Search for High-Molecular Weight Linear polymers for the Formulation of Novel Solutions for the Fabrication of Micro-Fibers by Electromechanical Spinning

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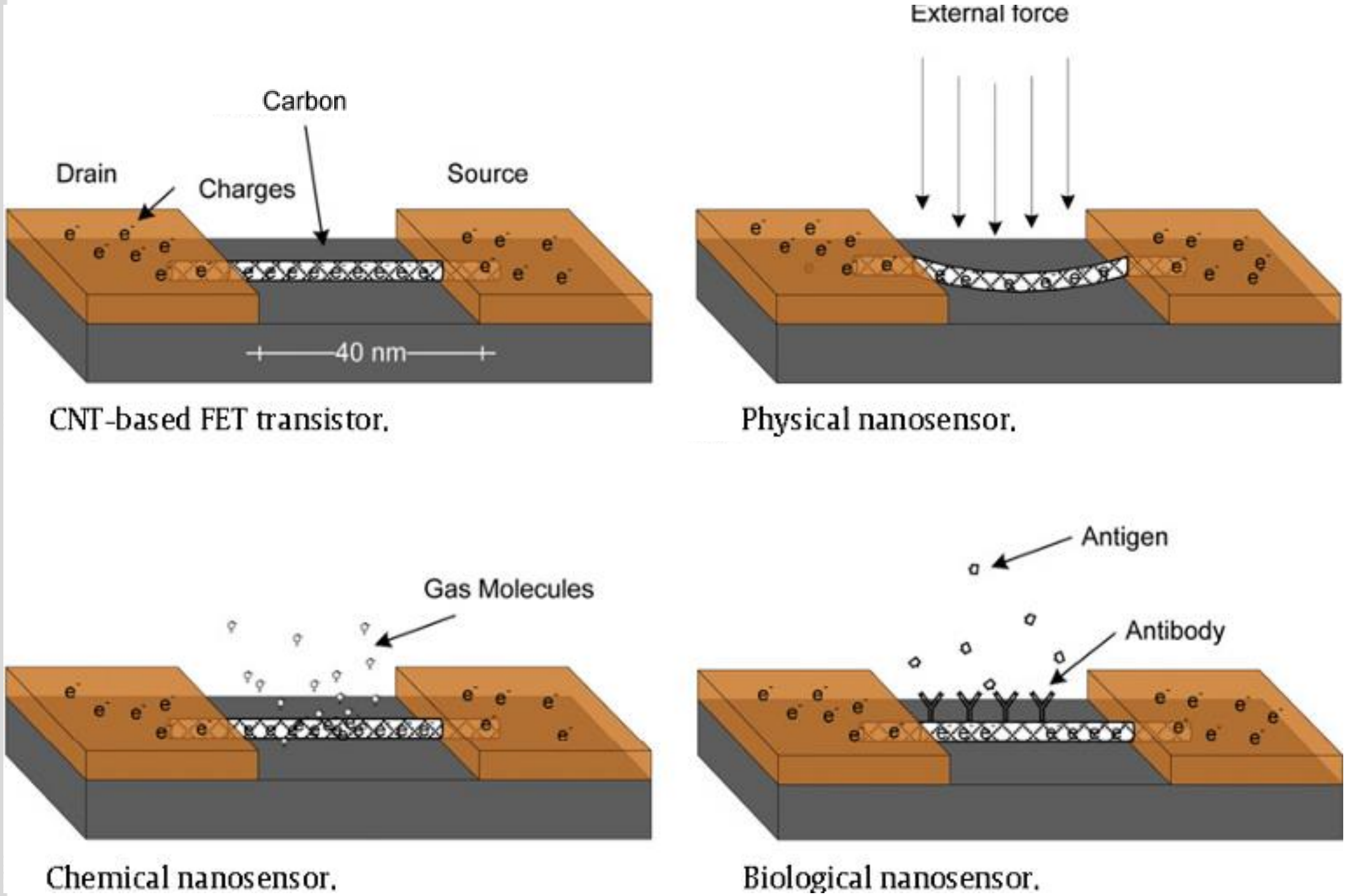
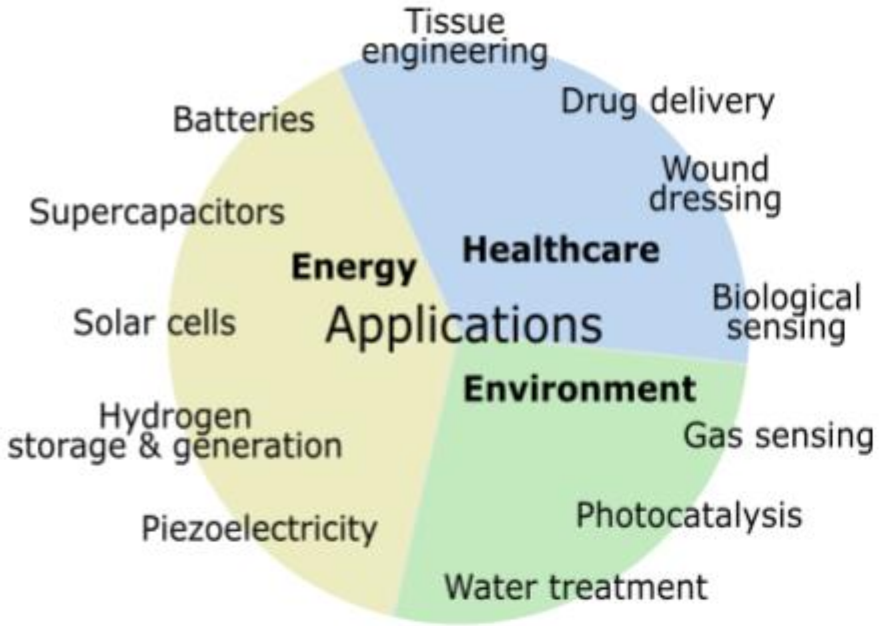
Committee Member:	**Dr. Marc Madou**
Committee Member:	**Dr. Jaime Bonilla Ríos**

02 Dec 2020

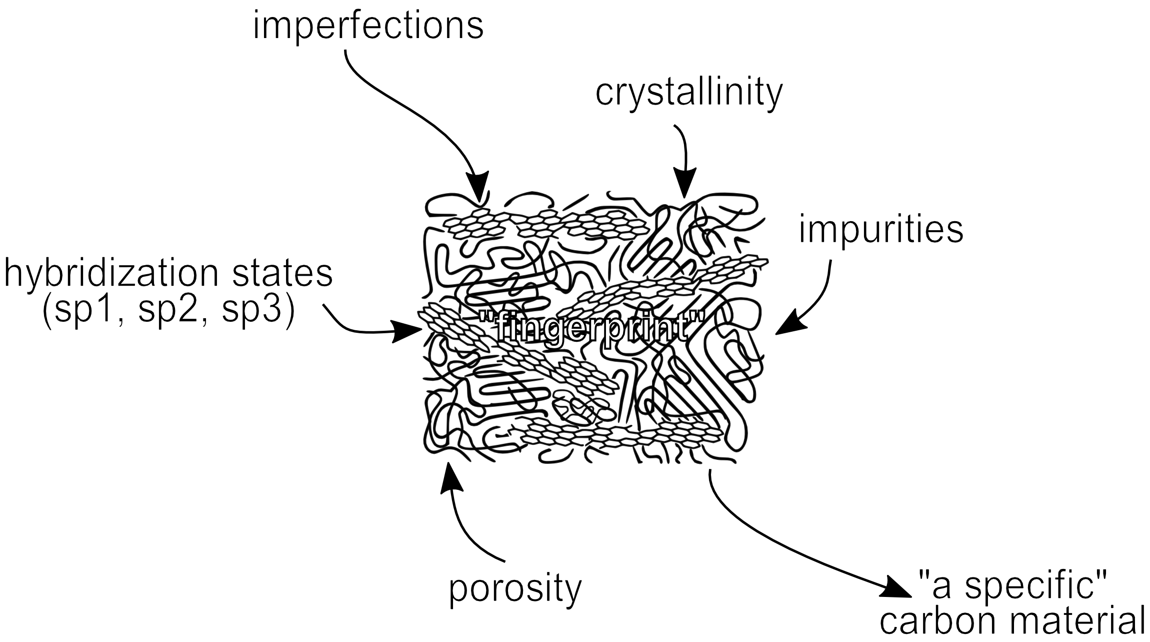
Glass-like Carbon NWs: Applications





V. Baudrit J, Nanosensors, Int. J. Biosens. Bioelectron. 3 (2017) 368–375.https://doi.org/10.15406/ijbsbe.2017.03.00084.
R.L. McCreery, Chem. Rev. 108 (2008) 2646–2687. https://doi.org/10.1021/cr068076m.
G. Speranza, C — J. Carbon Res. 5 (2019) 84. https://doi.org/10.3390/c5040084.

Carbon Based Nanomaterials (CBNs)

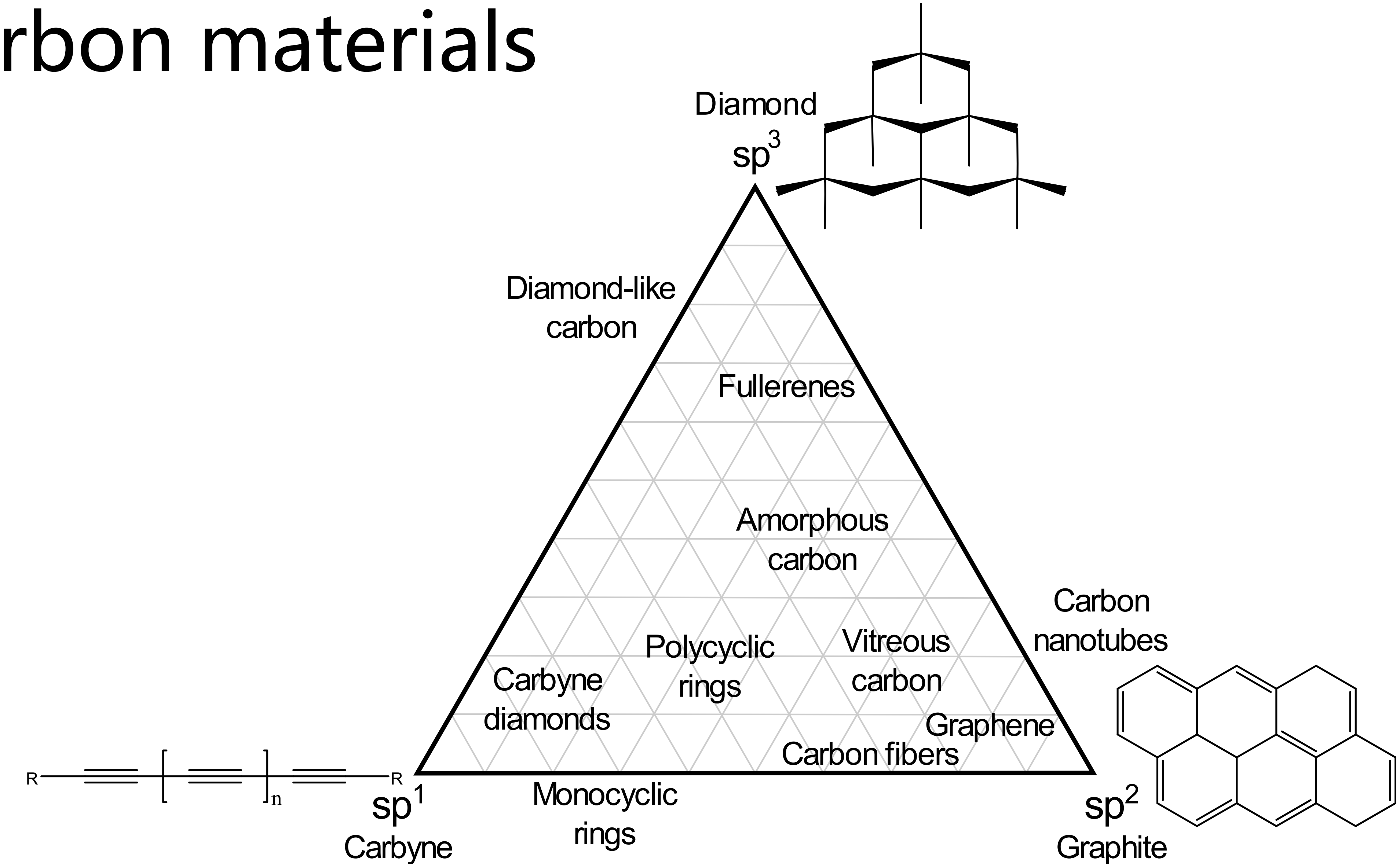


The crystallite size, molecular arrangement, and anisotropy determine the material's properties.

The interminable collection of CBNs range from soft, conductive lubricants to very hard, low conductivity solids; and from black colour, bulks to transparent, disordered thin films

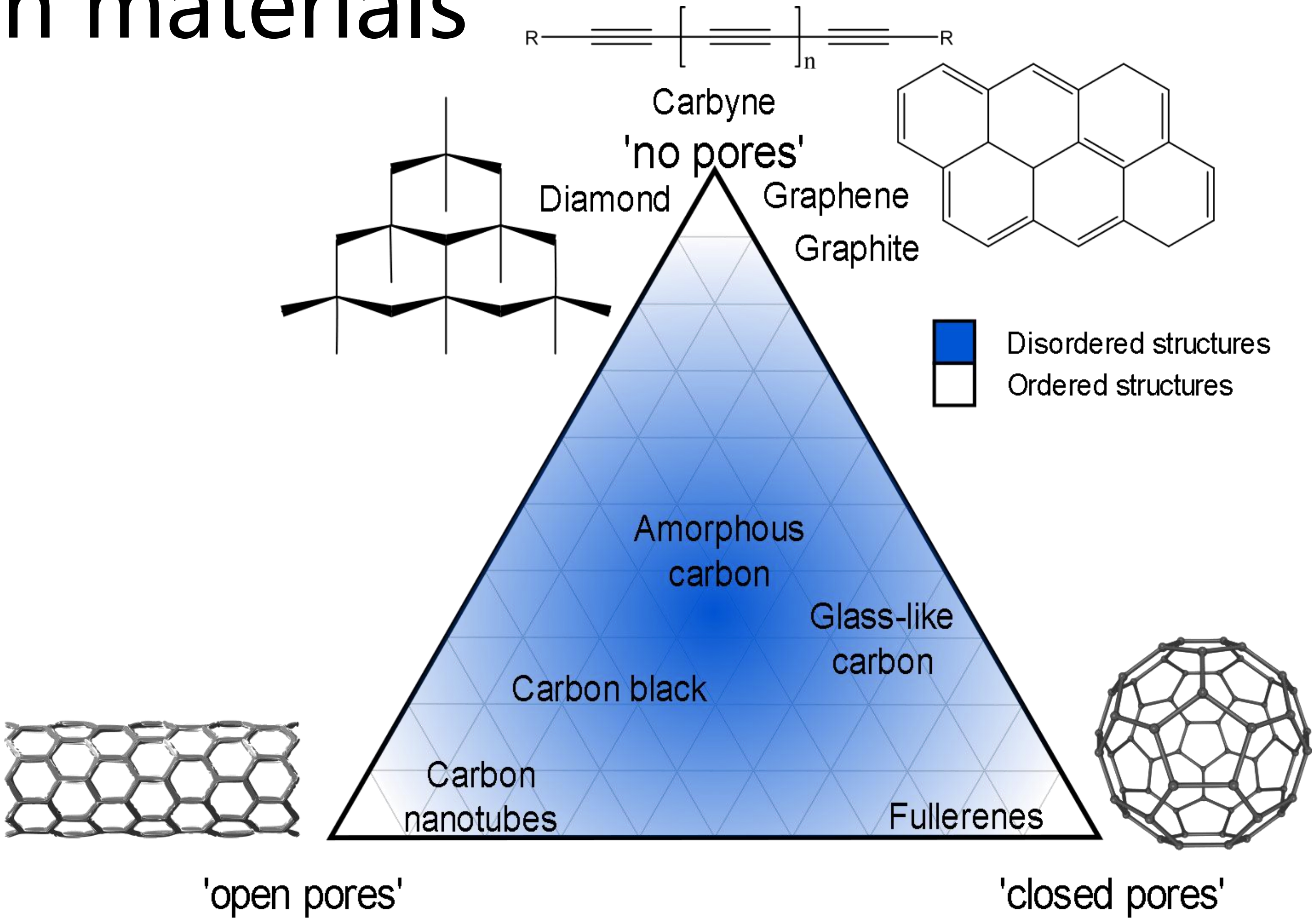
R.L. McCreery, Chem. Rev. 108 (2008) 2646–2687. https://doi.org/10.1021/cr068076m.
S. Beigi-Boroujeni, O. Katagiri-Tanaka, B. Cardenas-Benitez, S.O. Martinez-Chapa, A. Aguirre-Soto, Mater. Today Proc. (2020). https://doi.org/10.1016/j.matpr.2020.10.014.

Carbon materials



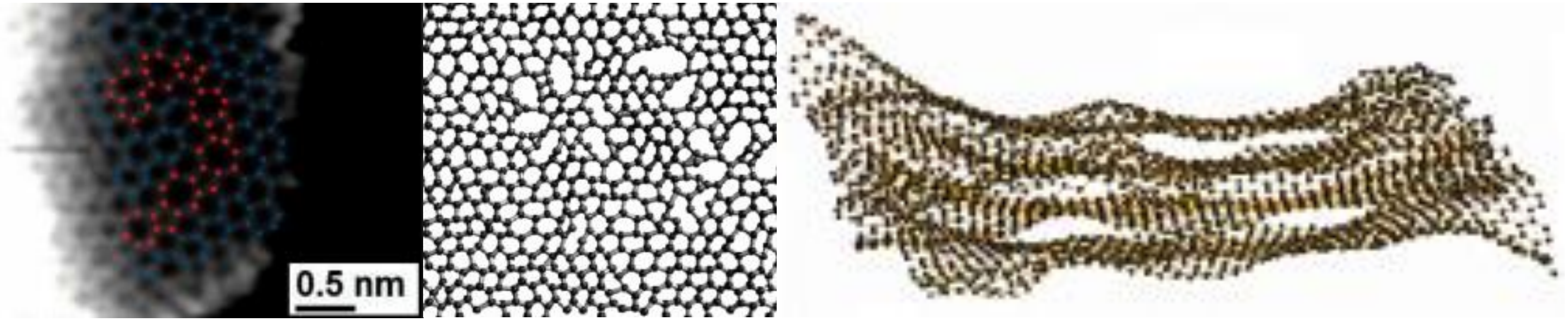
R.B. Heimann, S.E. Evsvukov, Y. Koga, Carbon N. Y. 35 (1997) 1654–1658. https://doi.org/10.1016/S0008-6223(97)82794-7.
E.A. Belenkov, Chelyabinsk State University, Chelyabinsk, Russia, 2003: p. 5.
M. Fedel, Elsevier, 2013: pp. 71–102. https://doi.org/10.1533/9780857093516.1.71.
M. Razeghi, Springer International Publishing, Cham, 2019. https://doi.org/10.1007/978-3-319-75708-7.
K. Alstrup Jensen, J. Bøgelund, P. Jackson, N. Raun Jacobsen, R. Birkedal, P. Axel Clausen, A. Thoustrup Saber, H. Wallin, U. Birgitte Vogel, The Danish Environmental Protection Agency, 2015.

Carbon materials



R.L. McCreery, Chem. Rev. 108 (2008) 2646–2687. https://doi.org/10.1021/cr068076m.
S. Beigi-Boroujeni, O. Katagiri-Tanaka, B. Cardenas-Benitez, S.O. Martinez-Chapa, A. Aguirre-Soto, Mater. Today Proc. (2020). https://doi.org/10.1016/j.matpr.2020.10.014.
Harry Marsh. Elsevier, Apr. 1989, p. 43. ISBN: 9780408038379. DOI: 10.1016/C2013- 0- 04111- 4. URL: https: //linkinghub.elsevier.com/retrieve/pii/C20130041114.
Pierson Hugh. Elsevier, 1994, p. 419. ISBN: 9780815513391.

Glass-like Carbon



Attractive for its electrochemical stability, thermal resistance, electrical conductivity, biocompatibility and is gas impermeable.

- It is used in the manufacture of semiconductors.

R.L. McCreery, Chem. Rev. 108 (2008) 2646–2687. https://doi.org/10.1021/cr068076m.
G. Speranza, C — J. Carbon Res. 5 (2019) 84. https://doi.org/10.3390/c5040084.

MicroChem's SU-8 & Tokai's recipe

Electrical resistivity, comparison:

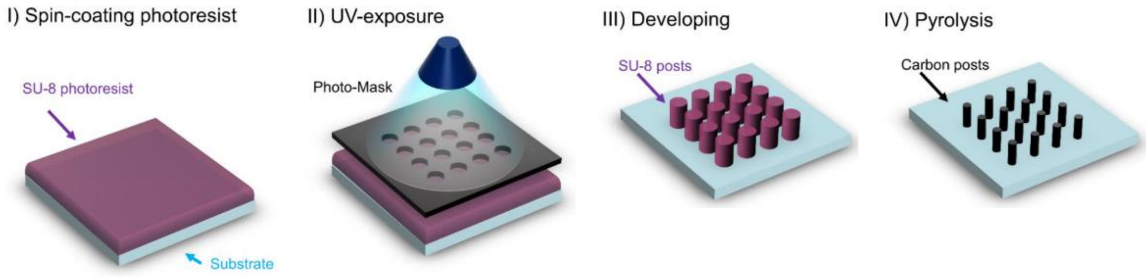
highly oriented pyrolytic graphite (HOPG)	< $\times 10^3$	TOKAI Glassy carbon	< x4	SU-8 glass-like carbon
		TOKAI CARBON		MICRO•CHEM

Tokai's recipe is a secret …

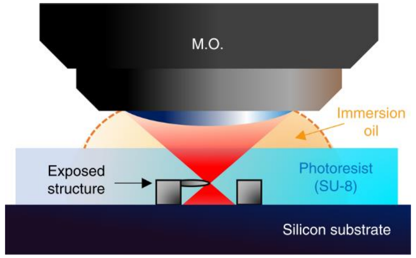
R.L. McCreery, Chem. Rev. 108 (2008) 2646–2687. https://doi.org/10.1021/cr068076m.
S. Beigi-Boroujeni, O. Katagiri-Tanaka, B. Cardenas-Benitez, S.O. Martinez-Chapa, A. Aguirre-Soto, Mater. Today Proc. (2020). https://doi.org/10.1016/j.matpr.2020.10.014.
G. Speranza, C — J. Carbon Res. 5 (2019) 84. https://doi.org/10.3390/c5040084.

Current approaches

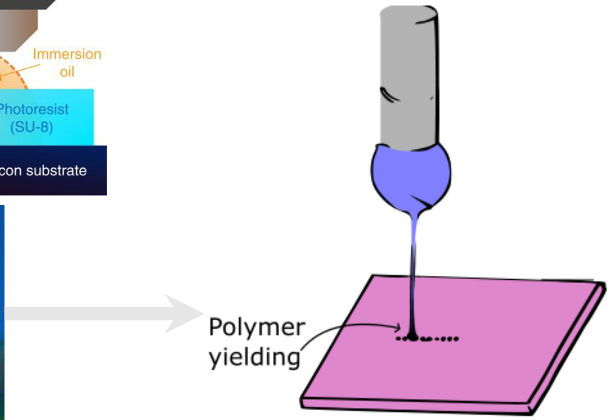
Photolithography
Physical & Optical Limitations



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

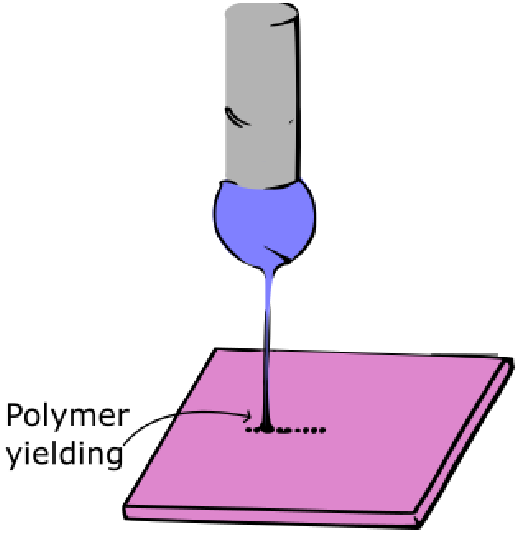


***Near-Field Electrospinning** (NFES)
Suspended Nanowires w/Spatial Control

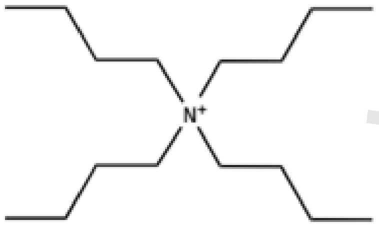


V. Galstyan, M. Bhandari, V. Sberveglieri, G. Sberveglieri, E. Comini, Metal Oxide Nanostructures in Food Applications: Quality Control and Packaging, Chemosensors. 6 (2018) 16. https://doi.org/10.3390/chemosensors6020016.
D. Kluge, J.C. Singer, B.R. Neugirg, J.W. Neubauer, H.-W. Schmidt, A. Fery, Top–down 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.

MicroChem's SU-8



However, SU-8 as is not electrospinnable
SU-8 does not have the right viscosity & solution conductivity.
SU-8 is design for photolithography.



Tetrabutylammonium tetrafluoroborate (TBF)

SU-8 + TBF + PEO formulation:
TBF to increase the solution conductivity

Poly(ethylene oxide) (PEO)

& PEO to provided the required viscosity

… both needed for smooth PEO flow during electrospinning

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

Problem Statement

- Properties of an electrospun fiber depend on many parameters,
- and each parameter also depends on the polymer-solvent system.

Solution Parameters:
- Concentration
- Molecular weight
- Viscosity
- Electrical conductivity

Ambient Parameters:
- Humidity
- Temperature

Process Parameters:
- Applied Voltage
- Flow rate
- Working distance

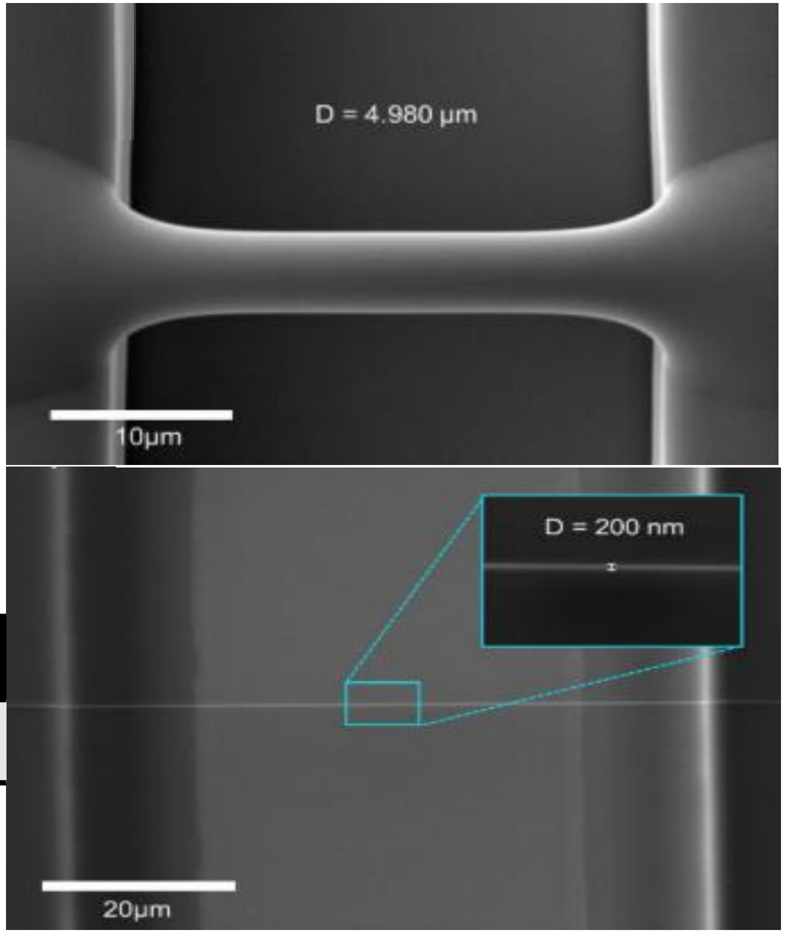
The interdependence between the process and solution parameters presents a challenge to predict the fiber diameter.

S.B. Gadkari, Scaling analysis for electrospinning, Springerplus. 3 (2014) 705. https://doi.org/10.1186/2193-1801-3-705.

Best Results so far by NFES (previous work)

Fiber yield rate of 81 %
Fiber diameter before pyrolysis of 4.966 µm
Fiber diameter after pyrolysis of 204 nm
Fiber length of 60.5 ± 4.3 µm
Fiber resistance from 407 KΩ to 1.727 MΩ

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



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B. Cárdenas Benítez, Advanced Manufacturing Techniques for the Fabrication and Surface Modification of Carbon Nanowires, Tecnológico de Monterrey, 2017.

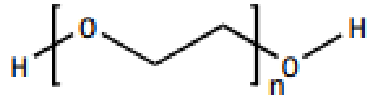
Implications of PEO

The fiber yield rate and fiber conductivity are impacted negatively as PEO introduces more oxygen to the solution

Some samples are destroyed during pyrolysis

High variance in the obtained conductivity across samples.

The addition of oxygen modifies the carbon structure.



Poly(ethylene oxide) (PEO)

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

Objectives

Objectives

General. Formulate polymer/solvent combinations that have the greatest potential to replace or modify the SU-8/PEO formulation for the fabrication of microscopic polymer fibers that may be converted to conductive suspended carbon nano-wires.

Specific1. Learn how the diameter of the electrospun polymer fiber can be controlled by appropriate tuning of the NFES parameters and solution properties.

Specific2. Through rheological analyses, determine if polymer solutions have comparative viscoelastic properties to those of the SU-8/PEO benchmark, and if they can be easily electrospun by NFES.

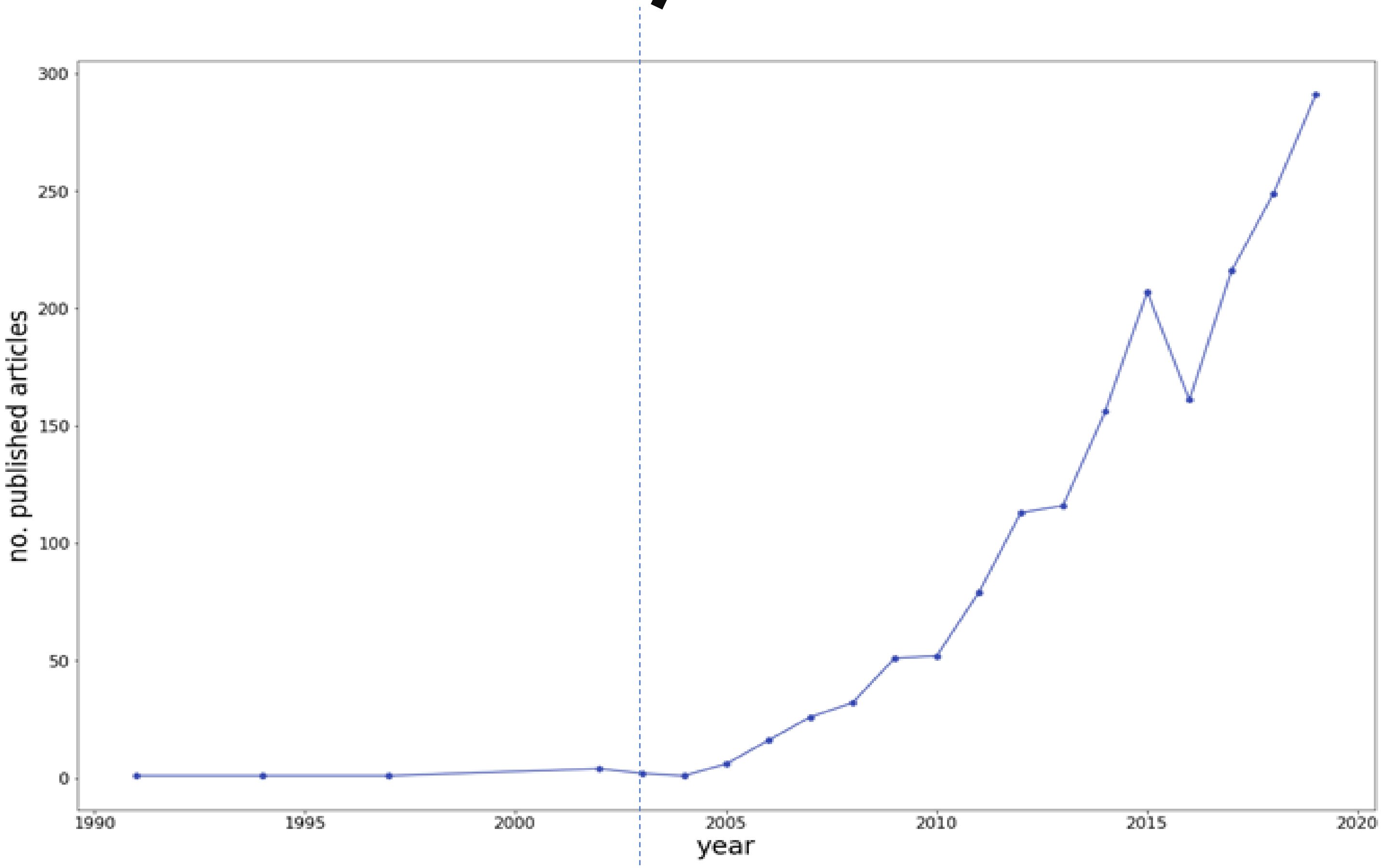
Specific3. Propose alternatives to the SU-8/PEO benchmark formulation for the production of microscopic polymer fibers with potential for the fabrication of carbon nano-wires.

NFES literature review

Specific Objective 1. Learn how the diameter of the electrospun polymer fiber can be controlled by appropriate tuning of the NFES parameters and solution properties.

Methods: NFES literature

(first NFES apparatus built in 2003 by J. Kameoka et al.)



- Thinnest polymeric fiber was achieved by C. Chang et al. with ~50 nm in diameter. (PEO in water)
  However, fiber yield rate was not reported

- Madou et al. recently achieved diameters as low as 4 nm after pyrolysis

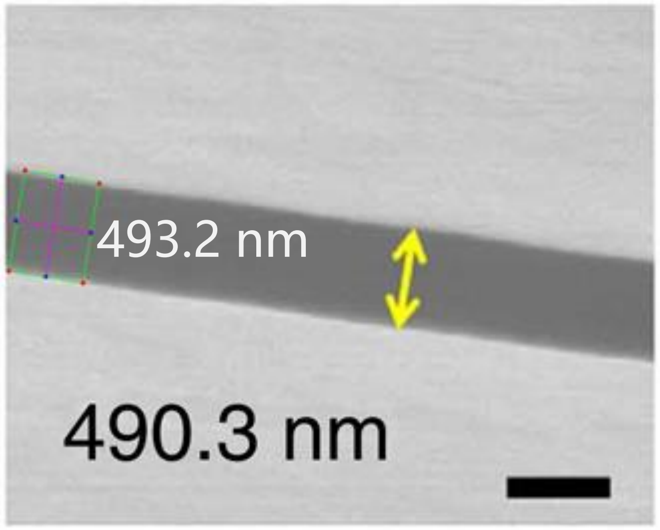
J. Deng, C. Liu, M. Madou, Nanoscale. (2020). https://doi.org/10.1039/D0NR00031K..
C. Chang, K. Limkrailassiri, L. Lin, Appl Phys Lett. (2008) 3. https://doi.org/10.1063/1.2975834.

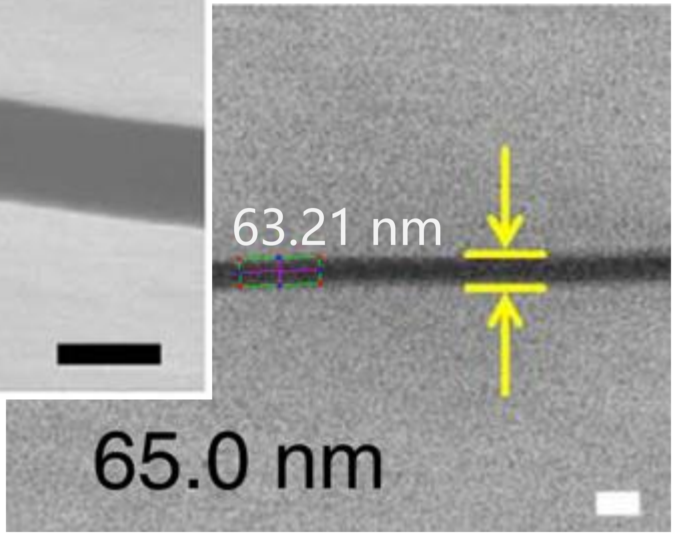
Methods: Data collection

(analysis of NFES articles from 2003 to 2020)

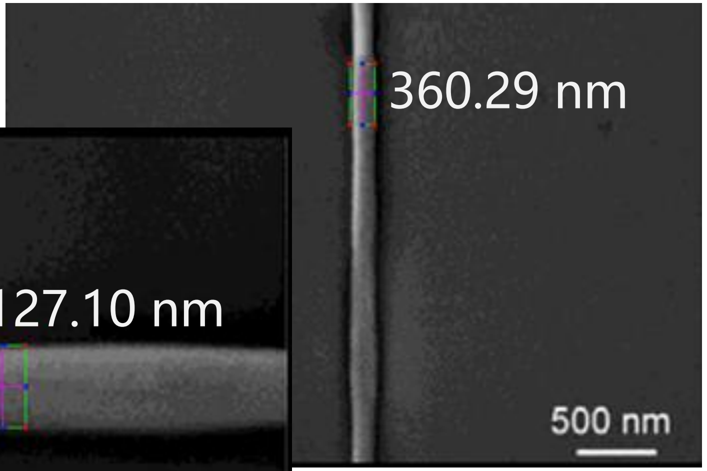
The author does not mention the fiber diameter in writing but provides a EM characterization.

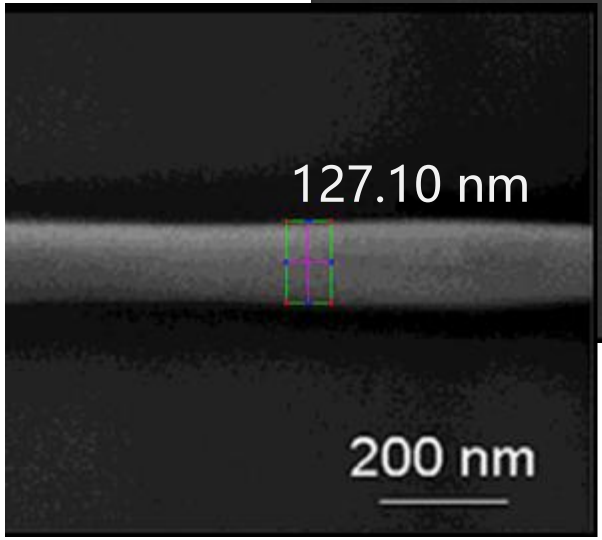
Python Image Analysis (with a 3.2% error in avg.):





Figures from Min2013



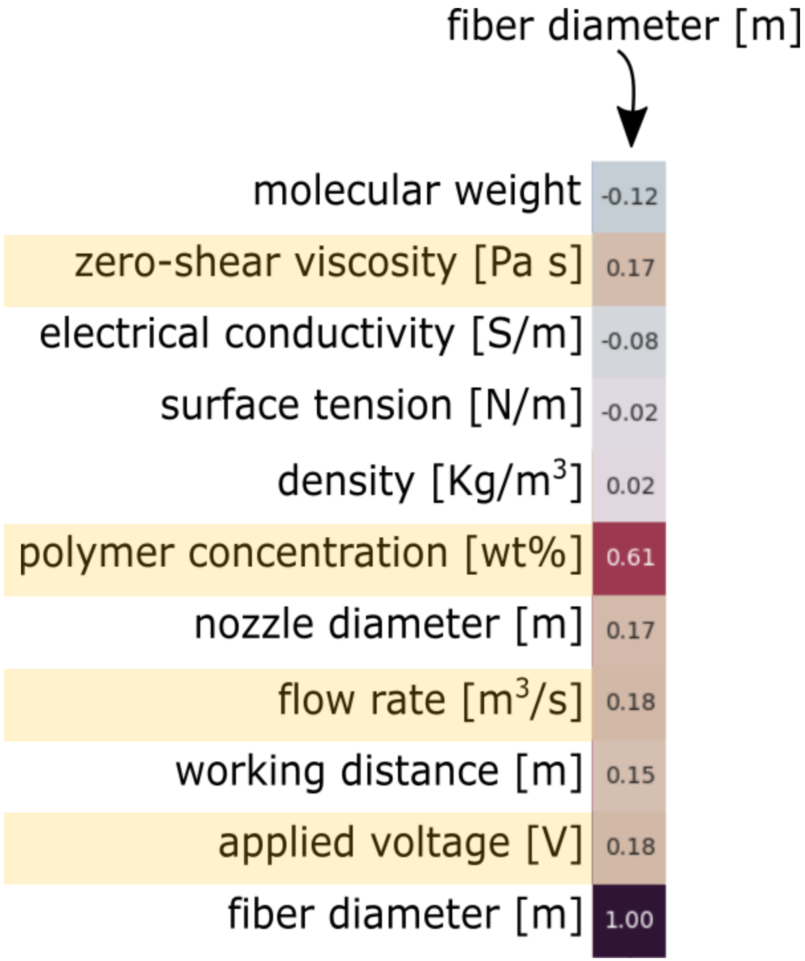


Figures from Camillo2013

S.-Y. Min, T.-S. Kim, B.J. Kim, H. Cho, Y.-Y. Noh, H. Yang, J.H. Cho, T.-W. Lee, Nat. Commun. 4 (2013) 1773. https://doi.org/10.1038/ncomms2785..
https://github.com/katagirimx/OpenCV-image-measuring
D. Di Camillo, V. Fasano, F. Ruggieri, S. Santucci, L. Lozzi, A. Camposeo, D. Pisignano, Nanoscale. 5 (2013) 11637–11642. https://doi.org/10.1039/C3NR03094F.

Relevant Parameters:

Matrix of Pearson linear correlation coefficients, built with Python's seaborn package.



- Zero-shear viscosity,
- Polymer Concentration,
- Solution Flow Rate,

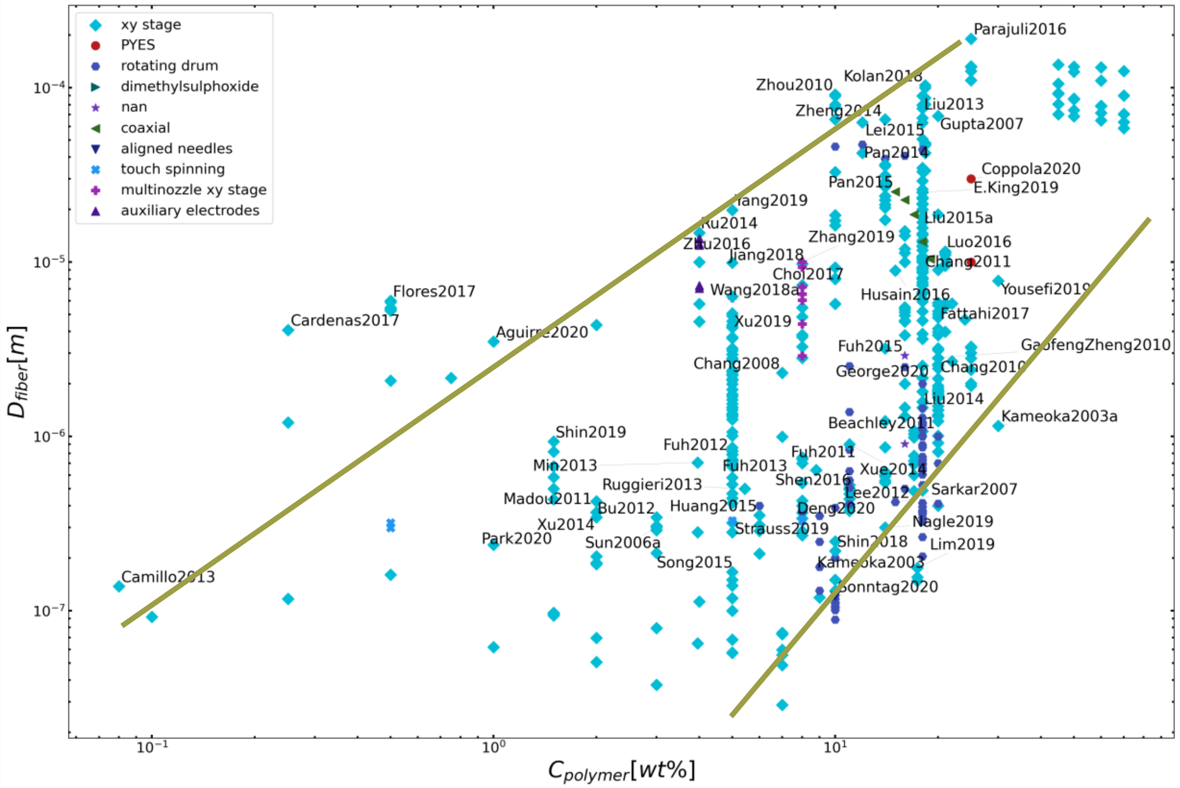
  &

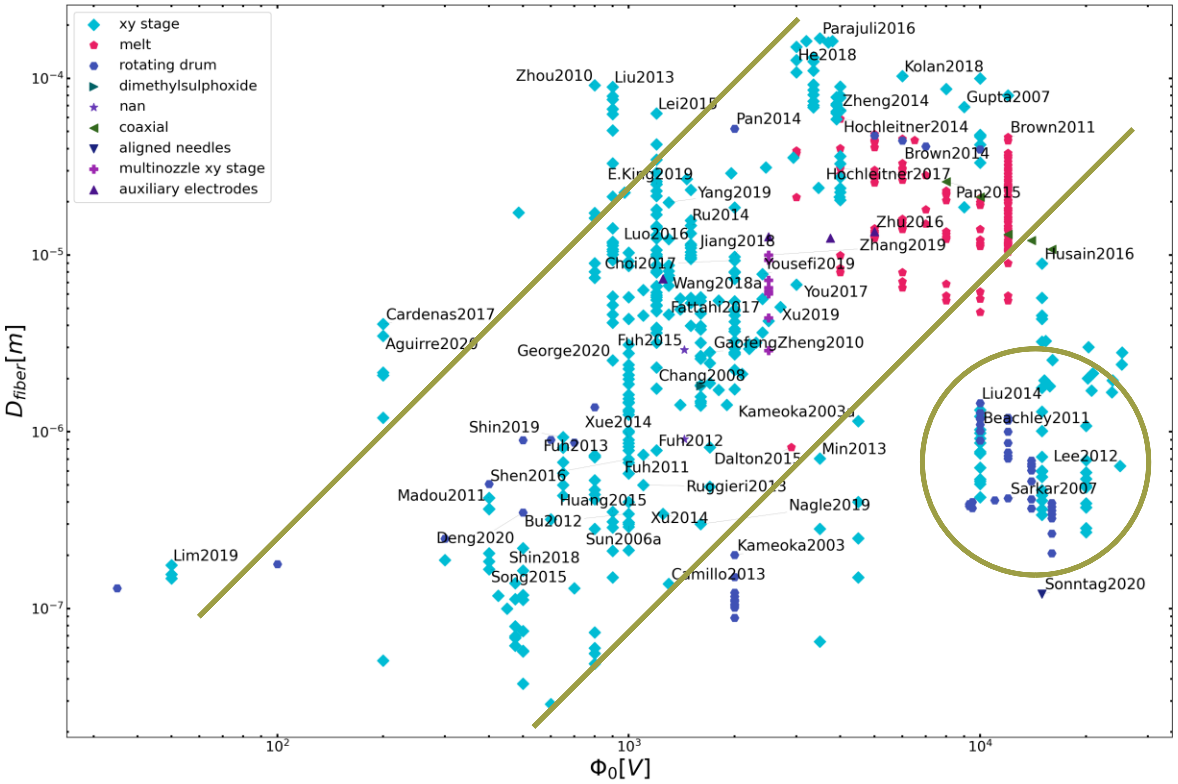
- Applied Voltage

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

Conclusion 1.2: Let's focus on polymer concentration

Polymer concentration is the most reliable process parameter to control the morphology of electrospun fibers. (regardless the type of NFES process)





Diameter Prediction of Electrospun Fibers

The fiber morphology not only depends on the process parameters, but also on the type of electrospinning process and on polymer-solvent system.

"[…] the fiber diameter decreases as the applied voltage increases."
Helgeson et al.

"[…] neither the collecting distance nor the applied voltage has large influences on fiber diameter […]"
Zhang et al.

"[…] while decreasing the voltage could also be used to reduce the average fiber diameter."
Brown et al.

The existing interdependence between the process and solution parameters adds complexity and ambiguity to the effect of each parameter

Siddharth B. Gadkari. In: SpringerPlus 3.1 (Dec. 2014), p. 705. ISSN: 2193-1801. DOI: 10.1186/2193-1801-3-705.
B. Zhang, F. Kang, J.-M. Tarascon, J.-K. Kim, Prog. Mater. (2016) https://doi.org/10.1016/j.pmatsci.2015.08.002.
M.E. Helgeson, K.N. Grammatikos, J.M. Deitzel, N.J. Wagner, Polymer (2008) https://doi.org/10.1016/j.polymer.2008.04.025.
T.D. Brown, F. Edin, N. Detta, A.D. Skelton, D.W. Hutmacher, P.D. Dalton, Mater. Sci. Eng. C. 45 (2014) 698–708. https://doi.org/10.1016/j.msec.2014.07.034.

Diameter Prediction of Electrospun Fibers

Helgeson and Wagner have presented an adimensional analysis to predict the fiber diameter with conservation equations of momentum, mass, electric charge and four dimensionless numbers:

$$\text{Peclet number } Pe = \frac{2\bar{\varepsilon} v_0}{K R_0} \qquad \text{Reynold number } Re = \frac{\rho v_0 R_0}{\eta_0} \qquad \text{Weber number } We = \frac{\rho {v_0}^2 R_0}{\gamma}$$

Correlation between the electrostatic and viscous forces:

$$\Pi_1 = Re Pe \Psi = \frac{2\bar{\varepsilon}^2 {\Phi_0}^2}{K \eta_0 L^2}$$

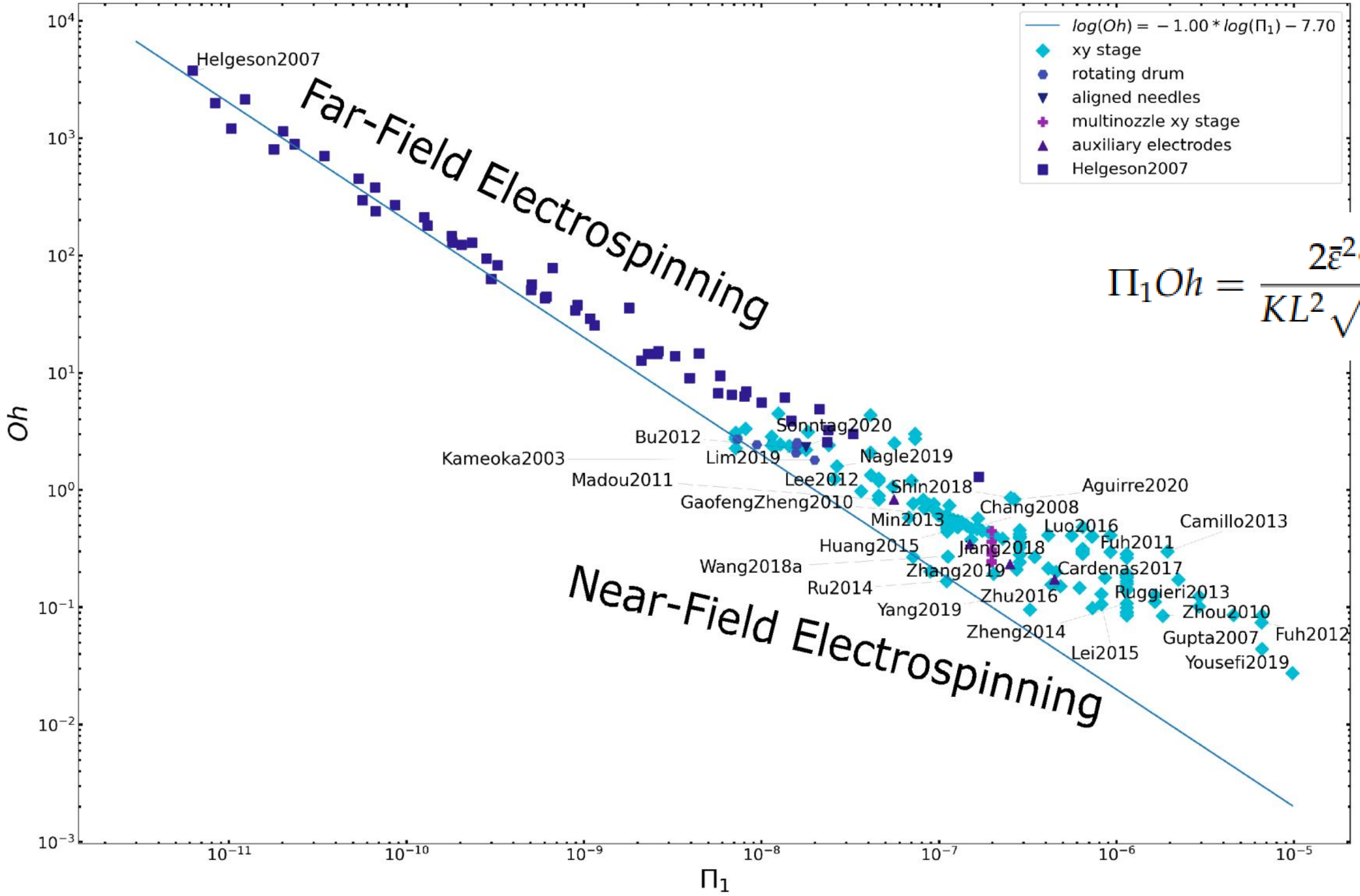
Ohnesorge number (jet behaviour and capillary rupture):

$$Oh = \frac{Re^2}{We} = \frac{\eta_0}{\sqrt{\rho \gamma R_{jet}}}$$

Helgeson gets rid of unknown or hard to measure parameters, such as the initial jet velocity.

M.E. Helgeson, N.J. Wagner, AIChE J. 53 (2007) 51–55. https://doi.org/10.1002/aic.11056.

Diameter Prediction of Electrospun Fibers



$$\Pi_1 Oh = \frac{2\bar{\varepsilon}^2 {\Phi_0}^2}{KL^2\sqrt{\rho\gamma R_{jet}}} = 2.5 \pm 0.2 \times 10^{-8}$$

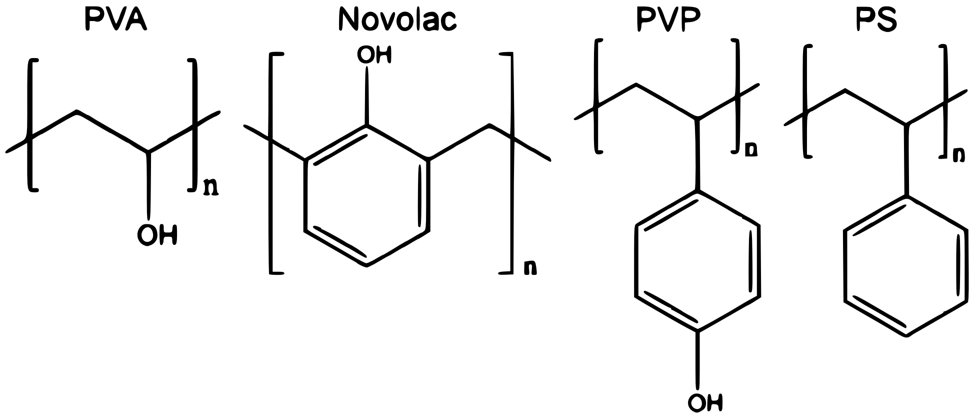
M.E. Helgeson, N.J. Wagner, AIChE J. 53 (2007) 51–55. https://doi.org/10.1002/aic.11056.

Rheology Analyses

Specific Objective 2. Through rheological analyses, determine if polymer solutions have comparative viscoelastic properties to those of the SU-8/PEO benchmark, and if they can be easily electrospun by NFES.

Selection of Polymer-Solvent combinations

Zhenan Bao et al. investigated the effect of the polymer chemical Structure of:



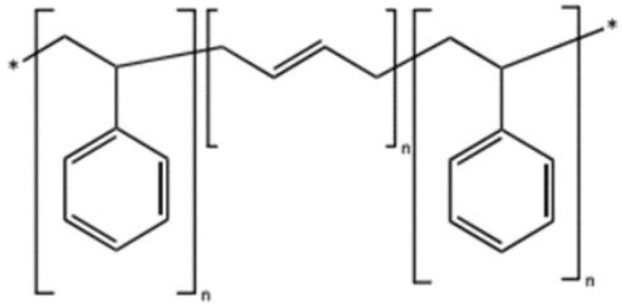
- higher sp2 carbon content translates into higher graphitization degree and higher electrical conductivity

- polymers with functional groups are required for the creation of smooth and continuous fibers.

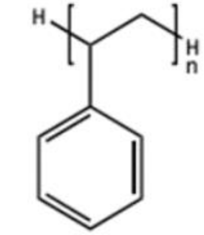
N. Liu, K. Kim, H.Y. Jeong, P.C. Hsu, Y. Cui, Z. Bao,, ACS Nano. 9 (2015) 9043–9049. https://doi.org/10.1021/acsnano.5b03134.

Conclusion1.3: Selection of Polymer-Solvent combinations

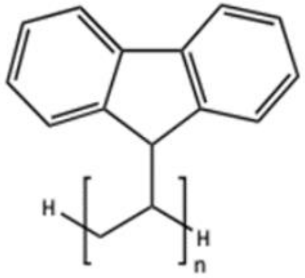
Polymers with **high carbon content** relative to **oxygen content**



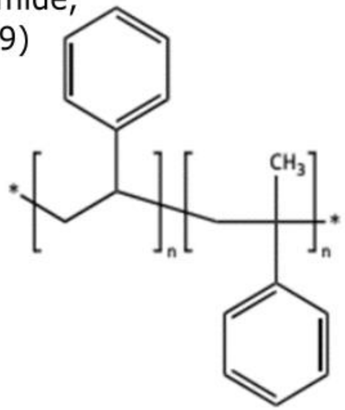
Poly(styrene-co-butadiene)
in Tetrahydrofuran, N,N-Dimethylformamide, and 1-Methyl-2-Pyrrolidinone (Fong1999)



Polystyrene (PS)
in Tetrahydrofuran (Yousefi2019)



Poly(9-Vinyl Carbazole) (PVK)
in Chloroform (Min2013)



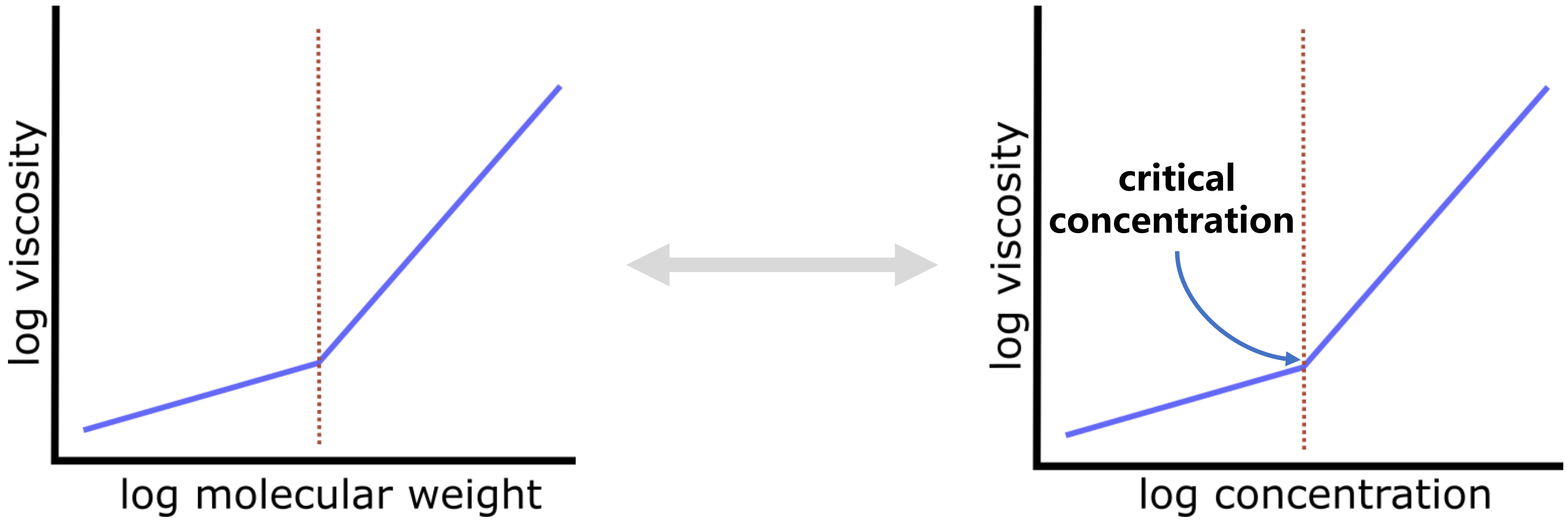
Poly(styrene-co-a-methylstyrene)
in N,N-Dimethylformamide (no records)

A.A. Yousefi, A.R. Mohebbi, S. Falahdoost Moghadam, S.A. Poursamar, L. Hao, Sol. Energy. 188 (2019) 1111–1117. ttps://doi.org/10.1016/j.solener.2019.07.007.
H. Fong, D.H. Reneker, J. Polym. Sci. Part B Polym. Phys. 37 (1999) 3488–3493. https://doi.org/10.1002/(SICI)1099-0488(19991215)37:24<3488::AID-POLB9>3.0.CO;2-M.
S.-Y. Min, T.-S. Kim, B.J. Kim, H. Cho, Y.-Y. Noh, H. Yang, J.H. Cho, T.-W, Nat. Commun. 4 (2013) 1773. https://doi.org/10.1038/ncomms2785.

Literature claims

- As "electrospinnability" is determined by the **polymer chain entanglement**,
- **chain entanglement** is controlled by *molecular weight*,
- increasing *molecular weight* increases viscosity, and
- viscosity is controlled by **polymer concentration**, then

The **critical/spinnable concentration** can be found in a **viscosity vs. concentration** plot



D.R. Flores, Role of rheological properties in near field electrospun fibers morphology, (2017) 130.
G.L. Wilkes, J. Chem. Educ. 58 (1981) 880. https://doi.org/10.1021/ed058p880.

Methods: # Sample Preparation (SU8-PEO)

Sample	Weight Percent $wt\%$		
	SU-8	**PEO**	**TBF**
1	99.50	0.00	0.50
2	99.25	0.25	0.50
3	99.00	0.50	0.50
4	98.75	0.75	0.50
5	98.50	1.00	0.50
density [g/ml]	1.123		

3.0 ml samples
on a heating plate at 160 rpm and 60°C, for 2 hours each.

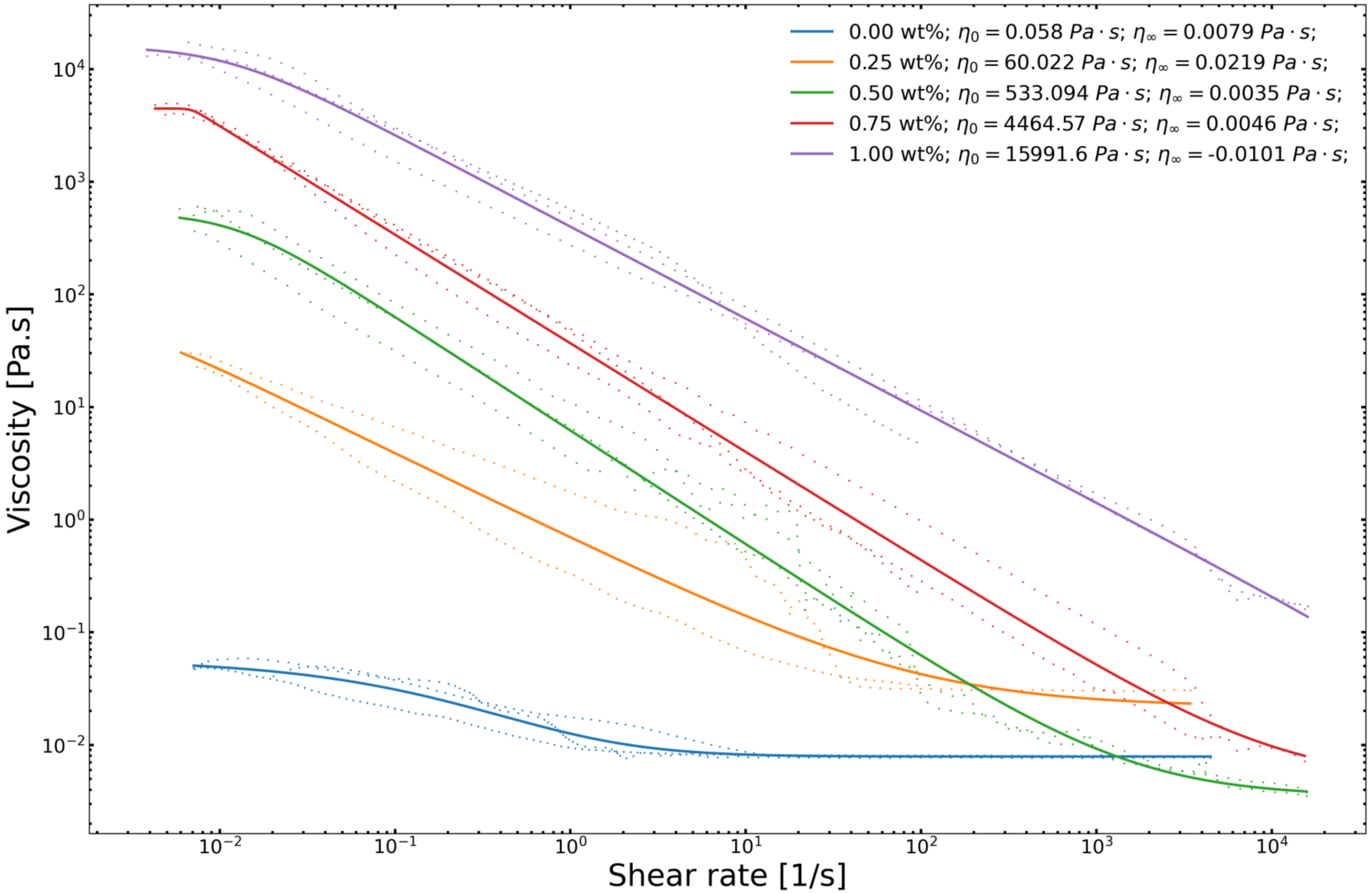
A salt (TBF) was added to all the samples to increase the electrical conductivity

Methods: Rheology – Frequency Sweeps

Geometry:
Steel cone plate, Peltier plate
(60.0 mm diameter, 0.9979° cone angle,
23 µm truncation)

Procedure:
Frequency sweep
(20°C, for 20 min
from 10^{-3} to 10^{4} 1/s shear rates)

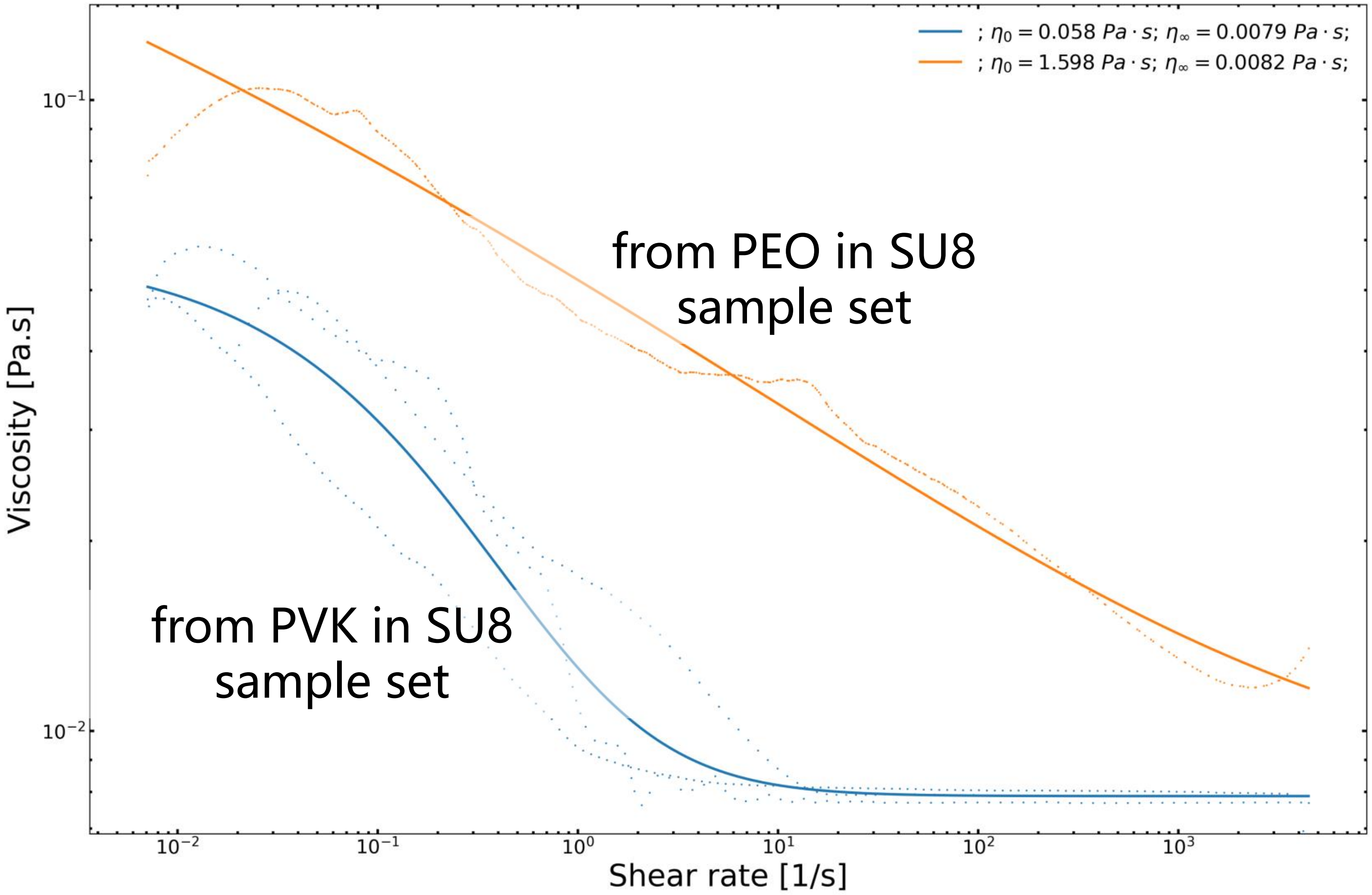
Methods: # The Carreau-Yasuda Model



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

η : viscosity
$\dot{\gamma}$: shear rate
η_∞ : infinite shear rate viscosity
η_0 : zero shear rate viscosity
κ : time constant
n : Power Law index
a : width of the transition region

Methods: Rheology results validation for 0wt% PEO and 0wt% PVK



Measured:

$(8.05 \pm 0.28)\ \mathrm{mPa \cdot s}$

vs.

MicroChem data sheet:

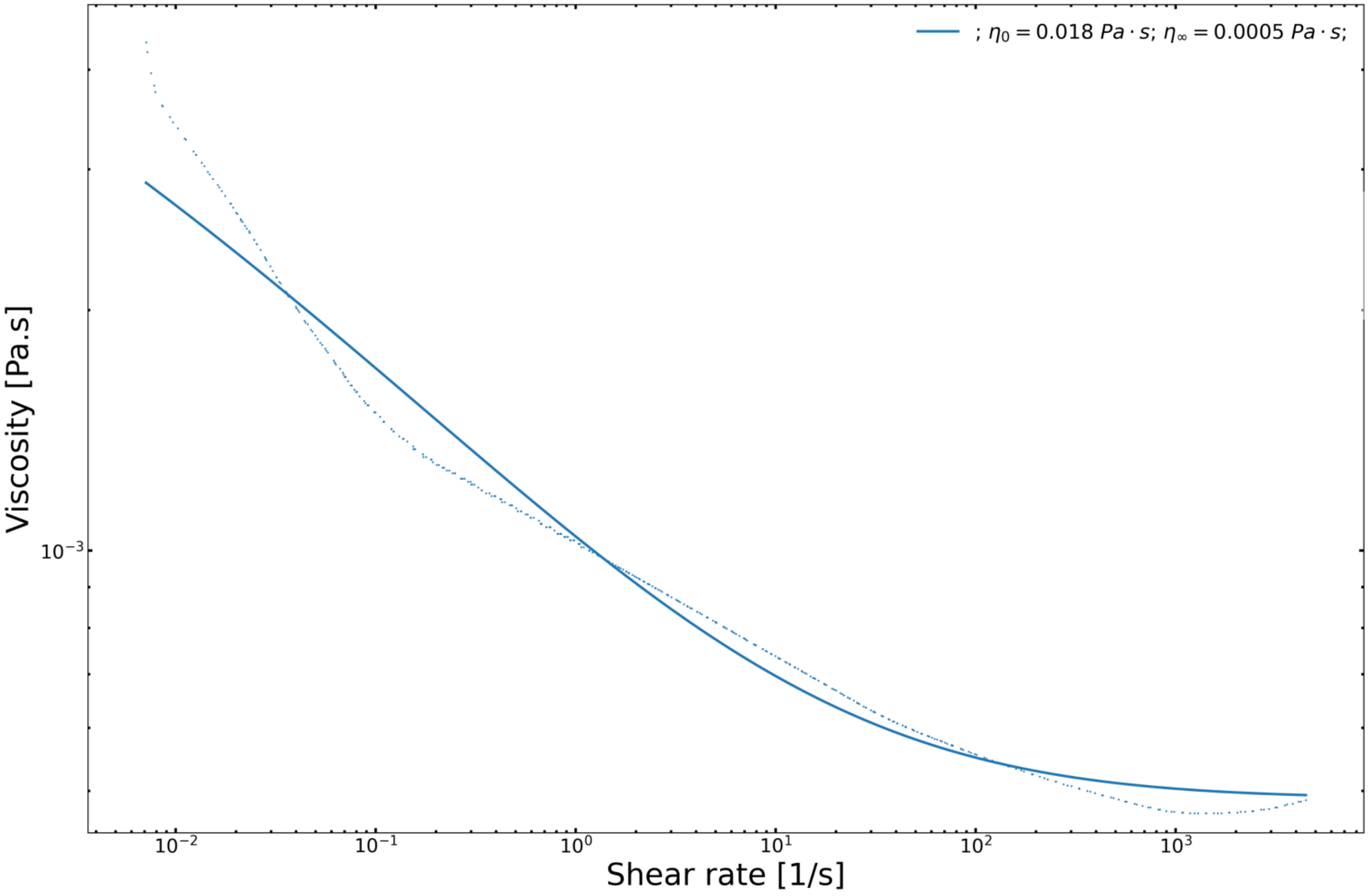
$$\frac{7.5\mathrm{cSt}\ (1.123\mathrm{g/ml})}{1000\mathrm{cSt} \cdot \mathrm{s} \cdot \mathrm{m} \cdot \mathrm{g/ml} \cdot \mathrm{Kg}}$$

$= 8.422\ \mathrm{mPa \cdot s}$

$1.09\ \% error$

Microchem, Su-8 2000.5, 2002, 2005, 2007, 2010, 2015, Microchem. (2018) 1–5. papers3://publication/uuid/859F51B9-0382-4DE8-88A9-267F936939A3.

Methods: Rheology results validation for 0wt% PVK



Measured CHL viscosity:
$0.499\ \mathrm{mPa \cdot s}$

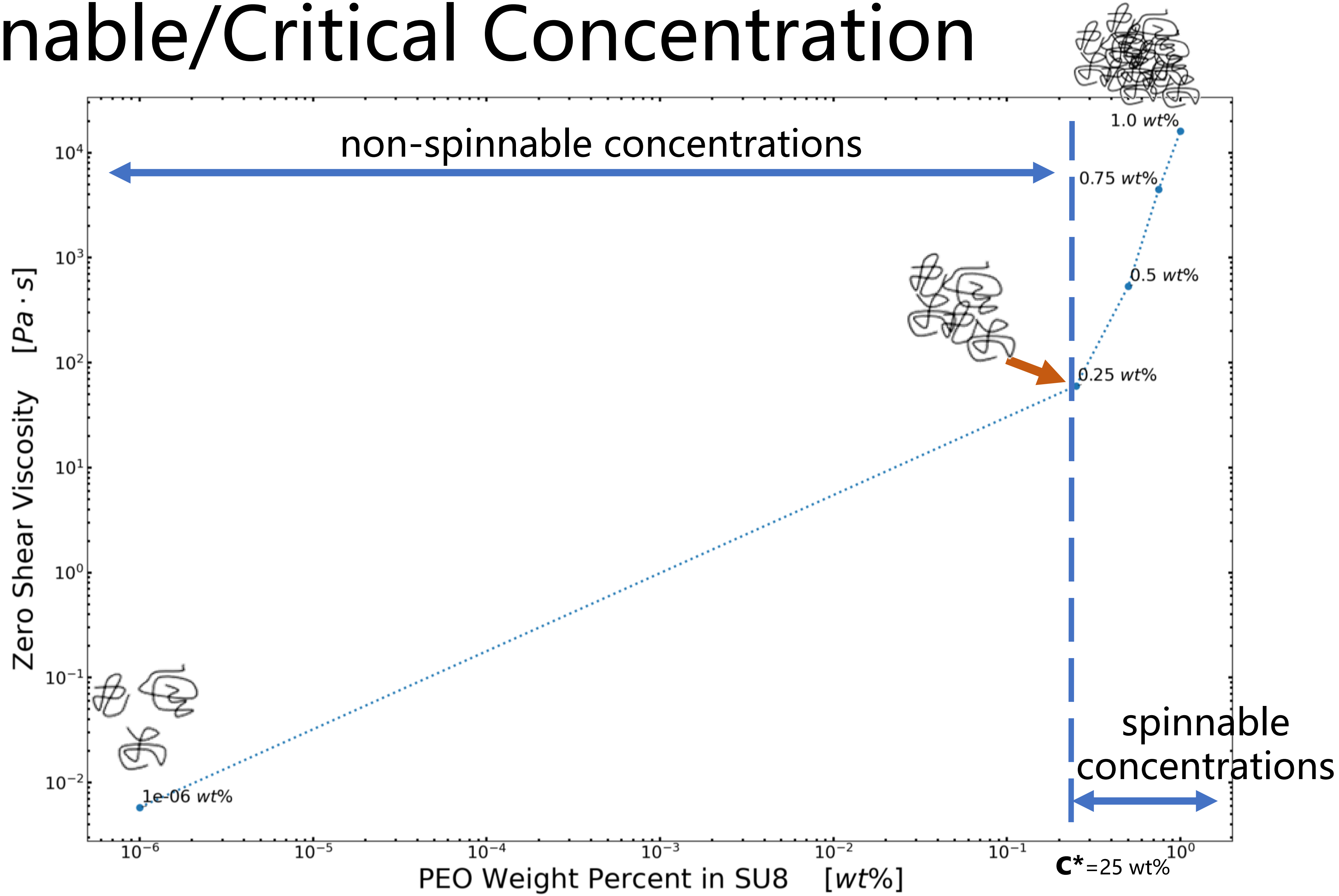
vs.

Anton-Paar data sheet:
$0.563\ \mathrm{mPa \cdot s}$

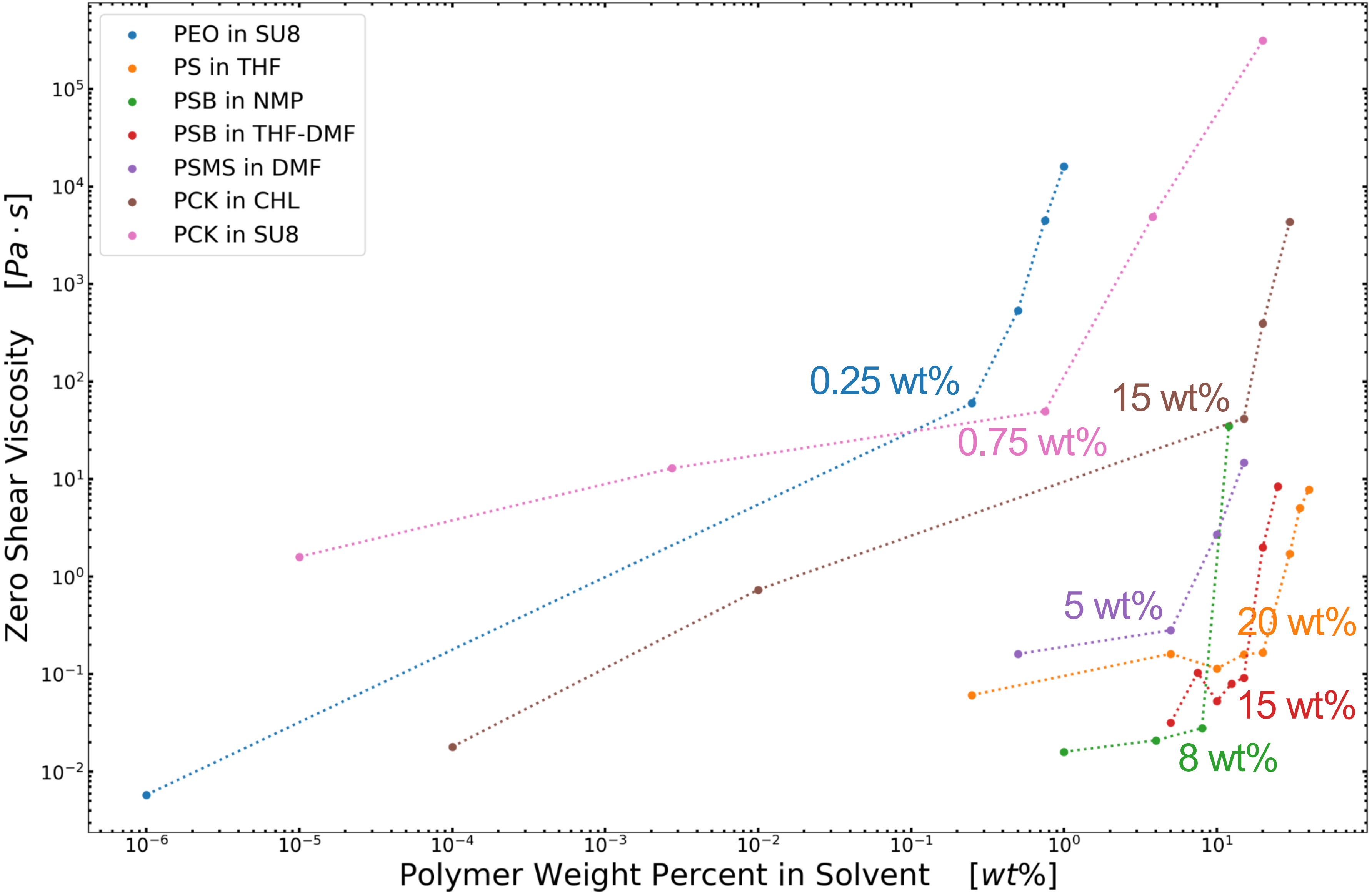
$11.36\ \% error$

https://wiki.anton-paar.com/en/chloroform/

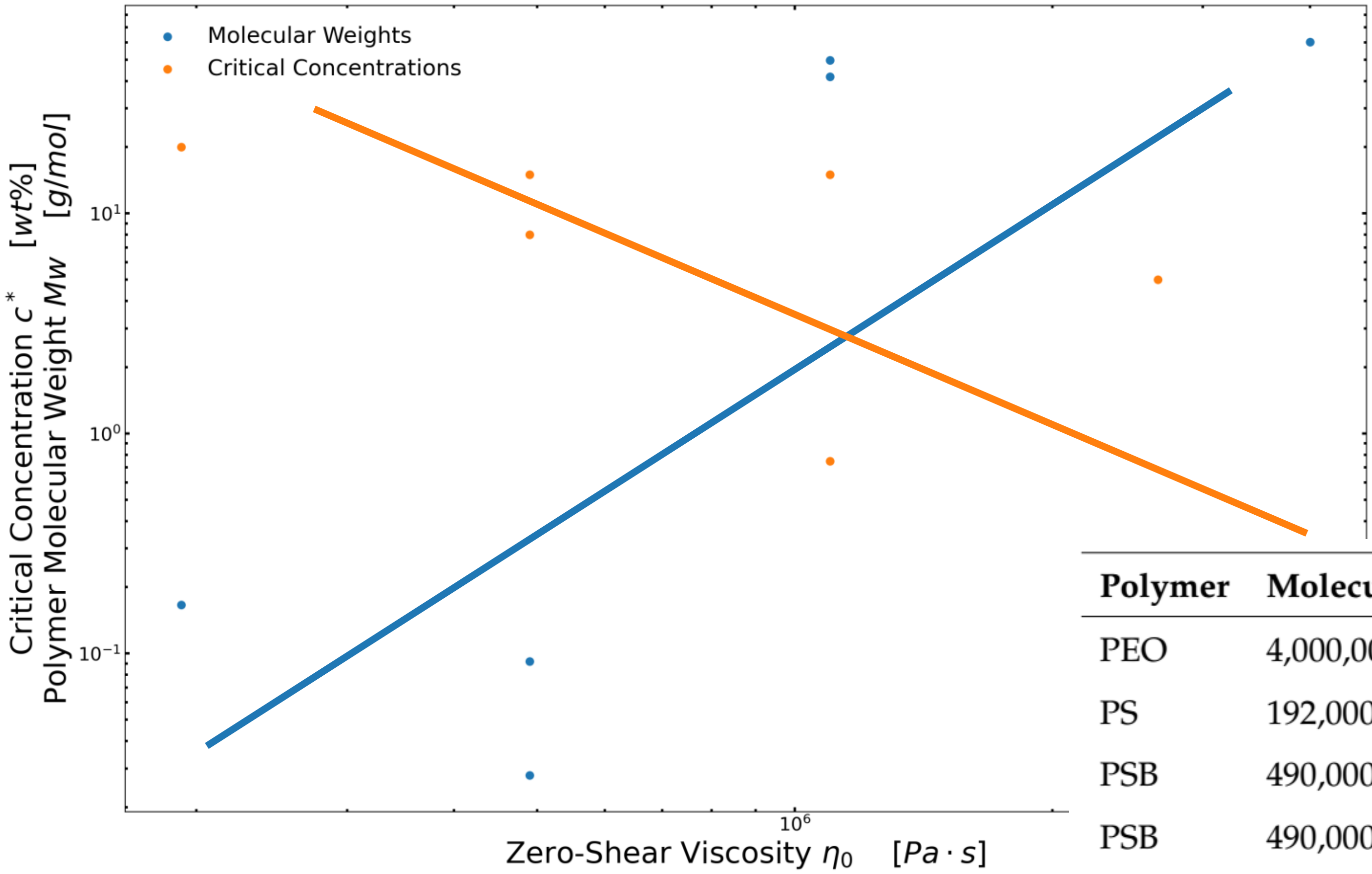
Spinnable/Critical Concentration



Spinnable/Critical Concentration



Conclusion2.1: Spinnable/Critical Concentration



A low molecular weight shall be compensated with higher concentrations to reach a spunable viscosity.

Polymer	Molecular Weight [$g \cdot mol$]	Solvent	c^*[wt%]	η_0[$Pa \cdot s$]
PEO	4,000,000	CPO (SU-8)	0.25	60.022
PS	192,000	THF	20.00	0.166
PSB	490,000	NMP	8.00	0.028
PSB	490,000	THF and DMF	15.00	0.092
PSMS	2,658,076	DMF	5.00	0.282
PVK	1,100,000	CHL	15.00	41.861
PVK	1,100,000	CPO (SU-8)	0.75	49.657

Vu Anh Doan et al. In: Journal of Materials Science 48.5 (Mar. 2013), pp. 2046–2052. ISSN: 0022-2461. DOI: 10.1007/s10853- 012- 6974- 1. URL: http://link.springer.com/10.1007/s10853-012-6974-1.
Ralph H. Colby, Lewis J. Fetters, and William W. Graessley. In: Macromolecules 20.9 (Sept. 1987), pp. 2226–2237. ISSN: 0024-9297. DOI: 10 . 1021 / ma00175a030.

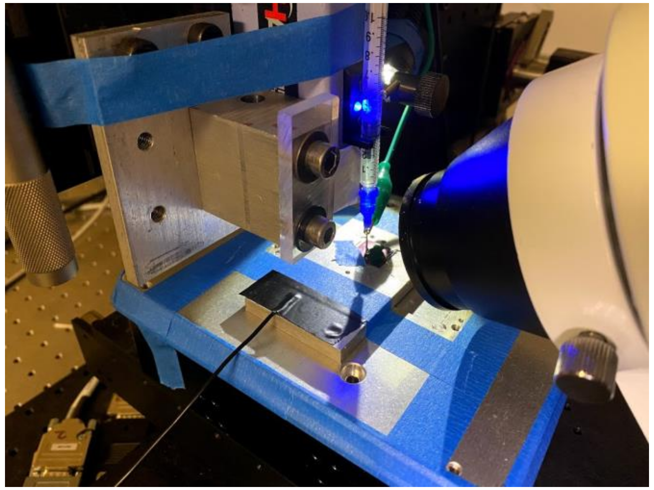
Fabrication & Characterization

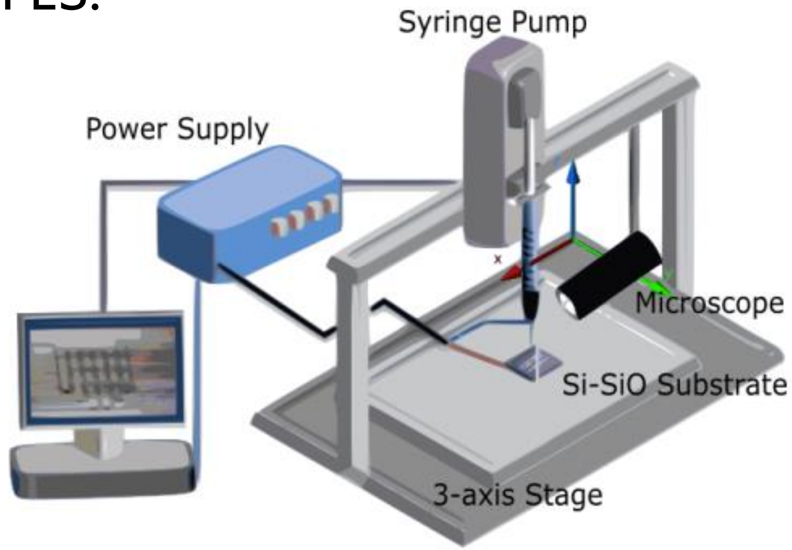
Specific Objective 3. Propose alternatives to the SU-8/PEO benchmark formulation for the production of microscopic polymer fibers with potential for the fabrication of carbon nano-wires.

Methods: Design of experiments / NFES

Given the results of previous work, the experiments shall reflect:

- The SU8-PEO sample set is the control
- The calculated critical concentration were used for each sample set.
- Each sample was electrospun at different applied voltages from 200 to 600V
  - Other process parameters (working distance, stage velocity, flow rate) are to be tuned and remain constant during NFES.



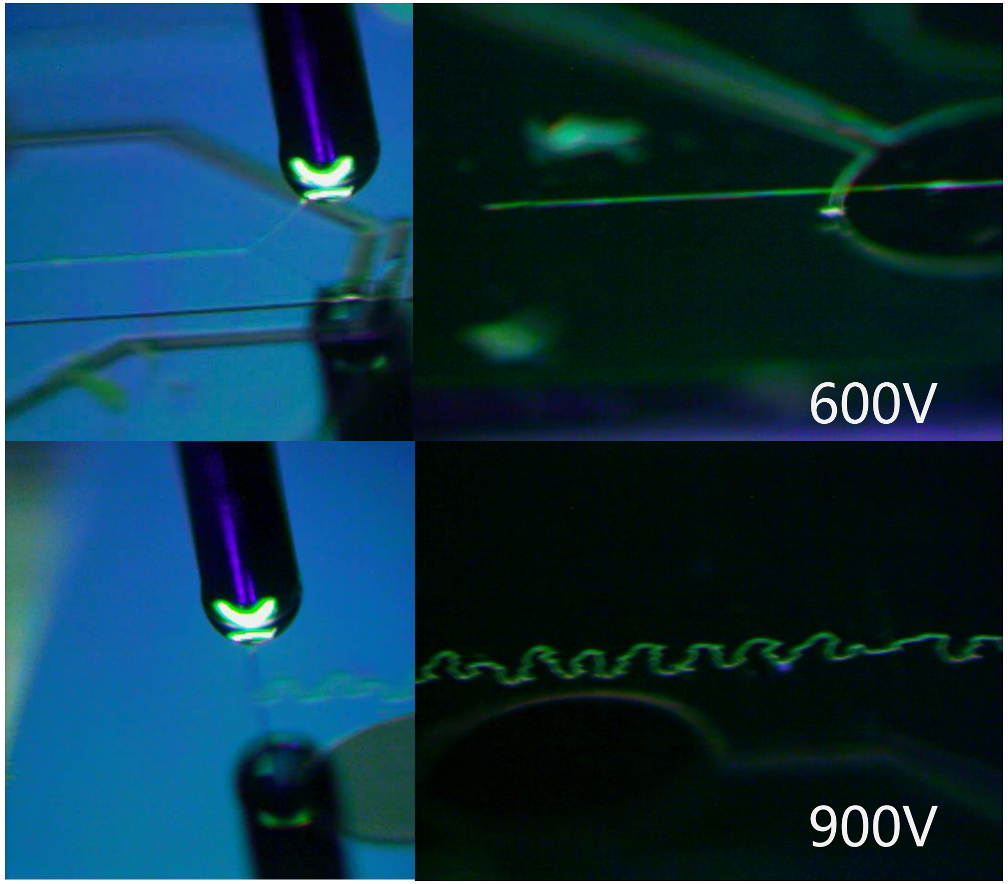


Domingo R Flores-hernandez et al. In: (2020). DOI: 10.3390/polym12061358.

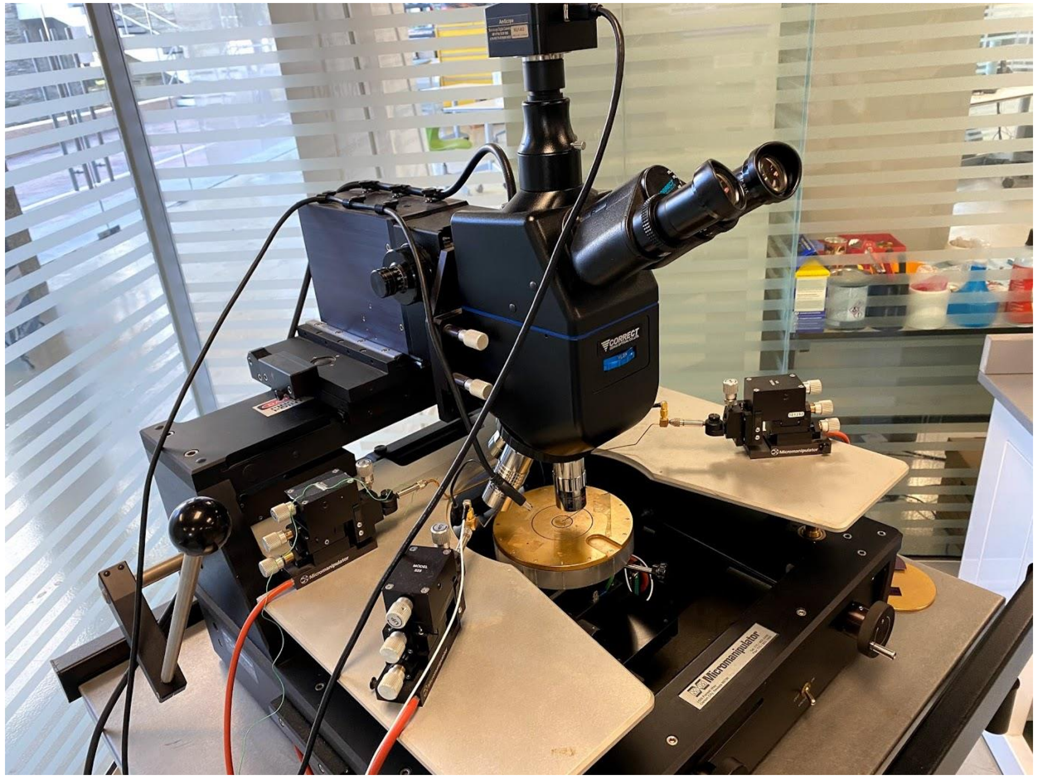
Fabrication: Process Parameters

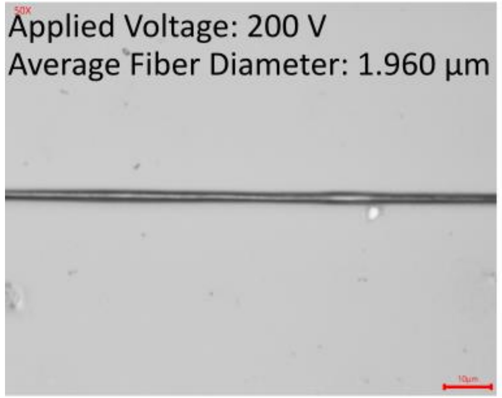
- Fabrication velocity: 10 mm/s
- Working distance: 0.5 mm
- Applied voltage: 200V to 600V
- Applied current: 10 uA
- Flow rate: 0.04 uL/min
- Spacing: 10um

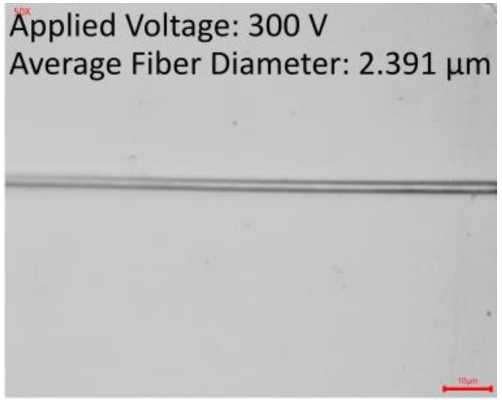
0.25 wt% PEO in SU-8

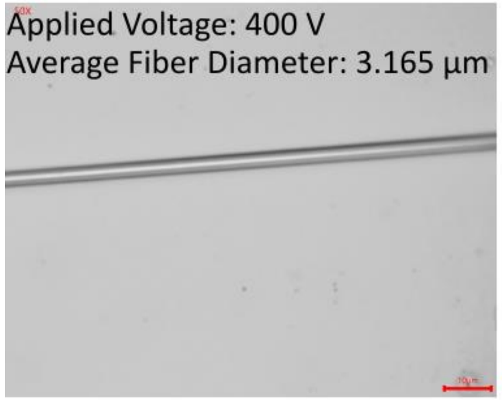


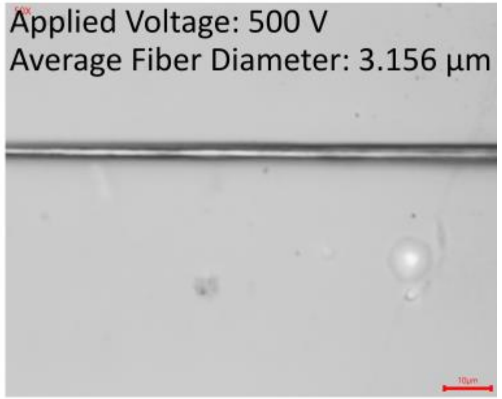
Characterization:



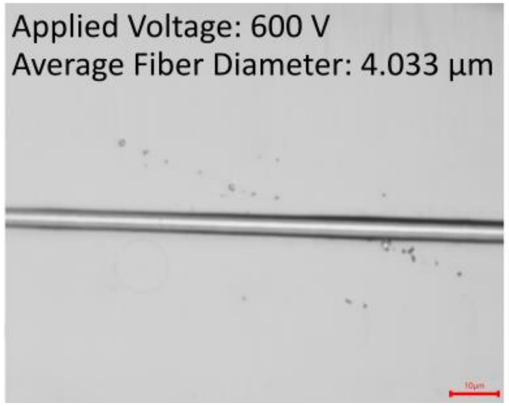








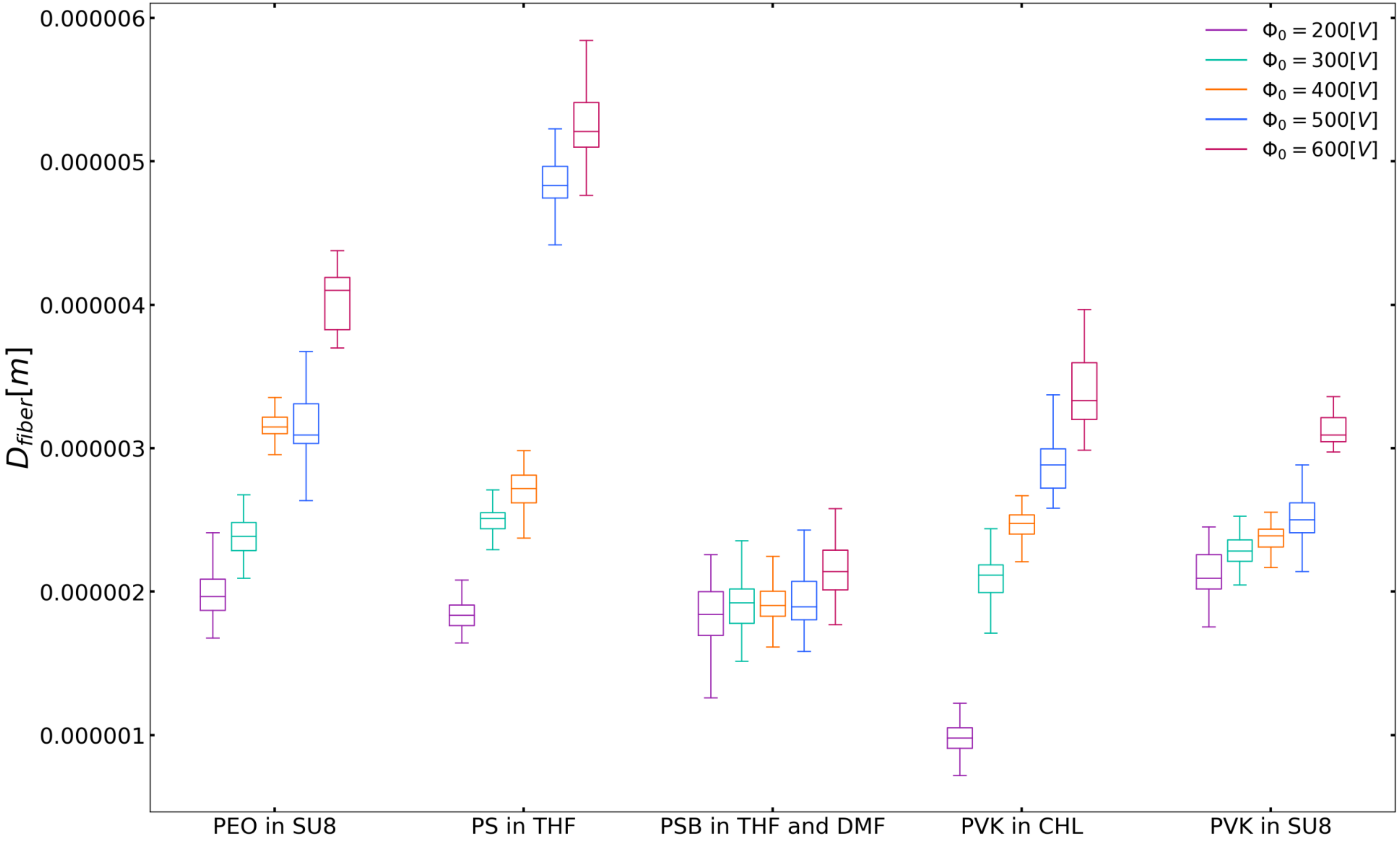
PEO in SU-8



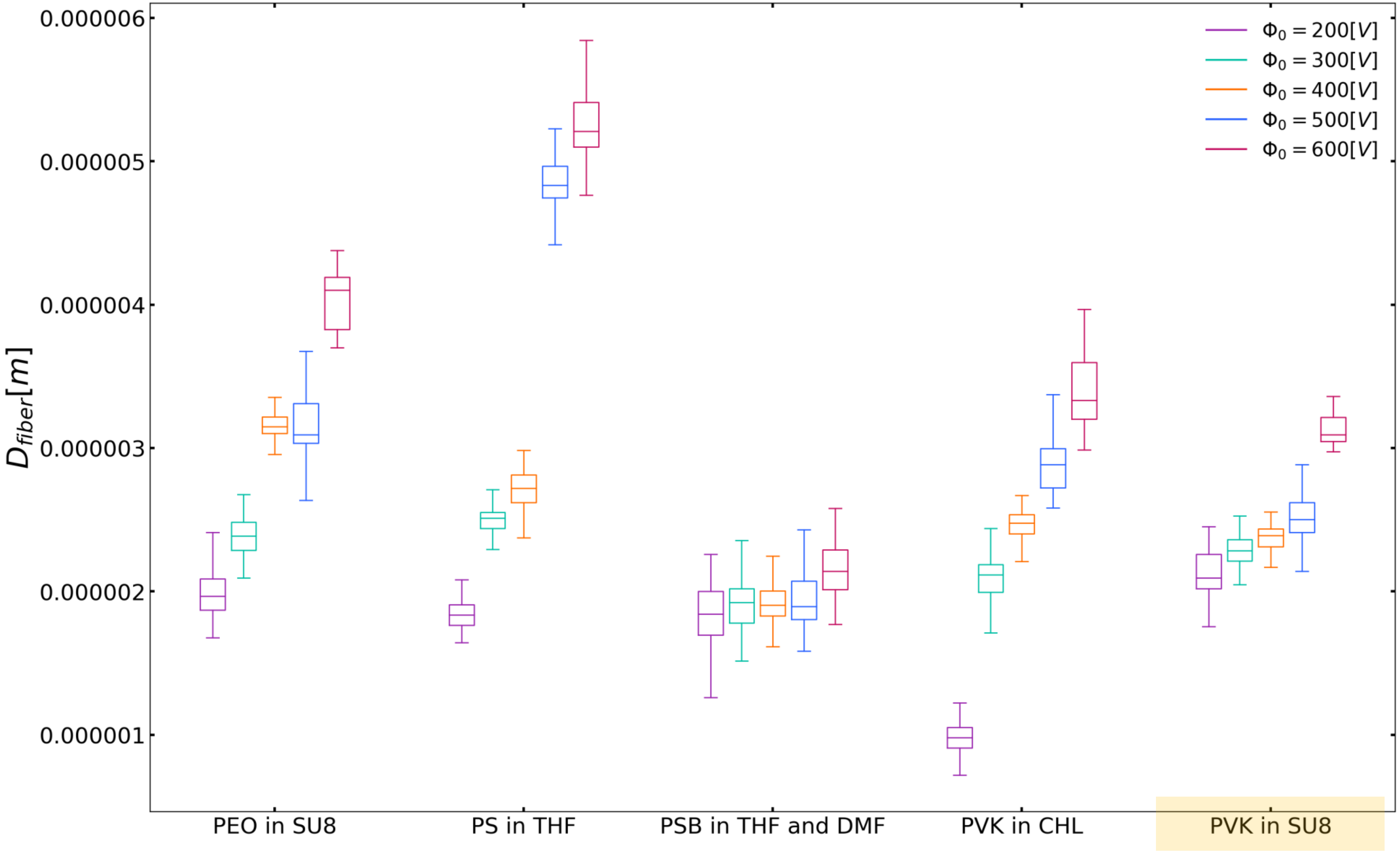
non-spinnable solutions

Polymer / Solvent	Critical concentration	Rationale
Poly(Styrene-co-alpha-Methylstyrene) (**PSMS**) in N,N-Dimethylformamide(**DMF**)	5 wt% (and 10, 15 wt%)	Fibres were broken into agglomerates / dust
Poly(Styrene-co-Butadiene) (**PSB**) in 1-Methyl-2-Pyrrolidinone (**NMP**)	8.00 wt%	Development of a shell around the drop.

Results: Spinnable solutions



Results: Spinnable solutions



Conclusions & Future Work

Helgeson's Dimensionless analysis

Helgeson's model was thought to work with far-field electrospinning, hence the deviation of the NFES data from the model trend.

For an accurate NFES fiber diameter prediction, the mechanical stresses introduced by the moving stage shall be considered in the model

Pyrolysis Process

This work verifies the electro-spinnability of four new formulations and one modification to the PEO/SU-8 solution, however fibers were not carbonized into carbon structures.

Further work shall study the pyrolysis process of the proposed fibers to get carbon structures with good electrical conductivity.

A photo-polymerization process could be introduced before pyrolysis to increase the order of the molecules and achieve carbon with higher
conductivity.

Process Parameters

The viscosity-concentration plot is a helpful tool to estimate the critical spinnable concentration of a polymer-solvent system as NFES solutions require specific viscosities to initiate a polymer jet. However there is room for improvement as this method only considers rheological data.

Other methods could be adopted to better tune other process parameters such as stage velocity, and applied voltage.

Thank You

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Any Questions?

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02 Dec 2020