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

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CONACYT

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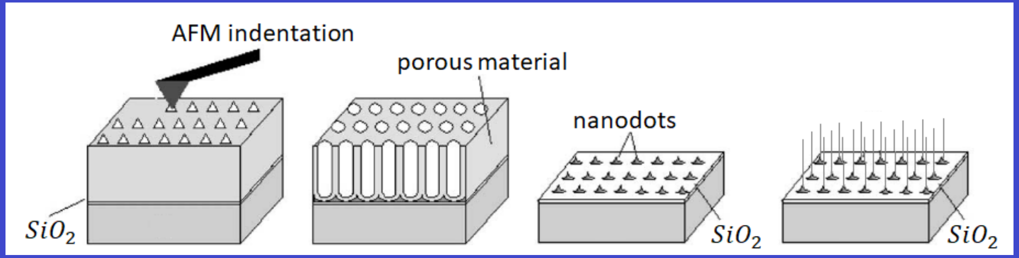
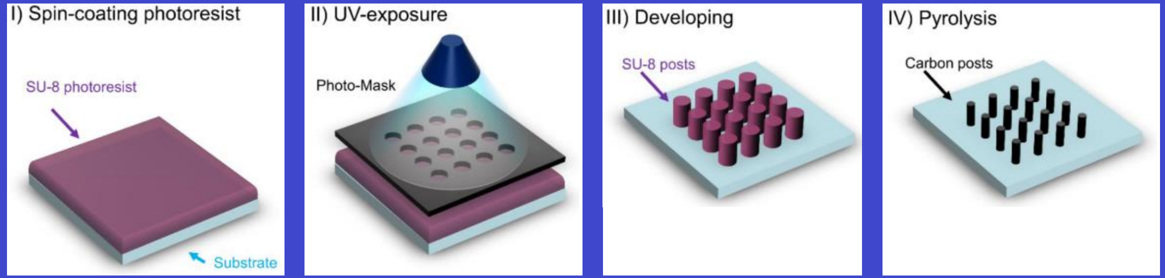
Motivation & Problem Statement

Current approaches for the fabrication of carbon nanostructures

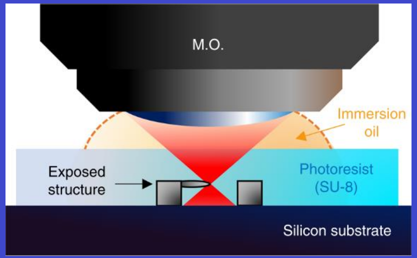
Self-assembly
Limited Length and Random Orientation



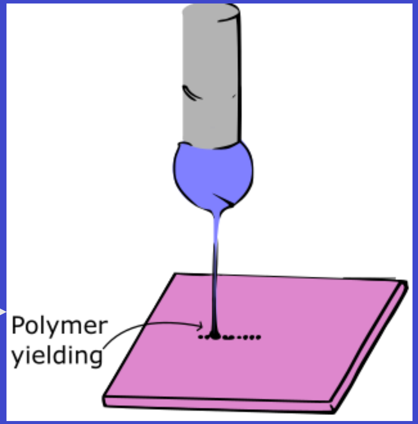
Photolithography
Physical & Optical Limitations



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



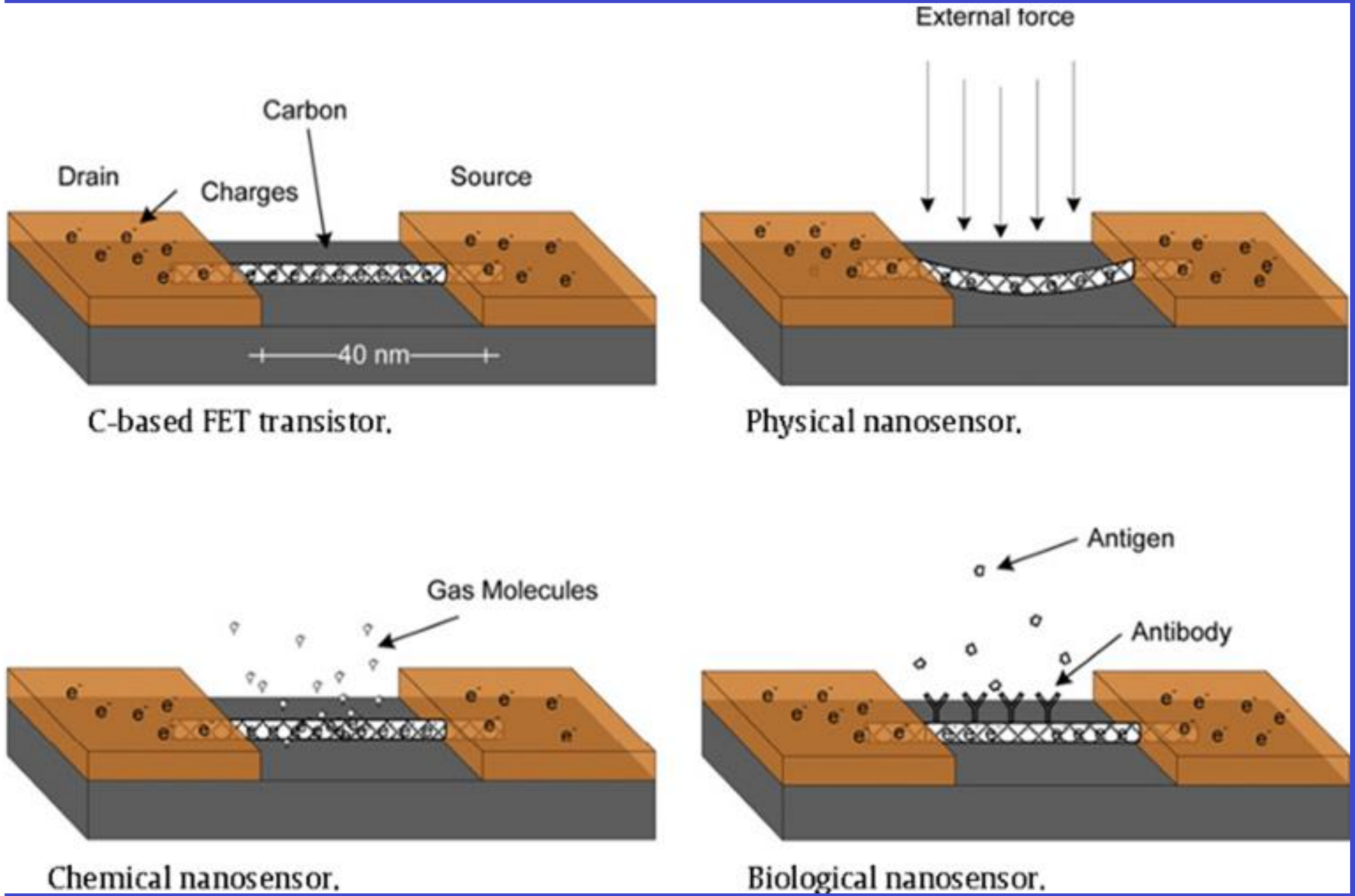
* Near-Field Electrospinning (NFES)
Suspended Nanowires w/Spatial Control



V. Galstyan, M. Bhandari, V. Sberveglieri, G. Sberveglieri, E. Comini, Metal Oxide Nanostructures in Food Applications: Quality Control and Packaging, Chemosensors. 6 (2018) 16.

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.

Applications of Carbon Nanowires (CNWs)



The carbon nanostructure changes its electrical properties with:

- deformation (mass, pressure, force or displacement)
- absorption/attachment of chemicals
- biological processes such as antibody/antigen interaction, DNA interaction and cellular communication

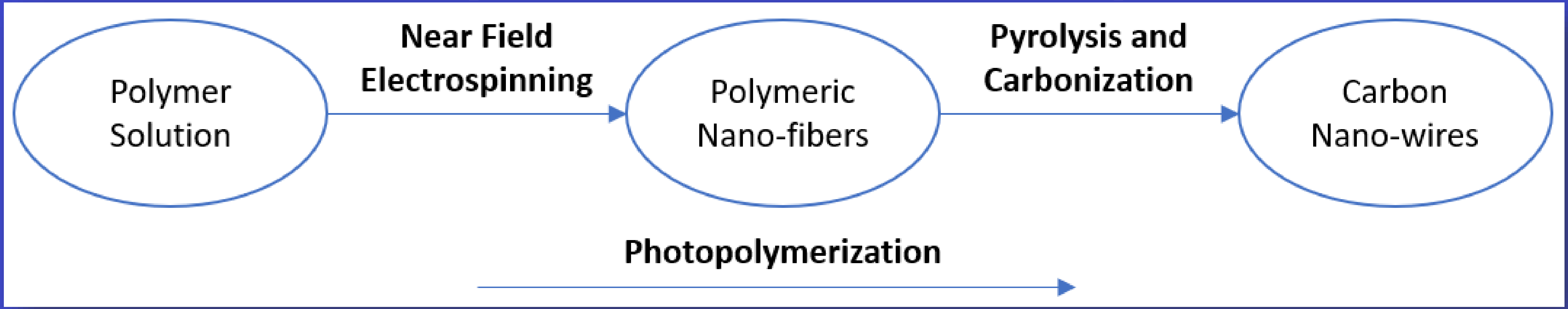
I.F. Akyildiz, J.M. Jornet, Electromagnetic wireless nanosensor networks, Nano Commun. Netw. 1 (2010) 3–19. https://doi.org/10.1016/j.nancom.2010.04.001.
N. Rikhtegar, M. Keshtgary, A Brief Survey on Molecular and Electromagnetic Communications in Nano-Networks, Int. J. Comput. Appl. 79 (2013) 16–28. https://doi.org/10.5120/13721-1510.

Thesis Overview – CNWs fabrication process

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

spatial control

carbon structures



good conductivity

Polymer Solution Parameters

SU-8 Carbon Structures

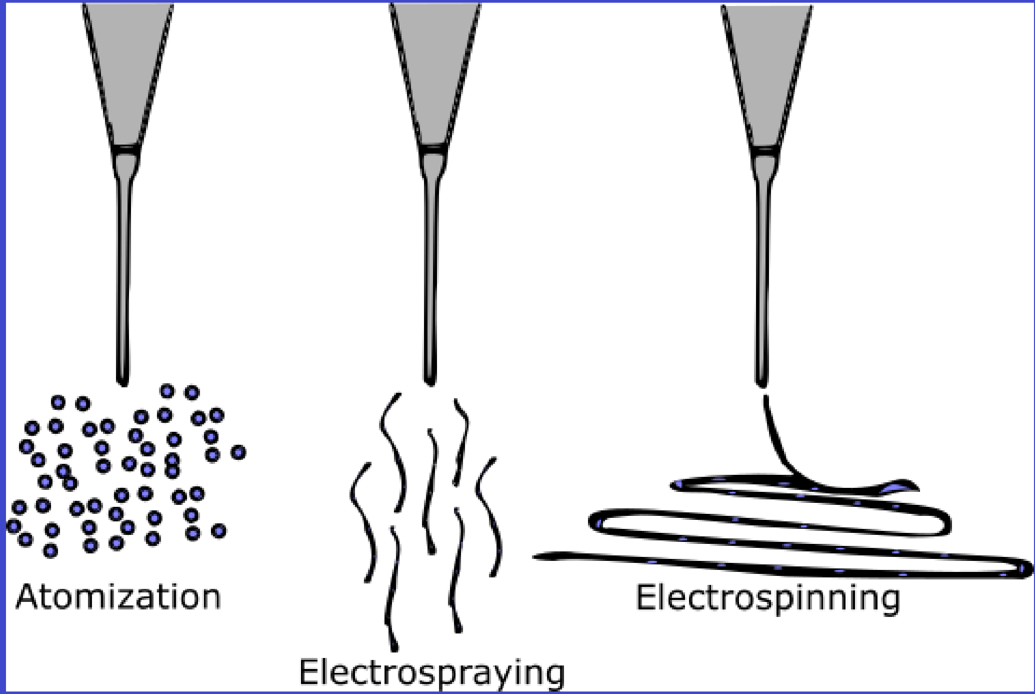
The production of C-MEMS:

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

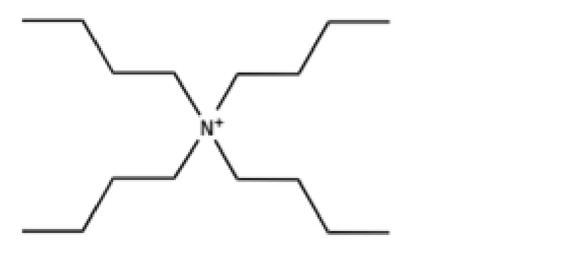
SU-8 is design for photolithography



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

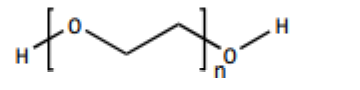
Making SU-8 spunable (by Braulio & Ricardo)

SU-8 + TBF + PEO



Tetrabutylammonium tetrafluoroborate (TBF)

→ To increase the solution conductivity



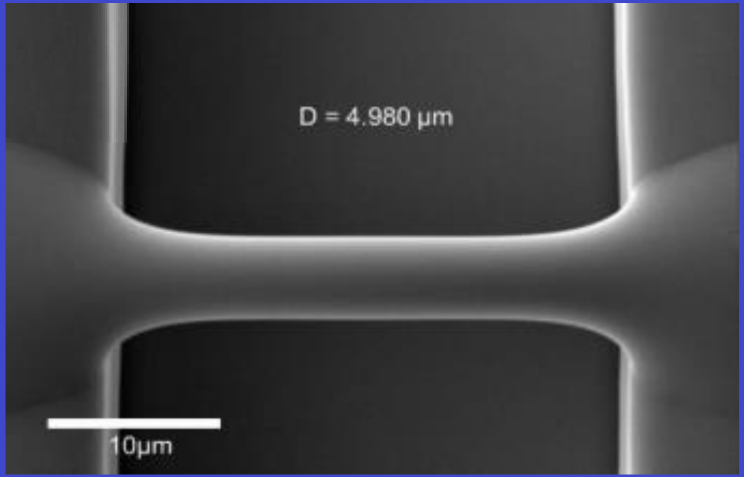
Poly(ethylene oxide) (PEO)

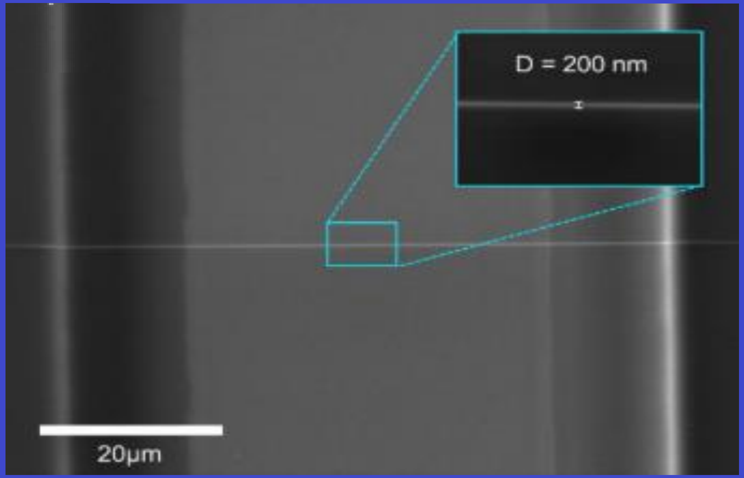
→ To provided the required viscosity

… 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:

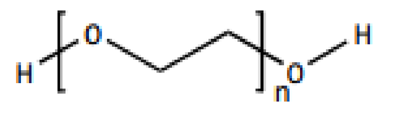
wt% PEO	SU-8 2002 [mg]	PEO [mg]	TBT [mg]
0.25	2246	5.65	11.32

= 2 ml of solution

B. Cárdenas, Advanced Manufacturing Techniques for the Fabrication and Surface Modification of Carbon Nanowires, (2017) 160.

Implications of PEO, as it introduces oxygen to the solution

The fiber yield rate and fiber conductivity are impacted negatively.



Poly(ethylene oxide) (PEO)

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.

The Carreau-Yasuda Model

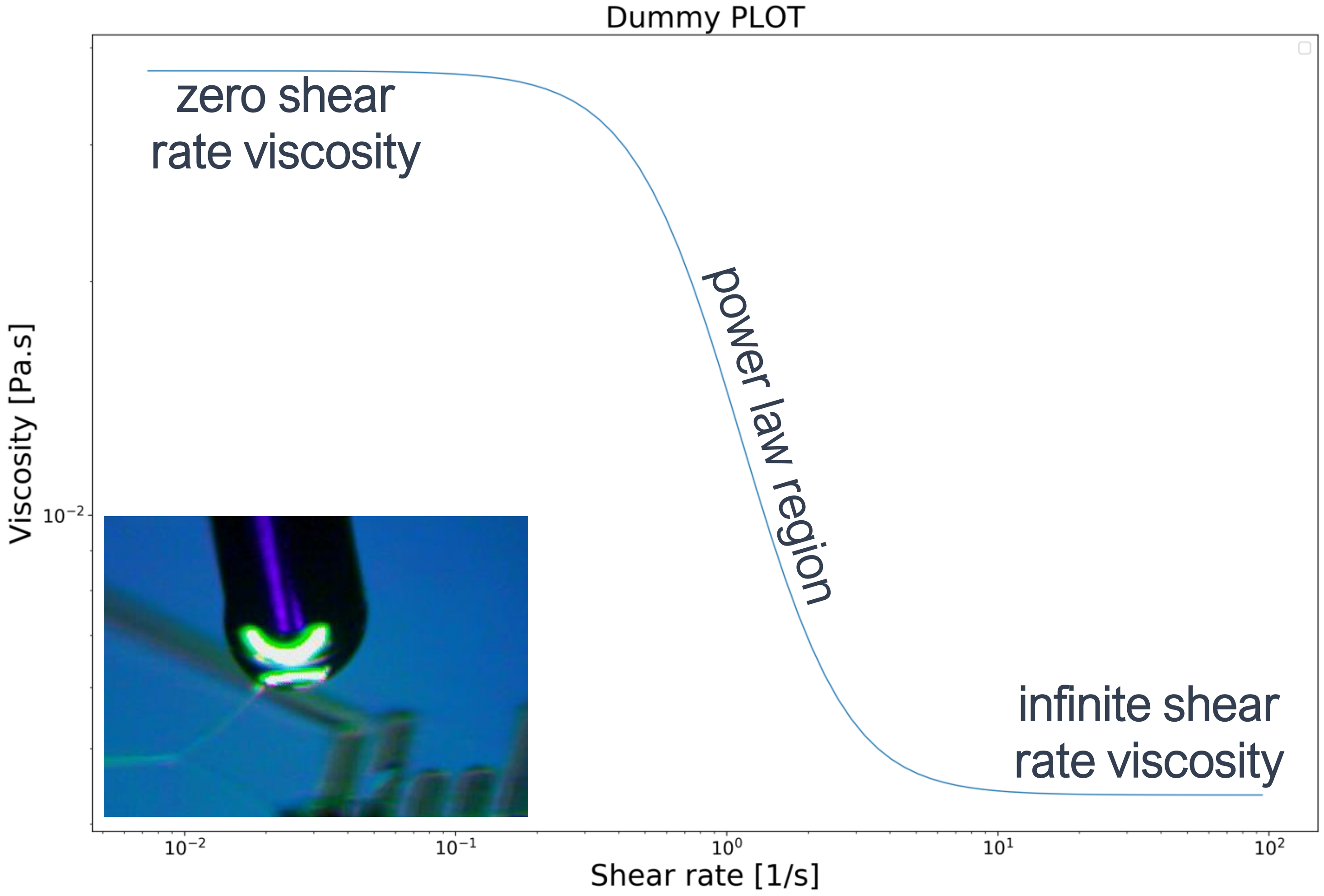
$$\frac{\eta - b}{a - b} = \frac{1}{\left[1 + (c\dot{\gamma})^{e}\right]^{\frac{1-d}{e}}}$$

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{\left[1 + (\kappa\dot{\gamma})^{a}\right]^{\frac{(1-n)}{a}}}$$

$$\eta = \frac{\eta_0 - \eta_\infty}{\left[1 + (\kappa\dot{\gamma})^{a}\right]^{\frac{(1-n)}{a}}} + \eta_\infty$$

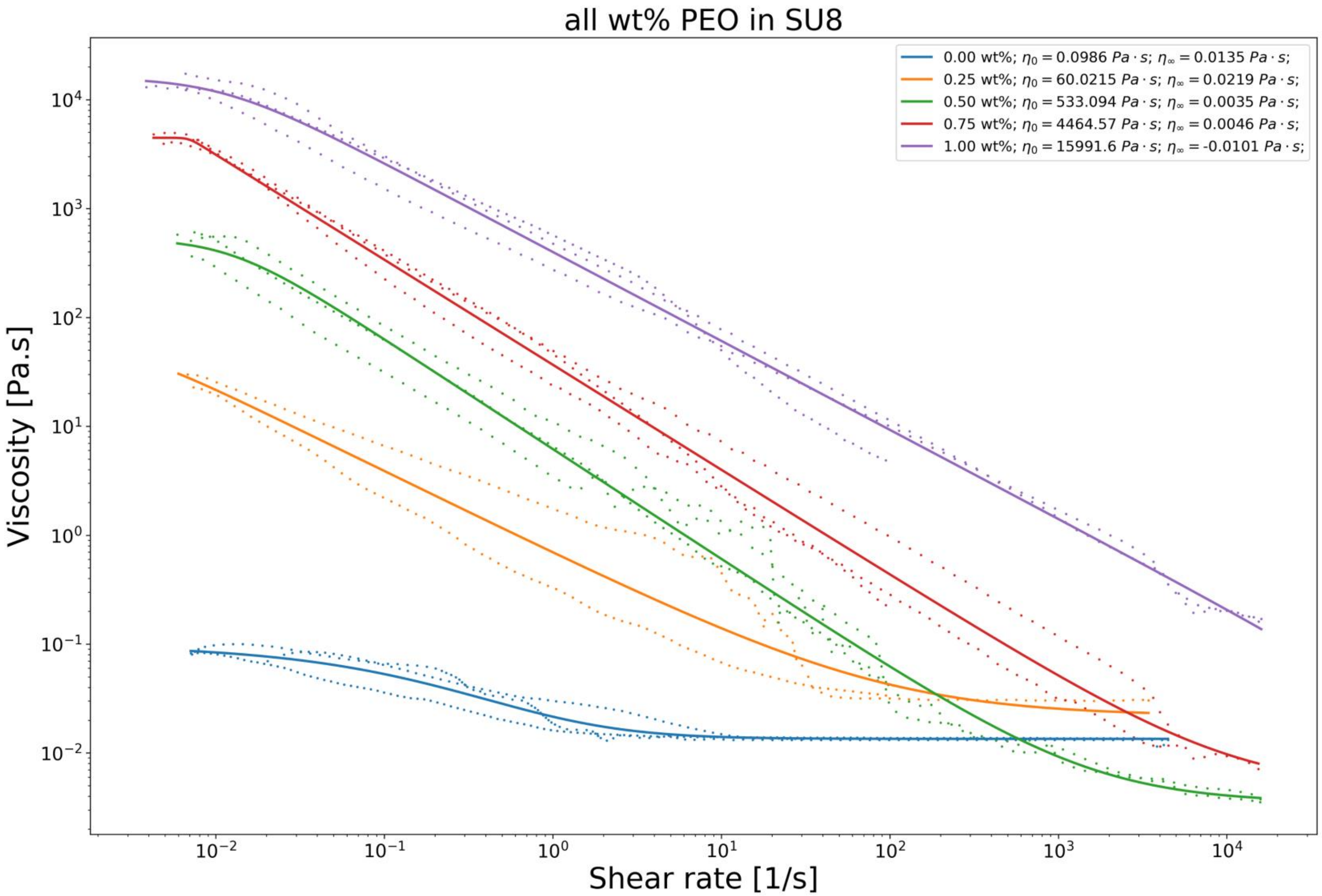
where:

η = Viscosity
$\dot{\gamma}$ = Shear rate
η_∞ = Infinite shear rate viscosity
η_0 = Zero shear rate viscosity
κ = Time constant
n = The Power Law index
a = The width of the transition region between the zero shear viscosity and the Power Law region



Osswald, T., Rudolph, N., Osswald, T., & Rudolph, N. (2014). Generalized Newtonian Fluid (GNF) Models. Polymer Rheology, 59–99. https://doi.org/10.3139/9781569905234.003

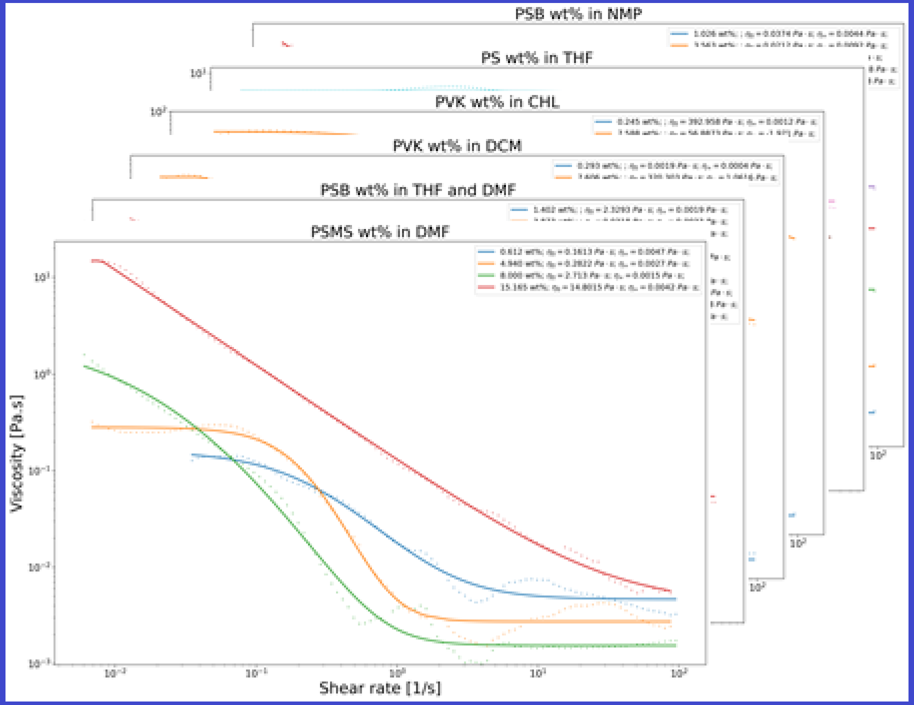
Rheology of the amended SU-8 solution (0.25 wt%)



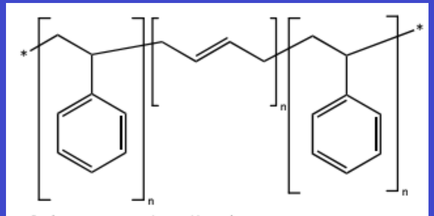
The 0.25 wt% sample (orange line) has a zero-shear viscosity (ZSV) of 60 Pa.s spunable at 600 V

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

Rheology of the proposed polymer solutions

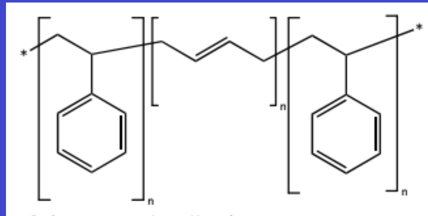


15 wt% in NMP



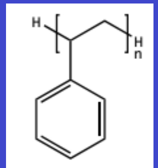
Poly(styrene-co-butadiene)

25 wt% in THF & DMF



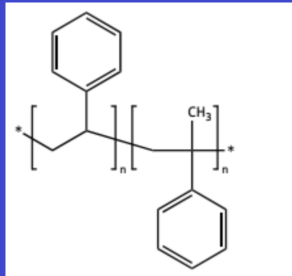
Poly(styrene-co-butadiene)

35 wt% in THF



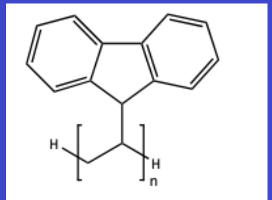
Polystyrene (PS)

15 wt% in DMF



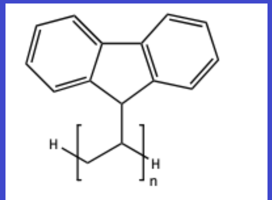
Poly(styrene-co-a-methylstyrene)

8 wt% in CHL



Poly(9-Vinyl Carbazole) (PVK)

7 wt% in DCM



Poly(9-Vinyl Carbazole) (PVK)

Solutions with similar rheology of that of the 0.25wt% PEO SU-8 solution with about **60 Pa.s** ZSV each.

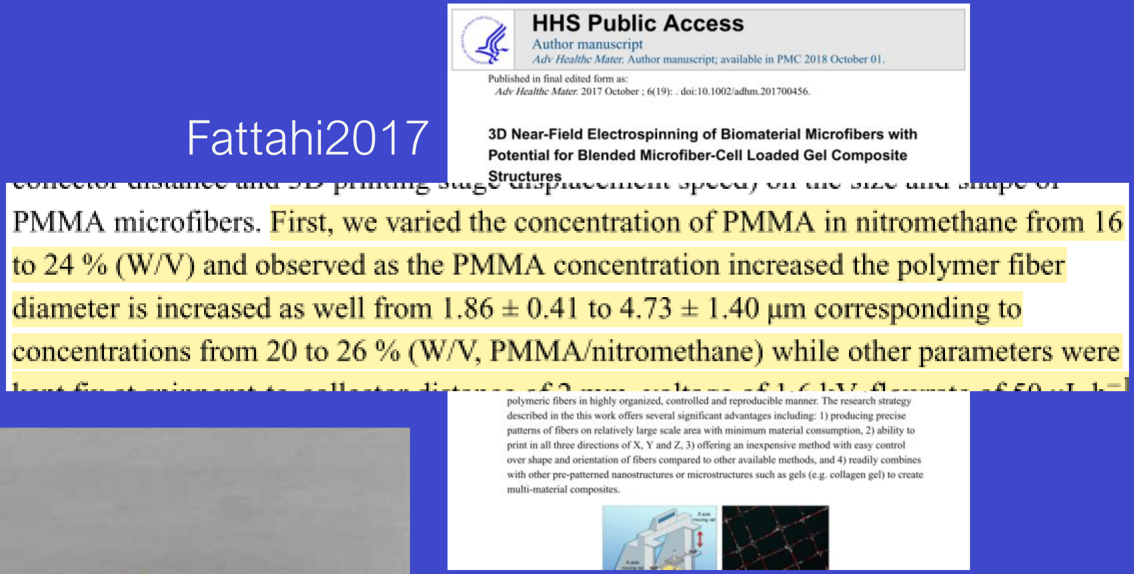
NFES Process Parameters

Data collection of NFES literature

(90+ papers from 2003 to 2020)

Use case 1 (ideal case): The author mentions the process parameters and fiber properties within the article in writing.

Fattahi2017



HHS Public Access

Author manuscript

Adv Healthc Mater. Author manuscript; available in PMC 2018 October 01.

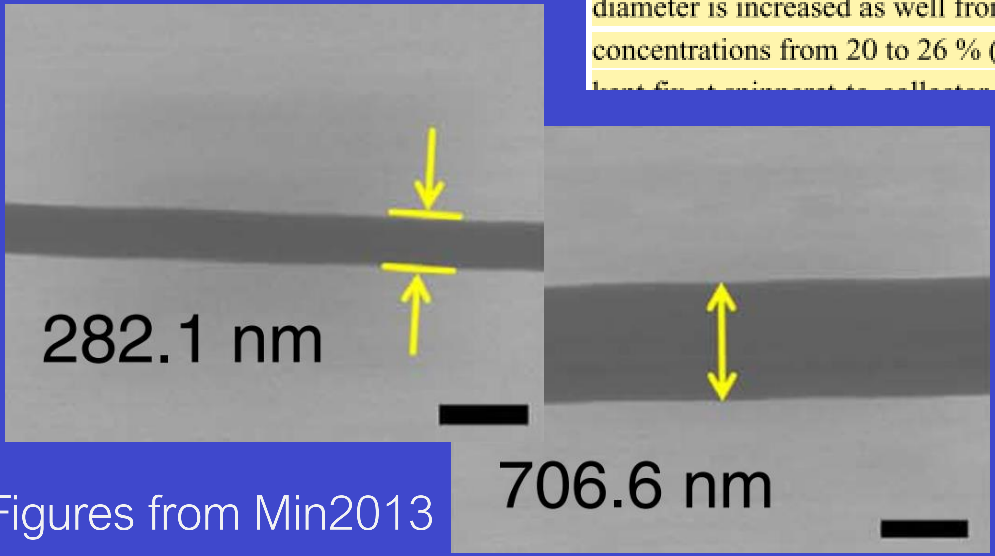
Published in final edited form as:

Adv Healthc Mater. 2017 October ; 6(19): . doi:10.1002/adhm.201700456.

3D Near-Field Electrospinning of Biomaterial Microfibers with Potential for Blended Microfiber-Cell Loaded Gel Composite Structures

PMMA microfibers. First, we varied the concentration of PMMA in nitromethane from 16 to 24 % (W/V) and observed as the PMMA concentration increased the polymer fiber diameter is increased as well from 1.86 ± 0.41 to 4.73 ± 1.40 μm corresponding to concentrations from 20 to 26 % (W/V, PMMA/nitromethane) while other parameters were

polymeric fibers in highly organized, controlled and reproducible manner. The research strategy described in the this work offers several significant advantages including: 1) producing precise patterns of fibers on relatively large scale area with minimum material consumption, 2) ability to print in all three directions of X, Y and Z, 3) offering an inexpensive method with easy control over shape and orientation of fibers compared to other available methods, and 4) readily combines with other pre-patterned nanostructures or microstructures such as gels (e.g. collagen gel) to create multi-material composites.



Figures from Min2013

Data collection of NFES literature
(90+ papers from 2003 to 2020)

Use case 2 (typical case): The author provides the data in plots and graphs.

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

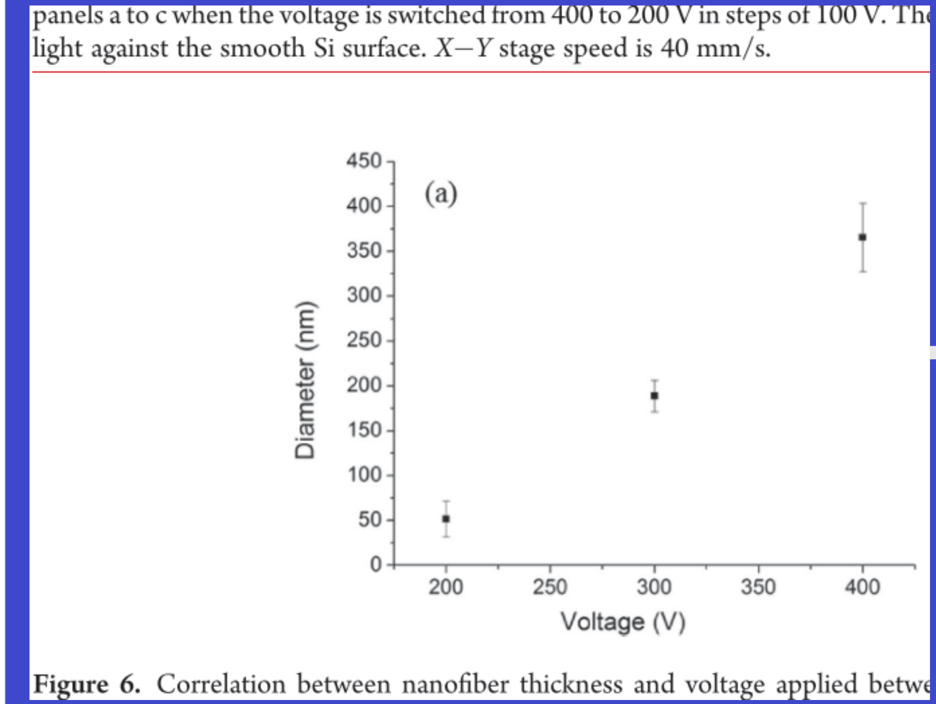
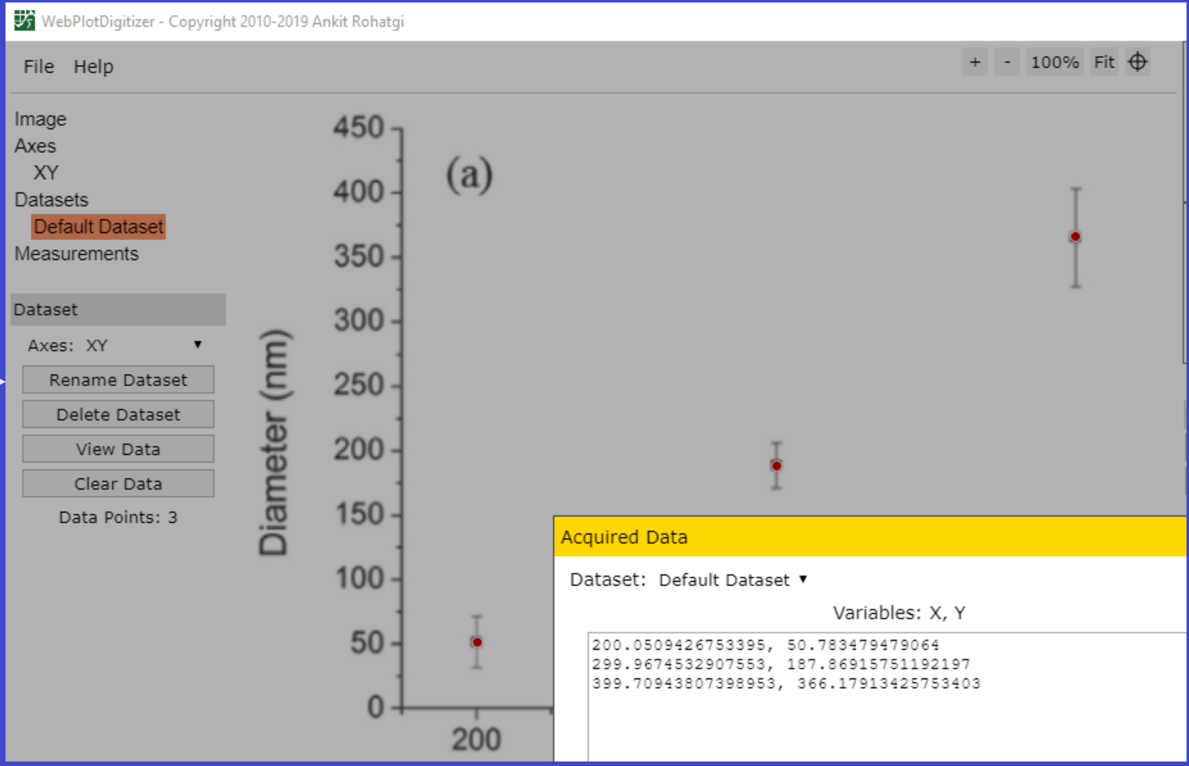

panels a to c when the voltage is switched from 400 to 200 V in steps of 100 V. The
light against the smooth Si surface. X−Y stage speed is 40 mm/s.

Figure 6. Correlation between nanofiber thickness and voltage applied betw



M.J. Madou, D. Dunn-Rankin, L. Kulinsky, A. Mirsepassi, G.S. Bisht, S. Oh, G. Canton, Controlled Continuous Patterning of Polymeric Nanofibers on Three-Dimensional Substrates Using Low-Voltage Near-Field Electrospinning, Nano Lett. 11 (2011) 1831–1837. https://doi.org/10.1021/nl2006164.

Applied voltage vs. fiber diameter by Madou2011

Data collection of NFES literature
(90+ papers from 2003 to 2020)

Use case 3 (difficult case): The author does not mention the fiber diameter in writing but provides a EM characterization.

Python Image Analysis:

Figures from Min2013

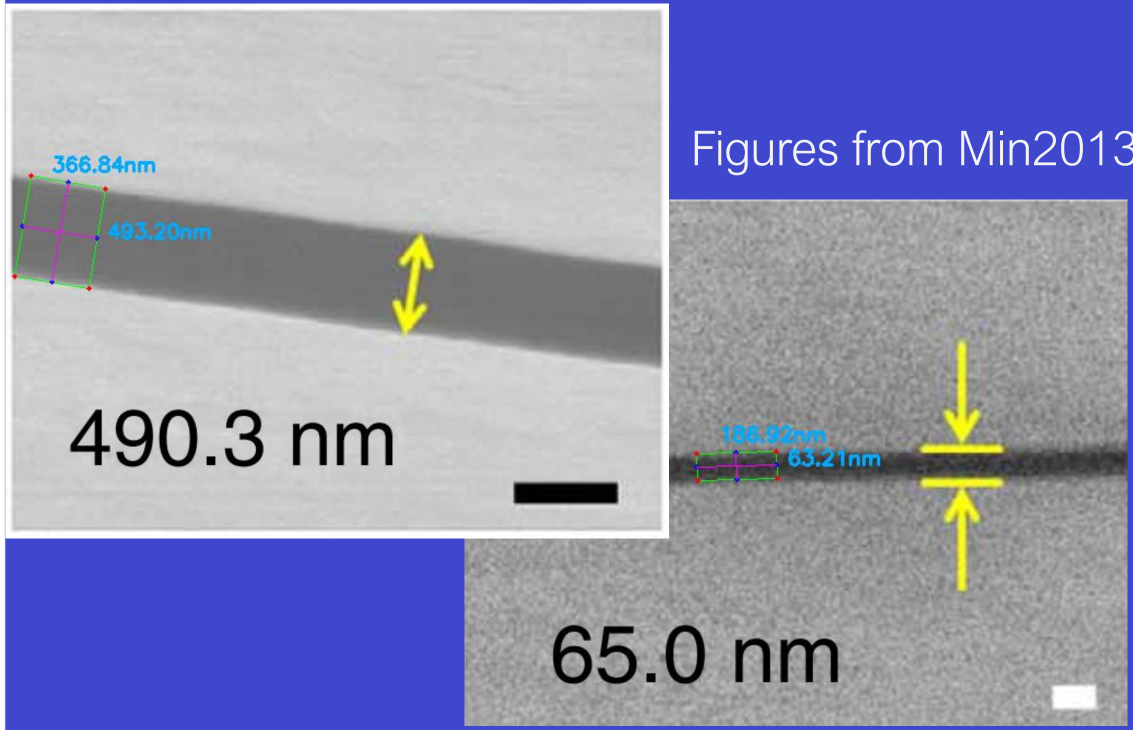
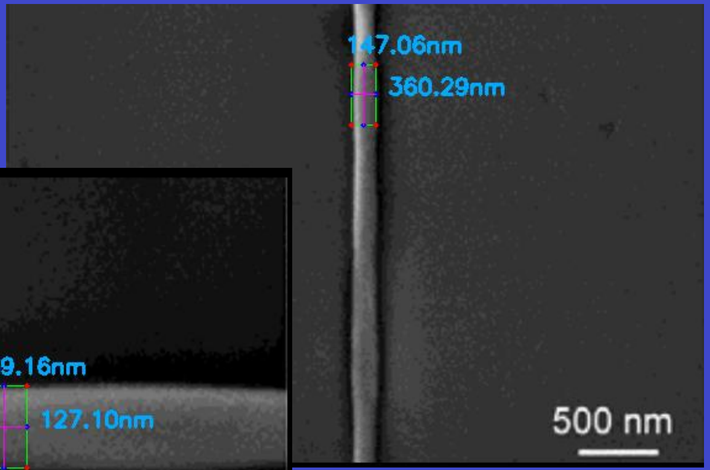


Figure from Camillo2013



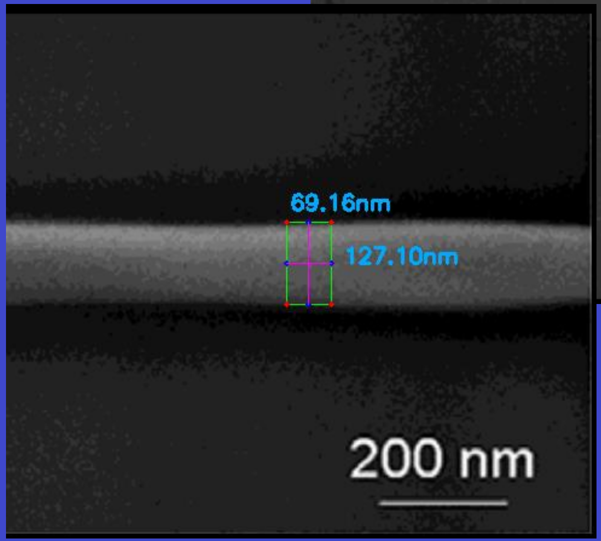
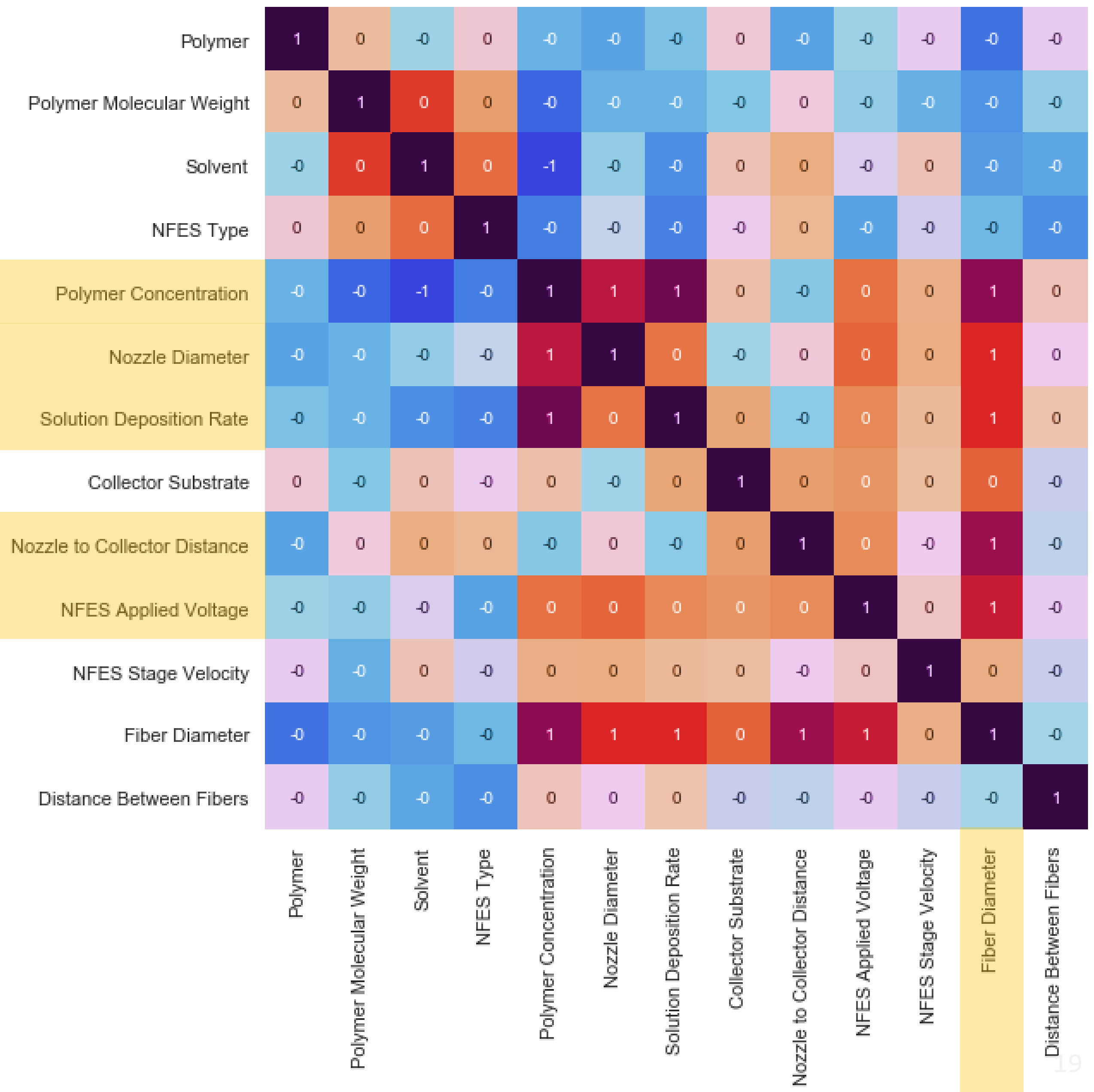


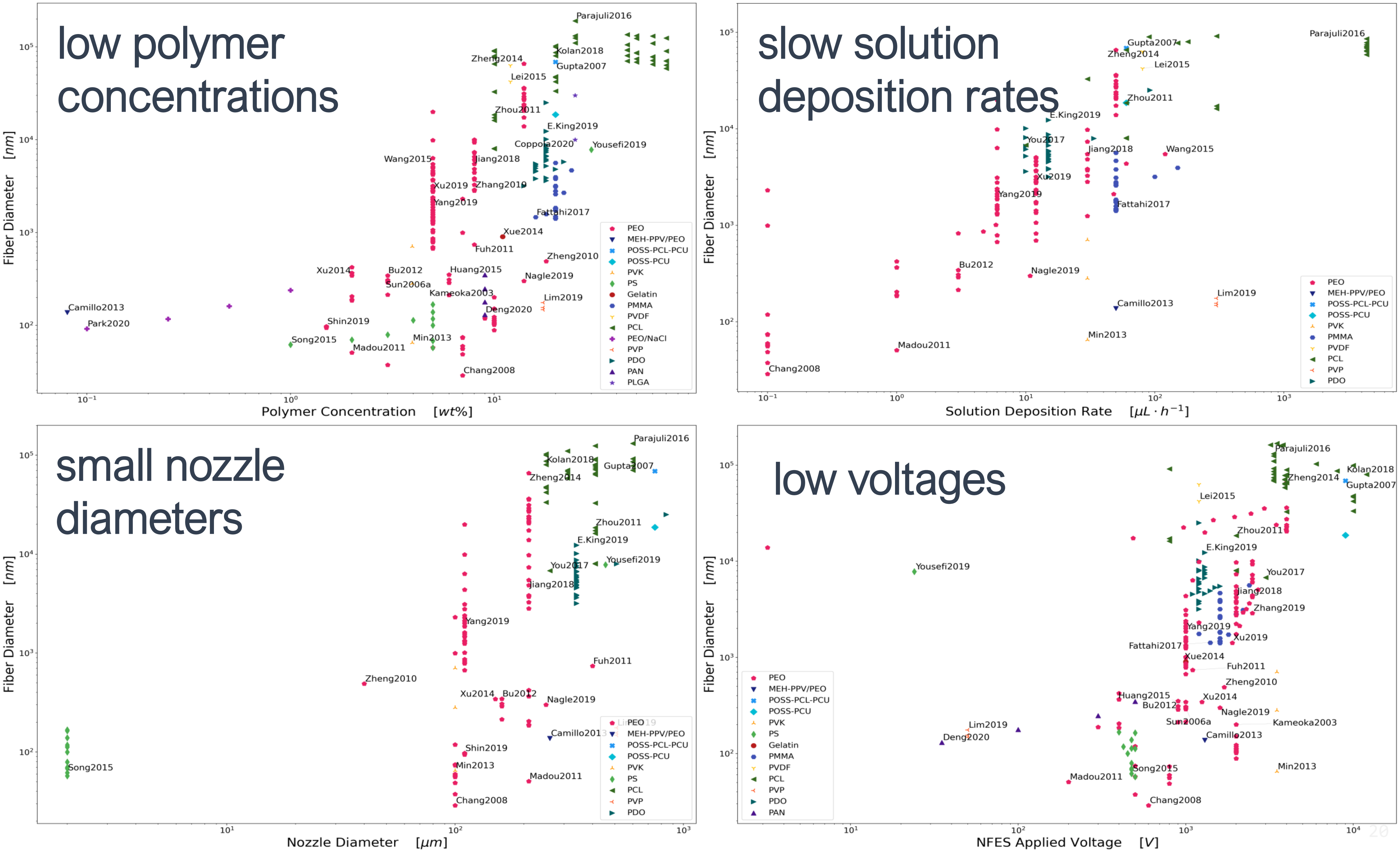
Figure from Camillo2013

https://github.com/katagirimx/OpenCV-image-measuring

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

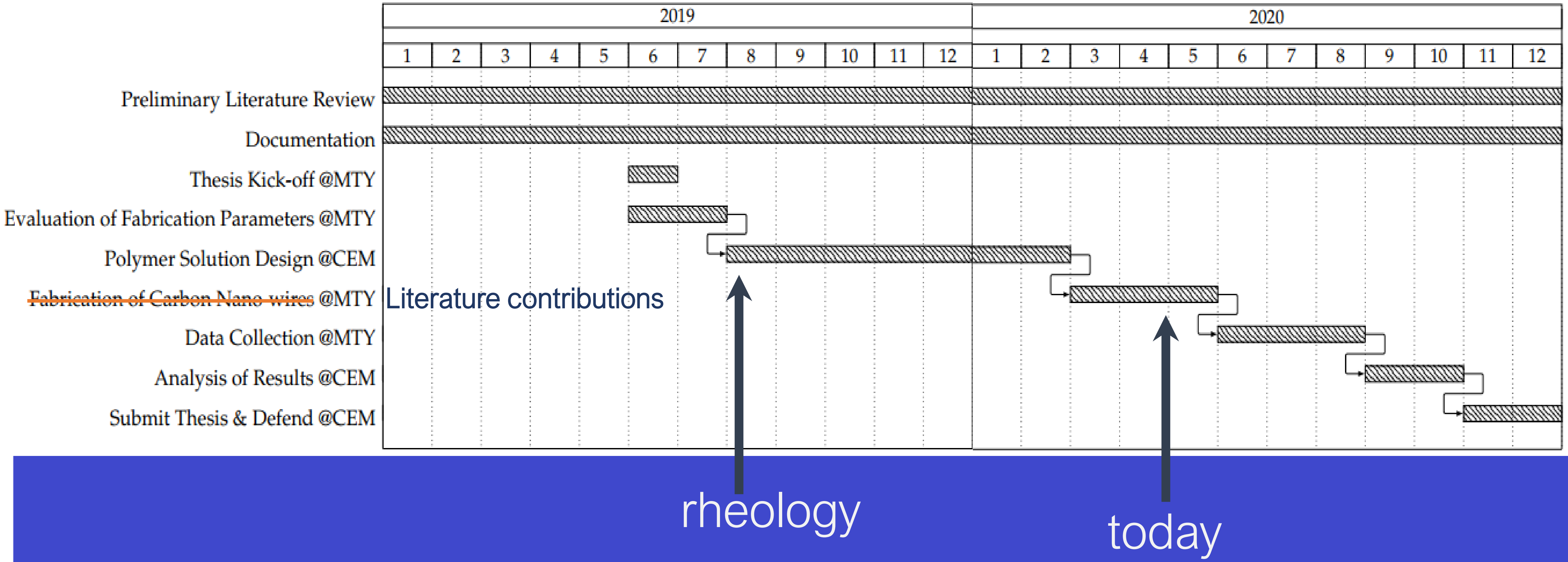
are the main drivers of the final Fiber Diameter




low polymer concentrations
Fiber Diameter [nm]
Polymer Concentration [wt%]
PEO
MEH-PPV/PEO
POSS-PCL-PCU
POSS-PCU
PVK
PS
Gelatin
PMMA
PVDF
PCL
PEO/NaCl
PVP
PDO
PAN
PLGA
slow solution deposition rates
Fiber Diameter [nm]
Solution Deposition Rate [μL · h⁻¹]
small nozzle diameters
Fiber Diameter [nm]
Nozzle Diameter [μm]
low voltages
Fiber Diameter [nm]
NFES Applied Voltage [V]

Overall Progress & Next Steps

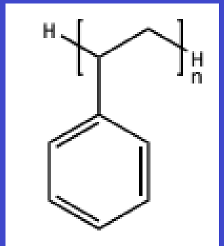
Current Work Plan



Next step: Study/Test the proposed polymer solutions

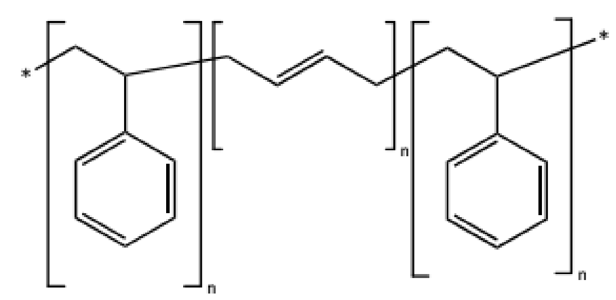
high carbon polymers and no oxygen

+35 wt% in THF



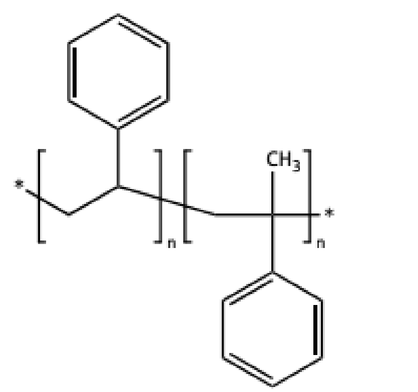
Polystyrene (PS)

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

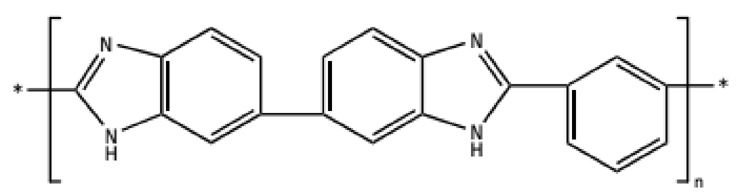


Poly(styrene-co-butadiene)

+15 wt% in DMF

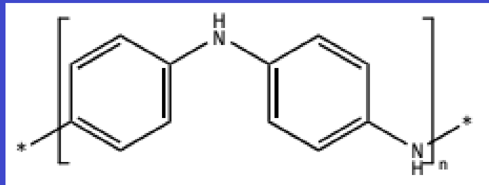


Poly(styrene-co-a-methylstyrene)



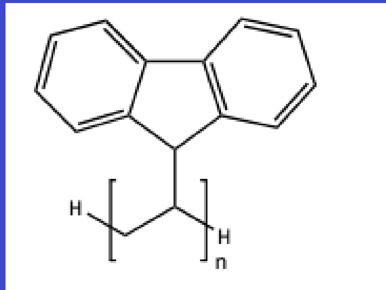
Polybenzimidazole (PBI)

No records



Polyaniline (PANI / emeraldine salt)

No records



Poly(9-Vinyl Carbazole) (PVK)

~8 wt% in CHL


Q
&
A