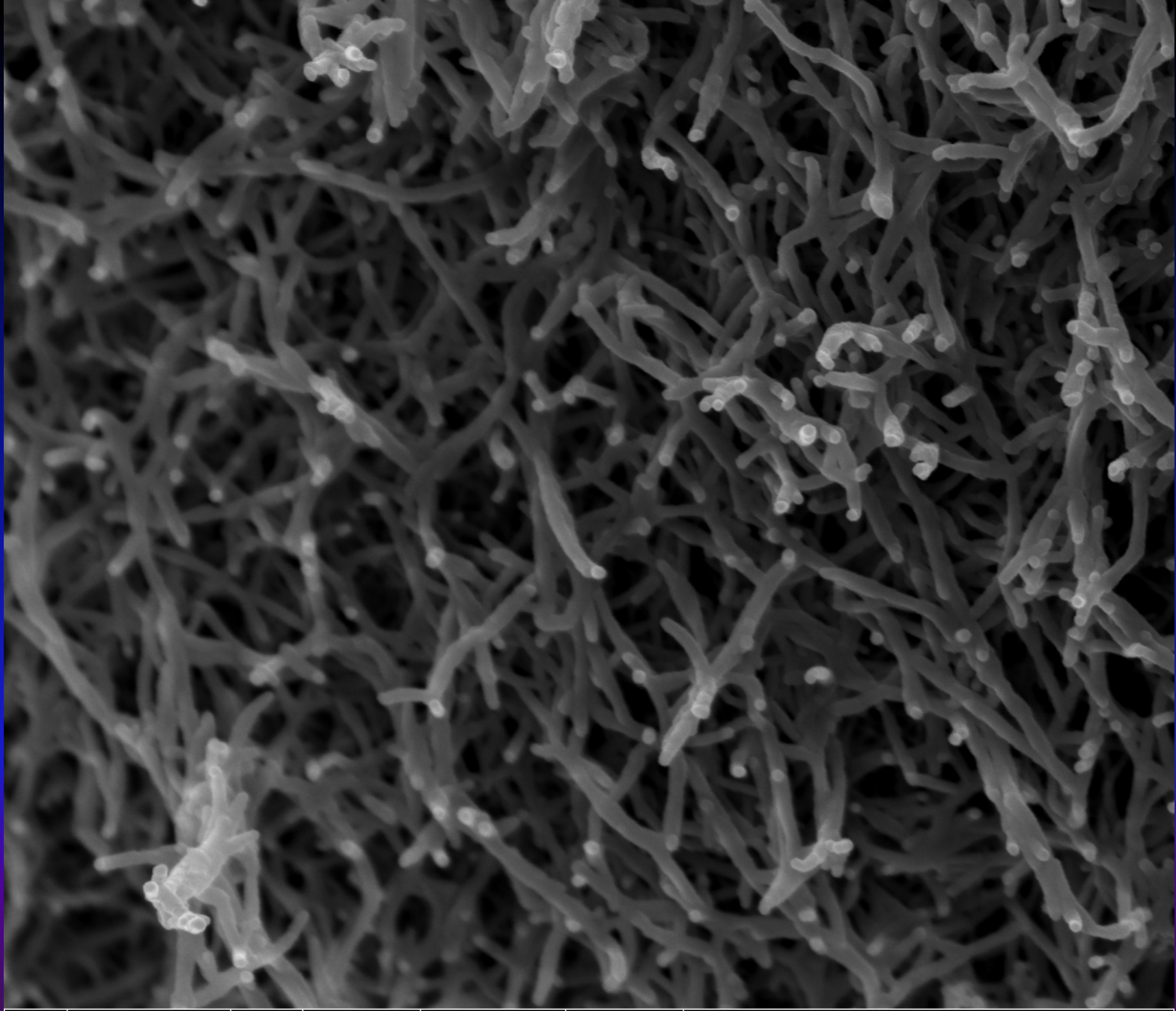
mag   
50 000 x


WD  
4.0 mm

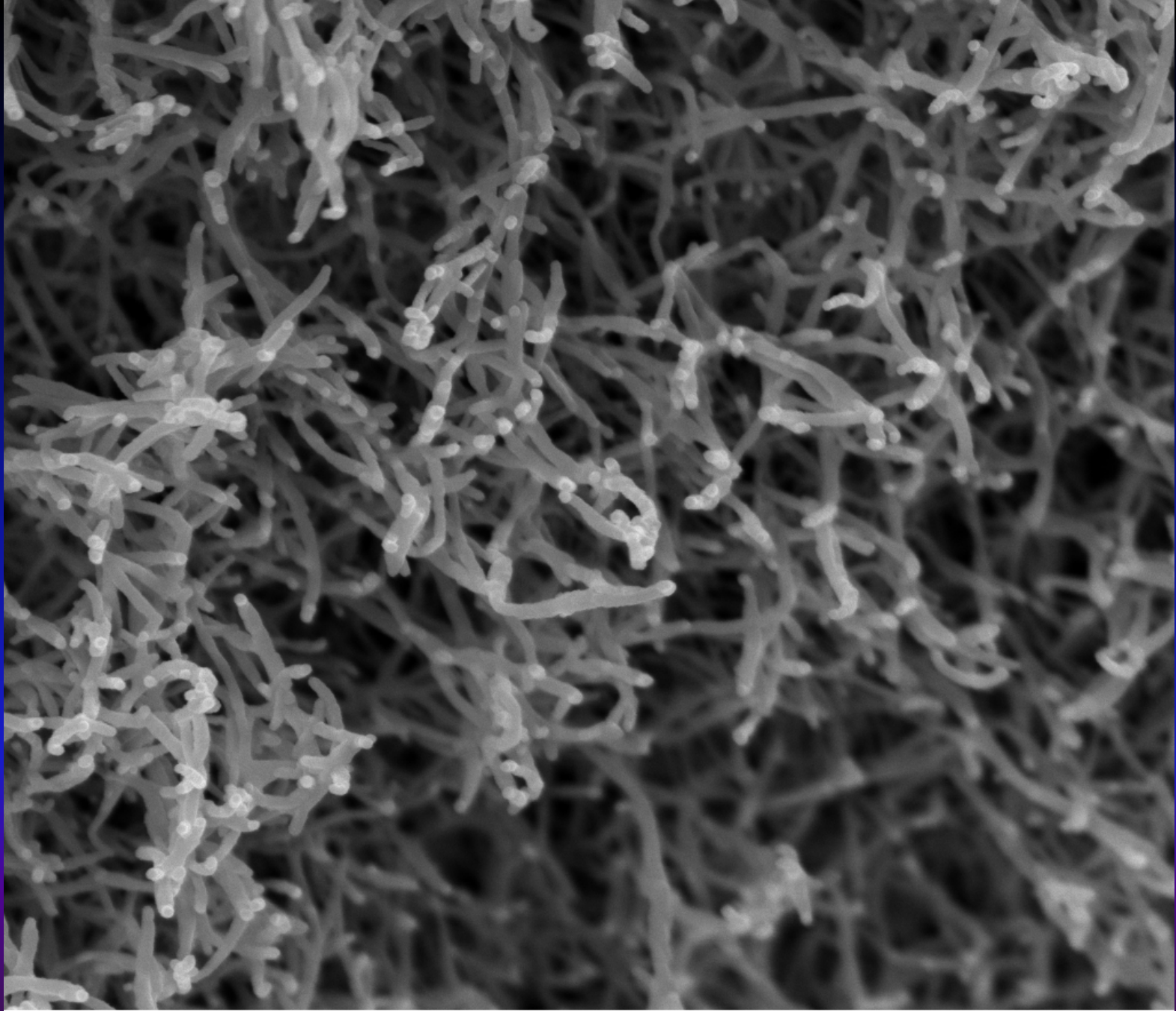
2  $\mu\text{m}$


Simonsen Sample

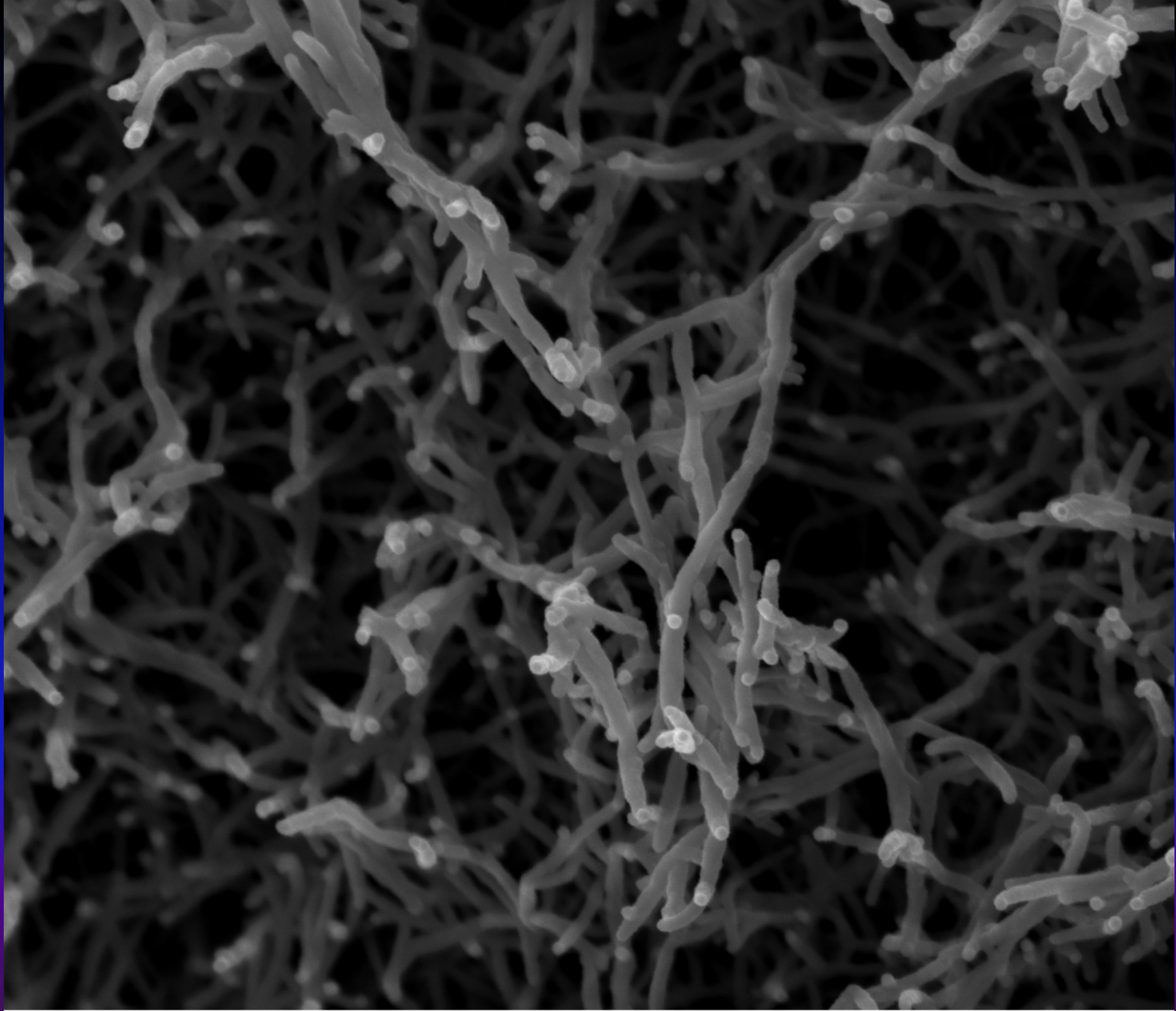





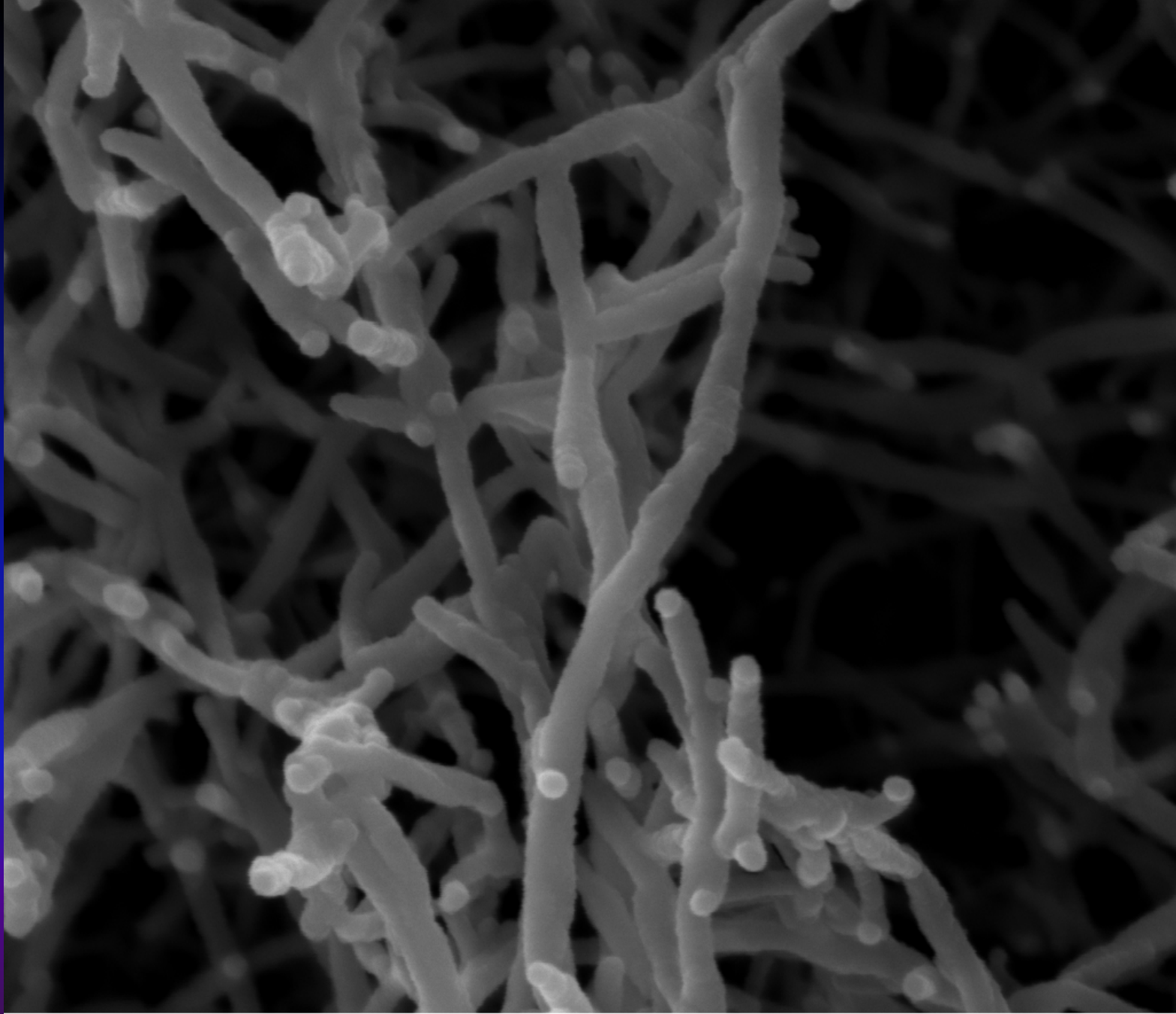
	3/23/2009	det	HFW	mag <input type="checkbox"/>	WD	1 $\mu$ m
	8:30:11 AM	TLD	2.56 $\mu$ m	100 000 x	3.2 mm	



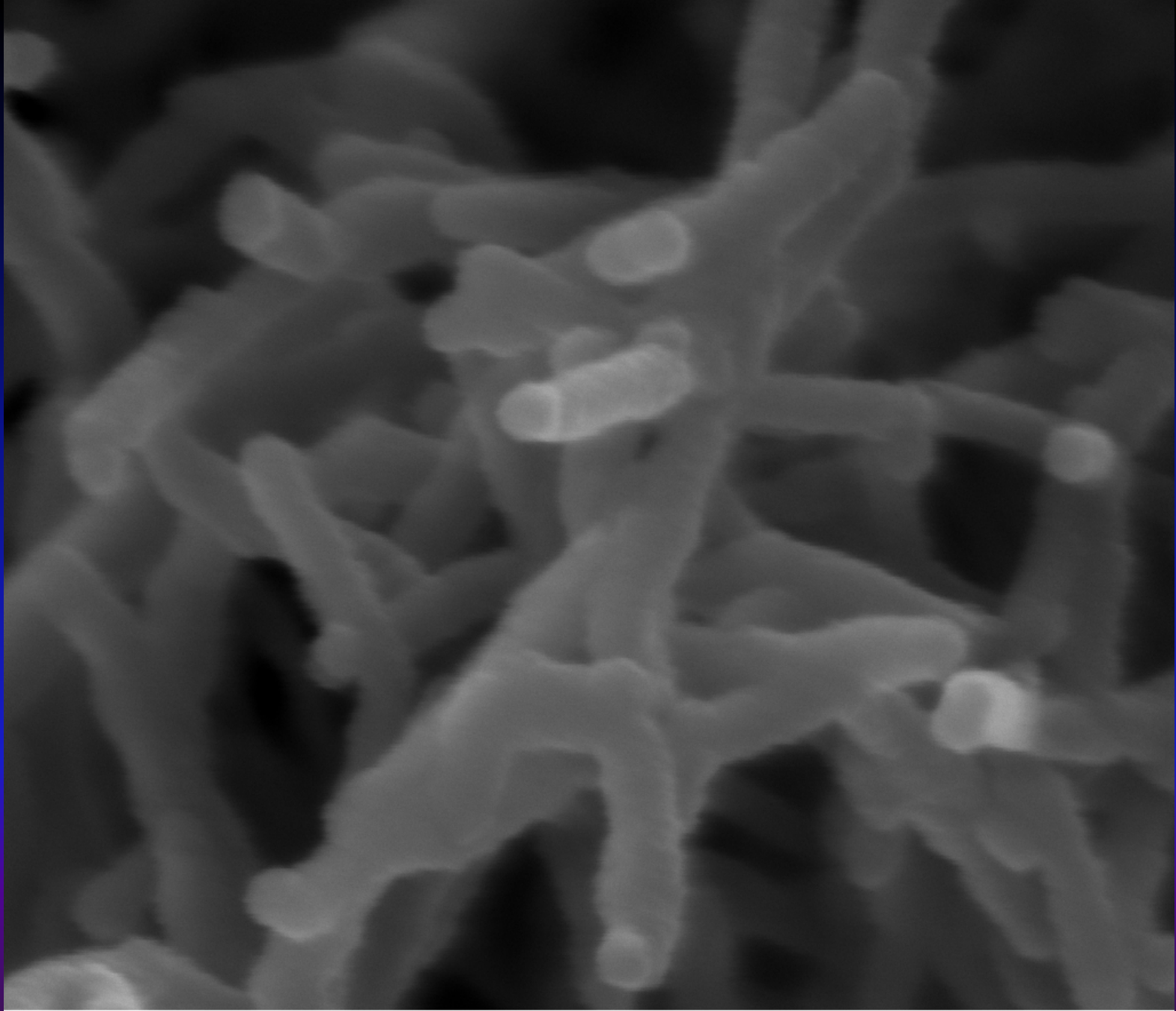
	3/23/2009	det	HFW	mag <input type="checkbox"/>	WD	← 1 μm →
	8:11:31 AM	TLD	2.56 μm	100 000 x	3.2 mm	



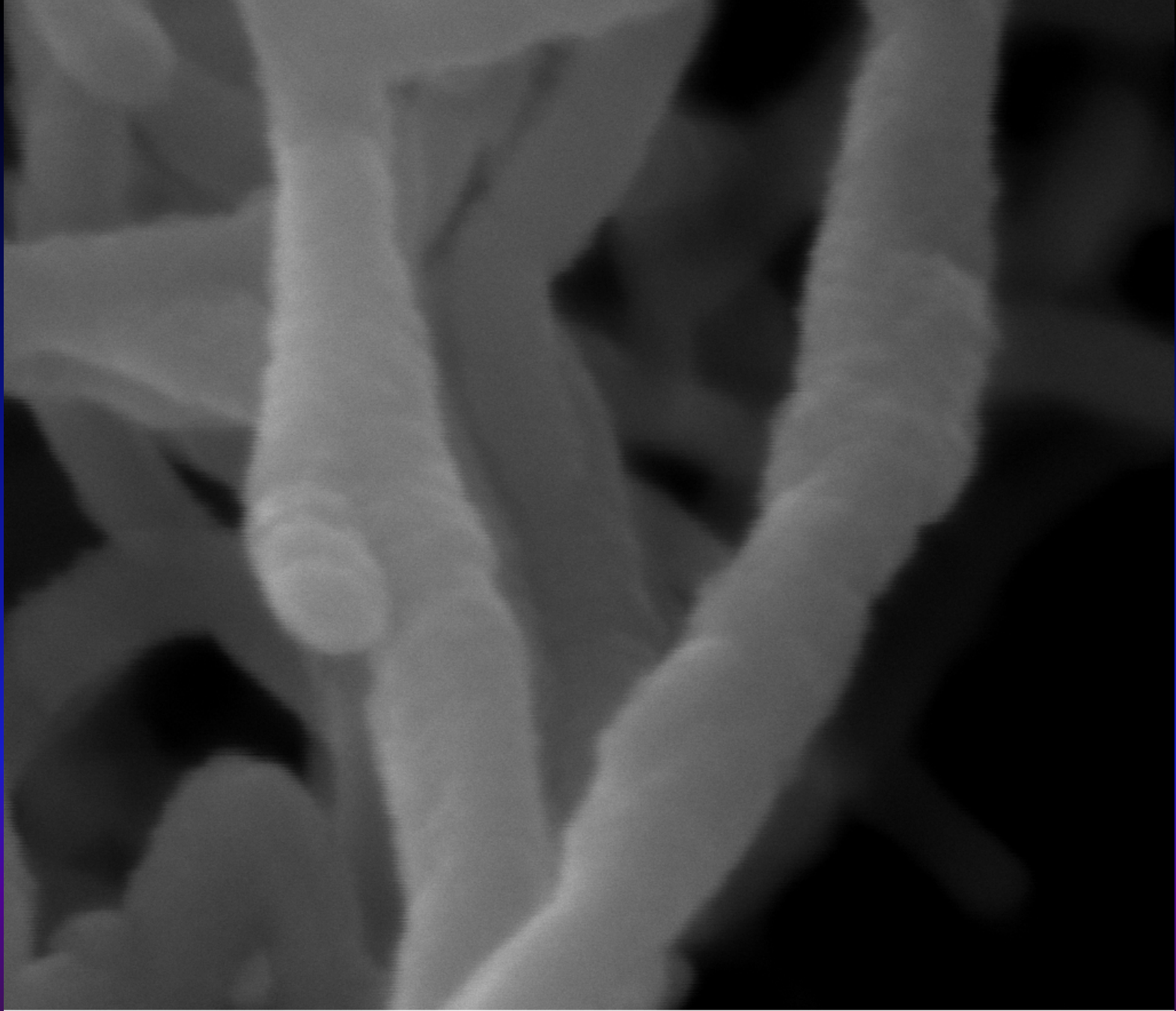
	3/23/2009	det	HFW	mag <input type="checkbox"/>	WD	500 nm
	8:37:34 AM	TLD	2.13 $\mu\text{m}$	120 000 x	3.2 mm	



	3/23/2009	det	HFW	mag <input type="checkbox"/>	WD	400 nm
8:39:23 AM	TLD	1.02 $\mu\text{m}$	250 000 x	3.2 mm	C.CNXL Control	



	3/23/2009	det	HFW	mag <input type="checkbox"/>	WD	200 nm
	8:25:33 AM	TLD	512 nm	500 000 x	3.1 mm	



	3/23/2009	det	HFW	mag	<input type="checkbox"/>	WD	100 nm
	8:42:43 AM	TLD	256 nm	1 000 000 x		3.2 mm	

# Aerogel stability

# Protocol

- ① Add water
- ② Wait at least one day before next addition
- ③ Evaluate visually



# No addition of water



39% H<sub>2</sub>O



47% H<sub>2</sub>O



60% H<sub>2</sub>O



70% H<sub>2</sub>O



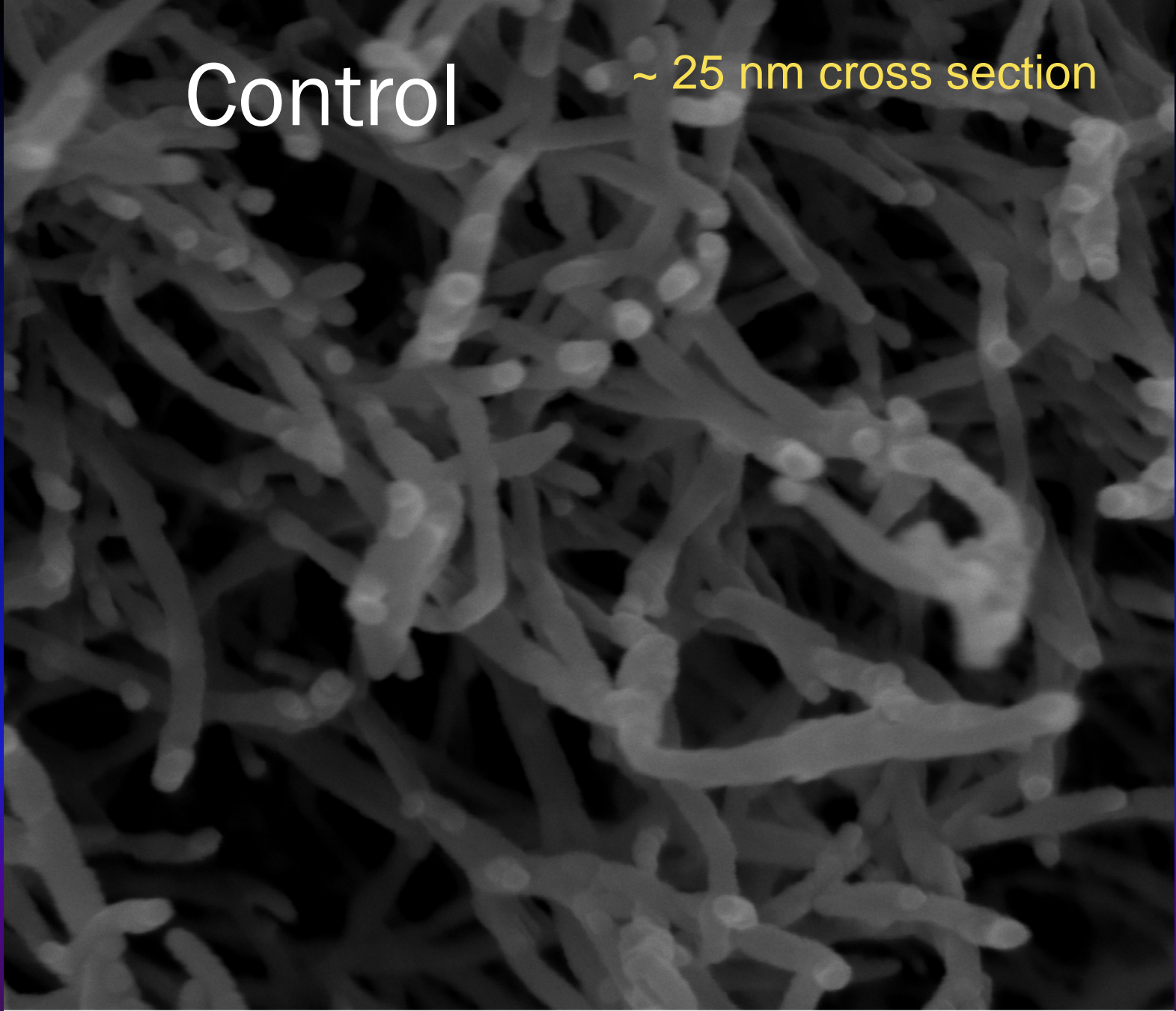
80% H<sub>2</sub>O




# Comparison of C.CNC aerogel treatments

# Control

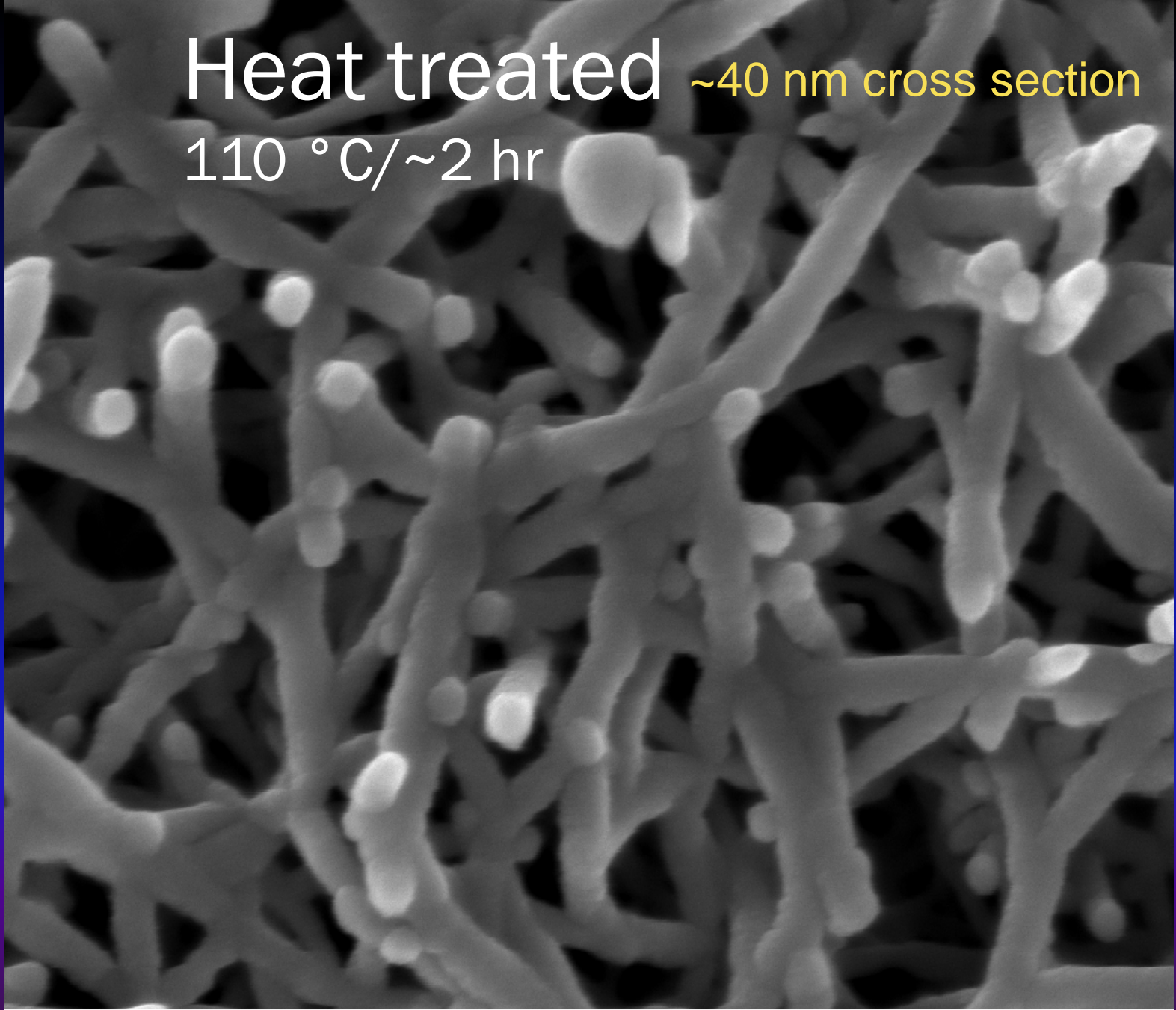
~ 25 nm cross section




	3/23/2009	det	HFW	mag <input type="checkbox"/>	WD	400 nm
	8:13:57 AM	TLD	1.02 $\mu\text{m}$	250 000 x	3.2 mm	



Heat treated  $\sim 40$  nm cross section  
110 °C/ $\sim 2$  hr




	2/18/2009	det	HFW	mag <input type="checkbox"/>	WD	400 nm
	9:21:41 AM	TLD	1.02 $\mu$ m	250 000 x	3.0 mm	

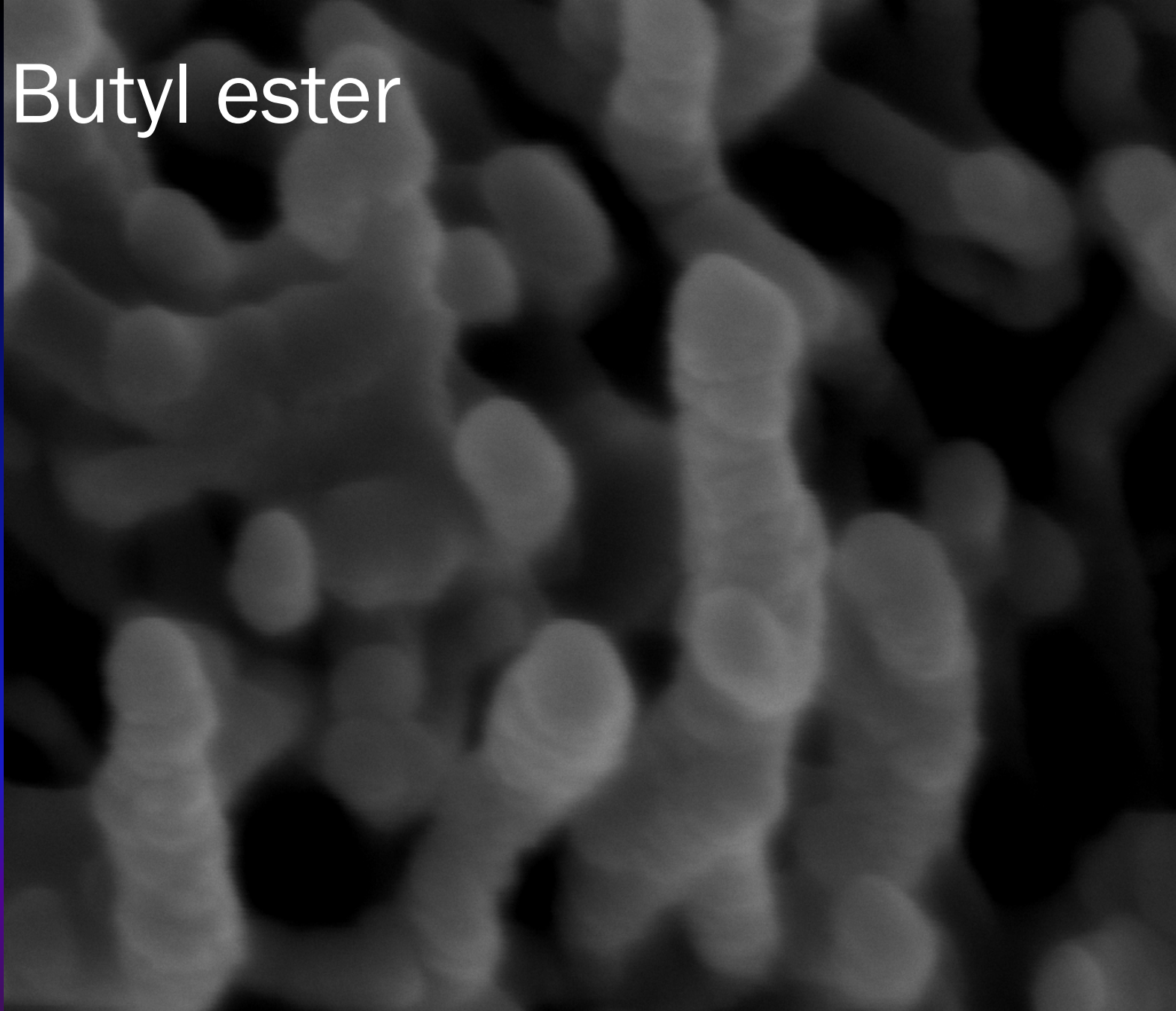
# Butyl ester


~50 nm cross section

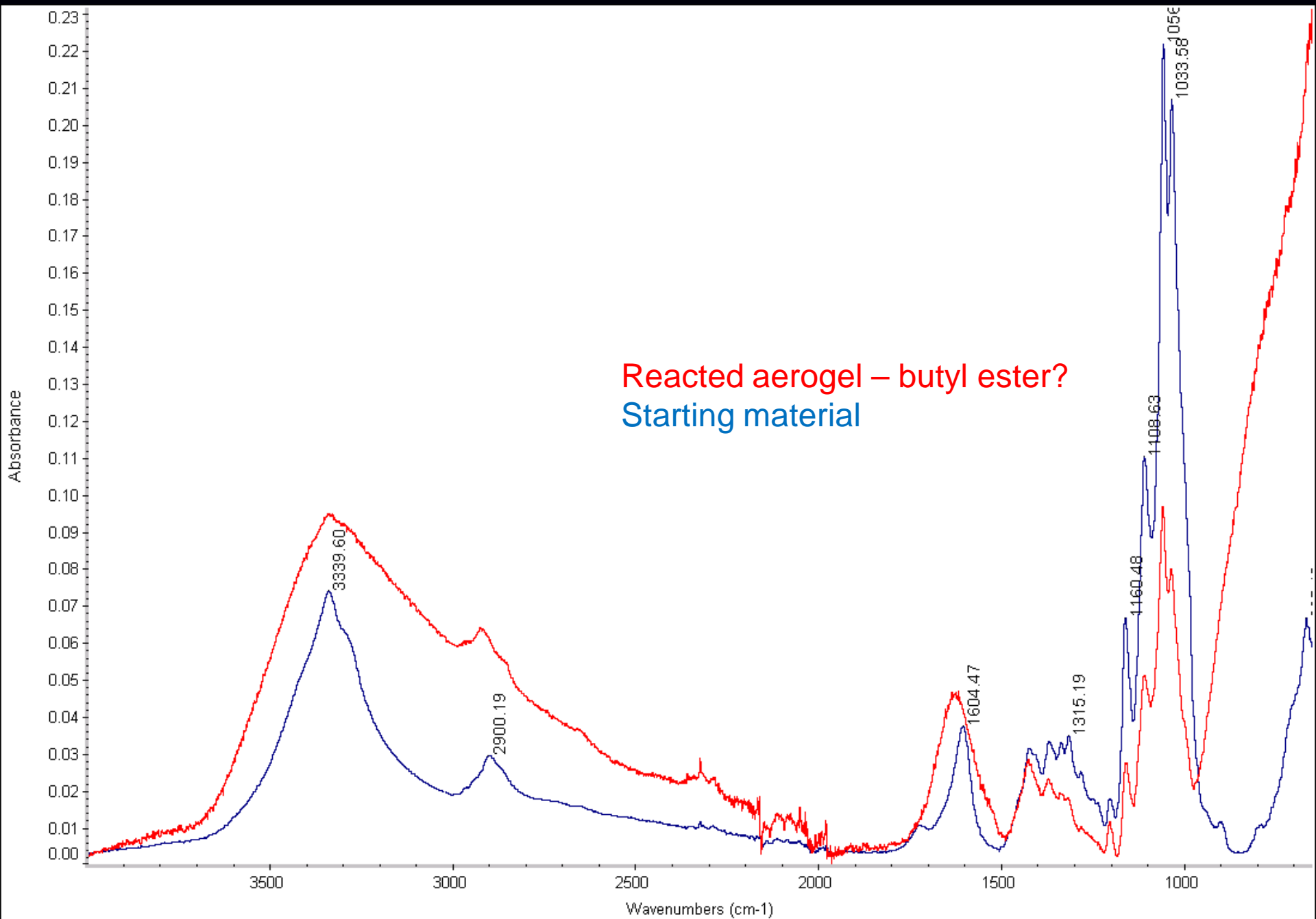


	2/18/2009	det	HFV	mag	WD	400 nm
	3:08:56 PM	TLD	1.02 $\mu$ m	250 000 x	4.2 mm	

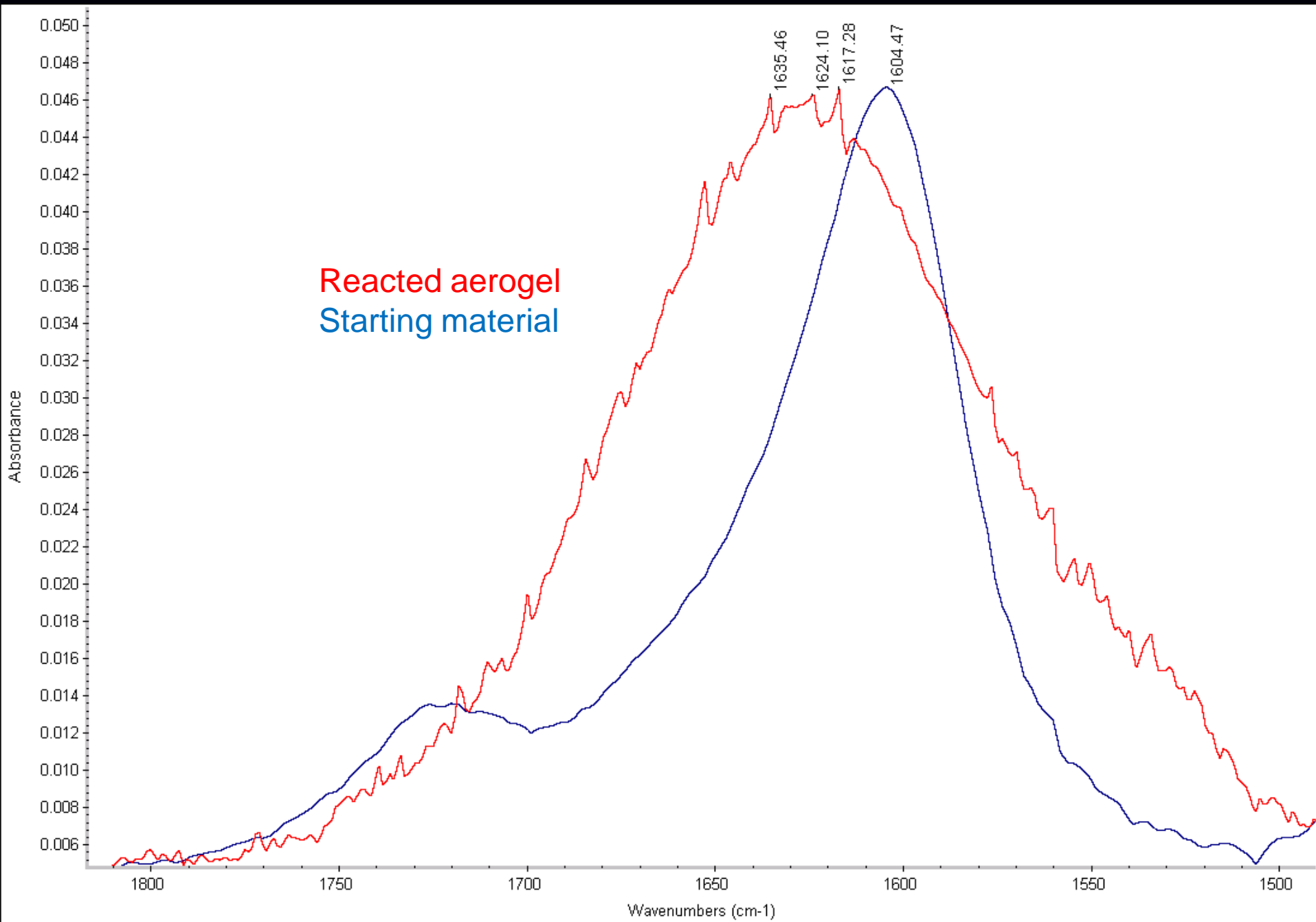
# Butyl ester



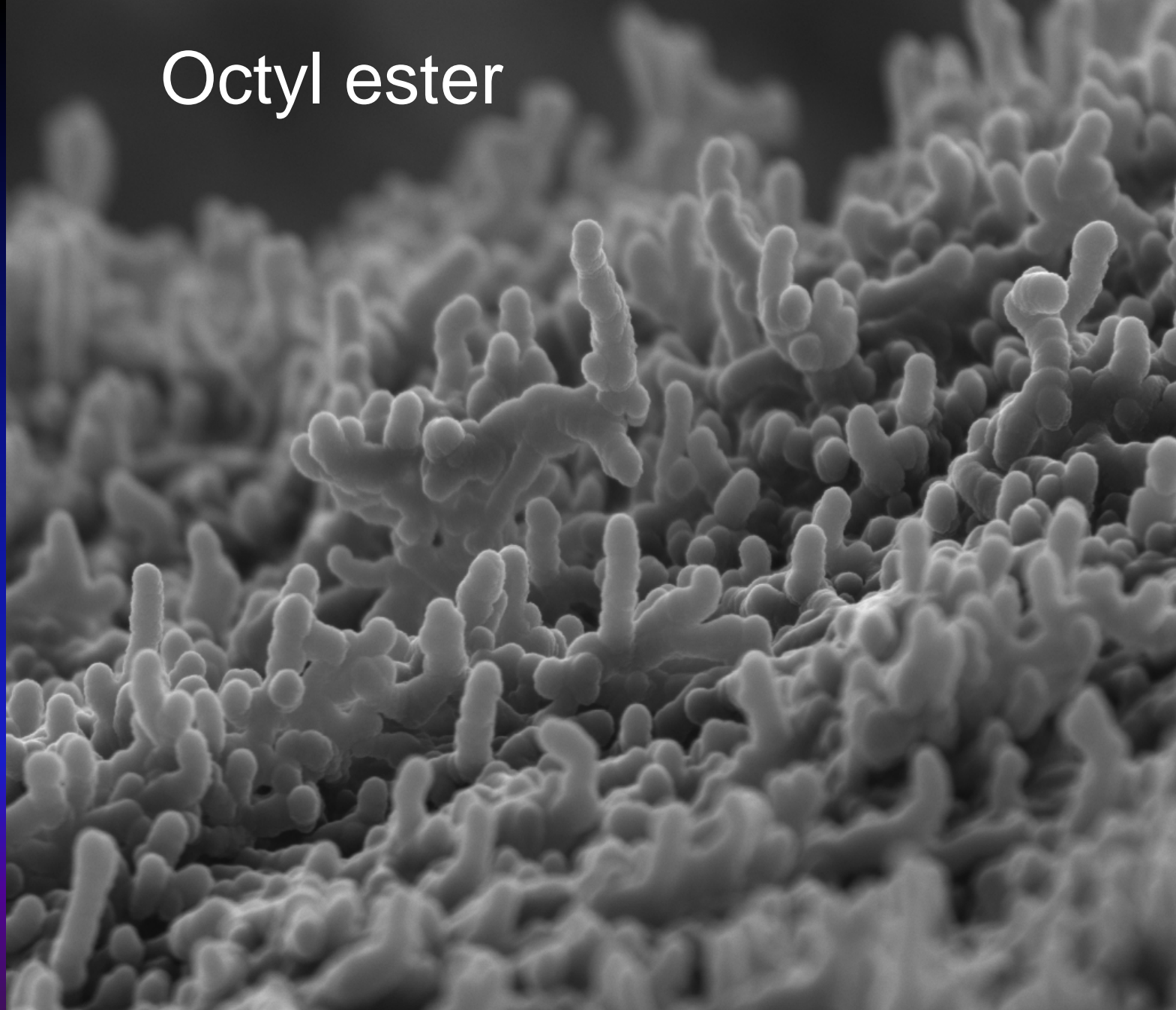
	2/18/2009	det	HFW	mag <input type="checkbox"/>	WD	← 200 nm → Butyl/Ester
	3:26:15 PM	TLD	512 nm	500 000 x	4.2 mm	




Reacted aerogel – butyl ester?  
Starting material

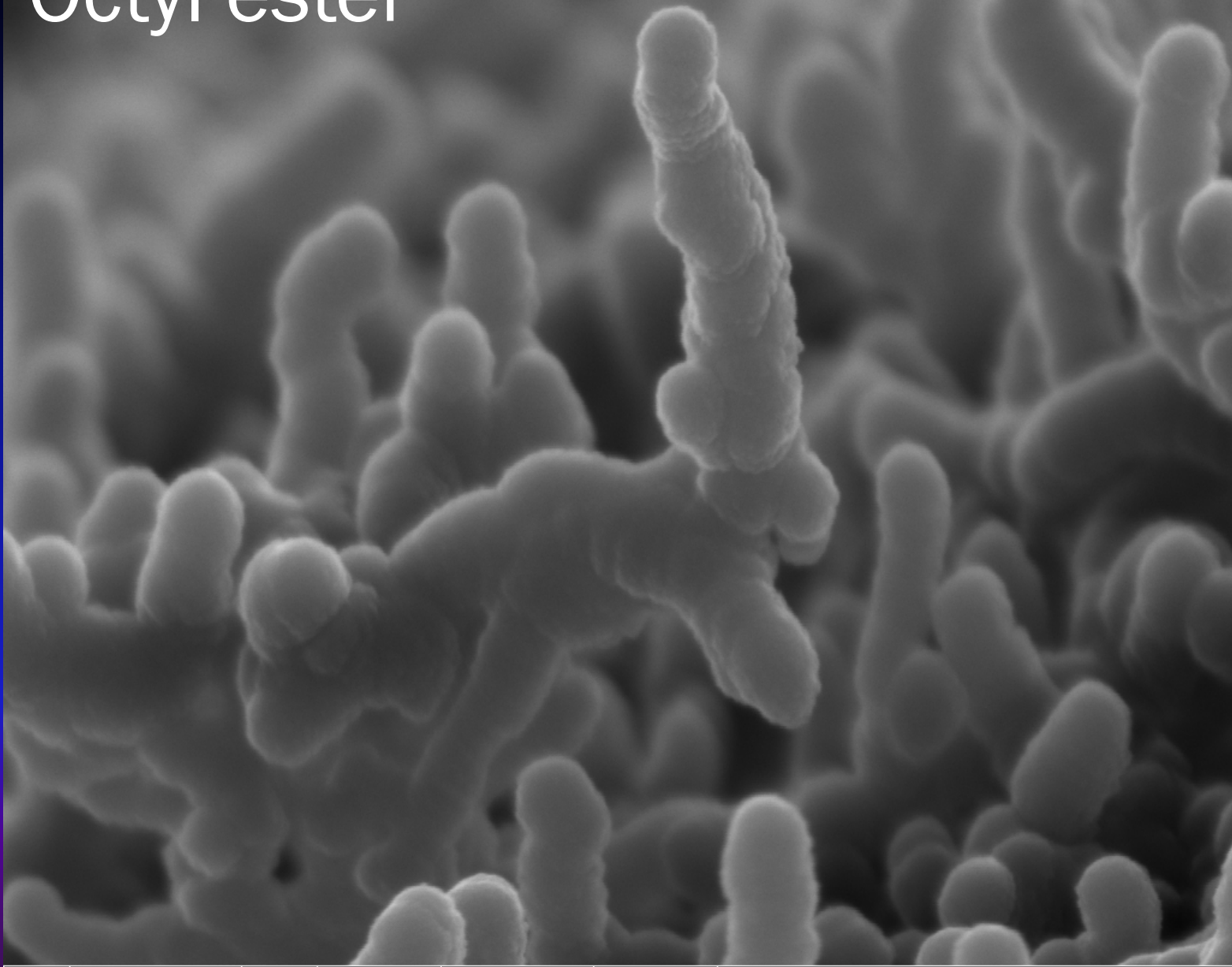



# Octyl ester



	2/25/2009	det	HFW	mag	WD	1 $\mu$ m
	3:15:26 PM	TLD	2.56 $\mu$ m	100 000 x	2.6 mm	

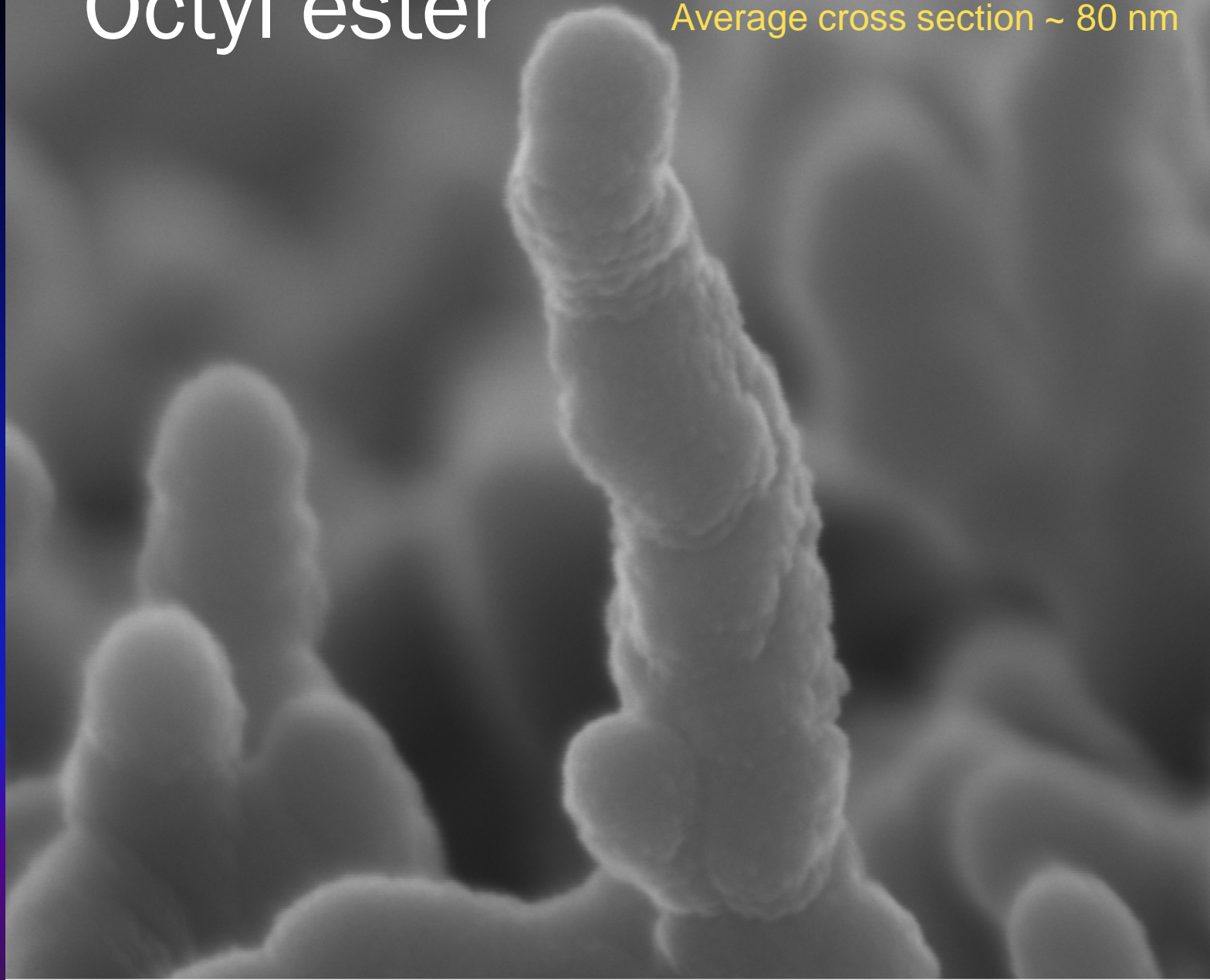
# Octyl ester




	2/25/2009	det	HFW	mag <input type="checkbox"/>	WD	← 400 nm →
	3:16:44 PM	TLD	1.02 $\mu\text{m}$	250 000 x	2.6 mm	

# Octyl ester

Average cross section ~ 80 nm



	2/25/2009	det	HFW	mag	<input type="checkbox"/>	WD	← 200 nm →
	3:18:49 PM	TLD	512 nm	500 000 x		2.6 mm	




# Octyl ester

→ ← 2-3 nm

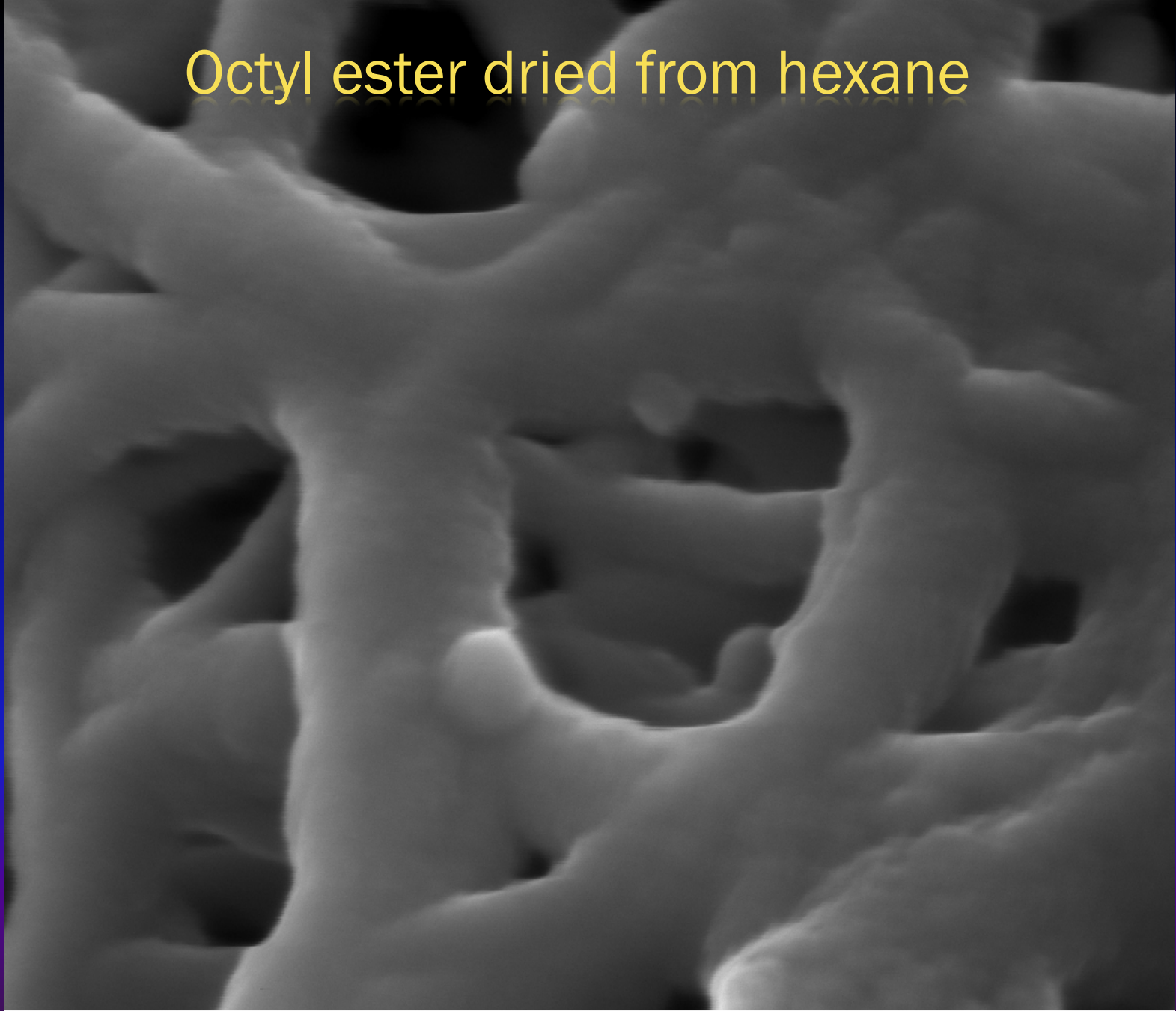
	2/25/2009	det	HFW	mag	□	WD	100 nm
	3:20:16 PM	TLD	256 nm	1 000 000 x		2.6 mm	


# Octyl ester dried from hexane

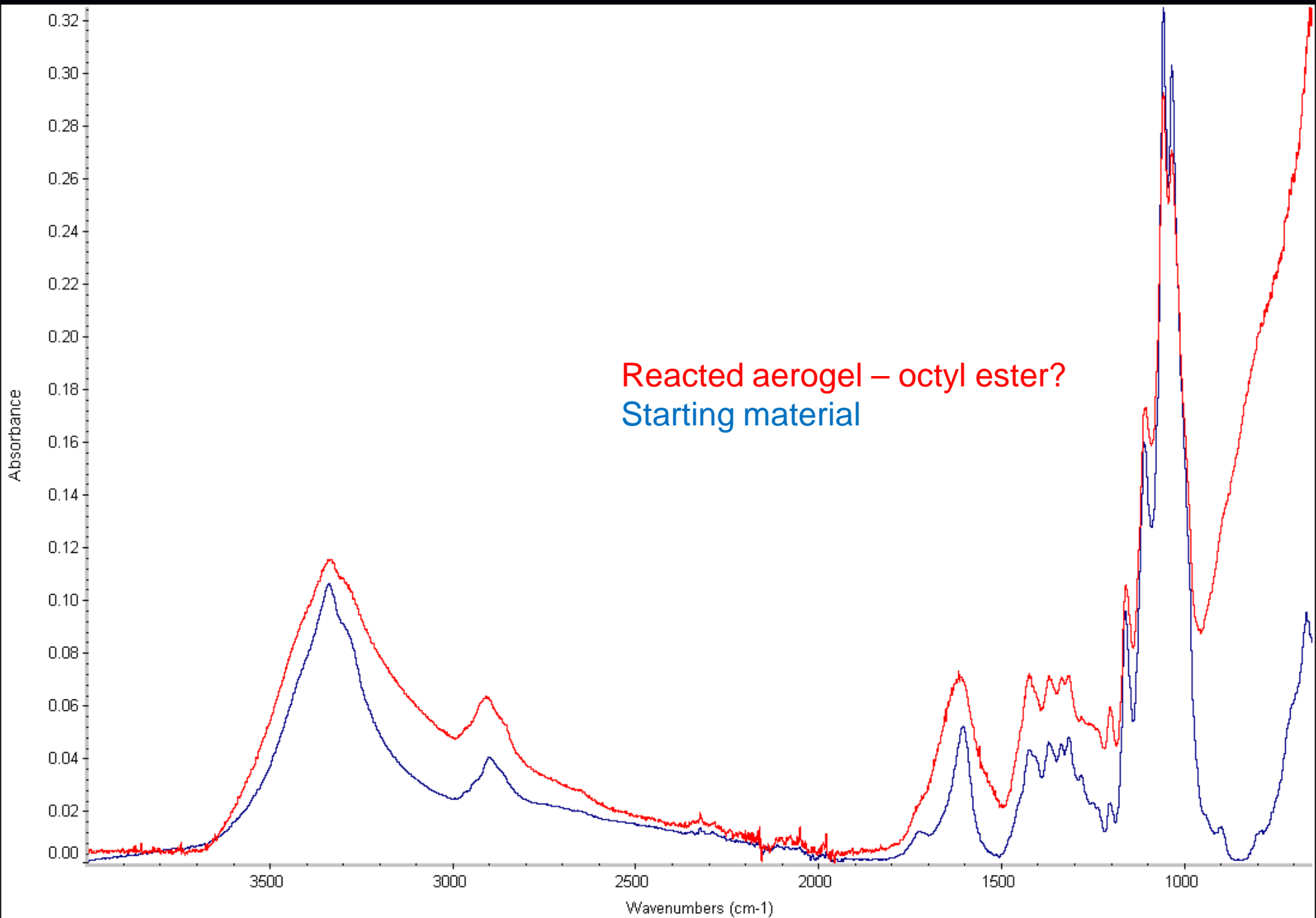
57 14 nm

	2/25/2009	det	HFW	mag <input type="checkbox"/>	WD	← 400 nm → JS8-68-1
	2:22:12 PM	TLD	1.02 $\mu\text{m}$	250 000 x	3.0 mm	

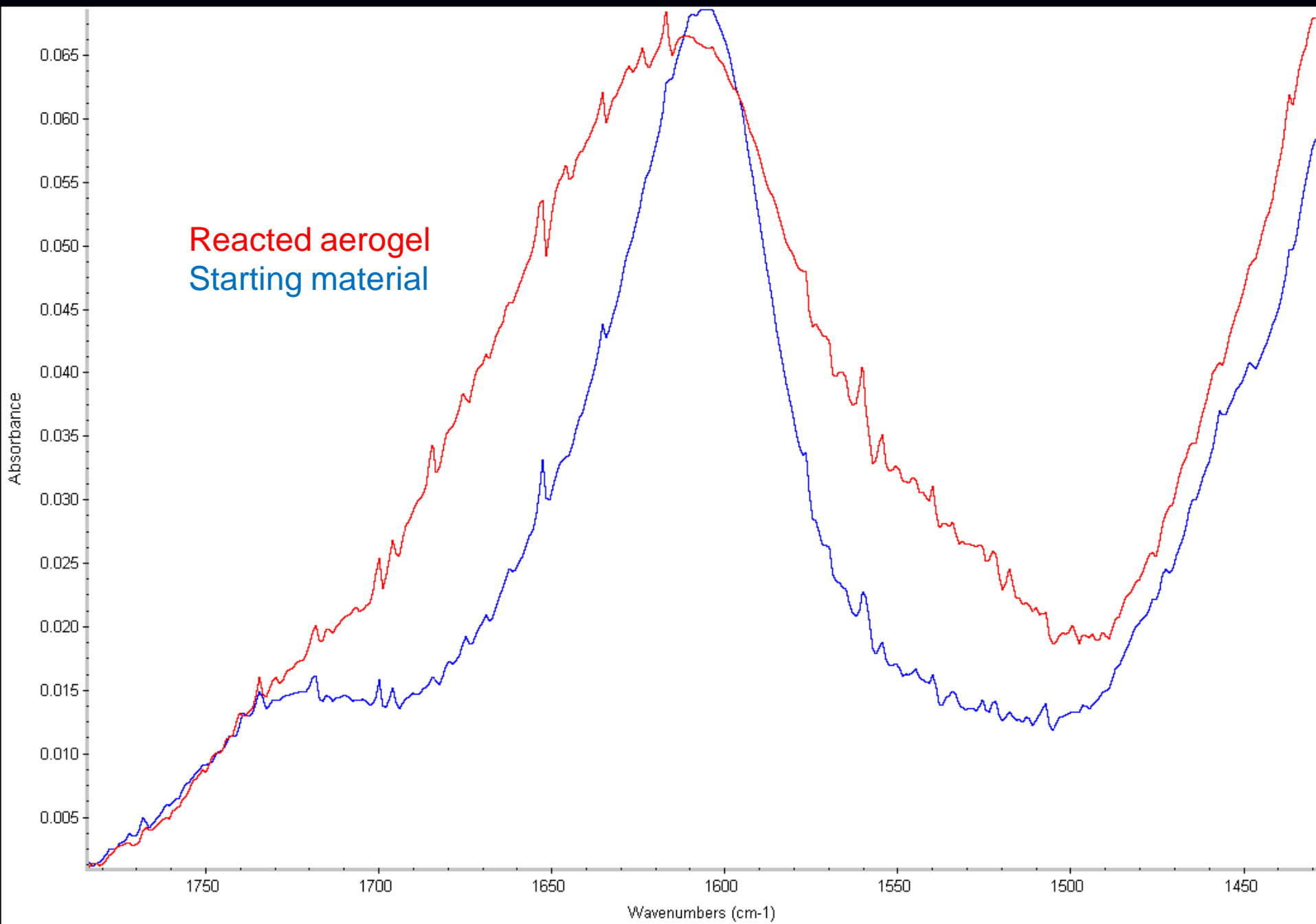
# Octyl ester dried from hexane



	2/25/2009	det	HFW	mag <input type="checkbox"/>	WD	← 200 nm →
	2:25:51 PM	TLD	512 nm	500 000 x	3.0 mm	

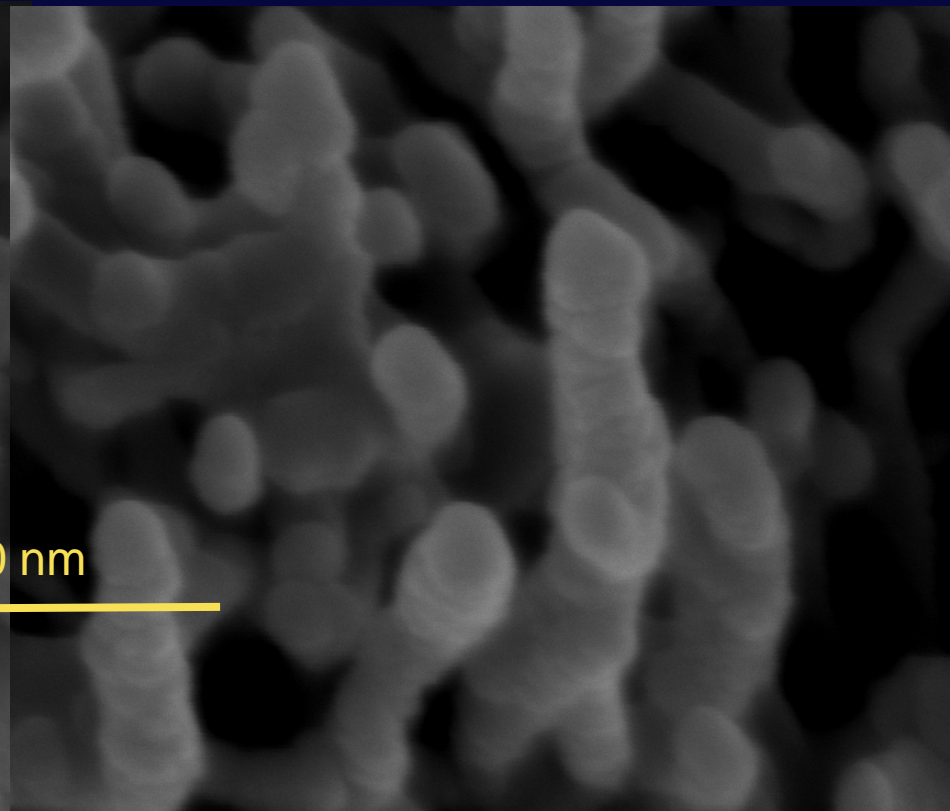
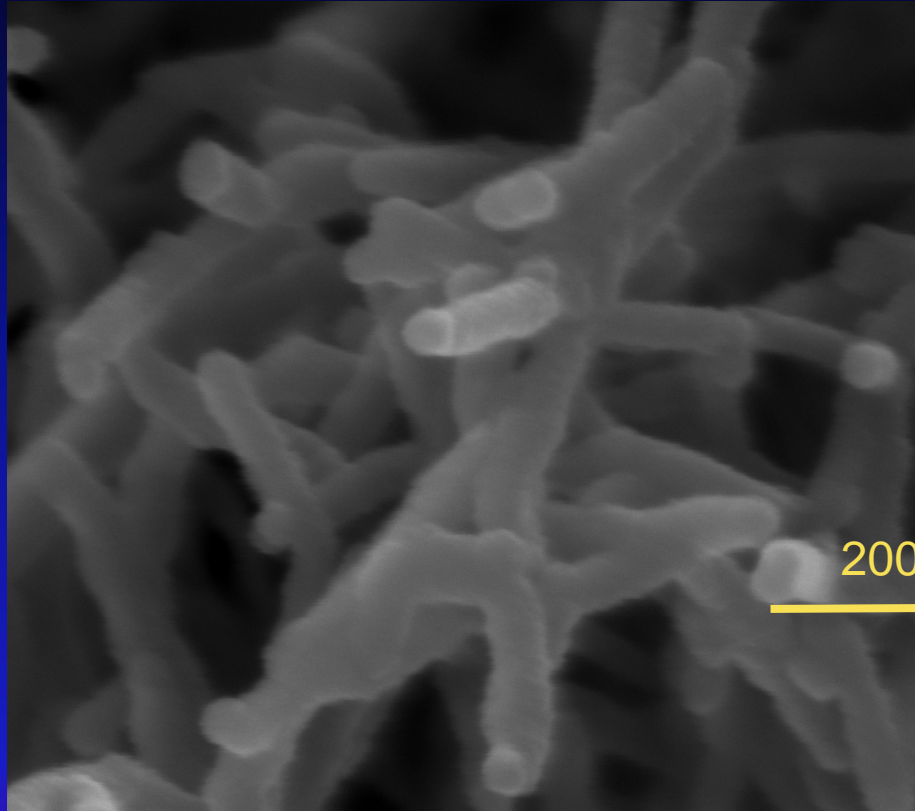


Reacted aerogel – octyl ester?  
Starting material



# Control

# Butyl ester



200 nm

	3/23/2009	det	HFW	mag	WD
	8:25:33 AM	TLD	512 nm	500 000 x	3.1 mm

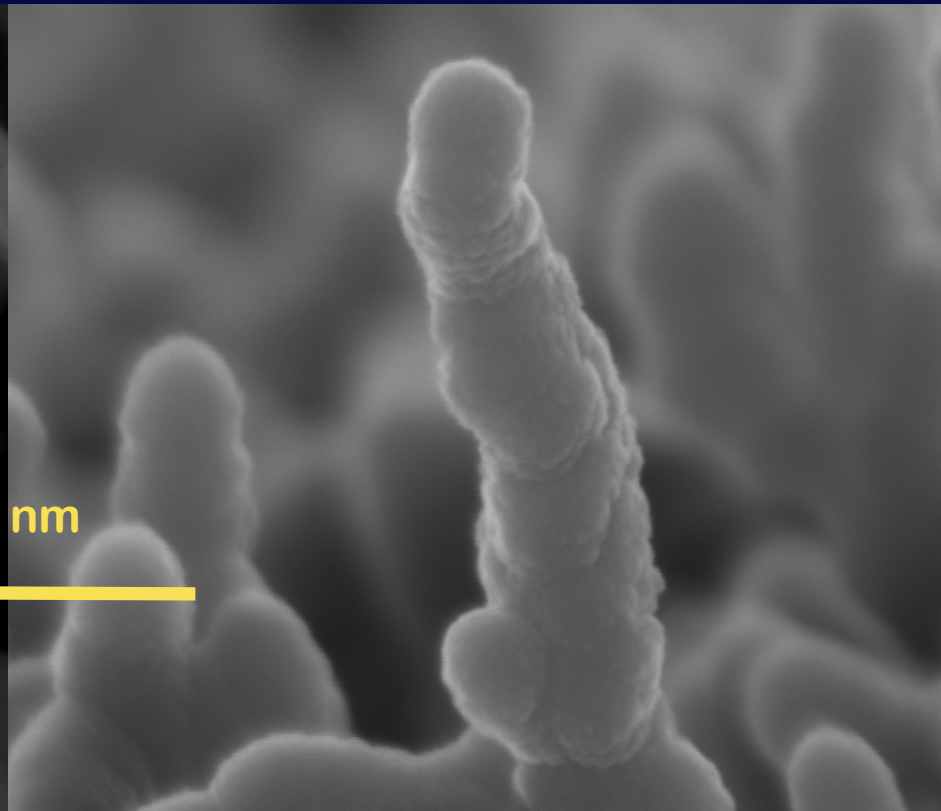
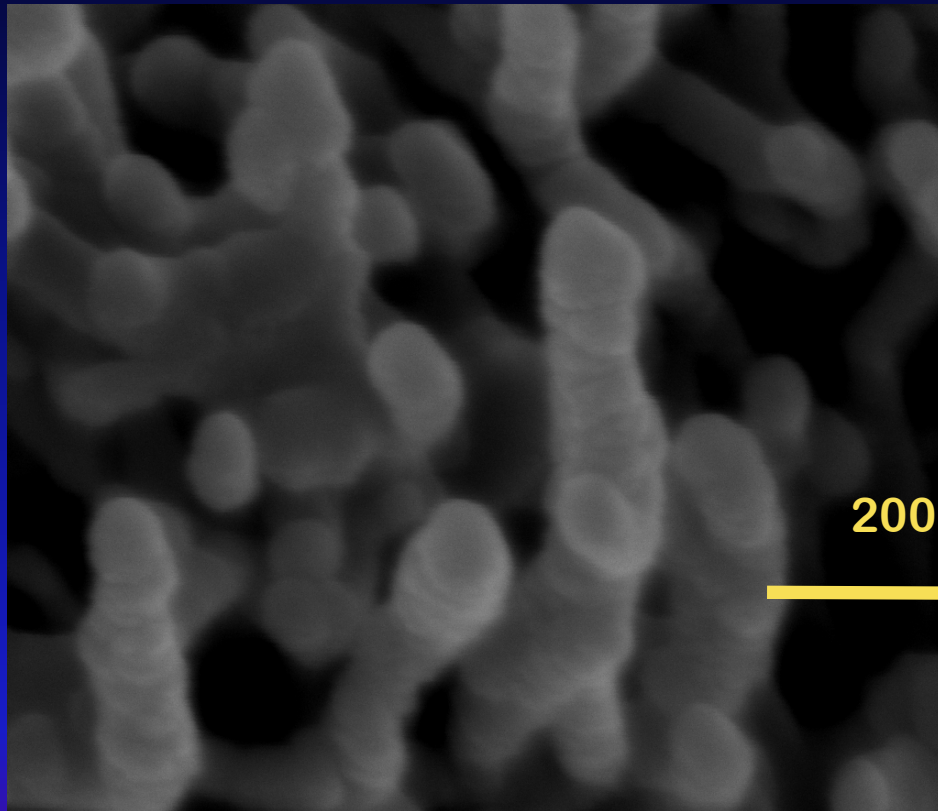
200 nm  
C.CNXL Control

	2/18/2009	det	HFW	mag	WD
	3:26:15 PM	TLD	512 nm	500 000 x	4.2 mm

200 nm  
Butyl/Ester

# Butyl ester

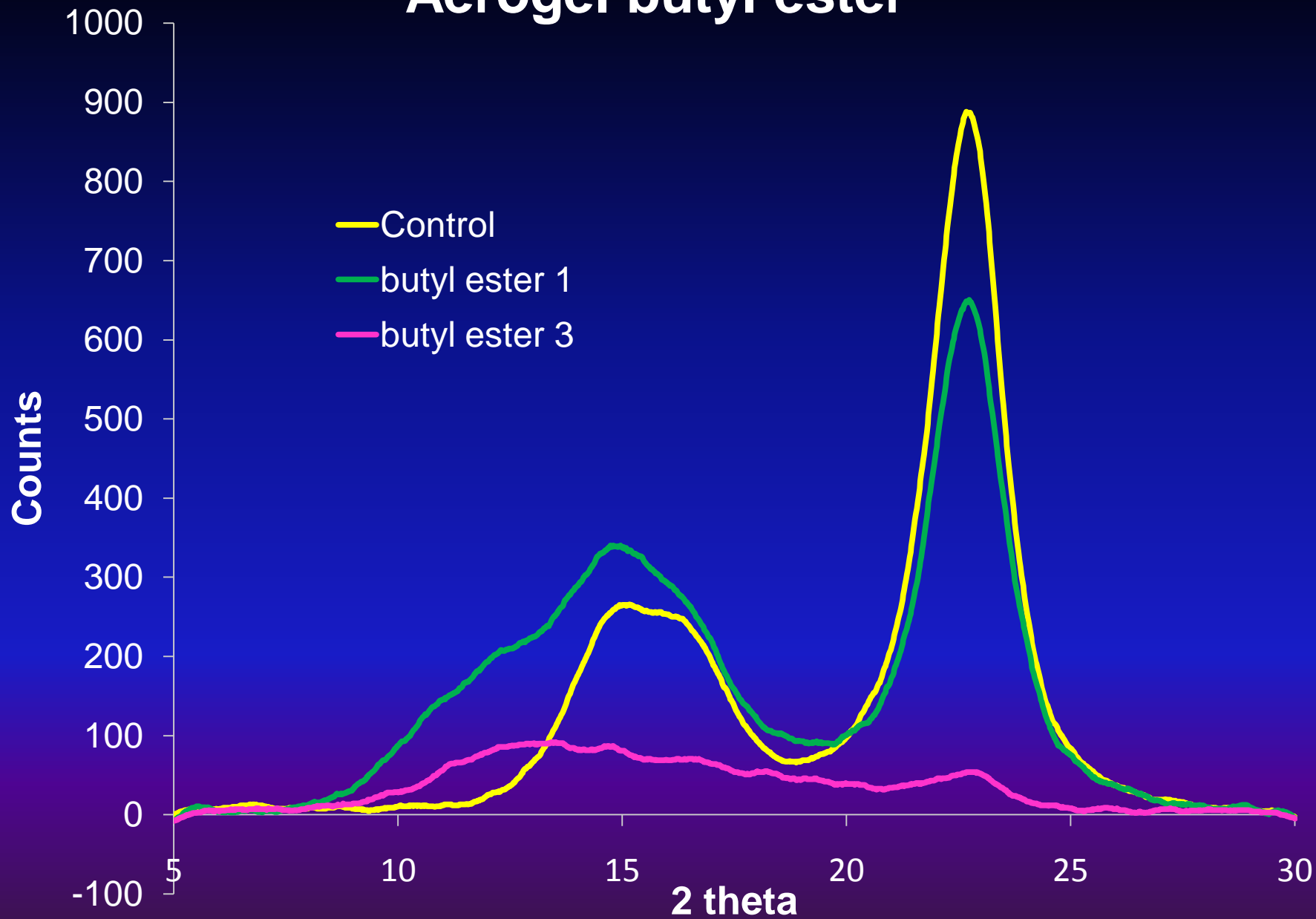
# Octyl ester



	2/18/2009	det	HFW	mag	WD	200 nm
3:26:15 PM	TLD	512 nm	500 000 x	4.2 mm	Butyl/Ester	

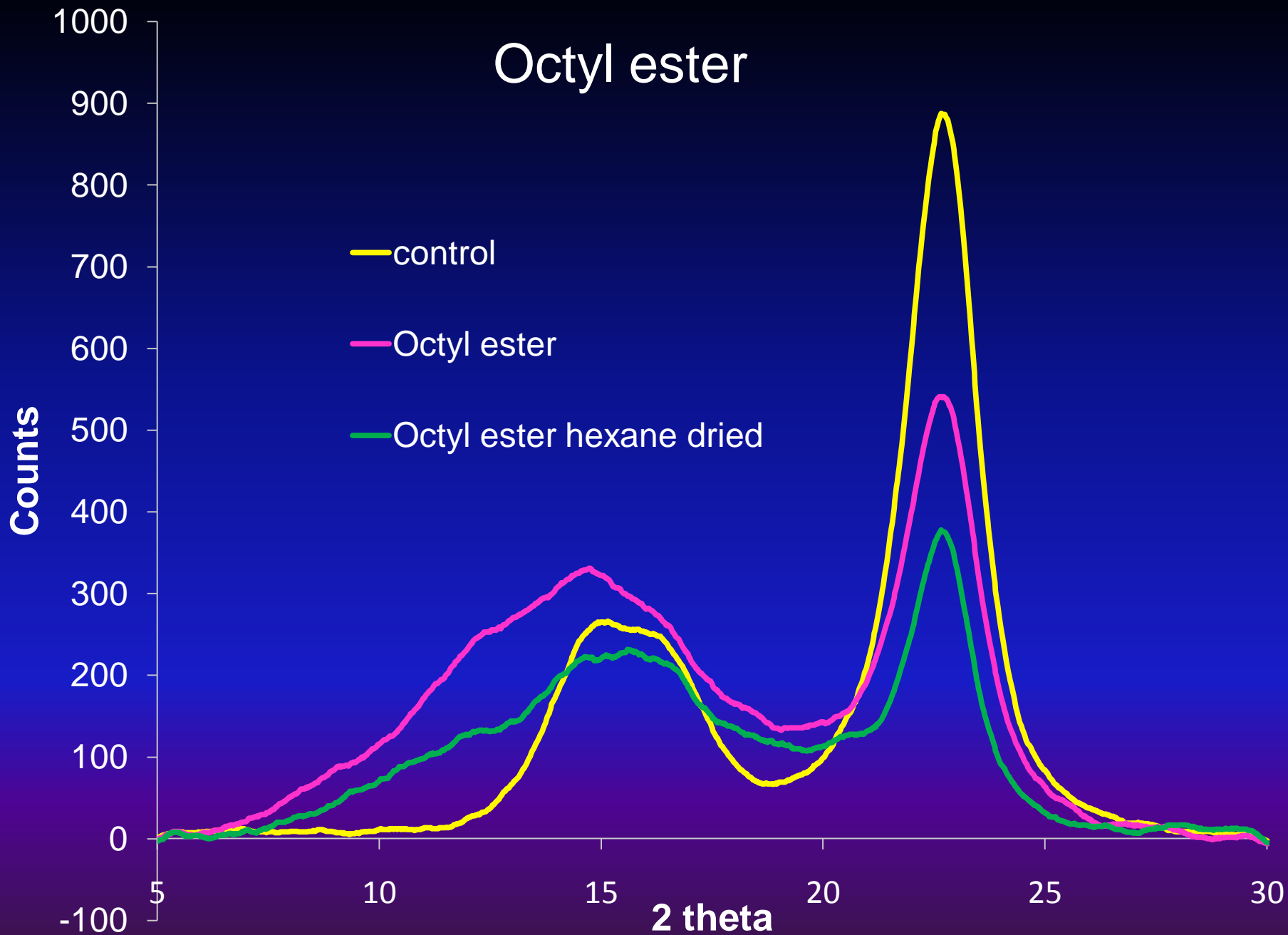
	2/25/2009	det	HFW	mag	WD	200 nm
3:18:49 PM	TLD	512 nm	500 000 x	2.6 mm	octyl/ester	

# Aerogel butyl ester

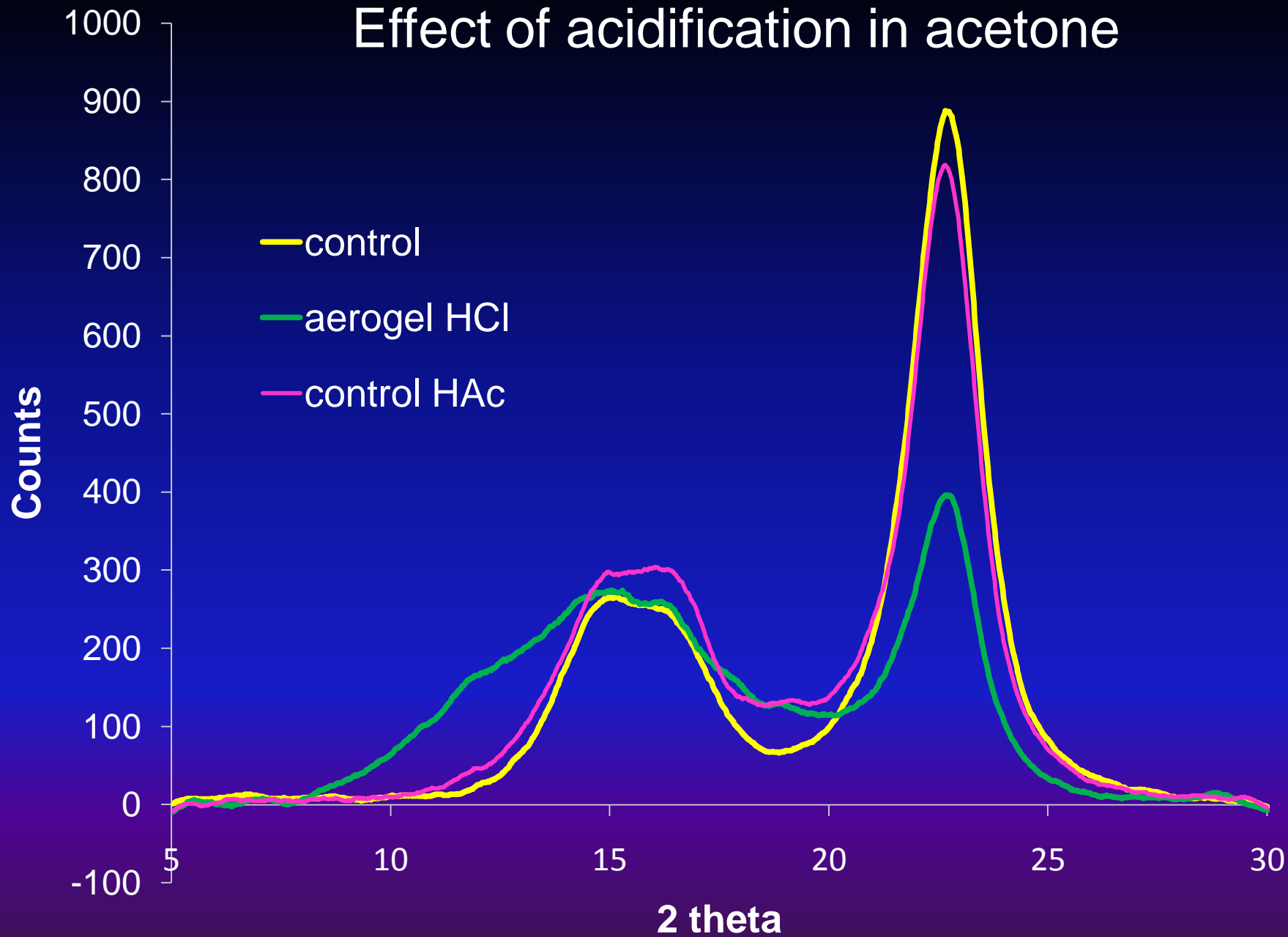




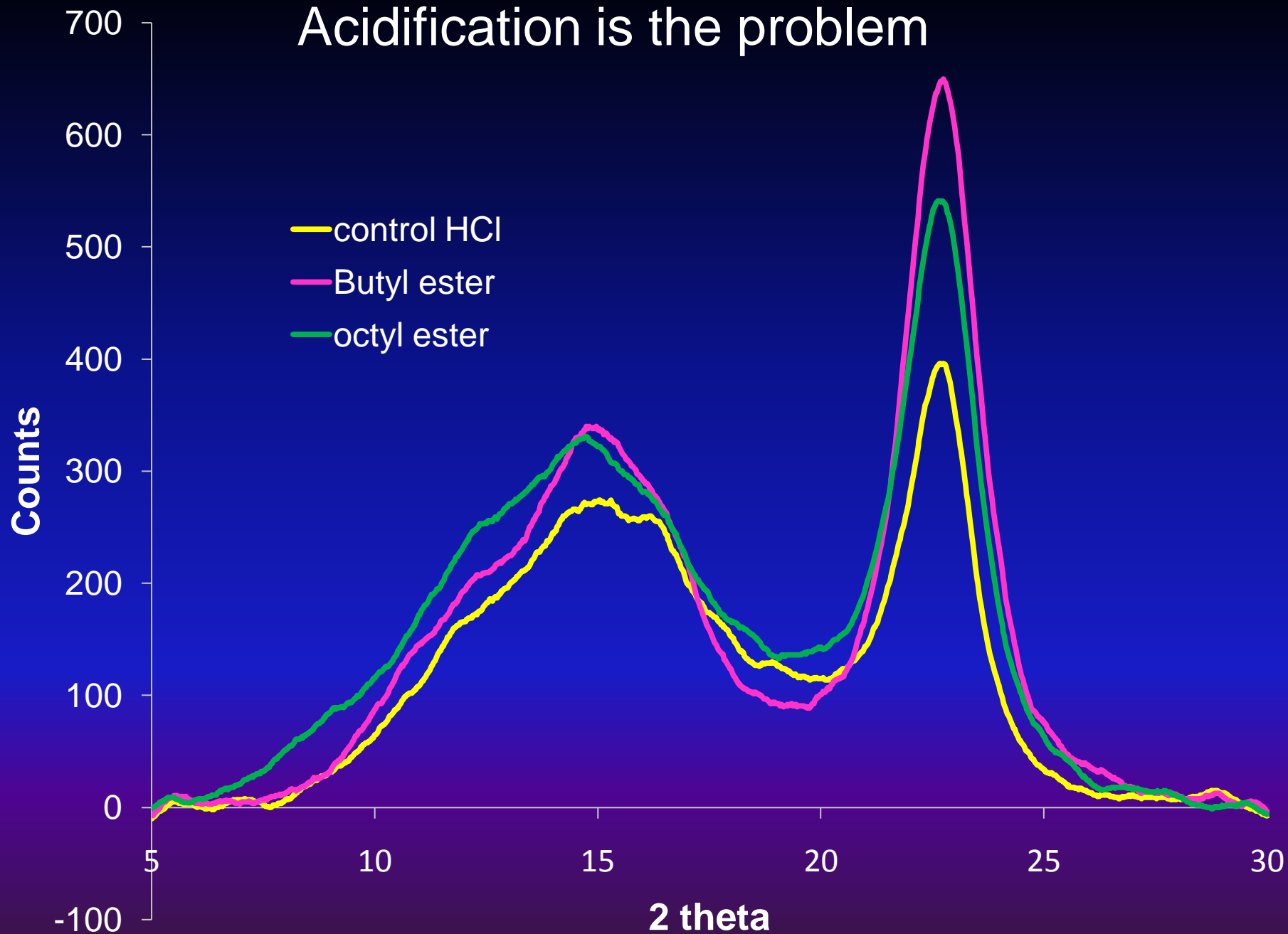
# Octyl ester



# Effect of acidification in acetone



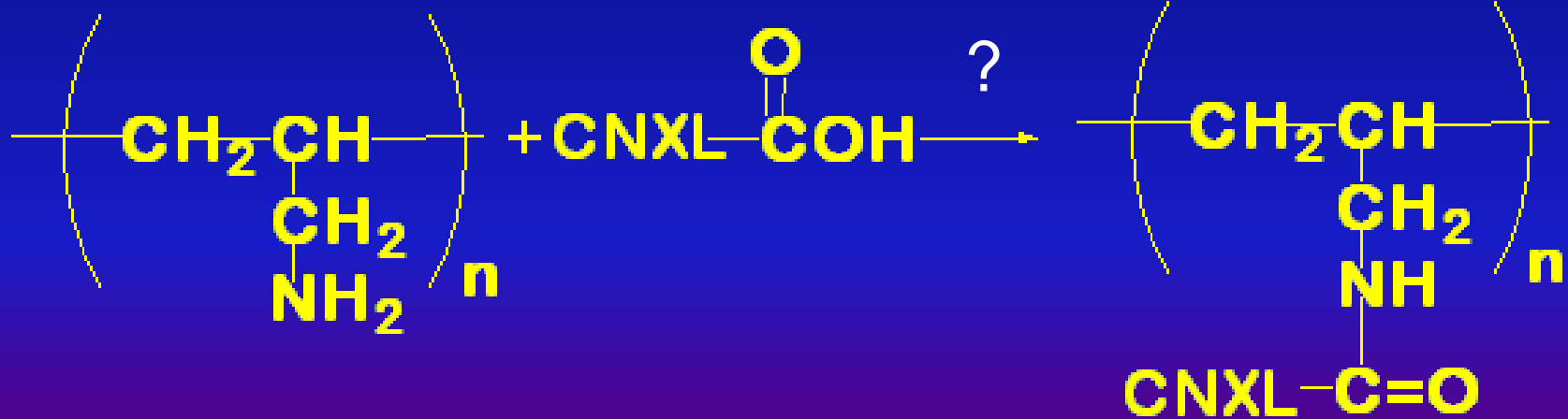
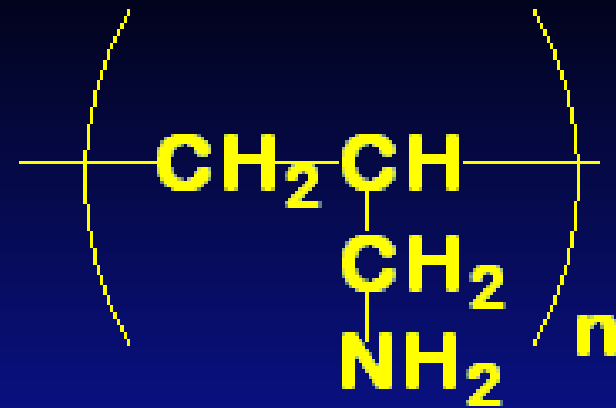
# Acidification is the problem



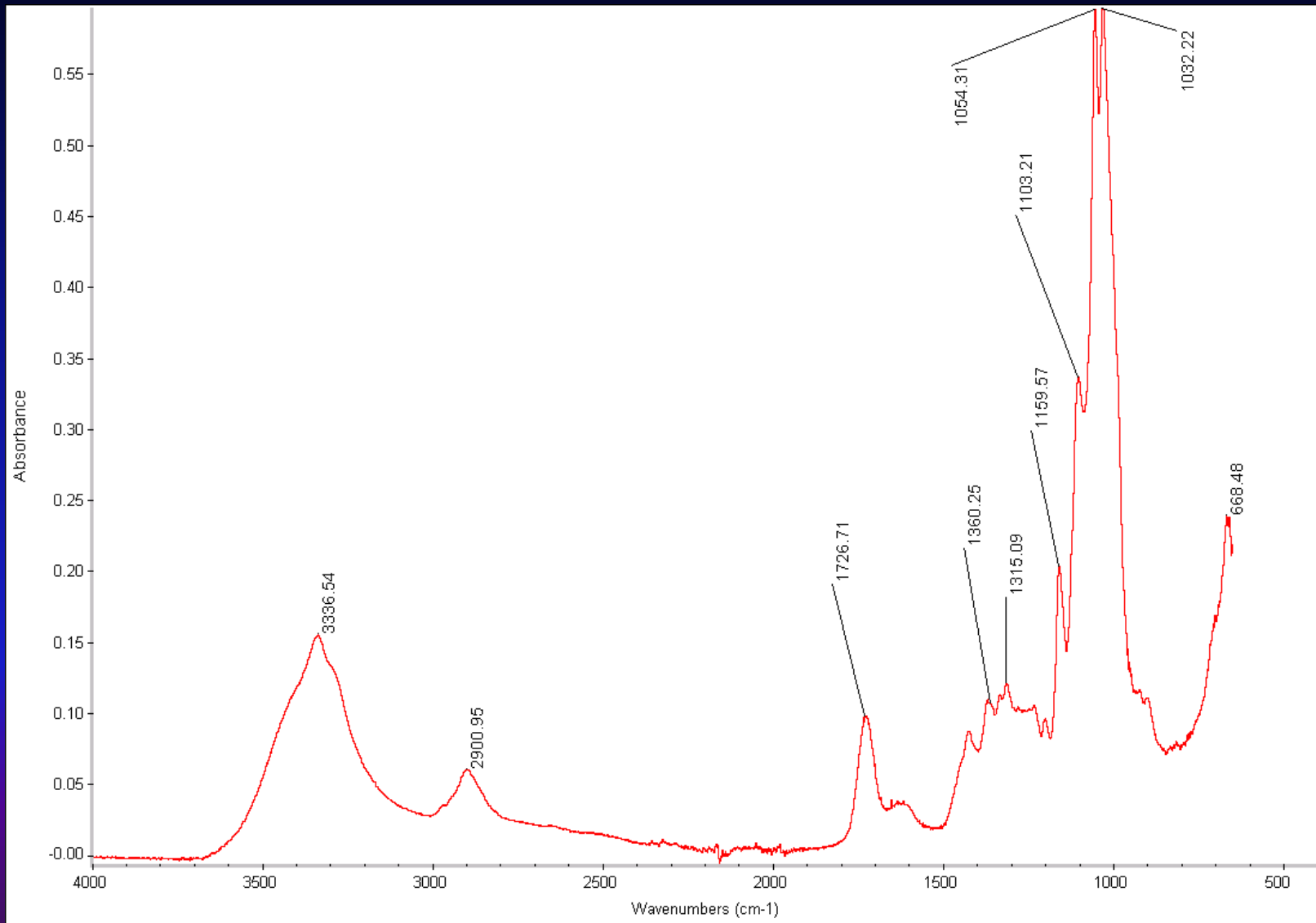
Poly(allyl amine)

# Poly(allyl amine)

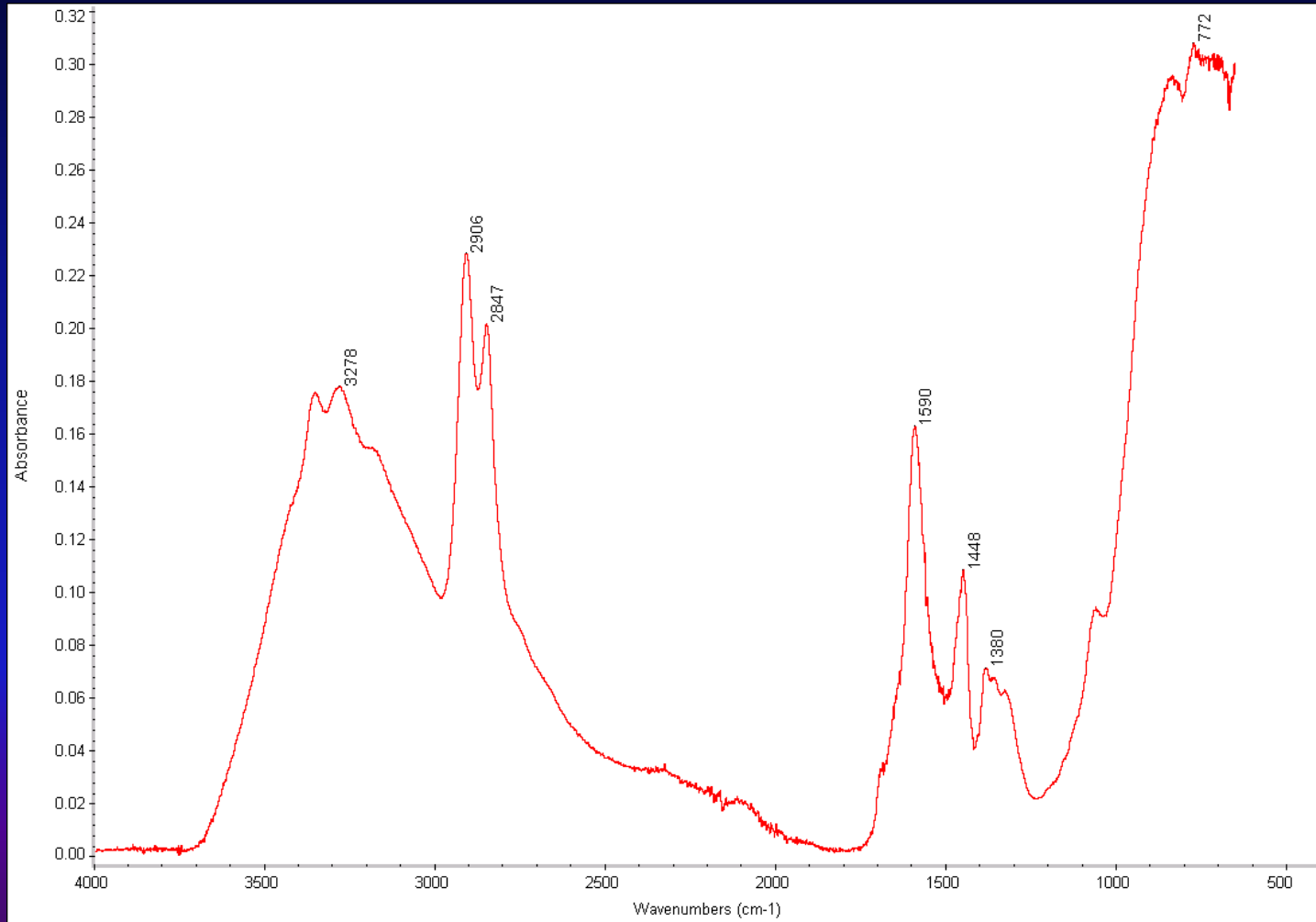
## PAAm



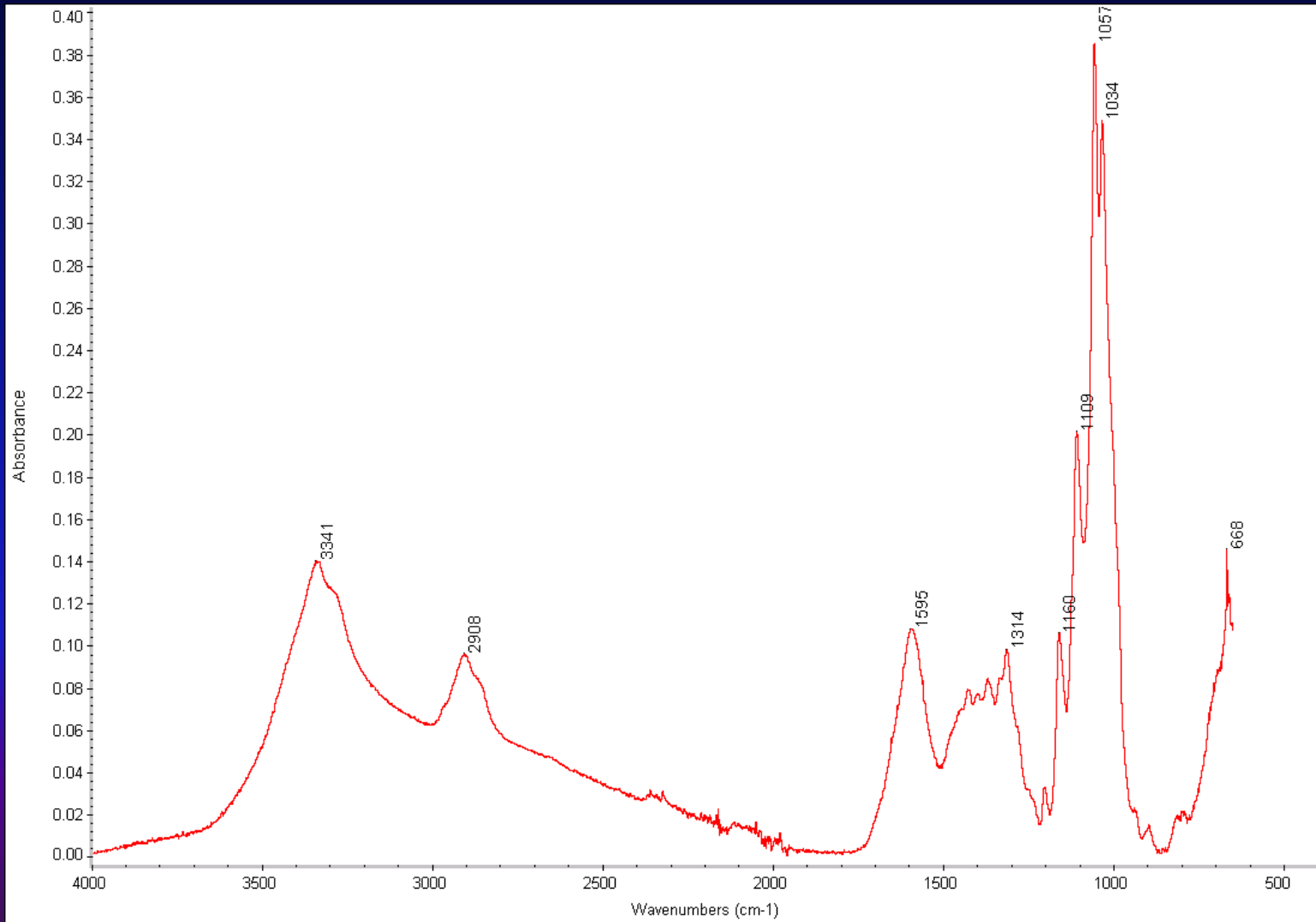
# Acidified cellulose aerogel



# PAAm

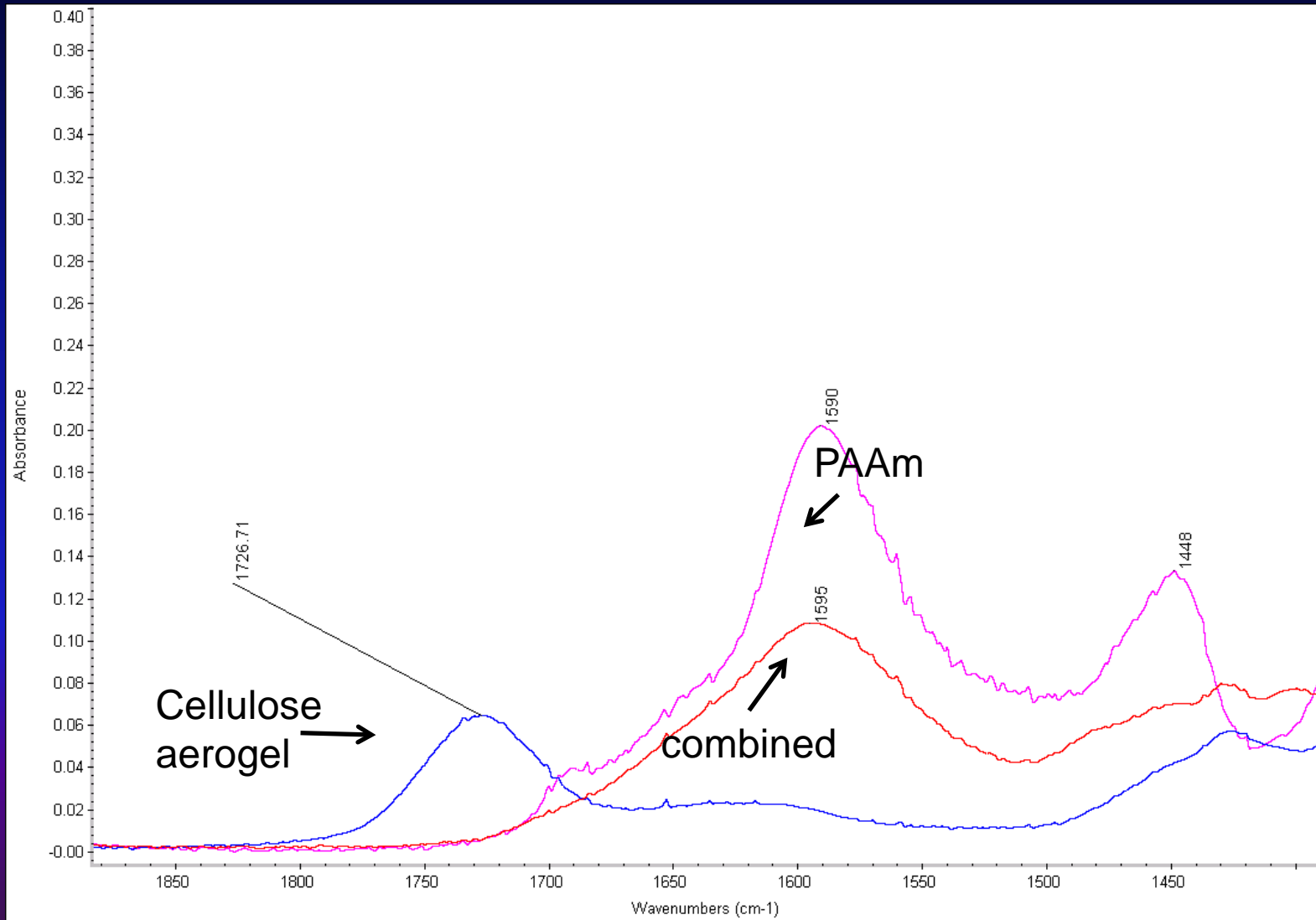


# Coated (reacted?) aerogel

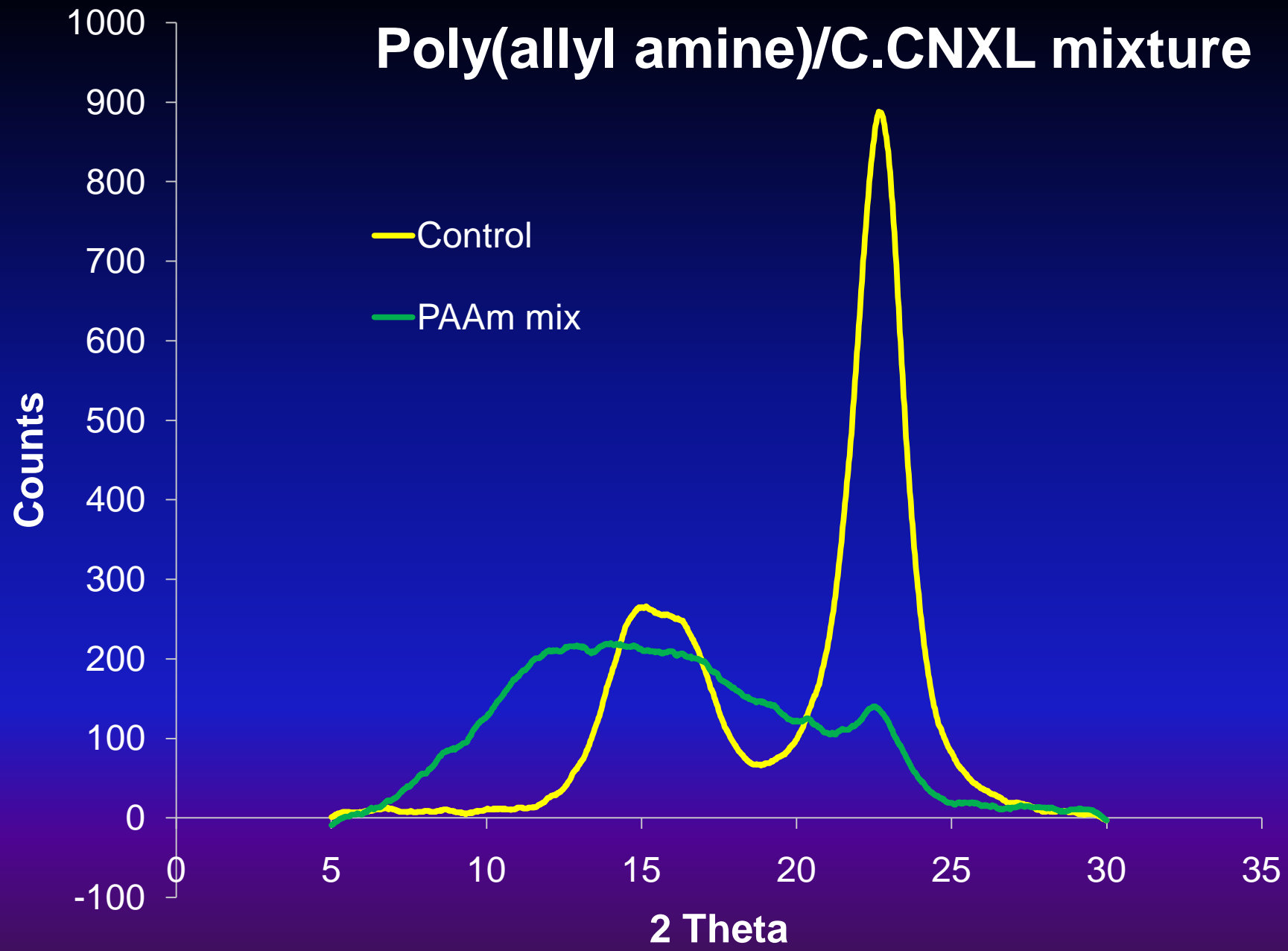


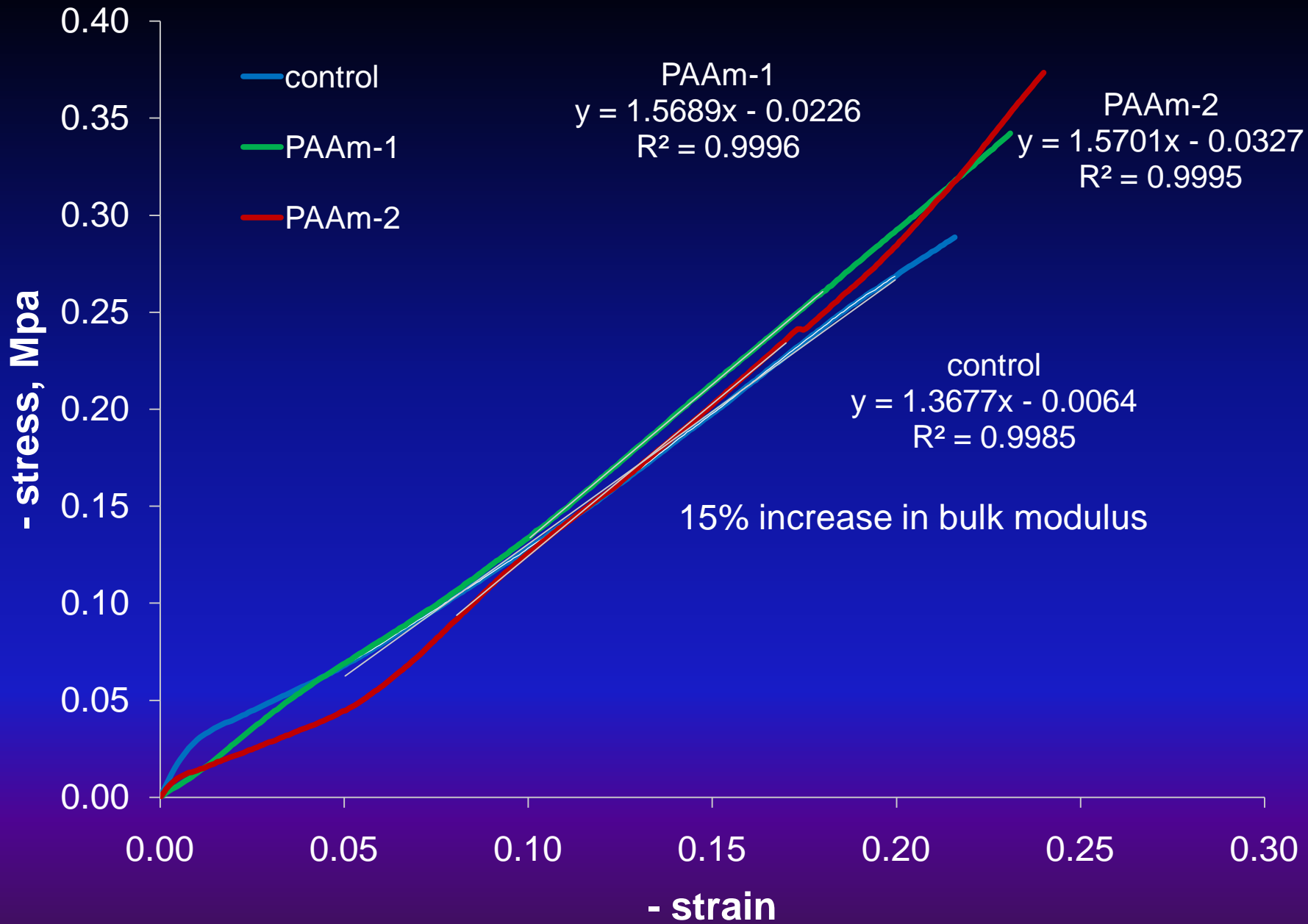


# Carbonyl region



# Poly(allyl amine)/C.CNXL mixture





# Conclusions

- CNC aerogels have a different diameter than that observed for dried suspensions using AFM or TEM
- The aerogel can be chemically modified
- Acidification in acetone with trifluoroacetic acid or HCl can hydrolyze the cellulose crystal

**Questions?**