Fabrication of graphitic-carbon suspended nanowires through mechano-electrospinning of photocrosslinkable polymers

A Osamu Katagiri Tanaka
A01212611@itesm.mx

08 Apr 2020

Motivation & Problem Statement

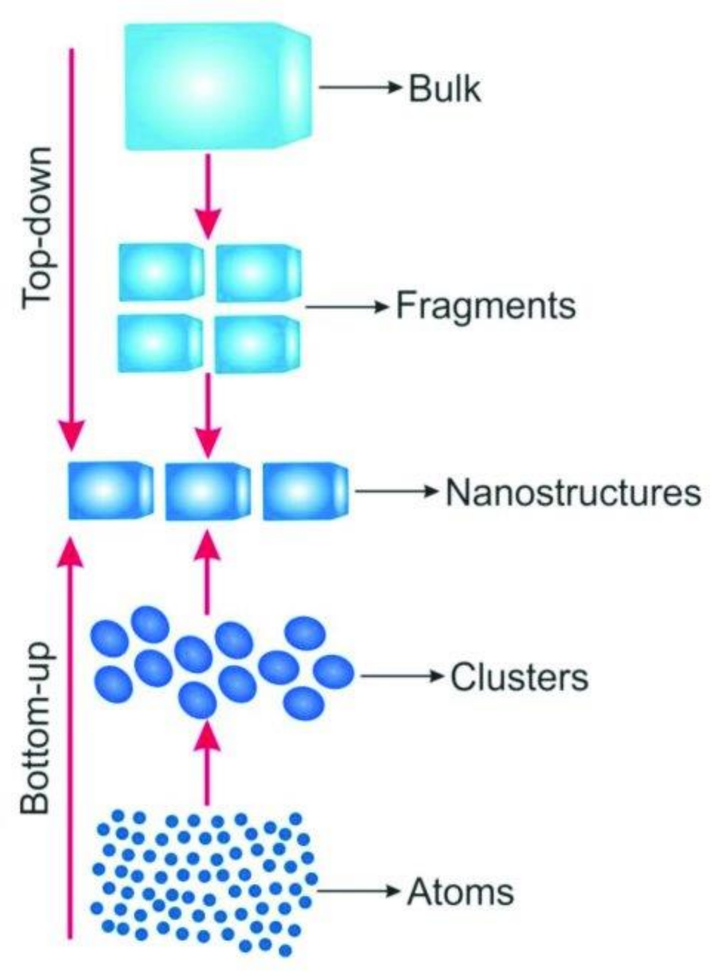
Current approaches for the fabrication of carbon nanowires (CNWs)

Lithography
Physical & Optical Limitations

Near-Field Electrospinning (NFES)
Can fabricate Suspended Nanowires w/Spatial Control

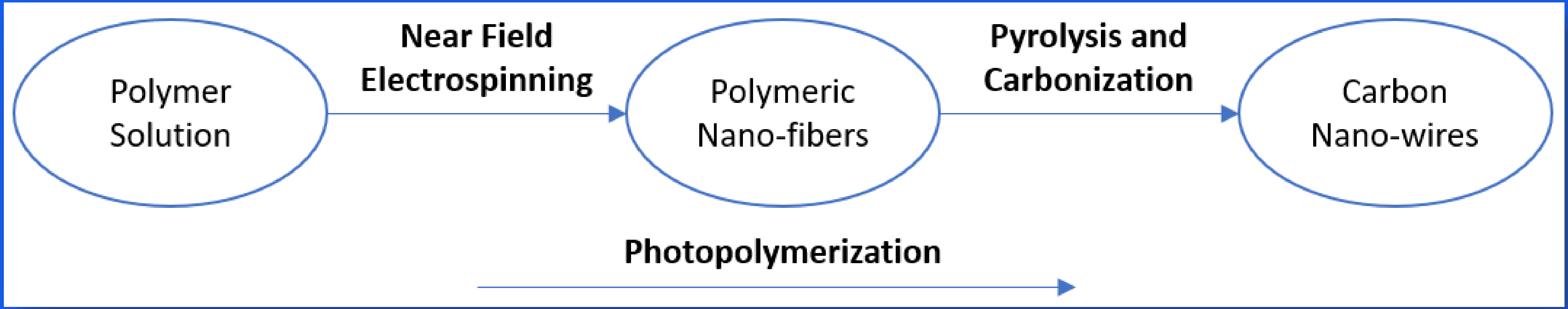
Self-assembly
Limited Length and Random Orientation

Two-Photon Polymerization (TPP)
Slow (mm per sec) & Expensive



V. Galstyan, M. Bhandari, V. Sberveglieri, G. Sberveglieri, E. Comini, Metal Oxide Nanostructures in Food Applications: Quality Control and Packaging, Chemosensors. 6 (2018) 16. https://doi.org/10.3390/chemosensors6020016.
D. Kluge, J.C. Singer, B.R. Neugirg, J.W. Neubauer, H.-W. Schmidt, A. Fery, Top–down meets bottom–up: A comparison of the mechanical properties of melt electrospun and self-assembled 1,3,5-benzenetrisamide fibers, Polymer (Guildf). 53 (2012) 5754–5759. https://doi.org/10.1016/j.polymer.2012.10.016.

Thesis Overview



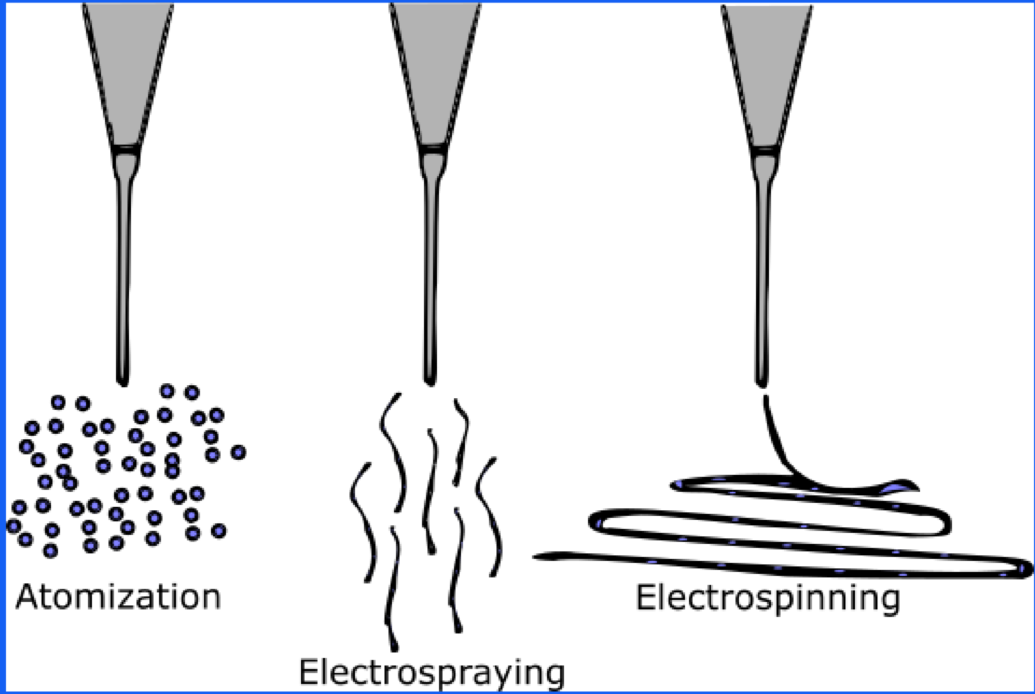
Design polymer solutions that can be electrospun by NFES, photopolymerized, and then pyrolyzed into conductive carbon nano-wires.

Polymer Solution Parameters

SU-8 Carbon Structures

The production of C-MEMS:

1. Polymer patterning through photolithography
2. Carbonization through pyrolysis



However, SU-8 as is can not electrospin

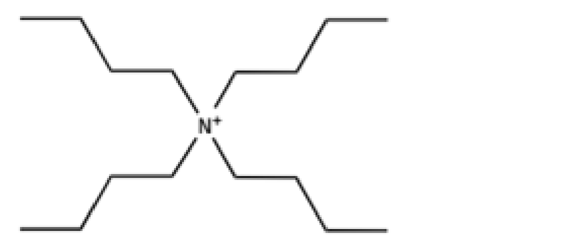
SU-8 does not have the right viscosity & solution conductivity

SU-8 is design for photolithography

Microchem, Su-8 2000.5-2015, 2000.5, 2002, 2005, 2007, 2010, 2015. (2006) 1–5. papers3://publication/uuid/859F51B9-0382-4DE8-88A9-267F936939A3.

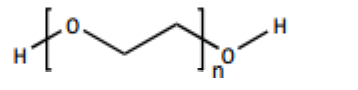
Making SU-8 spunable (by Braulio & Ricardo)

SU-8 + TBF + PEO



Tetrabutylammonium tetrafluoroborate (TBF)

→ To increase the solution conductivity



Poly(ethylene oxide) (PEO)

→ To provided the required viscosity

… both needed for smooth PEO flow during electrospinning

B. Cárdenas, Advanced Manufacturing Techniques for the Fabrication and Surface Modification of Carbon Nanowires, (2017) 160.
D.R. Flores, Role of rheological properties in near field electrospun fibers morphology, (2017) 130.

Results with amended SU-8

The modified solution is spunable

- Fiber diameter before pyrolysis of 4.966 µm
- Fiber diameter after pyrolysis of 204 nm

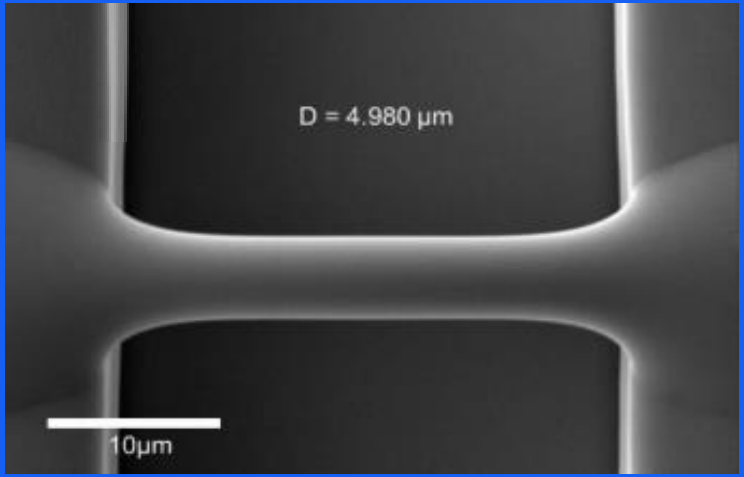
But, somewhat pyrolyzable

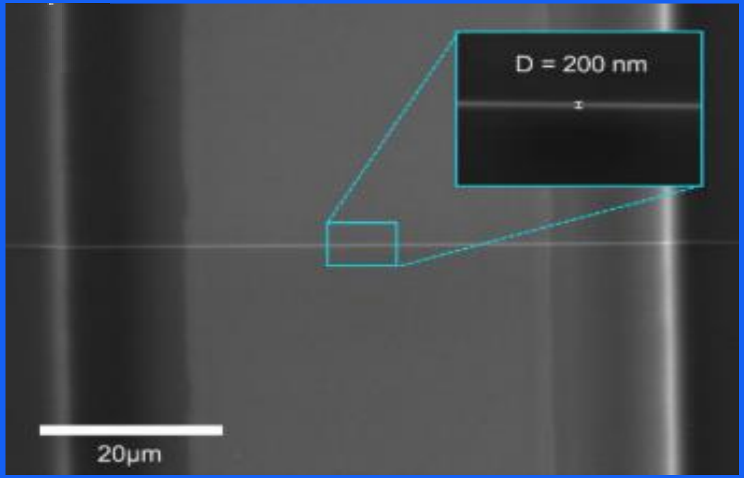
- Fiber resistivity from 407 KΩ to 1.727 MΩ
- Fiber yield rate of 81 %

Achieved with:

wt% PEO	SU-8 2002 [mg]	PEO [mg]	TBT [mg]
0.25	2246	5.65	11.32

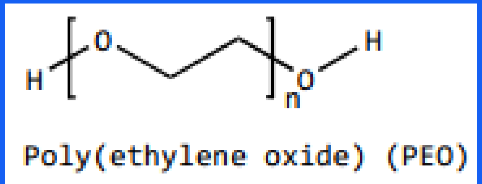
= 2 ml of solution





Implications of PEO, as it introduces oxygen to the solution

The fiber yield rate and fiber conductivity are impacted negatively.

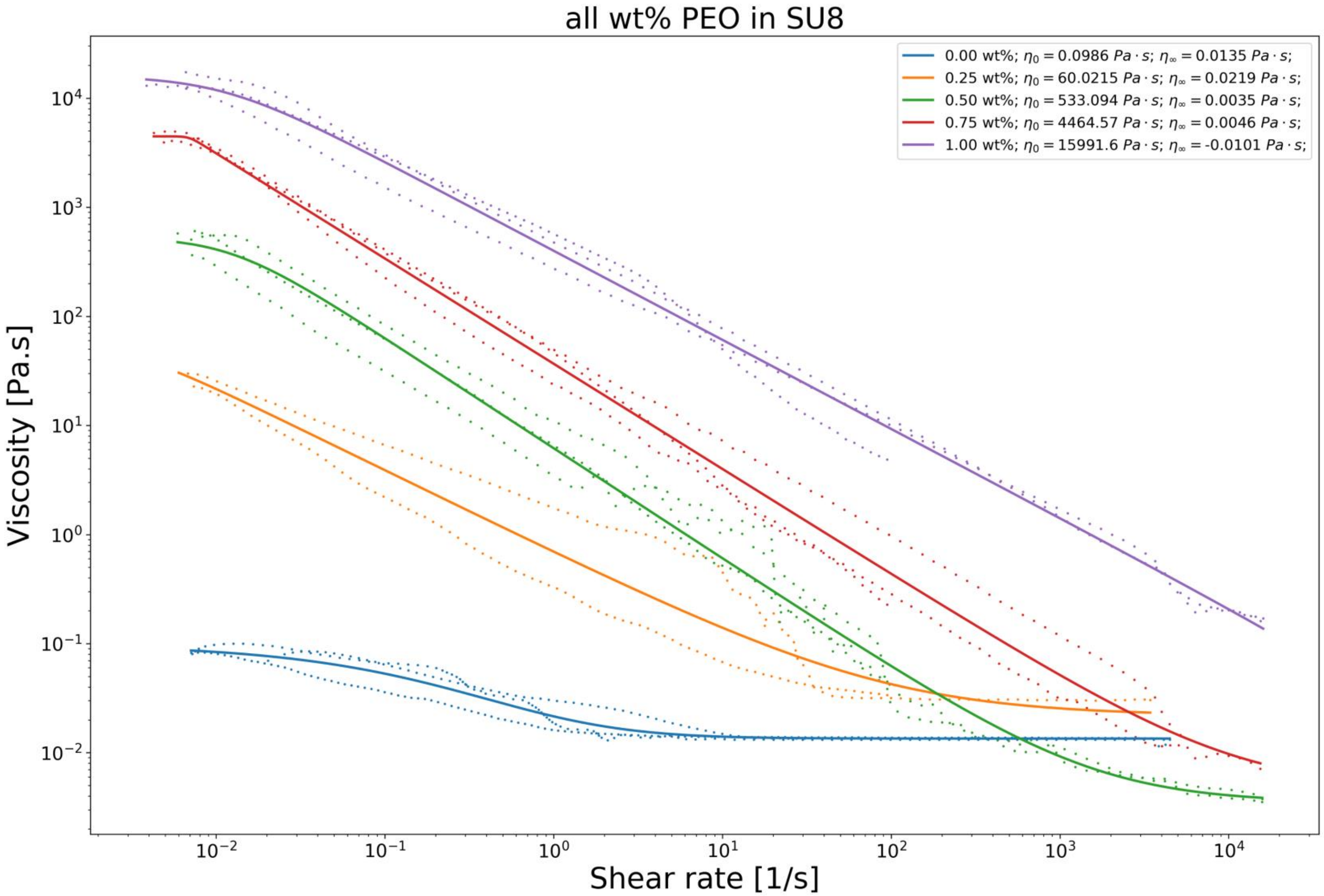


Some samples are destroyed during pyrolysis

High variance in the obtained conductivity across samples.

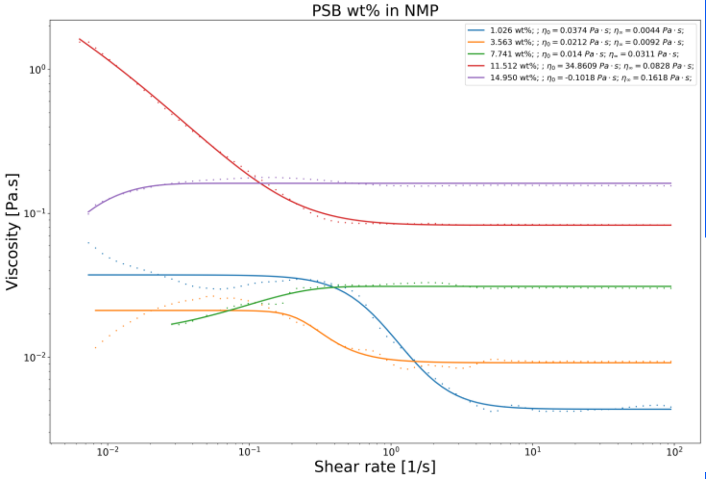
In the presence of oxygen, the char yield decreases. This is due to the oxidation on the char.

Rheology of the amended SU-8 solution (0.25 wt%)

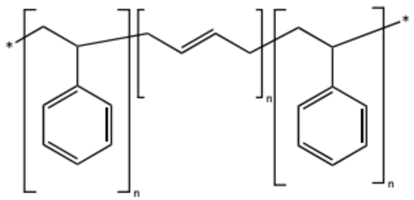


The 0.25 wt% sample (orange line) has a zero-shear viscosity (ZSV) of 60 Pa.s

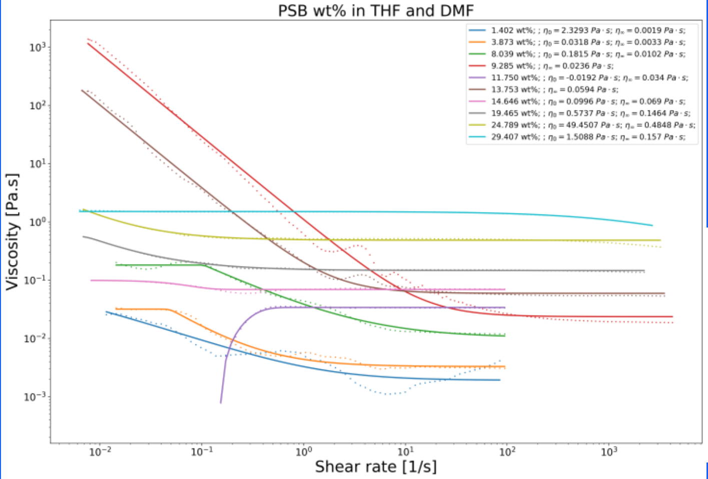
Let's discover new polymer solutions with similar rheology (and no oxygen)



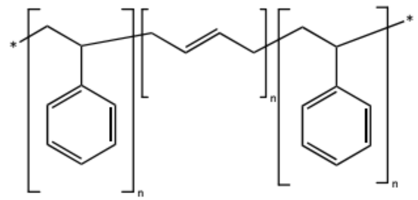
15 wt% in NMP



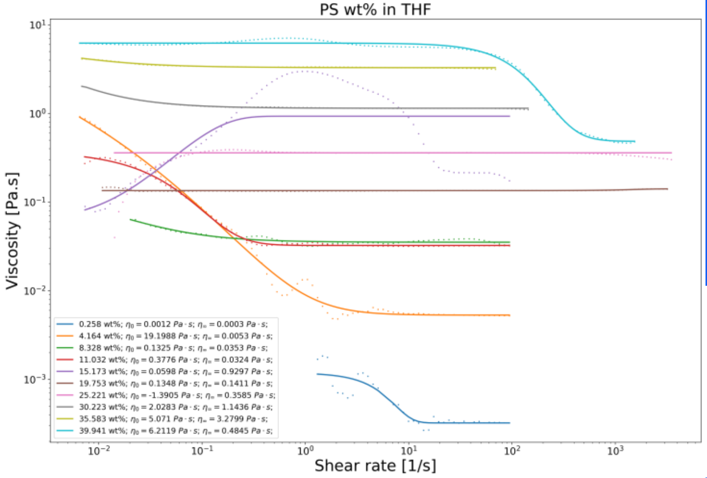
Poly(styrene-co-butadiene)



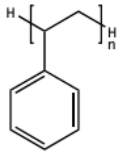
25 wt% in THF & DMF



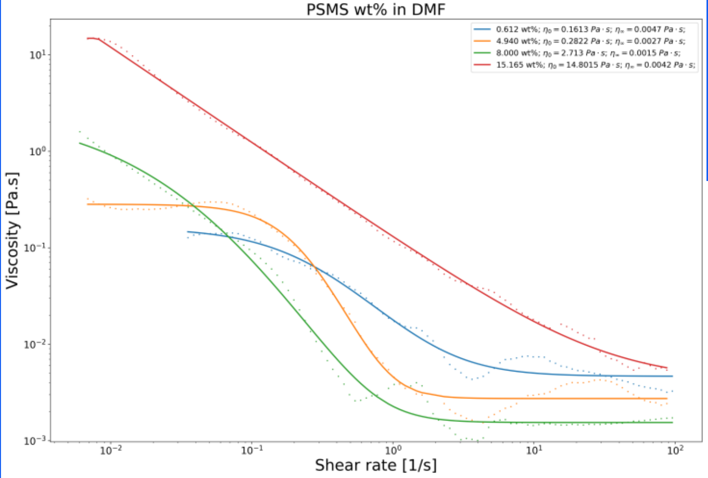
Poly(styrene-co-butadiene)



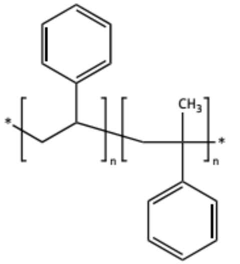
35 wt% in THF



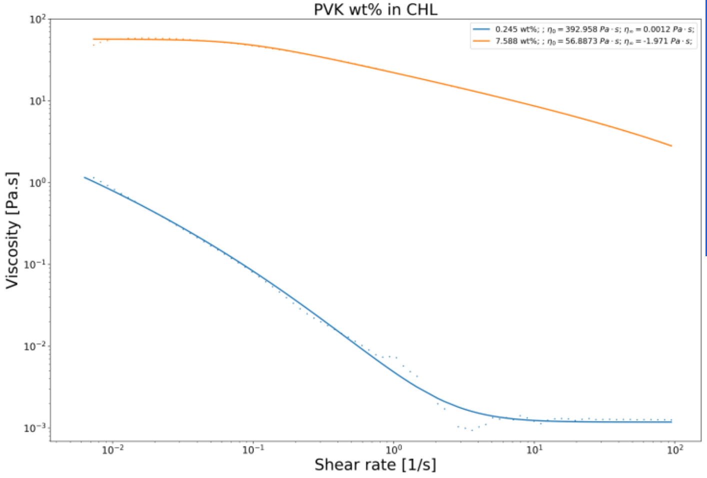
Polystyrene (PS)



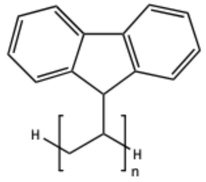
15 wt% in DMF



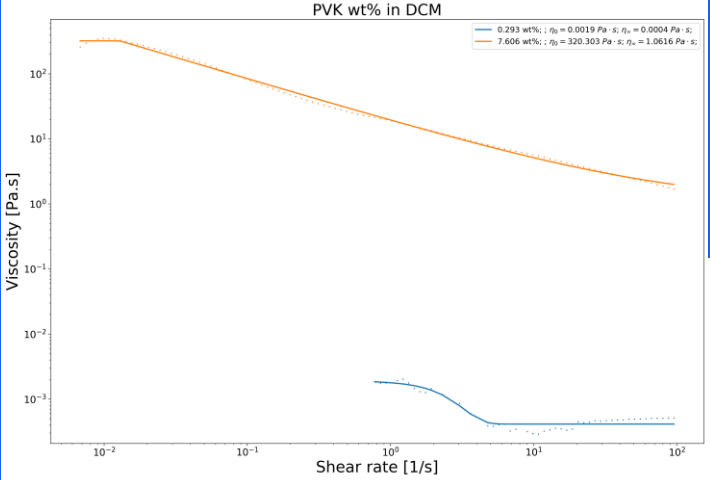
Poly(styrene-co-a-methylstyrene)



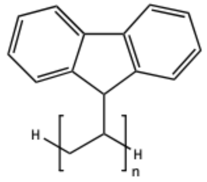
8 wt% in CHL



Poly(9-Vinyl Carbazole) (PVK)



7 wt% in DCM



Poly(9-Vinyl Carbazole) (PVK)

NFES Process Parameters

Data collection from 30+ NFES papers

Python Image Analysis

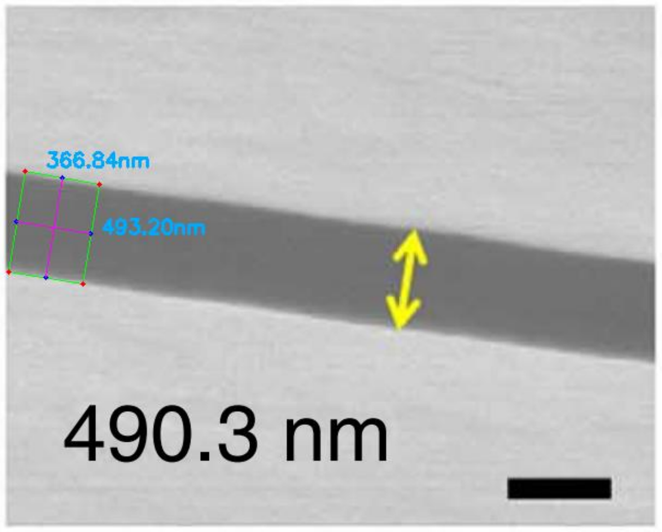


Figure from Min2013

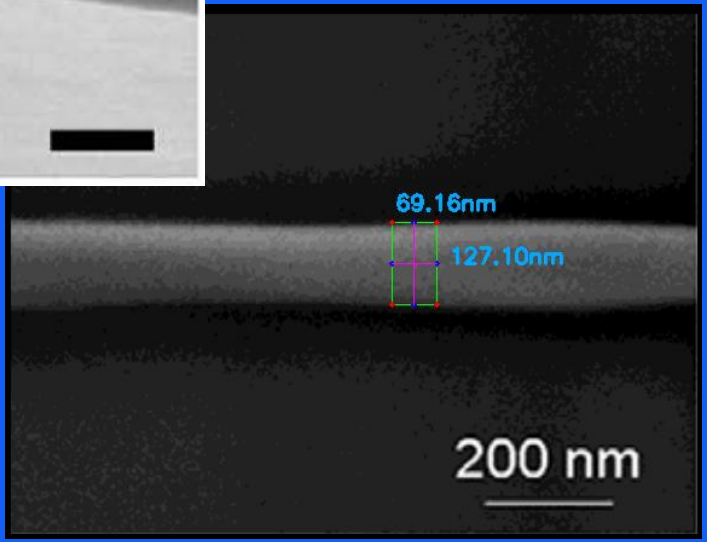
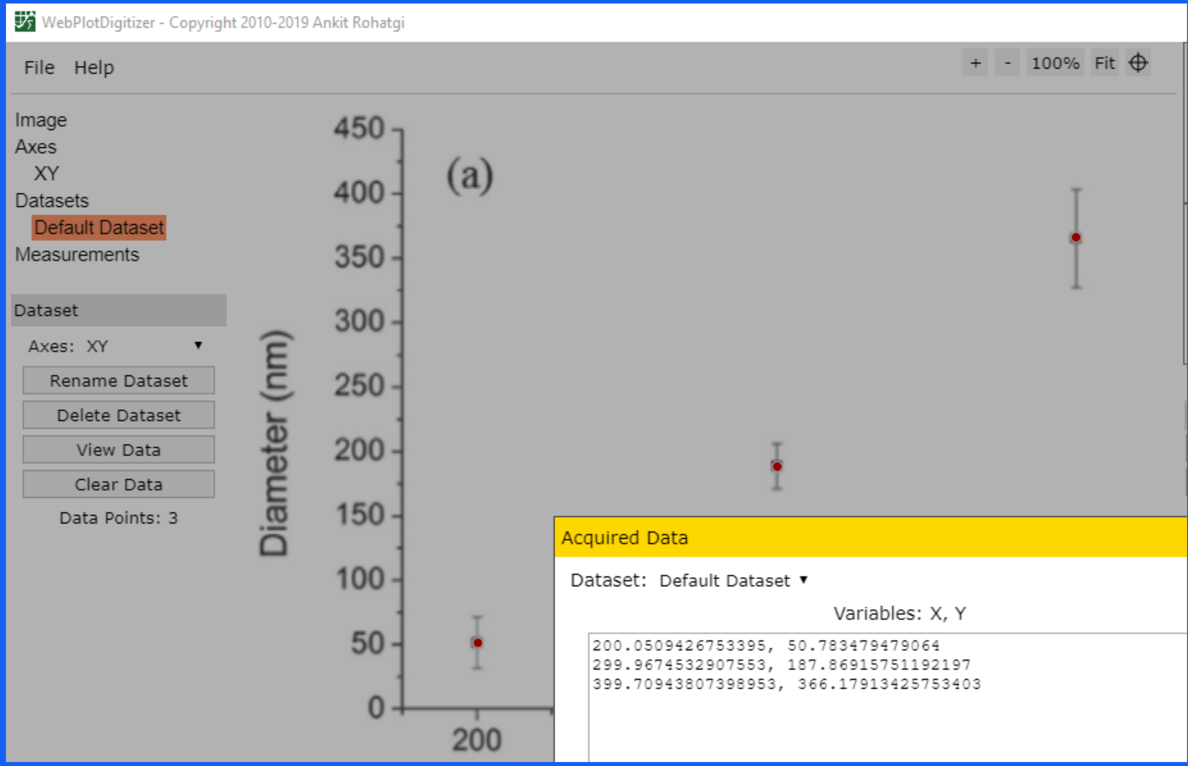


Figure from Camillo2013

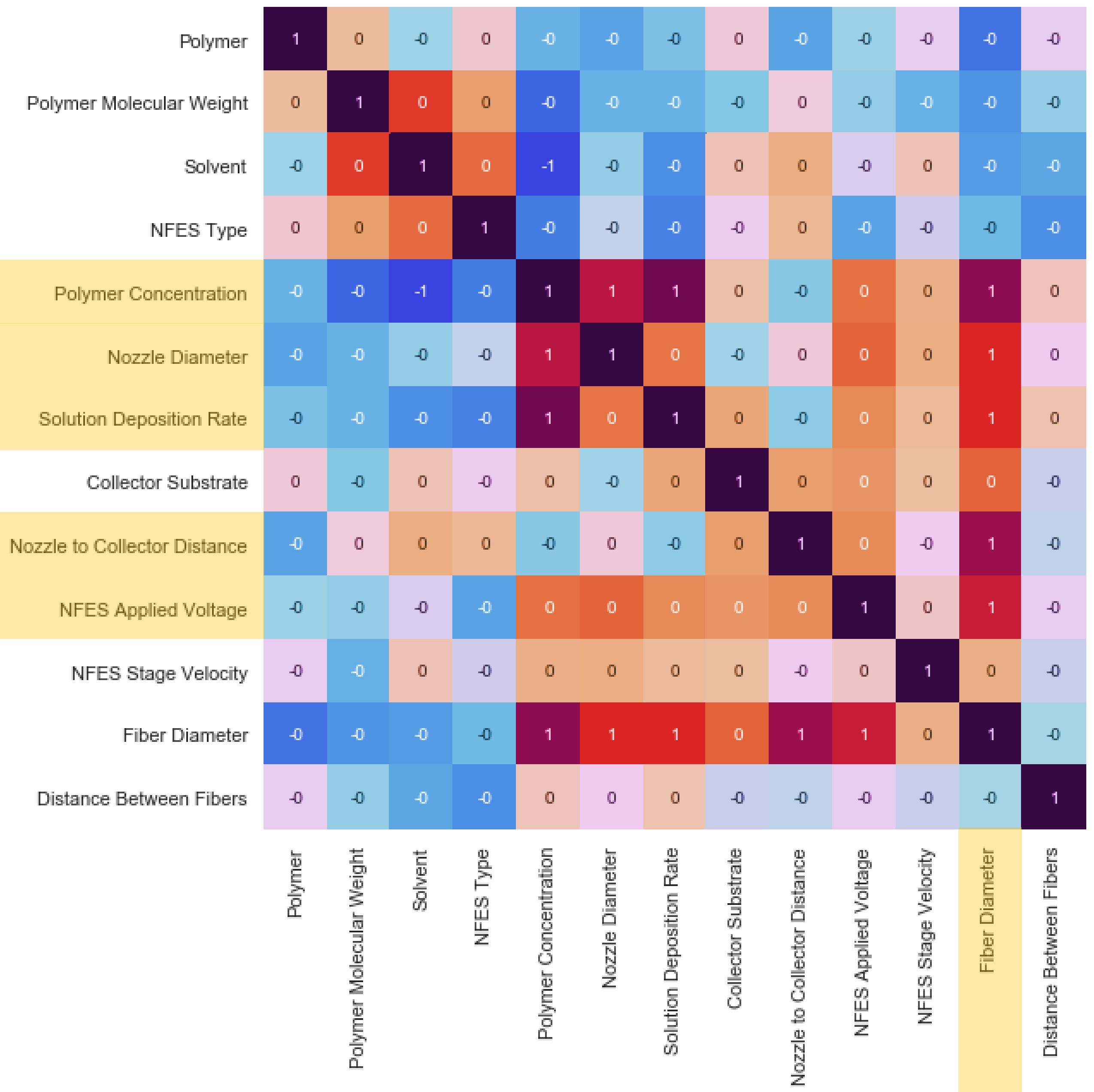
WebPlotDigitalizer https://github.com/ankitrohatgi/WebPlotDigitizer

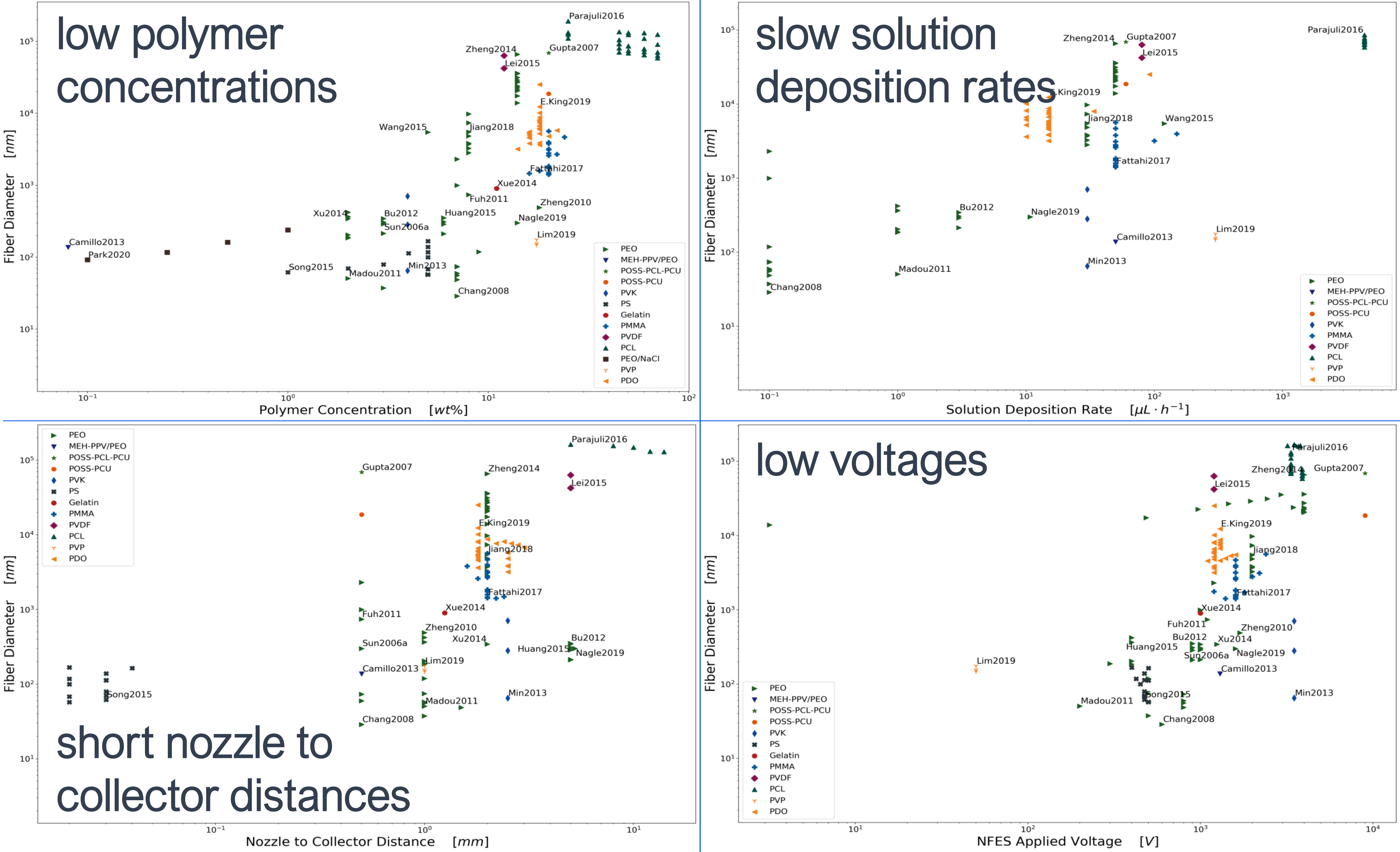


Applied voltage vs. fiber diameter by Madou2011

Polymer Concentration,
Nozzle Diameter,
Solution Deposition Rate,
Nozzle to Collector Distance &
Applied Voltage

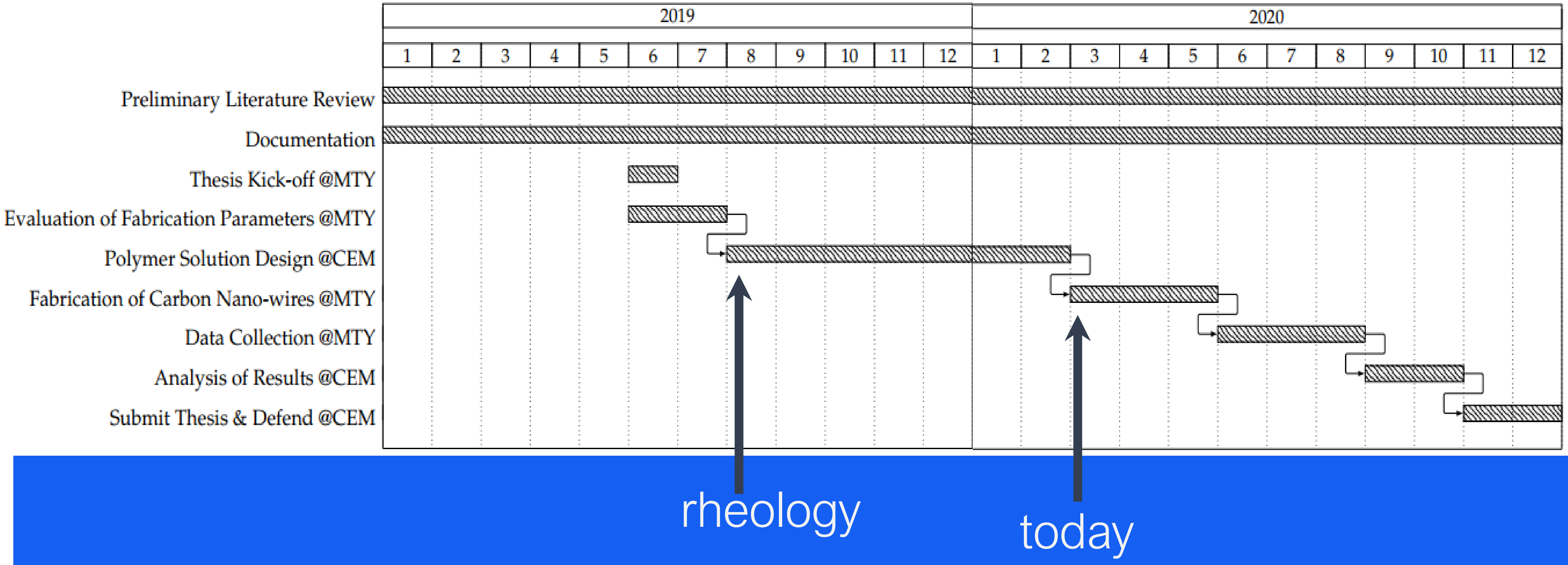
are the main drivers of the final **Fiber Diameter**




low polymer concentrations
Fiber Diameter [nm]
Polymer Concentration [wt%]
slow solution deposition rates
Fiber Diameter [nm]
Solution Deposition Rate [μL · h⁻¹]
short nozzle to collector distances
Fiber Diameter [nm]
Nozzle to Collector Distance [mm]
low voltages
Fiber Diameter [nm]
NFES Applied Voltage [V]
PEO
MEH-PPV/PEO
POSS-PCL-PCU
POSS-PCU
PVK
PS
Gelatin
PMMA
PVDF
PCL
PEO/NaCl
PVP
PDO
Parajuli2016
Zheng2014
Gupta2007
Lei2015
E.King2019
Wang2015
Jiang2018
Fattahi2017
Xue2014
Fuh2011
Zheng2010
Xu2014
Bu2012
Huang2015
Sun2006a
Nagle2019
Lim2019
Camillo2013
Park2020
Song2015
Madou2011
Min2013
Chang2008

Overall Progress & Next Steps

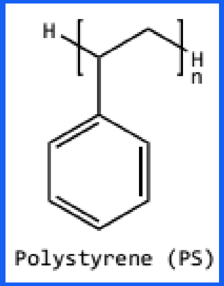
Current Work Plan



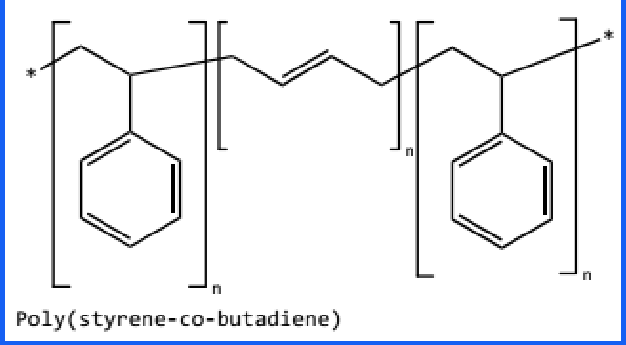
Next step: Study/Test the proposed polymer solutions

high carbon polymers and no oxygen

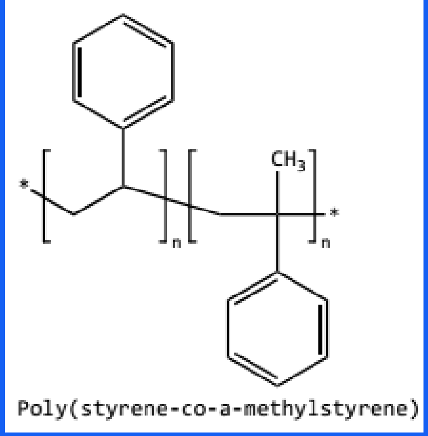
+35 wt% in THF

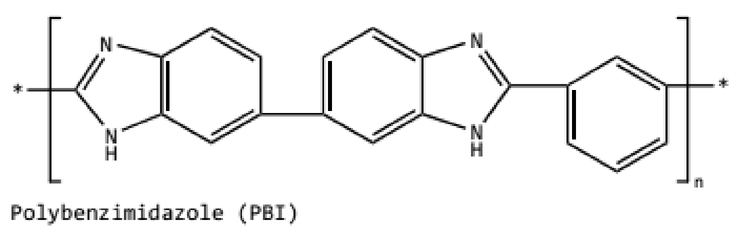


~15 wt% in NMP
~25 wt% in THF & DMF

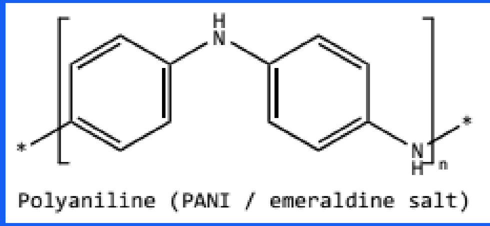


+15 wt% in DMF

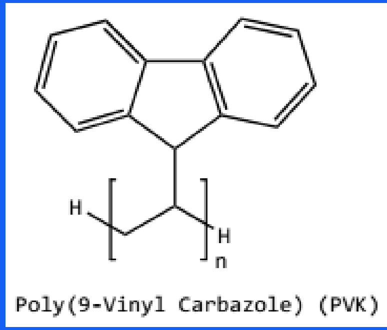




No records



No records



~8 wt% in CHL

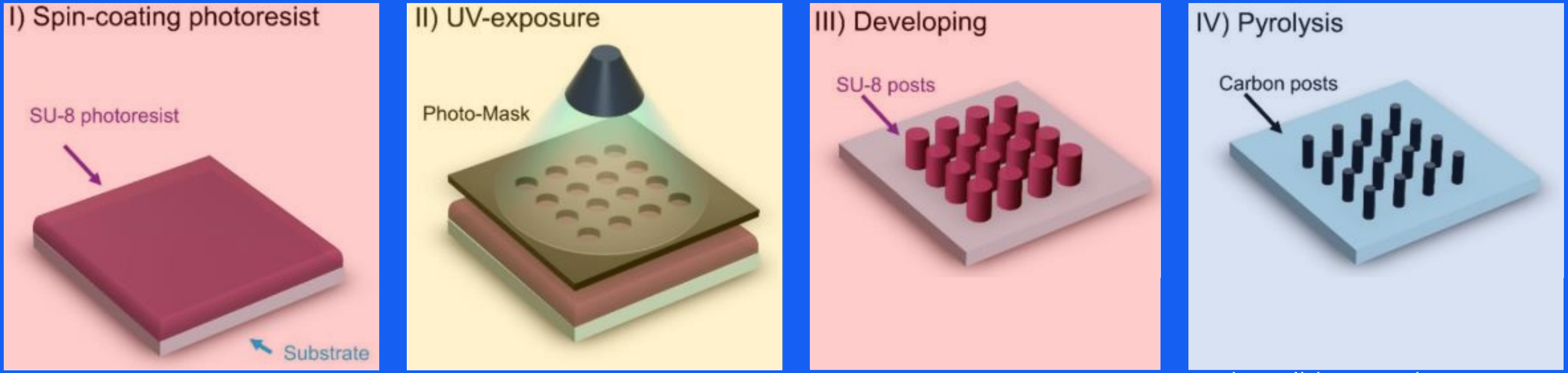

THE END

Q&A

Carbon nanostructures via Lithography

The production of C-MEMS:

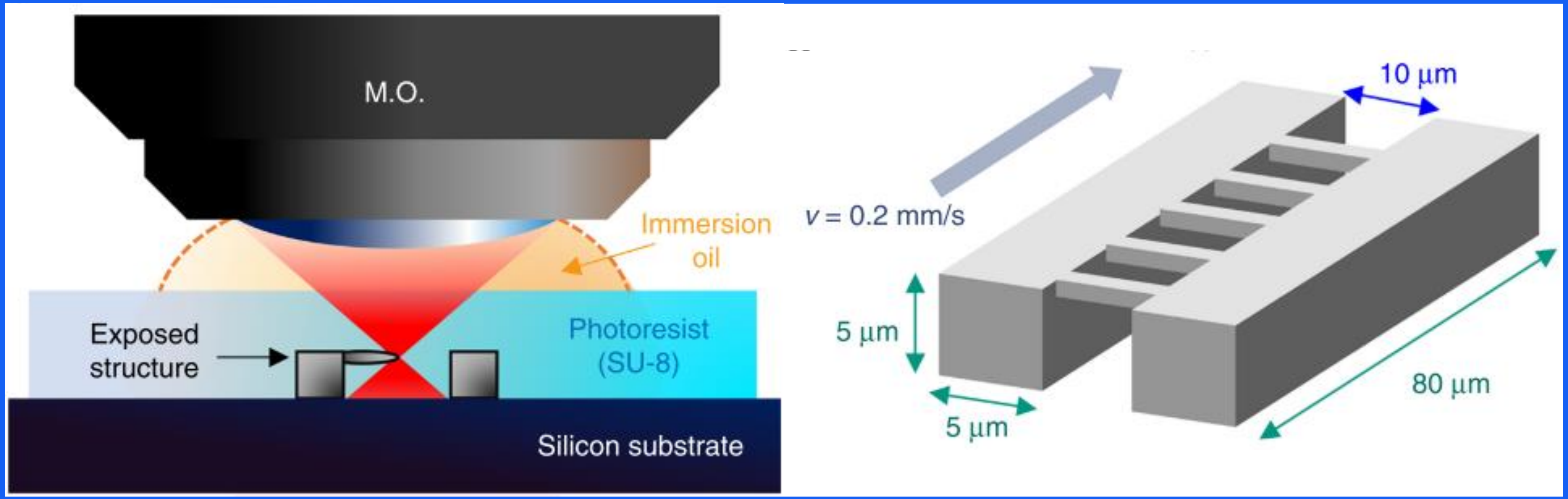
1. Polymer patterning through ~~photolithography~~ electrospinning
2. Carbonization through pyrolysis



photolithography process

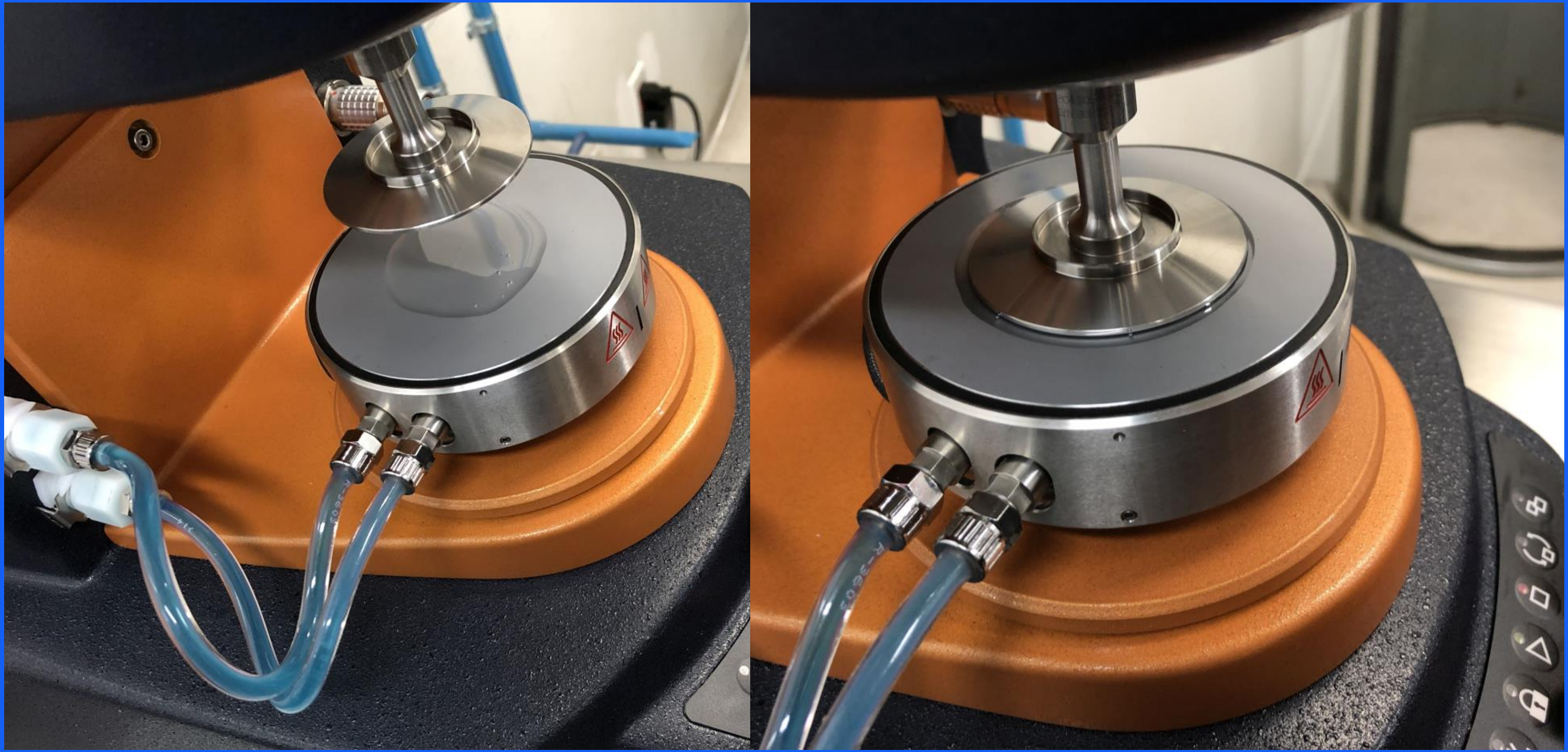
- SU-8 Waste
- Physical & Optical Limitations
- Structure Limitations

TPP – Two-Photon Polymerization



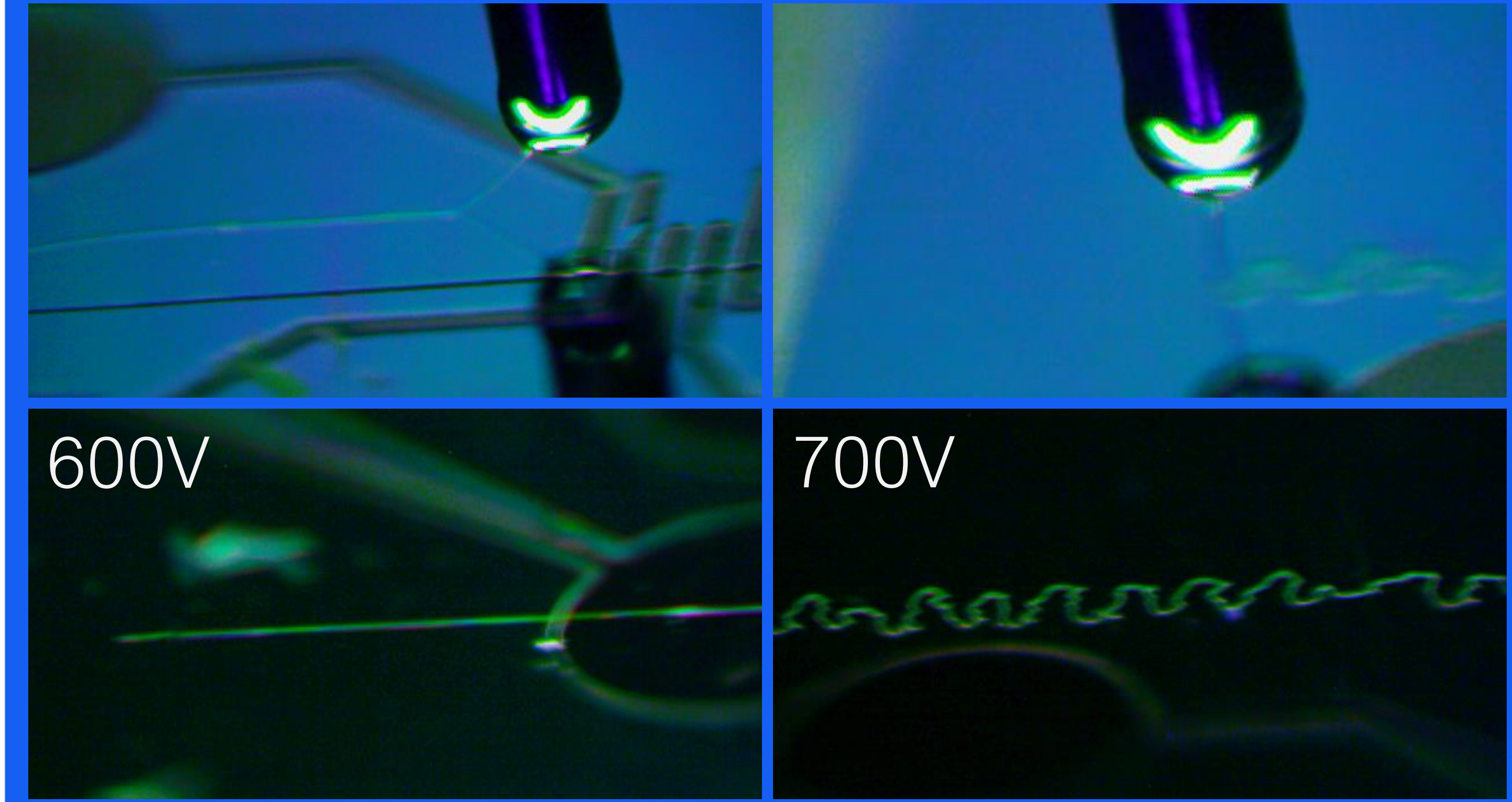
B. Cardenas-Benitez, C. Eschenbaum, D. Mager, J.G. Korvink, M.J. Madou, U. Lemmer, I. De Leon, S.O. Martinez-Chapa, Pyrolysis-induced shrinking of three-dimensional structures fabricated by two-photon polymerization: experiment and theoretical model, Microsystems Nanoeng. 5 (2019). https://doi.org/10.1038/s41378-019-0079-9.

Characterization of the 0.25 wt% PEO Solution

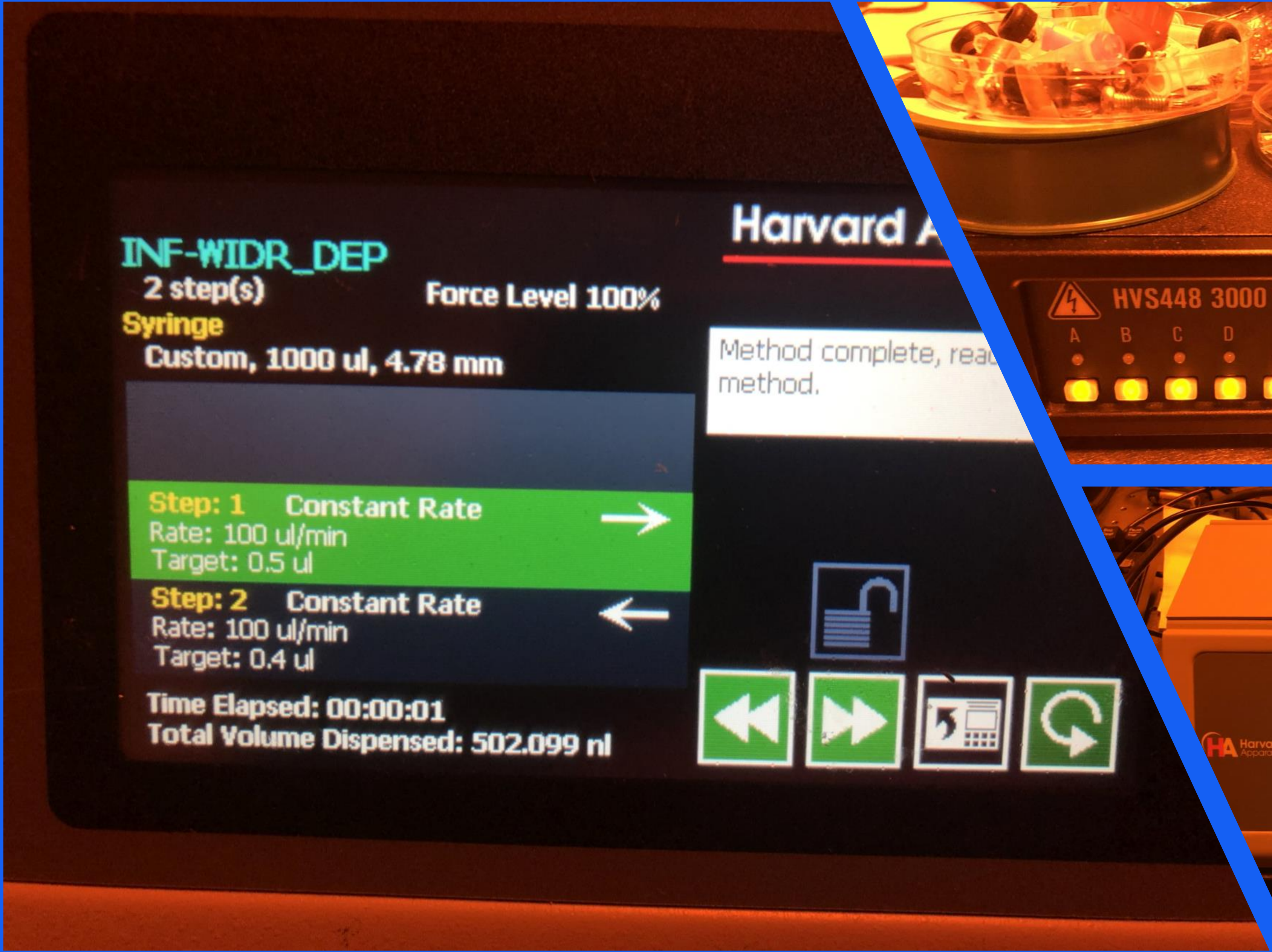


Characterization of the 0.25 wt% PEO Solution

Electrospun-able with an applied voltage of 600V.

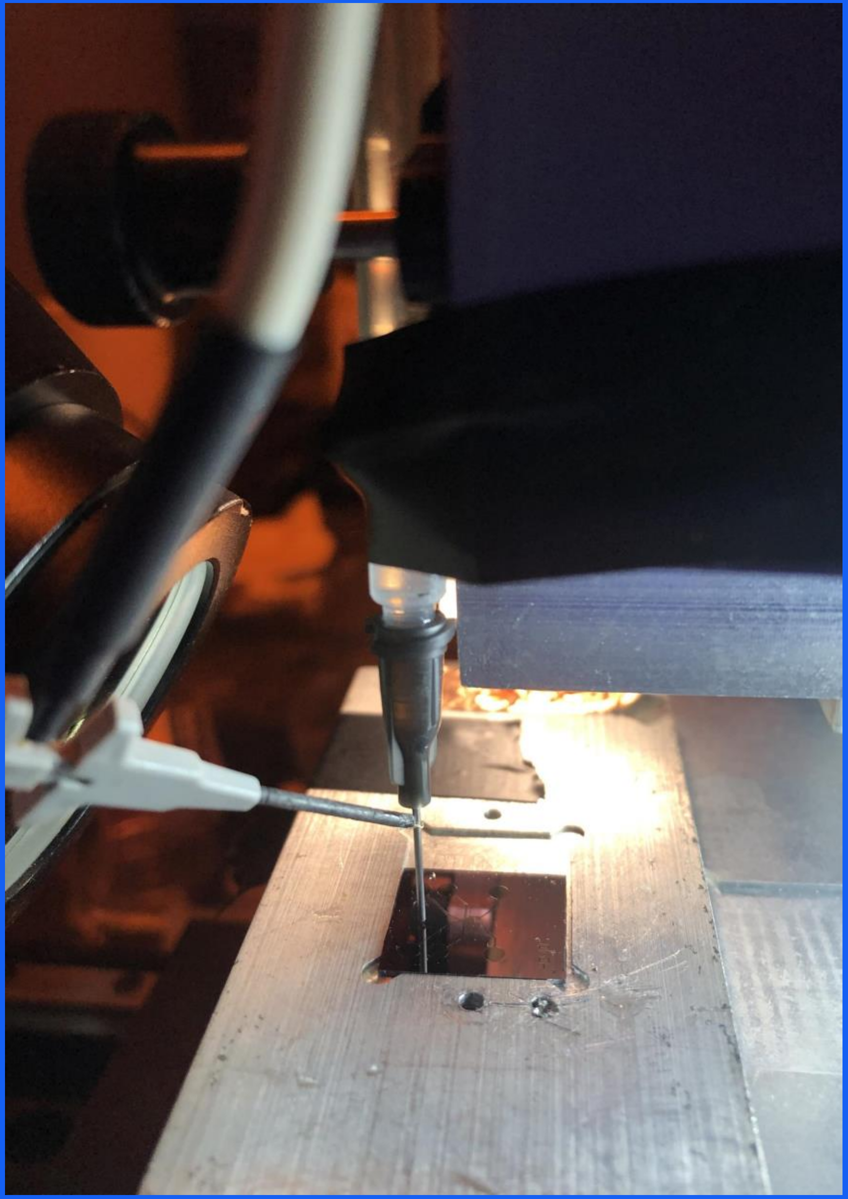


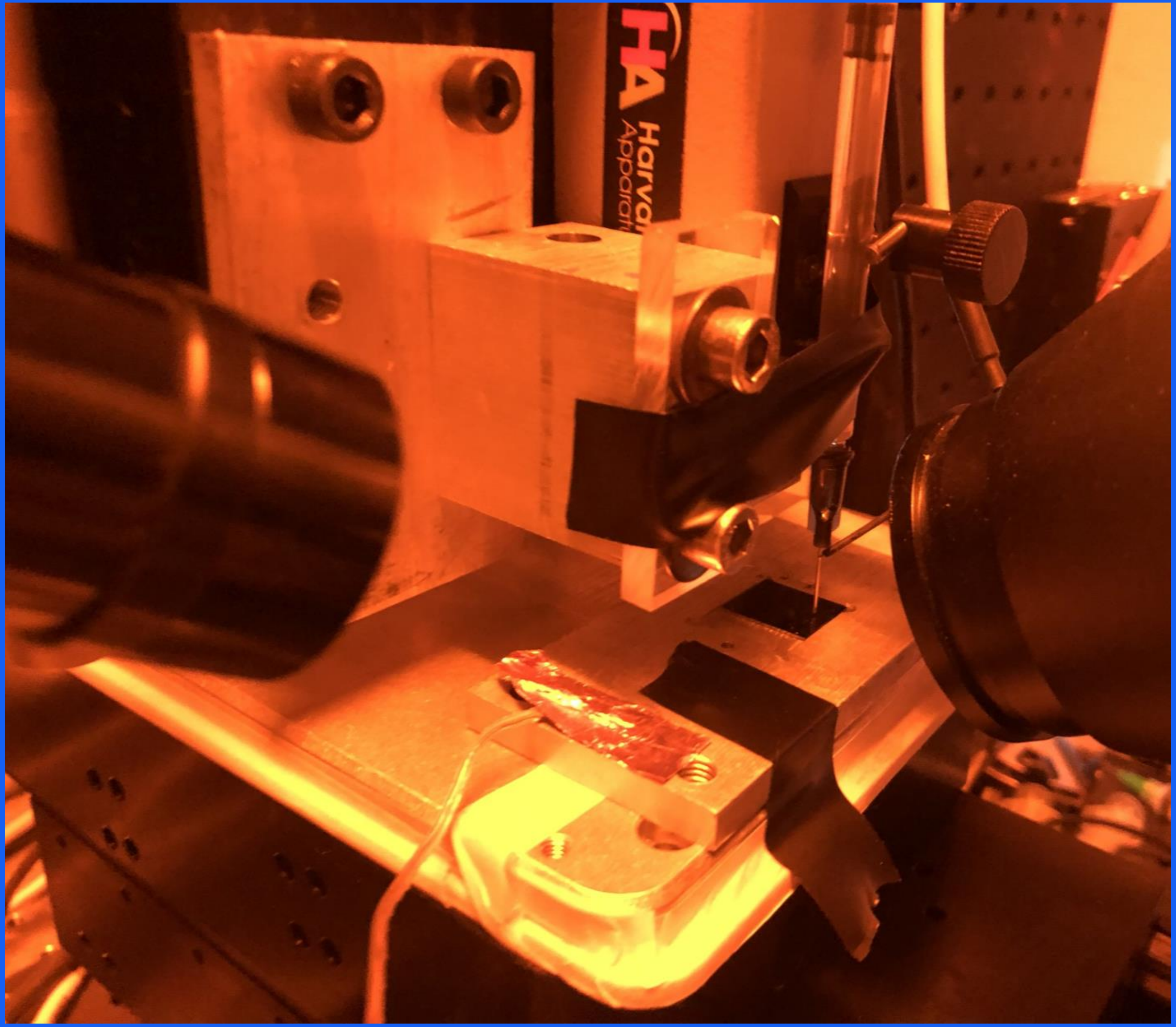
Unable to initiate the jet at 500V or lower.


INF-WIDR_DEP
2 step(s)
Force Level 100%
Syringe
Custom, 1000 ul, 4.78 mm
Harvard A
Method complete, read
method.
Step: 1 Constant Rate
Rate: 100 ul/min
Target: 0.5 ul
Step: 2 Constant Rate
Rate: 100 ul/min
Target: 0.4 ul
Time Elapsed: 00:00:01
Total Volume Dispensed: 502.099 nl


HVS448 3000 V High Voltage Sequencer
ENABLE
DISABLE
A B C D E F G H ALL
TRIGGER
PAUSE
RUN
STOP


Harvard Apparatus
Pump 11 Elite



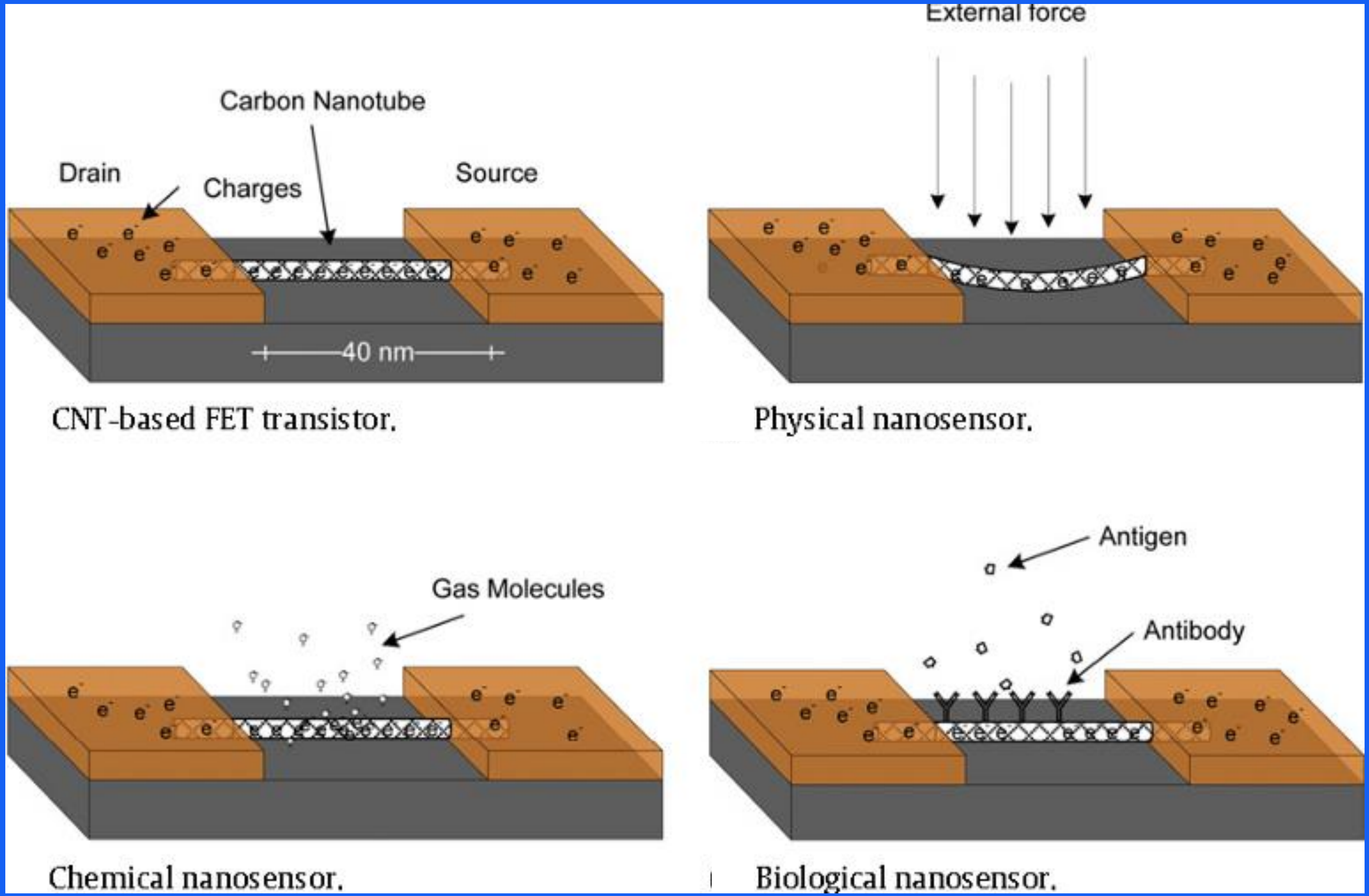

HA

PEO Solution

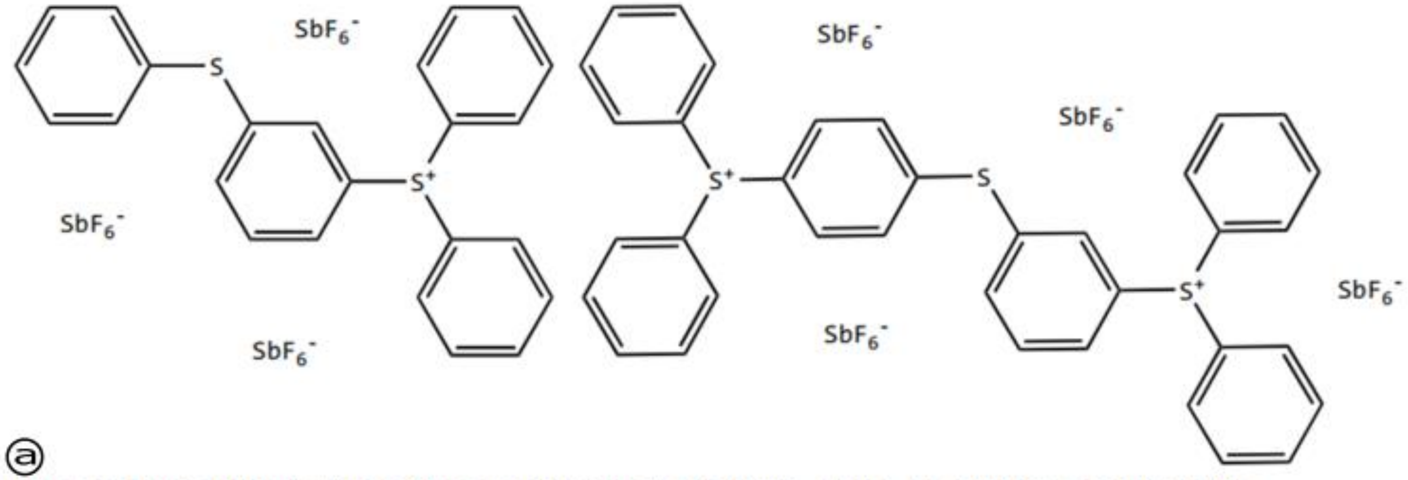
The EMS polymer solution consisted of
2ml of SU-8 2002 mixed with
0.5 wt% of Poly(ethylene oxide) (PEO, 4,000,000 MW; SigmaAldrich Inc., Cat. N. 189464) and
0.5 wt% Tetrabutylammonium Tetrafluoroborate salts (TBATFB; SigmaAldrich Inc., Cat. N. 217964) to increase its conductivity and allow smooth polymer flow during electrospinning.

All reagents were used as received. Magnetic stirring of these components was performed for 1hr at 75°C and low rpm (100-150 rpm).

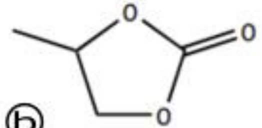
Applications of CNWs



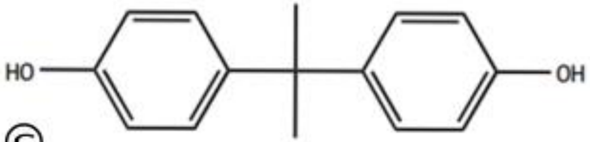
SU-8 (MicroChem,US)



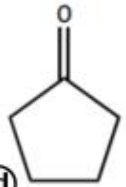
ⓐ
Mixed Triarylsulfonium/Hexafluoroantimonate Salt (CAS: 89452-37-9)/(CAS: 71449-78-0)



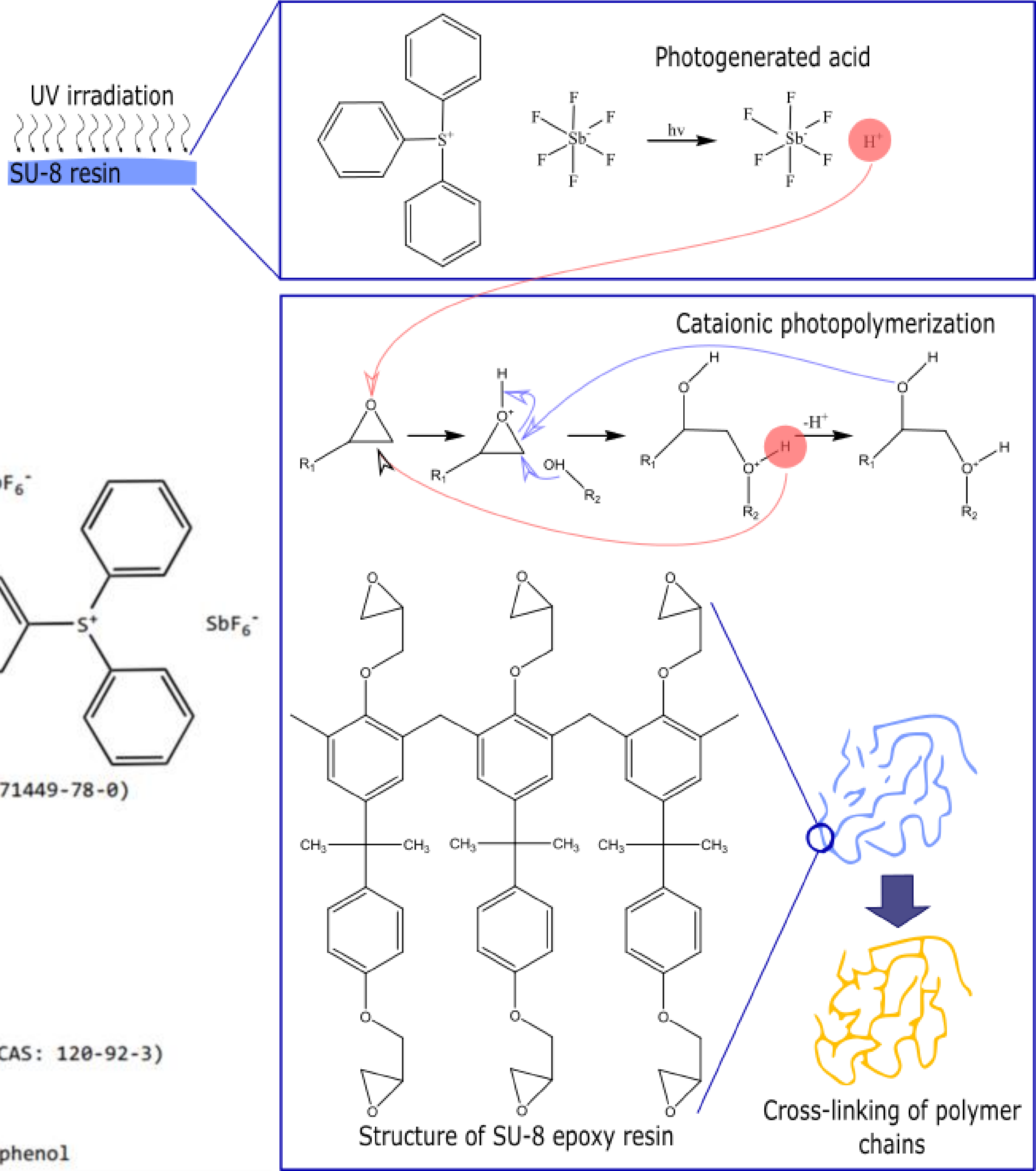
ⓑ
Propylene Carbonate (CAS: 108-32-7)



ⓒ
Epoxy Resin (CAS: 28906-96-9)
2-(Chloromethyl)oxirane; formaldehyde; 4-[2-(4-hydroxyphenyl)propan-2-yl]phenol



ⓓ
Cyclopentanone (CAS: 120-92-3)



SU-8 (MicroChem, US)

MICROCHEM CORP SU-8 2002 500ML

encompass

Manufacturer: MICROCHEM CORP Y111029

Catalog No.	NC0702370

$628.71 / Each

Qty Check Availability

Add to cart

https://www.fishersci.com/shop/products/NC0702370/nc0702370#?keyword=MICROCHEM+CORP+PHOTORESIST+SU-8

MICROCHEM CORP SU-8 DEVELOPER 4L

encompass

Catalog No.	NC9901158

$172.90 / Each

INGREDIENTS:
Cyclopentanone (CAS: 120-92-3); 23-78%.
Mixed Triarylsulfonium/ Hexafluoroantimonate Salt;
(CAS: 89452-37-9)/(CAS: 71449-78-0); 1-5%
Propylene Carbonate (CAS: 108-32-7); 1-5%
Epoxy Resin (CAS: 28906-96-9); 25-75%

https://www.fishersci.com/shop/products/NC9901158/nc9901158#?keyword=SU-8++developer

<subTitle>

<content> <key concept>