TECHNICAL UNIVERSITY OF LIBEREC

New Opportunities for the Development of Education at the Technical University of Liberec

Specific objective A2: Development in the field of distance learning, online learning and blended learning

NPO_TUL_MSMT-16598/2022

KNT_TNA_Material conditions

Ing. Radek Jirkovec, Ph.D.

Funded by the European Union
NextGenerationEU

CZECH RECOVERY PLAN

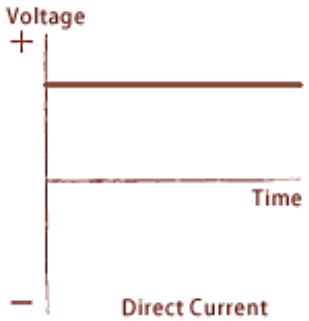
MINISTRY OF EDUCATION, YOUTH AND SPORTS

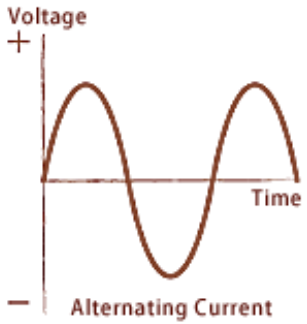
Repetition

- The process of fiber formation by the effect of an electric field
- Described as tugging between electrical and capillary forces

- High voltage DC power supply
  - It does not change its polarity over time
  - Positive / negative

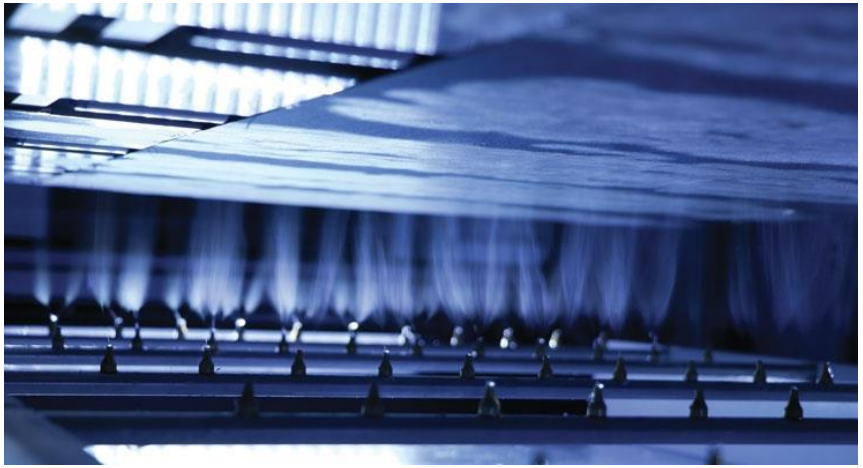
- From solutions or melts





Repetition

Needle electrospinning



Needle-less electrospinning

Electrode - charged / grounded

Collector - charged / grounded

Conditions affecting electrospinning

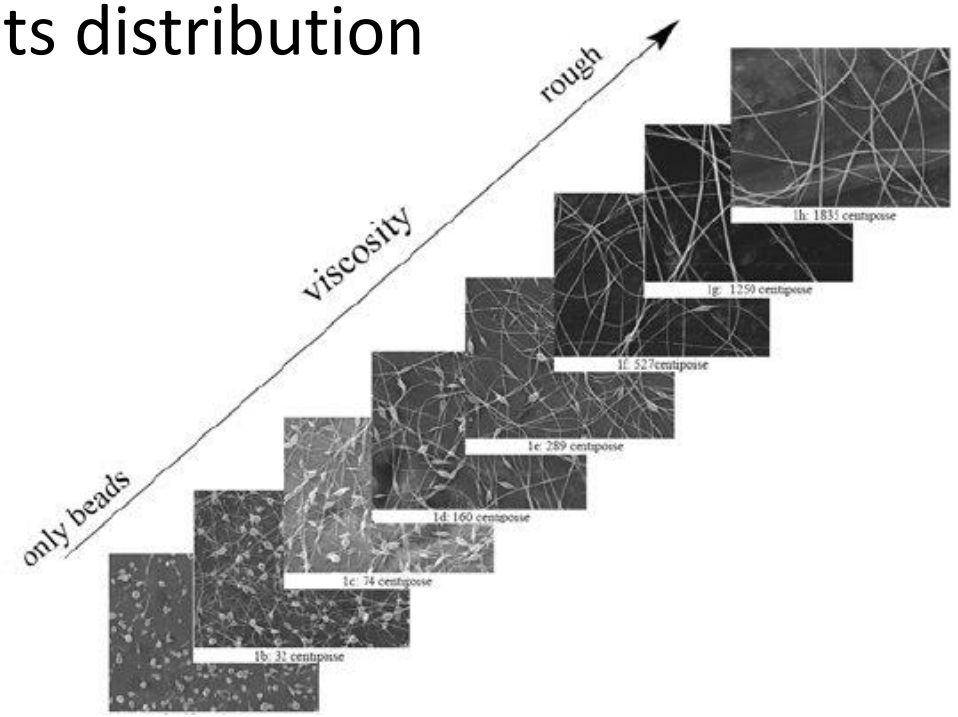
Process conditions *x* material conditions

Process conditions

- Spinner configuration
- Voltage
- Distance of the collector from the electrode
- Dosage of the solution
- Background material
- Temperature
- Humidity

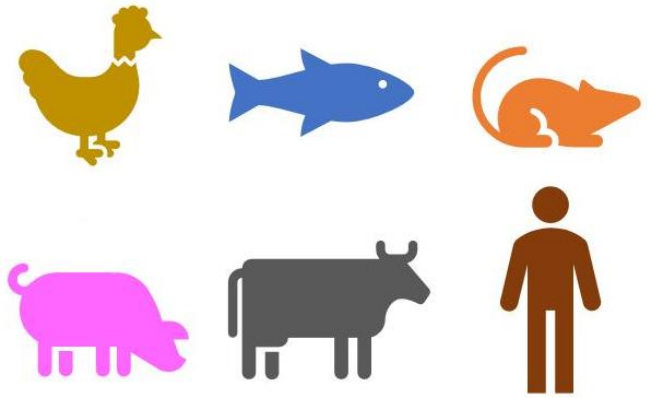
Material conditions

- Polymer type
- Molecular weight and its distribution
- Concentration
- Solvent system
- Electric conductivity
- Viscosity
- Surface tension
- Additives



Type of polymer

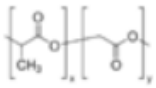
- Natural polymers
  - From what source?



- Synthetic polymers
  - Copolymers

Poly(D,L-lactide-*co*-glycolide)

7 Product Results | Match Criteria: Product Name



Synonym: **PLGA**

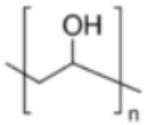
Linear Formula: $[C_3H_4O_2]_x[C_2H_2O_2]_y$

☐ P1941	lactide:glycolide (75:25), mol wt 66,000-107,000
☐ P2191	lactide:glycolide (50:50), mol wt 30,000-60,000
☐ P2066	lactide:glycolide 65:35, M_w 40,000-75,000

Type of polymer

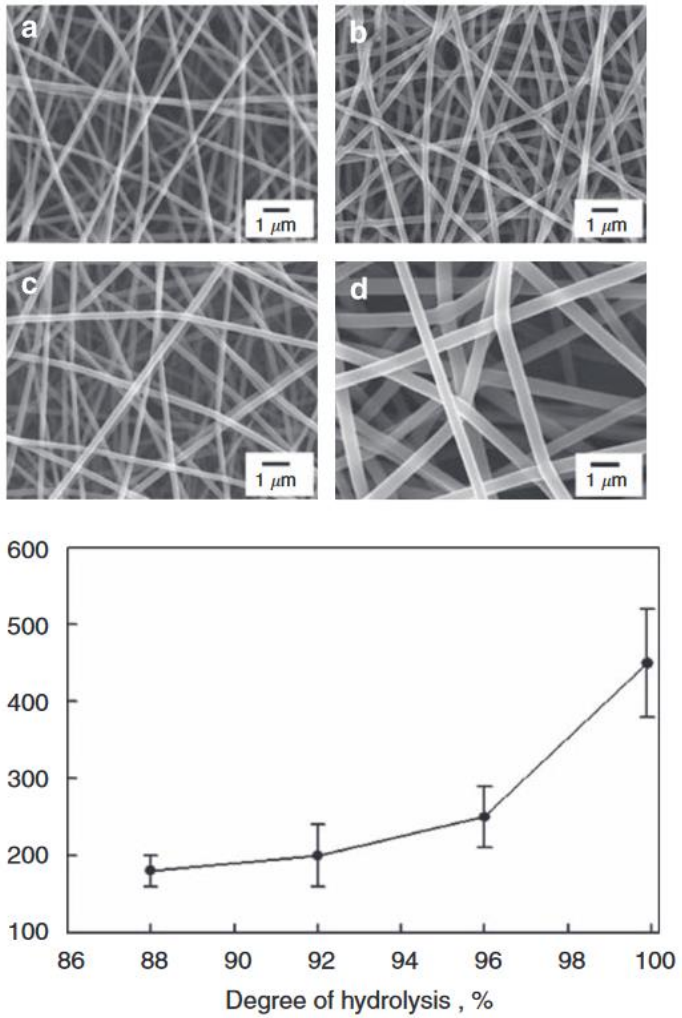
Poly(vinyl alcohol)

16 Product Results | Match Criteria: Product Name



Linear Formula: $[-CH_2CHOH-]_n$ | CAS Number: 9002-89-5

341584	M_W 89,000-98,000, 99+% hydrolyzed
P8136	87-90% hydrolyzed, average mol wt 30,000-70,000
360627	M_W 9,000-10,000, 80% hydrolyzed
363170	M_W 13,000-23,000, 87-89% hydrolyzed
363065	M_W 146,000-186,000, 99+% hydrolyzed
363146	M_W 85,000-124,000, 99+% hydrolyzed
363138	M_W 31,000-50,000, 98-99% hydrolyzed
363081	average M_W 85,000-124,000, 87-89% hydrolyzed



SEM images of electrospun PVA fibers with DH of (a) 88%, (b) 92%, (c) 96% and (d) 99.9% (top), and fiber diameters of the corresponding electrospun PVA fibers (bottom). The concentration of the PVA solution was 8.0wt%.

Molecular weight

- Mass of an amount of substance in a sample

$$M\ [g/mol]$$

- Weight average molecular weight

$$M_w = \frac{\sum m_i M_i}{\sum m_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \sum w_i M_i$$

- Numerically average molecular weight

$$M_n = \frac{\sum m_i}{\sum n_i} = \frac{\sum n_i M_i}{\sum n_i} = \sum x_i M_i$$

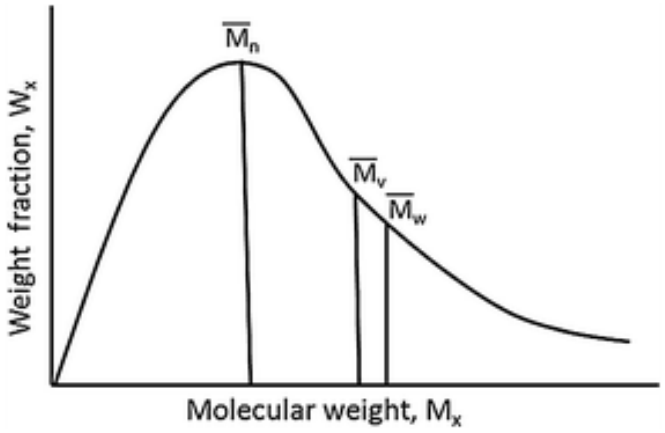
Molecular weight

- A mixture of molecular weight samples:

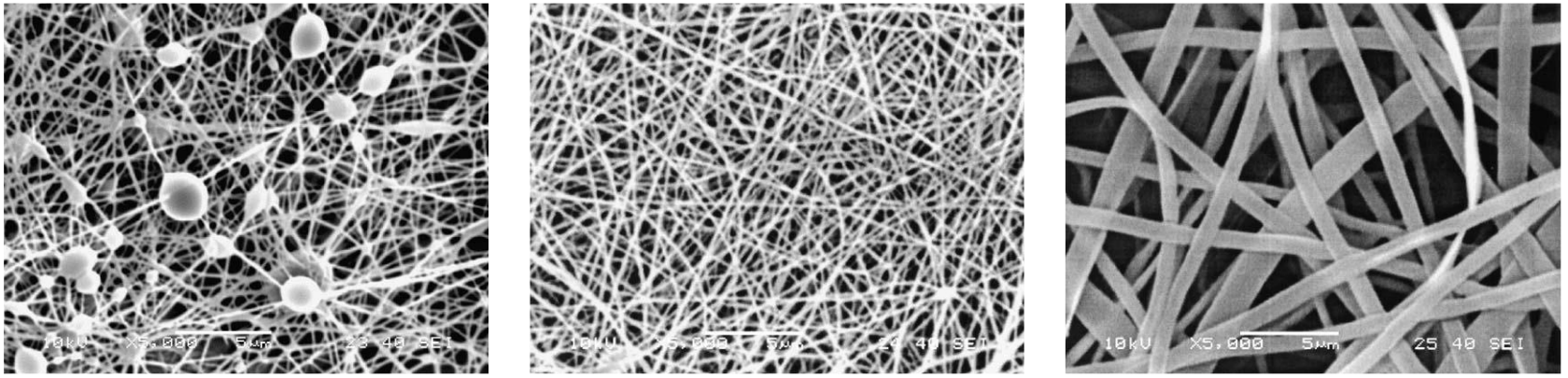
  10 000; 10 000; 10 000; 100 000

  - M_n 32 500; M_w 79 230

- Molecular weight distribution



Molecular weight

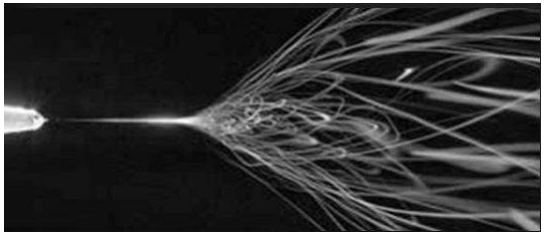


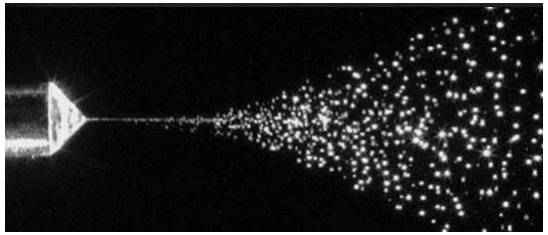
PVA (A) 9000–10,000 g/mol; (B) 13,000–23,000 g/mol; and (C) 31,000–50,000 g/mol (solution concentration: 25 wt.%).

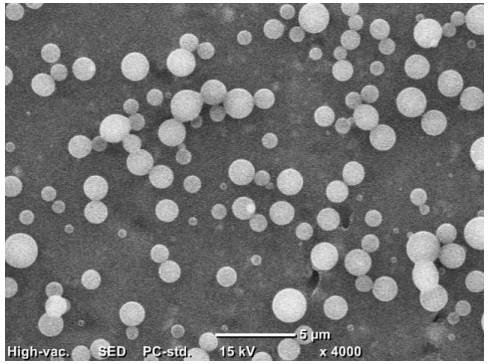
- It affects fiber diameters
- It is necessary to adjust the concentration of the solution

Concentration

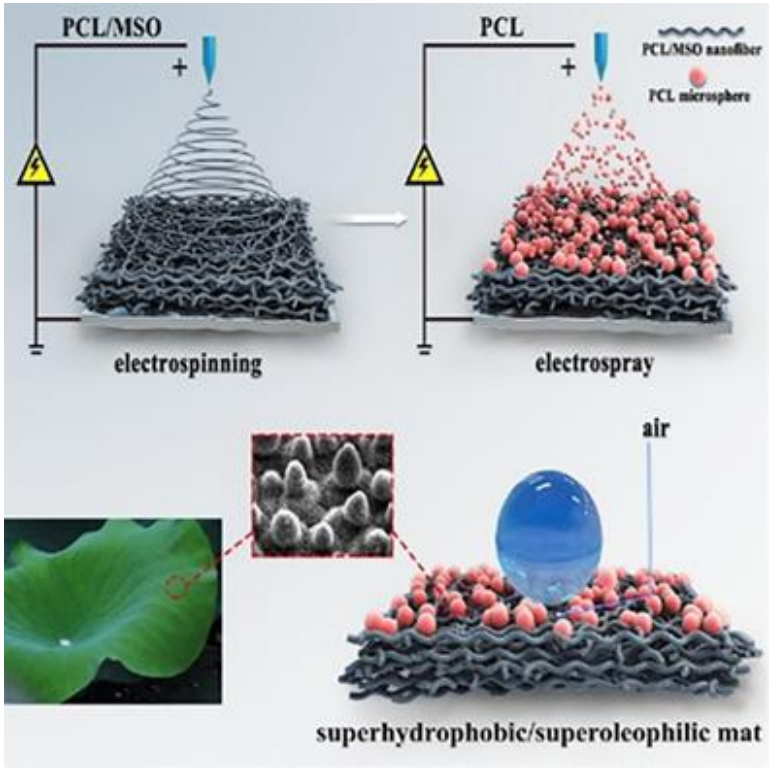
- An important property that affects the electrospinning process
- It affects viscosity, surface tension and electrical conductivity
- With a low concentration, we can create beads
- Electrospraying



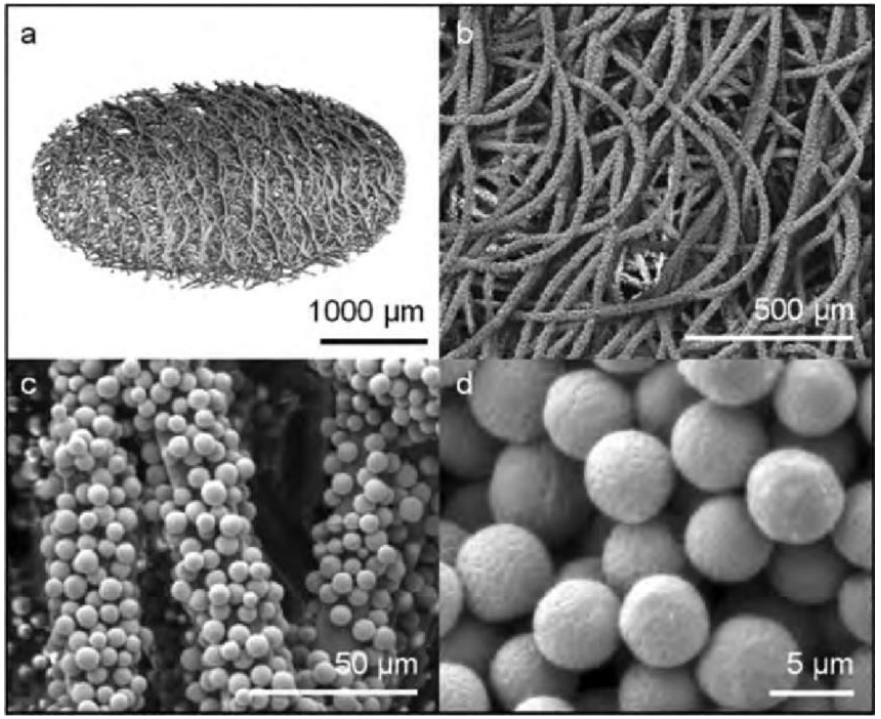




Concentration



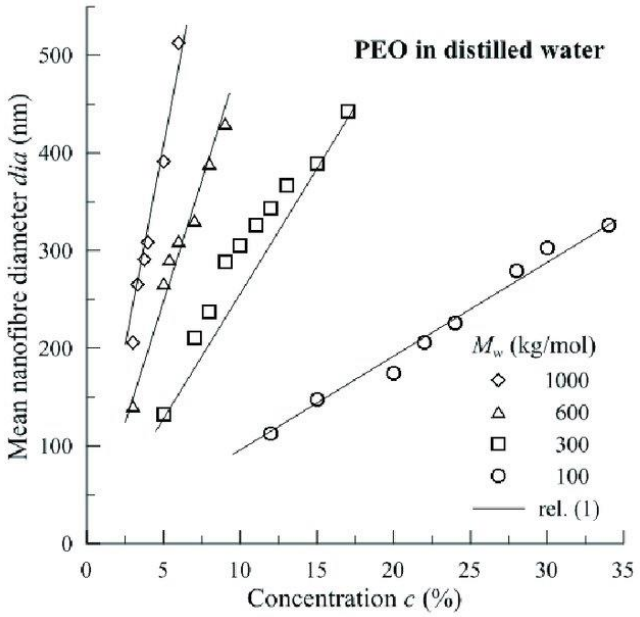
Schematic mechanism of superhydrophobic surface in PCL/MSO-PCL composite membrane



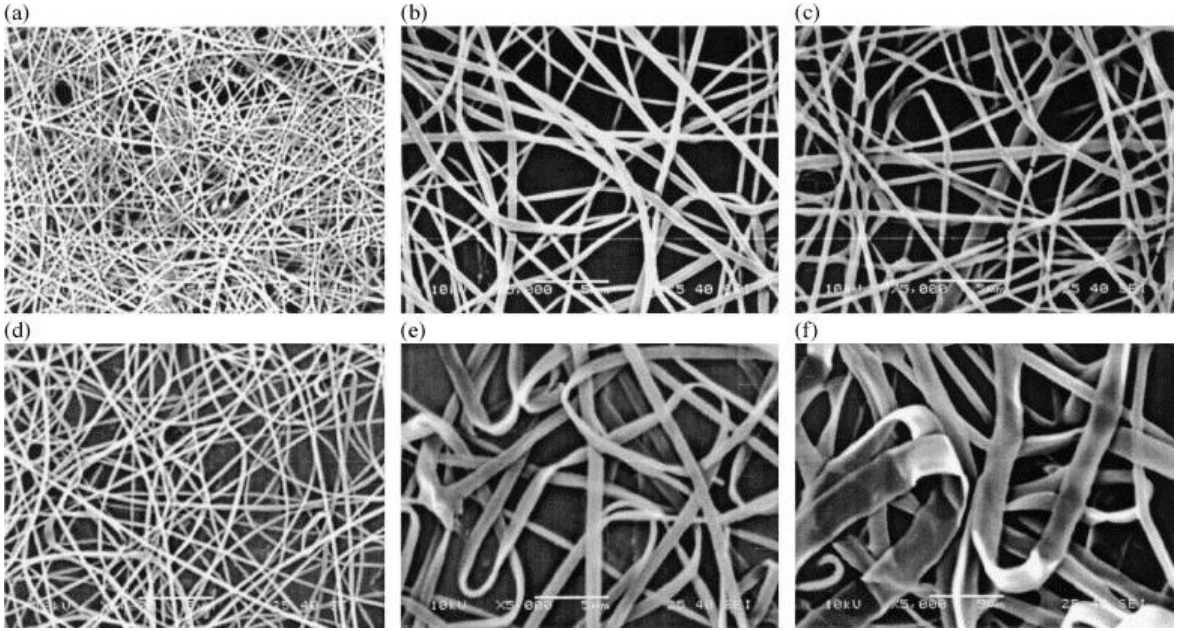
Overview of a PCL scaffold coated with electrosprayed PLGA particles after 1 h of electrospraying (80 mg PLGA). (a) mCT, (b)-(d) SEM, at different magnifications.

Concentration

- By changing the concentration, the fiber diameters change

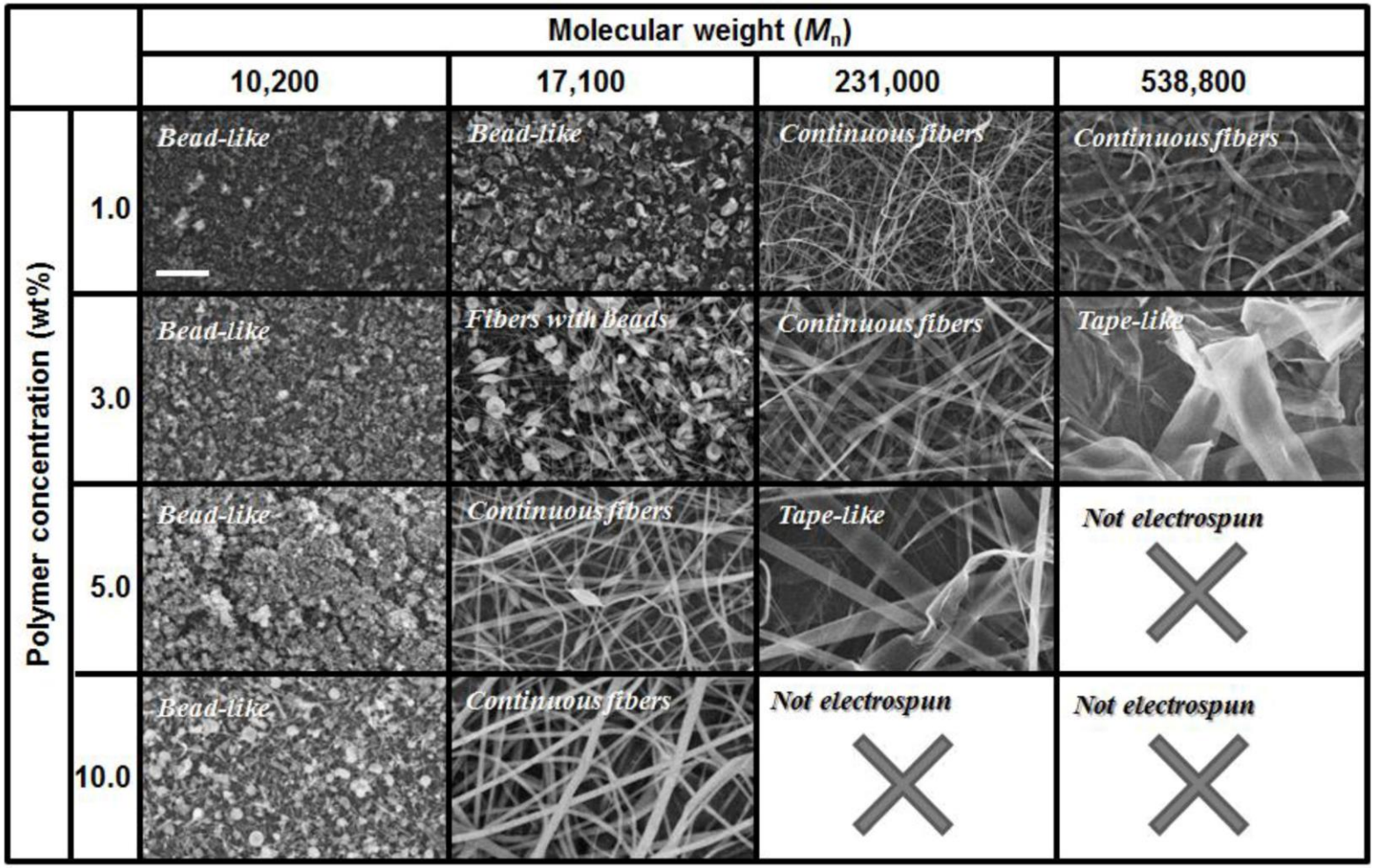


Dependence of mean nanofiber diameter on concentration (c) and molecular weight (Mw).



Photographs showing the effect of solution concentration on the structure in the electrospun polymer. Molecular weight=13,000–23,000 g/mol; (a) 21 wt.%; (b) 27 wt.%; and (c) 31 wt.%. Molecular weight=50,000–89,000 g/mol; (d) 9 wt.%; (e) 13 wt.%; (f) 17 wt.%.

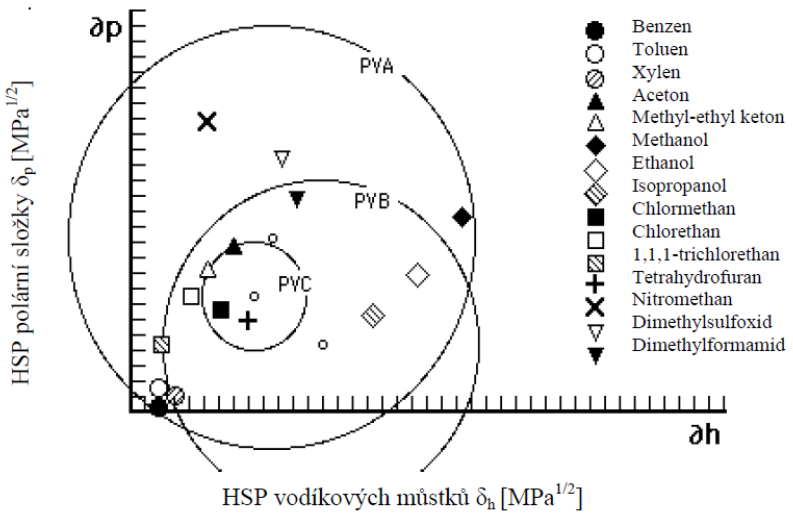
Concentration

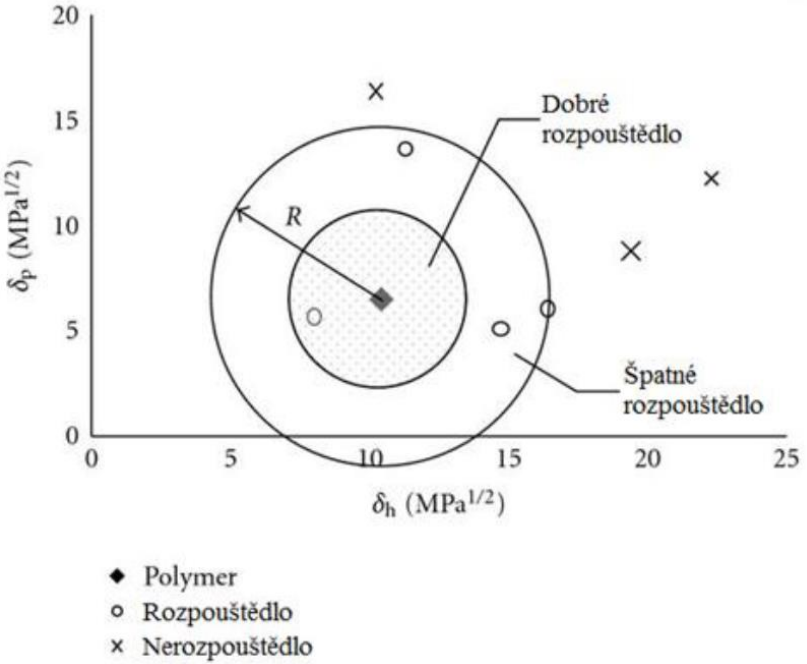


Effects of molecular weight and polymer concentration on the PNIPAAm fiber formation and morphologies (scale bar 10 μm).

Solvent system

- Polymer and solvent solubility parameters
- Hansen solubility parameters



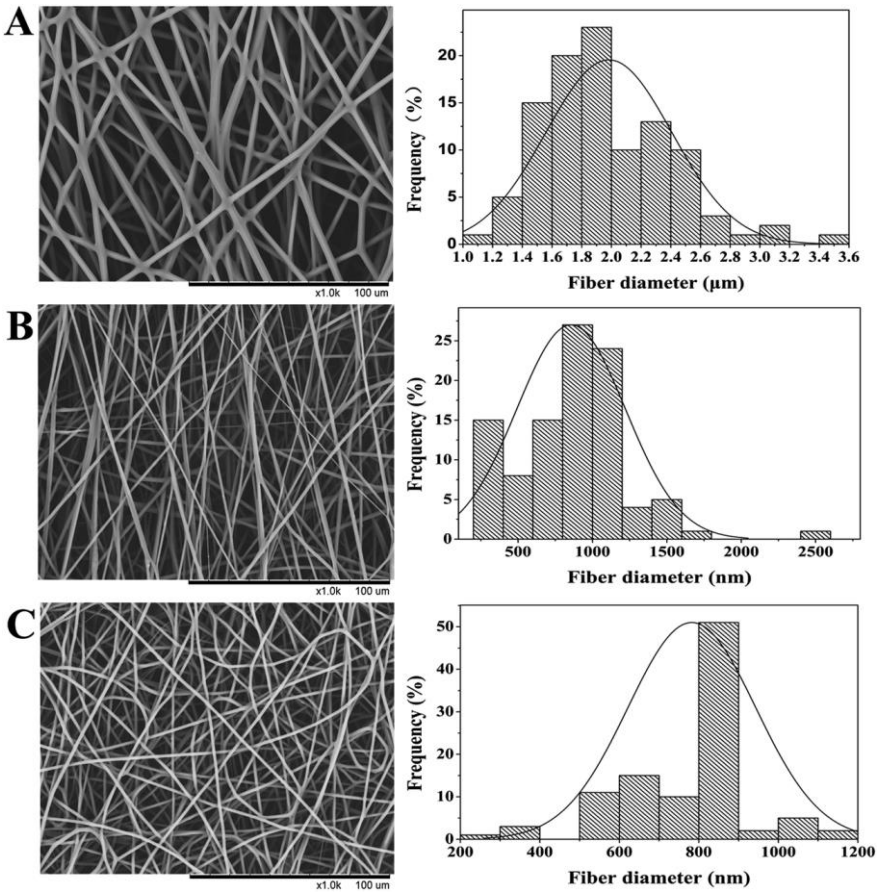


Solvent system

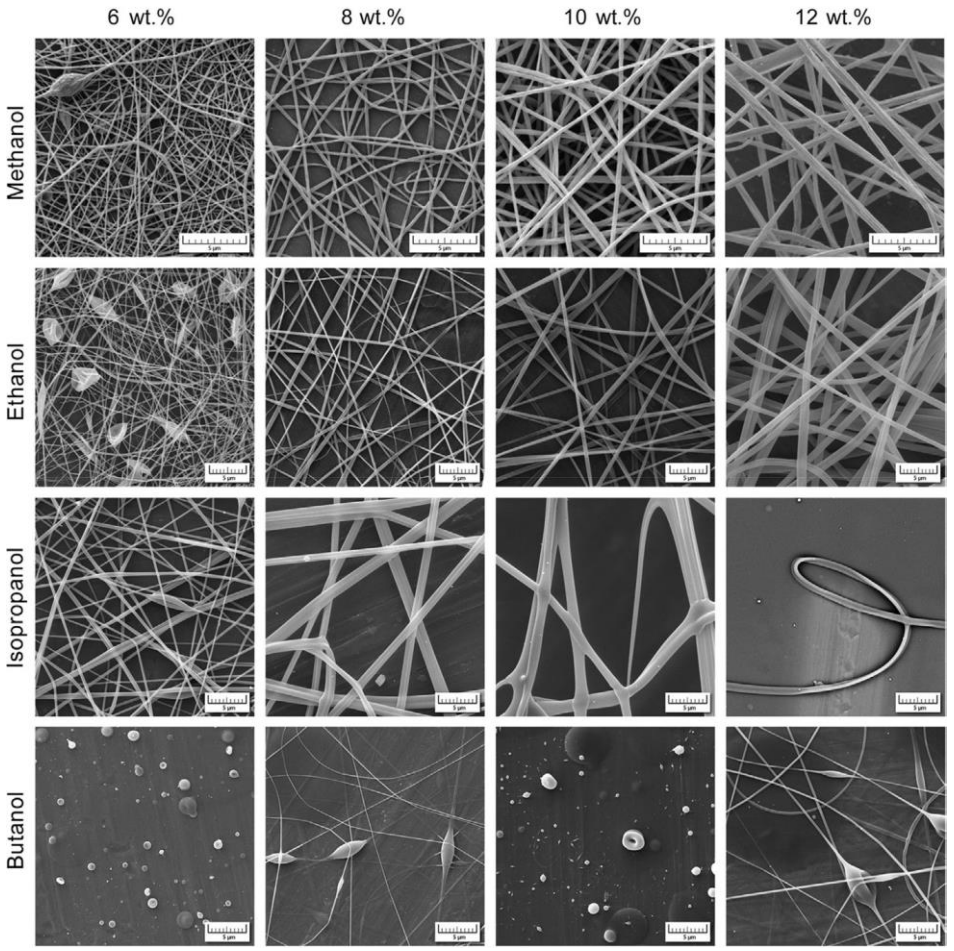
- Solubility parameters of polymer and solvent
- It affects electrical conductivity, viscosity and surface tension
- It therefore affects the electrospinning process and the morphology of the fiber layer

- Choice with respect to subsequent application

Solvent system



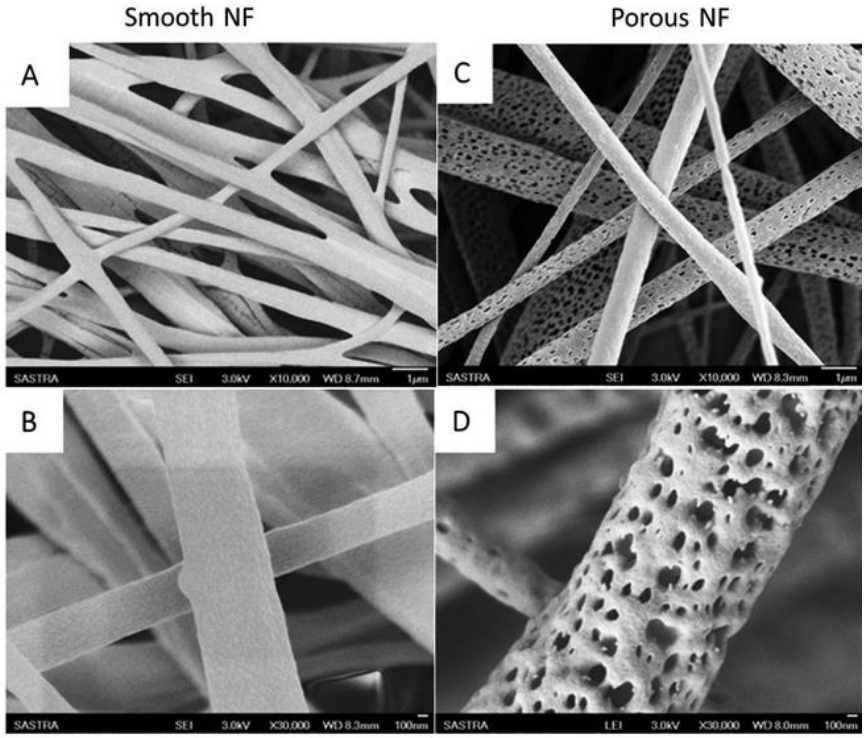
SEM images of PHBV/PEO electrospun fibers with fiber diameter distribution obtained from 10% (w/v) PHBV/PEO solution prepared by using different solvents: (A) Chloroform (B) Dichlormethane (C) Dichlormethane/etanol.



SEM images of PVB nanofibers

Solvent system

- Influencing surface morphology
- Possibility of creating porous nanofibers
- Very fast evaporation of the solvent
- Chloroform, acetone,…

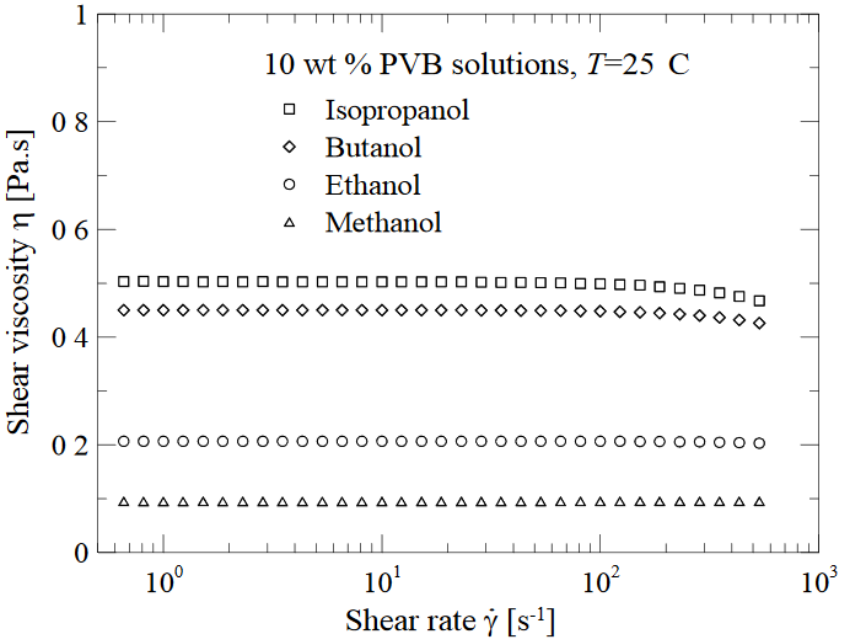


PLA nanofibers. The co-solvent mixture DCM/DMF yielded smooth structures (Fig. 3a, b) while DCM/acetone solvent mixture led to the formation of heterogeneous porous nano-features on nanofibers (Fig. 3c, d).

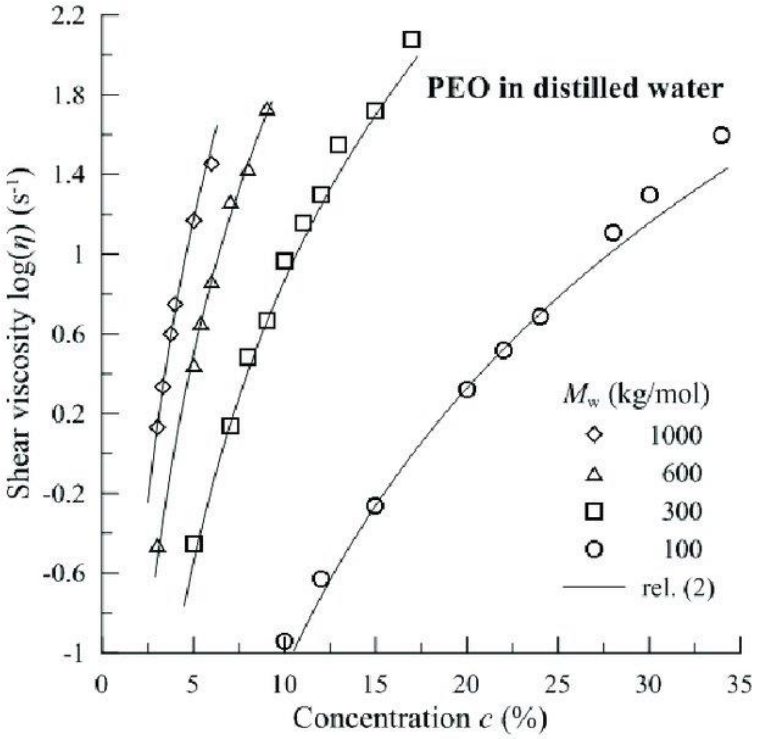
Viscosity

- Characterizes the internal friction of the fluid $\eta\ [Pa.s]$
- Dynamic viscosity $\tau = \eta \frac{dv}{dy}$
- Kinematic viscosity $\nu = \frac{\eta}{\rho}$
- It affects:
  - Molecular weight
  - Concentration
  - Solvent system

Viscosity

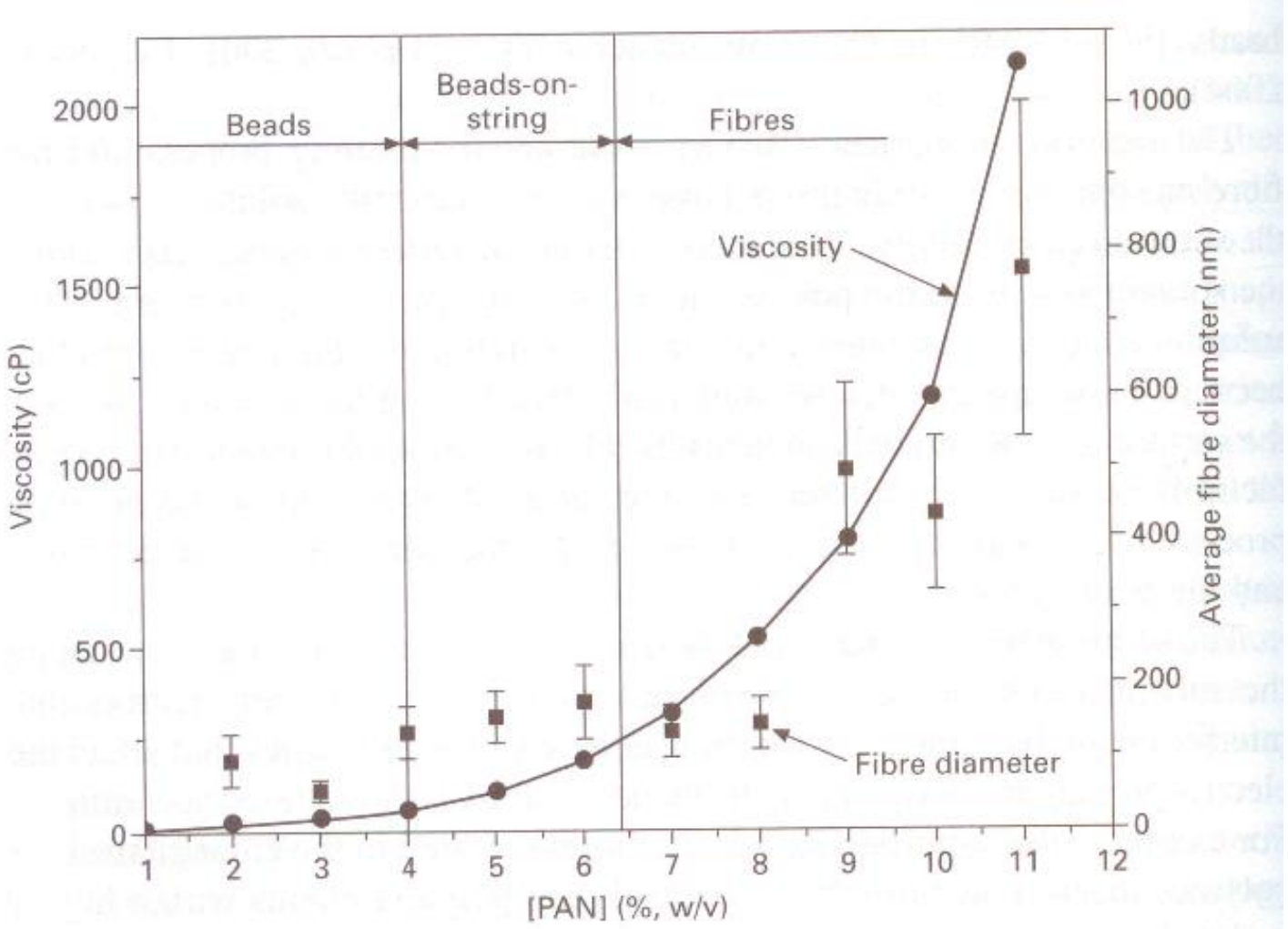


Shear viscosity of PVB solutions



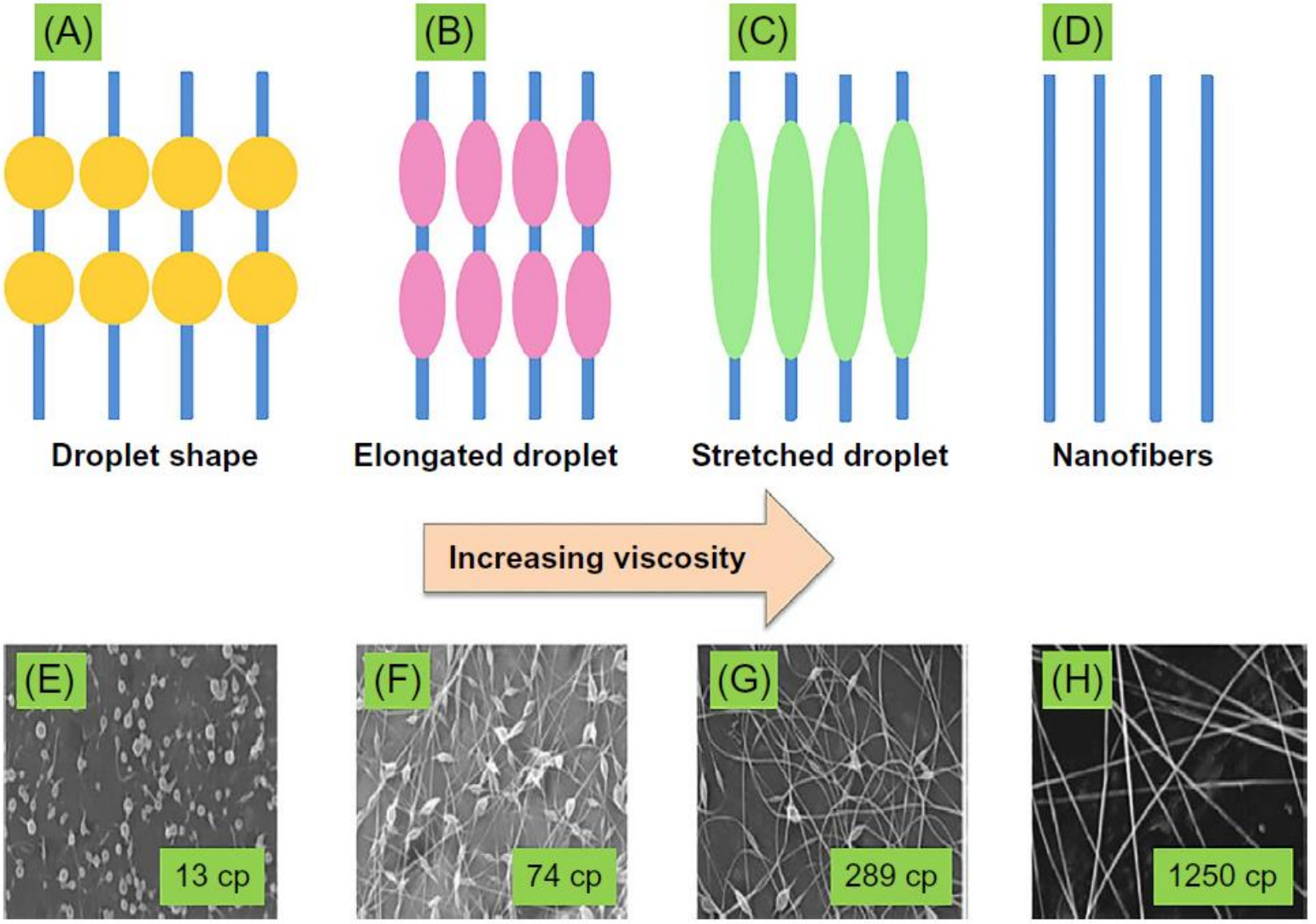
Dependence of shear viscosity (log(η)) on concentration (c) and molecular weight (Mw) in semi-log coordinates.

Viscosity



Relationship between polymer concentration, solution viscosity and diameter of electrospun polyacrylonitrile (PAN) fibres.

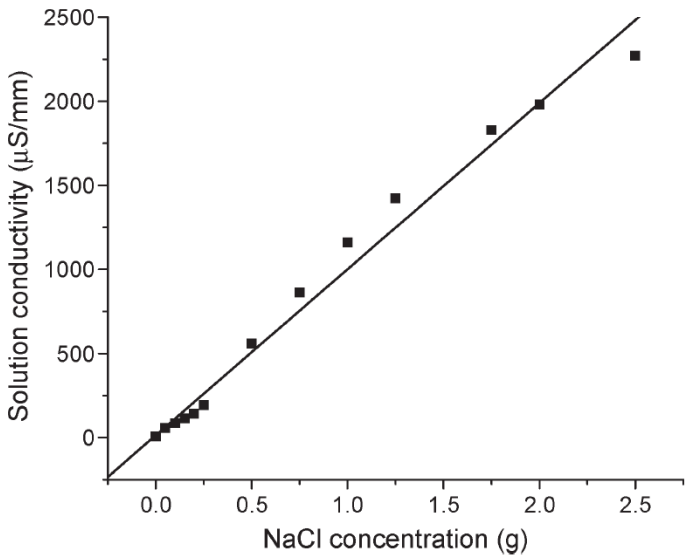
Viscosity


(A)
(B)
(C)
(D)
Droplet shape
Elongated droplet
Stretched droplet
Nanofibers
Increasing viscosity
(E)
13 cp
(F)
74 cp
(G)
289 cp
(H)
1250 cp

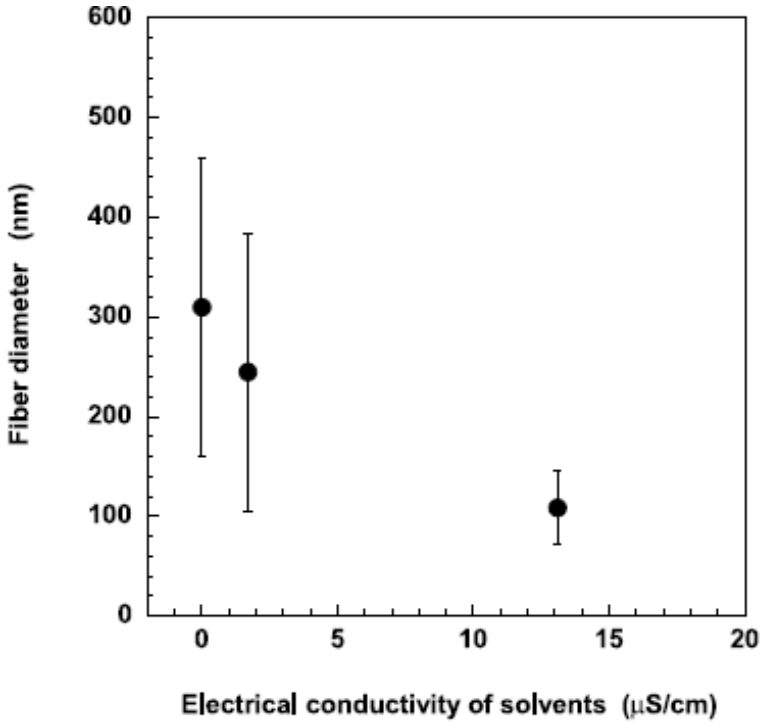
Electric conductivity

- The ability of a substance to conduct electric current $\sigma\ [S/m]$
- It affects:
  - Solvent system
  - Concentration
  - Additives

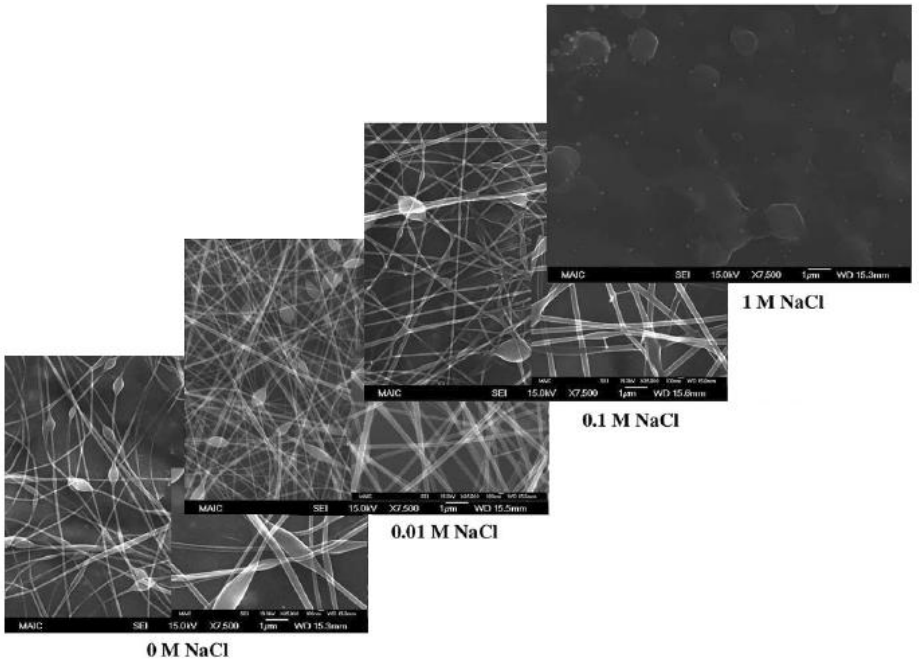
	Relative permittivity [-]	Specific conductivity [S/m]	Surface tension [mN/m]	Density [g/cm^3]
Methanol	32.7	$1.5*10^{-7}$	22.12	0.7899
Ethanol	24.5	$1.35*10^{-7}$	21.9	0.785
Isopropanol	19.9	$58*10^{-7}$	21.38	0.7813
Butanol	17.5	$9.12*10^{-7}$	24.5	0.806
PVB	3.60	$1*10^{-9}$	-	1.09



Electric conductivity



Solution conductivity effects on the diameter of electrospun P(LLA-CL) (70/30 wt%) fibers



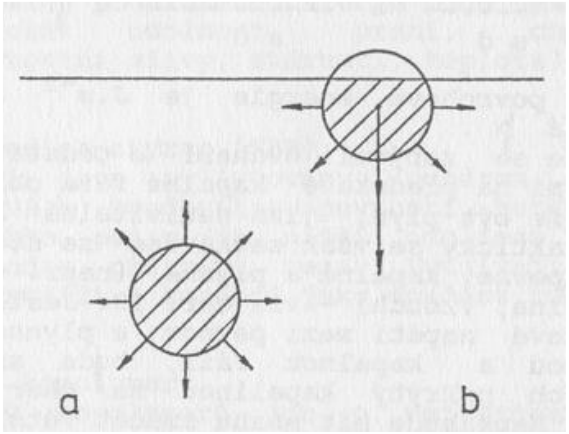
SEM images of PAA nanofibers with different NaCl concentrations

Surface tension

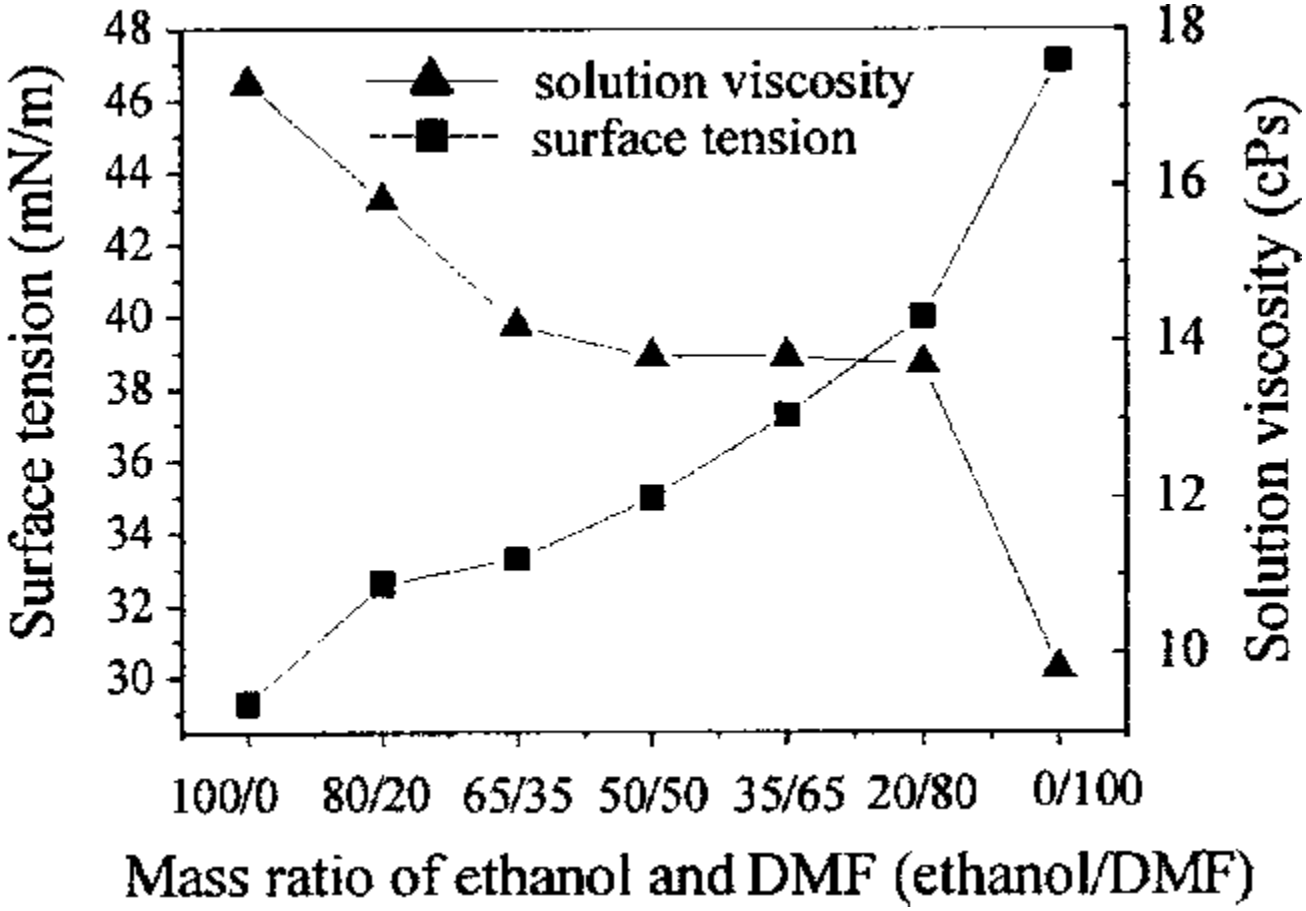
- The consequence of the interaction of the forces of the molecules or atoms that make up the surface layer
- The liquid tries to occupy the smallest possible area

$$\sigma = \frac{\Delta F}{\Delta l}$$

- Affected by:
  - Solvent system
  - Concentration
  - Additives

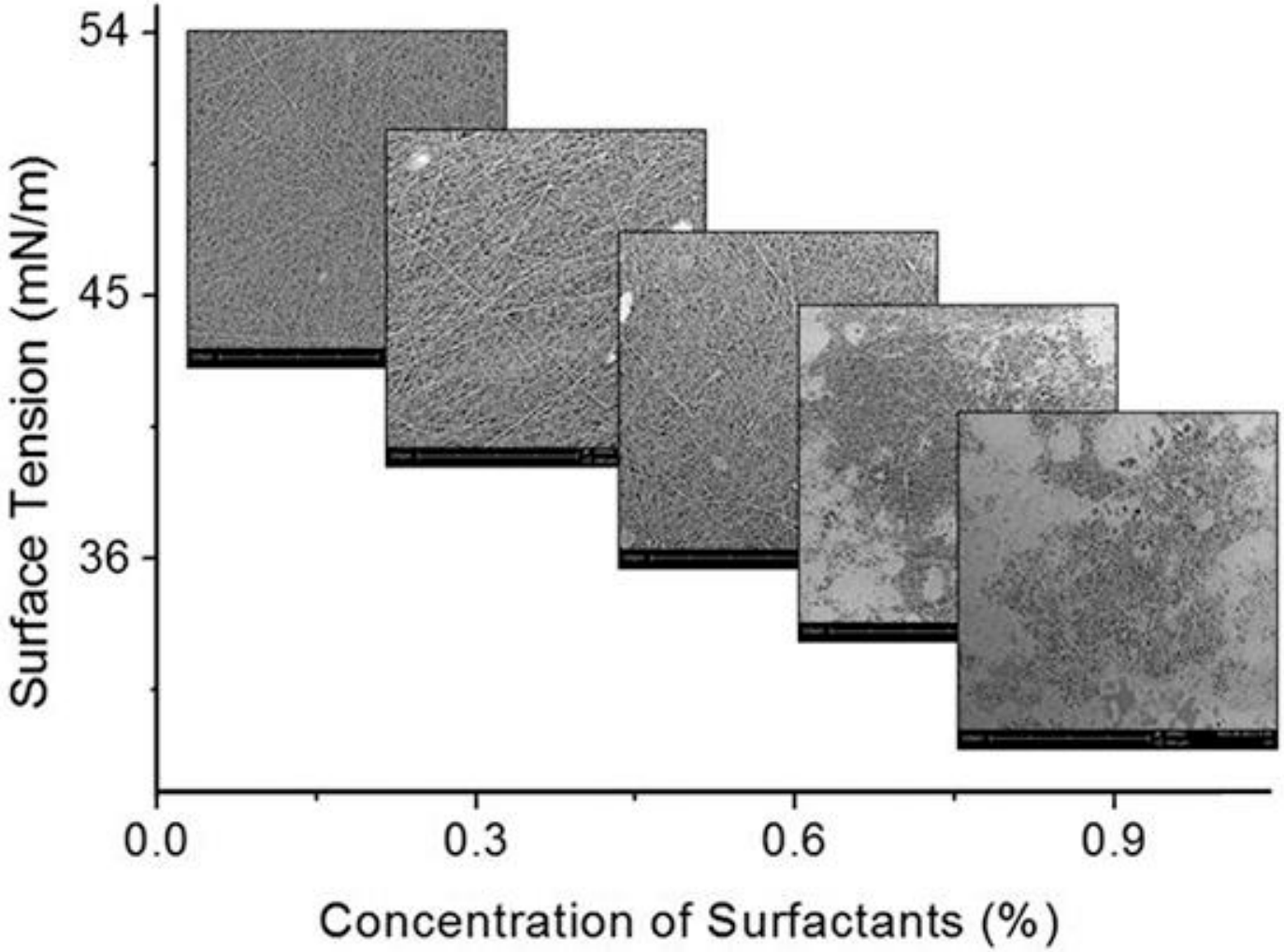


Surface tension



Surface tension and viscosity as functions of mass ratio of ethanol/DMF.

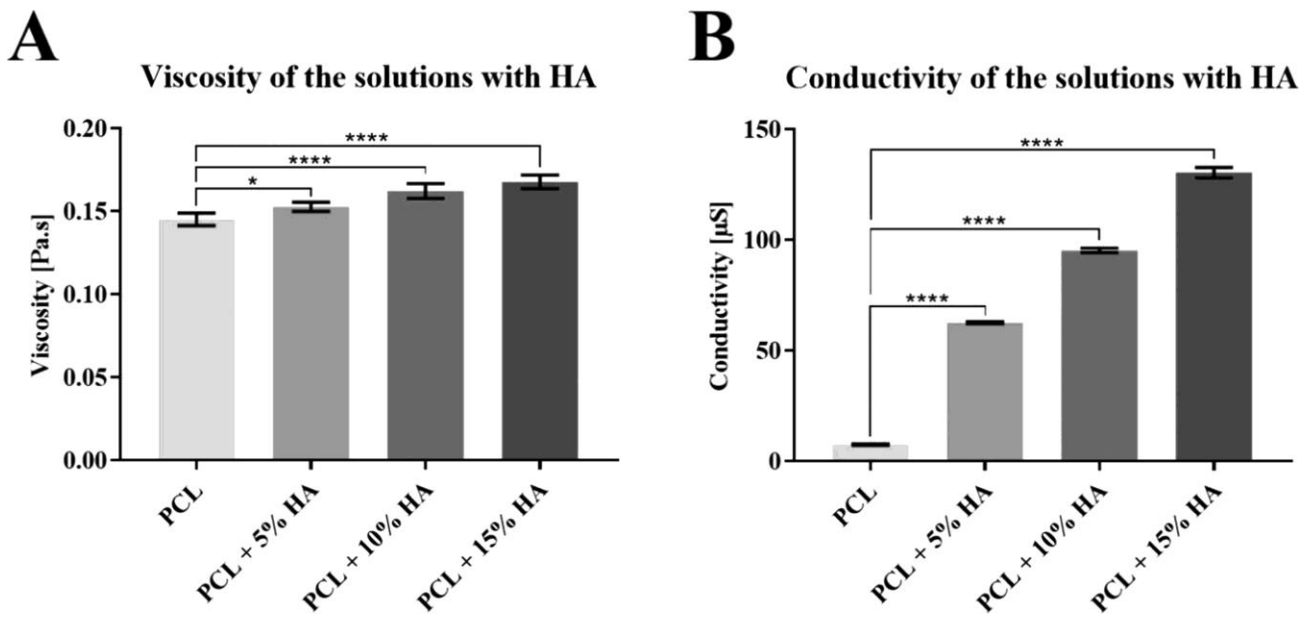
Surface tension



Effect of surface tension on the surface morphology of nanofibers

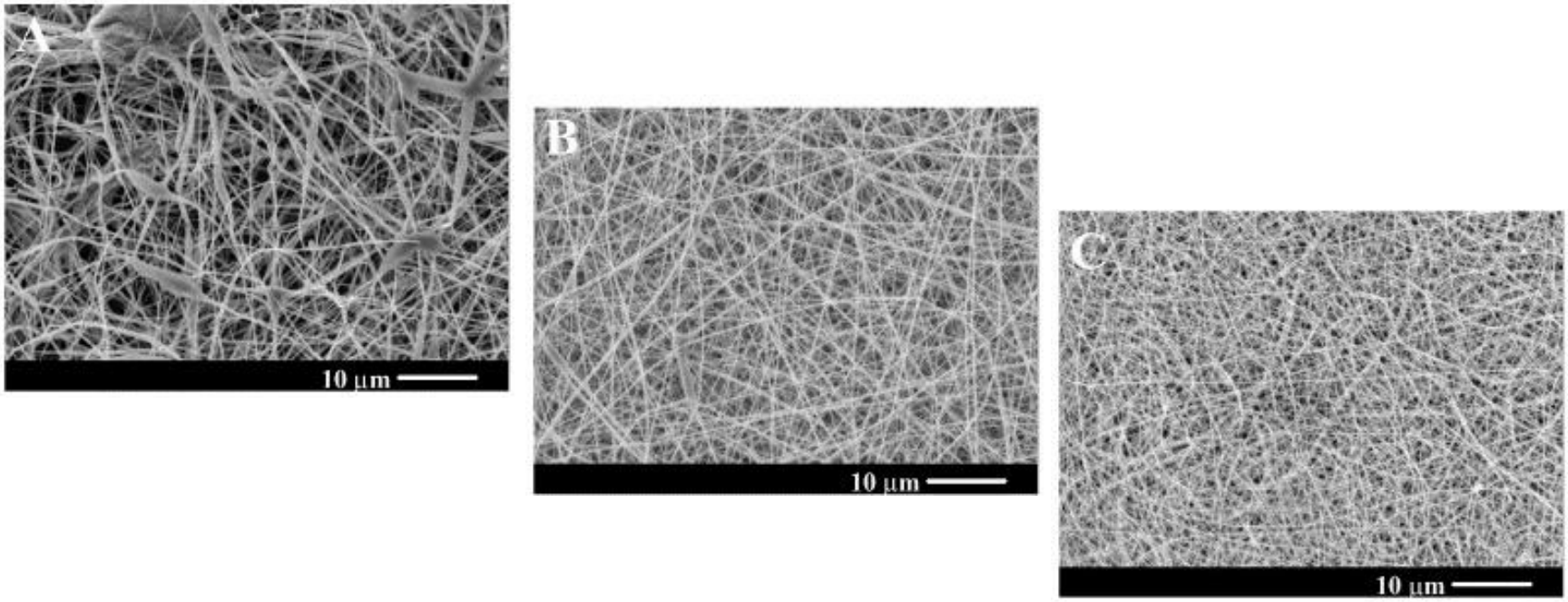
Additives

- They affect the surface tension, viscosity, electrical conductivity of the polymer solution
- All substances that are added to the solution



Parameters of the prepared PCL solutions with HA: (A) viscosity and (B) conductivity of the solutions.

Additives

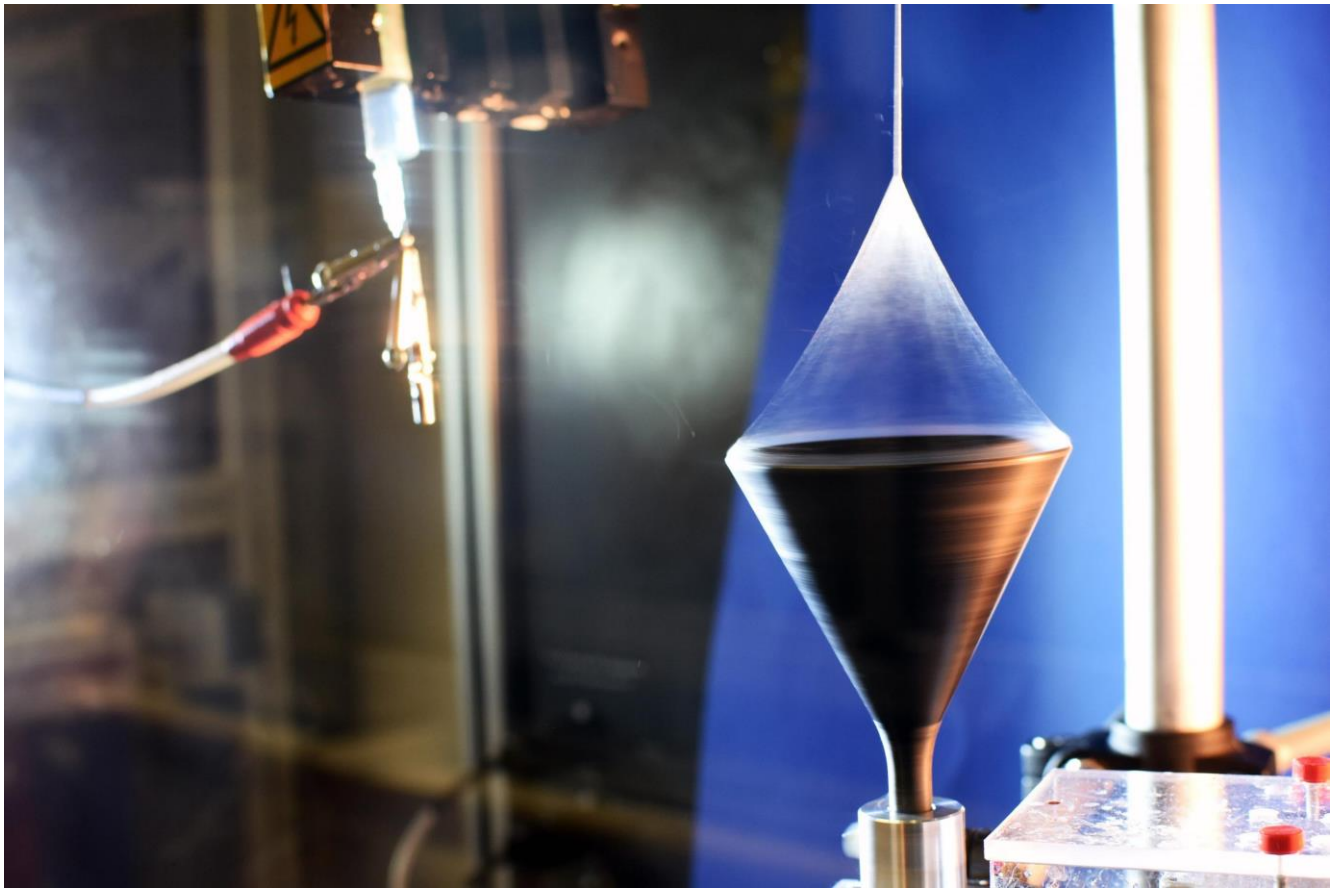


SEM images of PDLA membranes fabricated by electrospinning of a 30 wt% solution at voltage of 20 kV, feeding rate of 20 µl/min and with 1 wt% of (A) KH_2PO_4; (B) NaH_2PO_4 and (C) NaCl.

Summary

- The properties of the solution affect the electrospinning process
- For optimal spinning it is necessary:
  - Find a match between the molecular weight and the concentration of the polymer in the solution
  - Choose a suitable solvent system
  - Ensure optimal conductivity and surface tension for the given polymer and solvent system

Thank you for your attention!



TEST

- What material conditions affect the spinning process?
- How does molecular weight affect the concentration of a polymer solution?
- How does the concentration of the polymer solution affect the diameter of the fibers?