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A large, stylized graphic of a nanofiber structure, consisting of many concentric, overlapping rings of fine lines, creating a tunnel-like appearance. It is rendered in a light blue color against the dark blue background.

# NANOFIBRES

by electro-spinning of polymer solution

# Nanofibres background

## 1. Nanofibres properties

Increase of the surface to volume ratio -> solar and light sails and mirrors in space

Reduction of characteristic dimension -> nano-biotechnology, tissue engineering, chemical catalysts, electronic devices

Bio-active fibres: catalysis of tissue cells growth

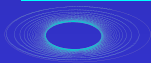
Mechanical properties improvement -> new materials and composite materials by alignment in arrays and ropes

## 2. Nanofibres production:

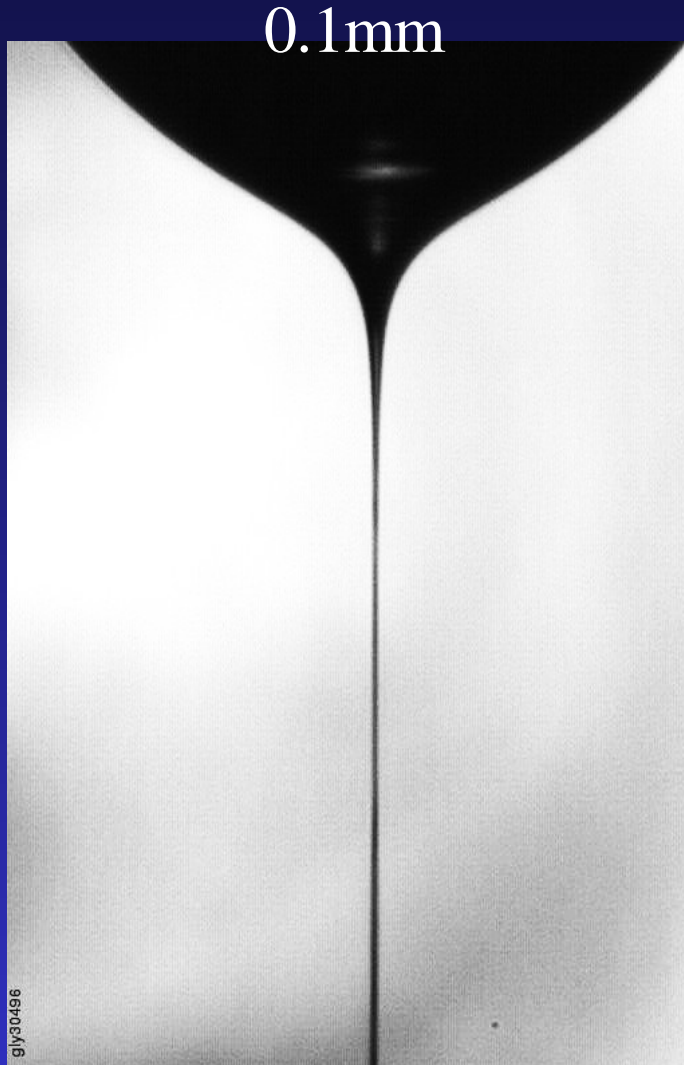
Air-blast atomisation

Pulling from melts

Electrospinning of polymer solutions



# Classical liquid jet

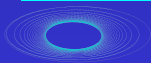


Orifice – 0.1mm

Primary jet diameter  $\sim 0.2\text{mm}$

Micro-jet diameter  $\sim 0.005\text{mm}$

- Gravitational, mechanical or electrostatic pulling limited to  $l/d \sim 1000$  by capillary instability
- To reach nano-range:
  - jet thinning  $\sim 10^{-3}$
  - draw ratio  $\sim 10^6$ !



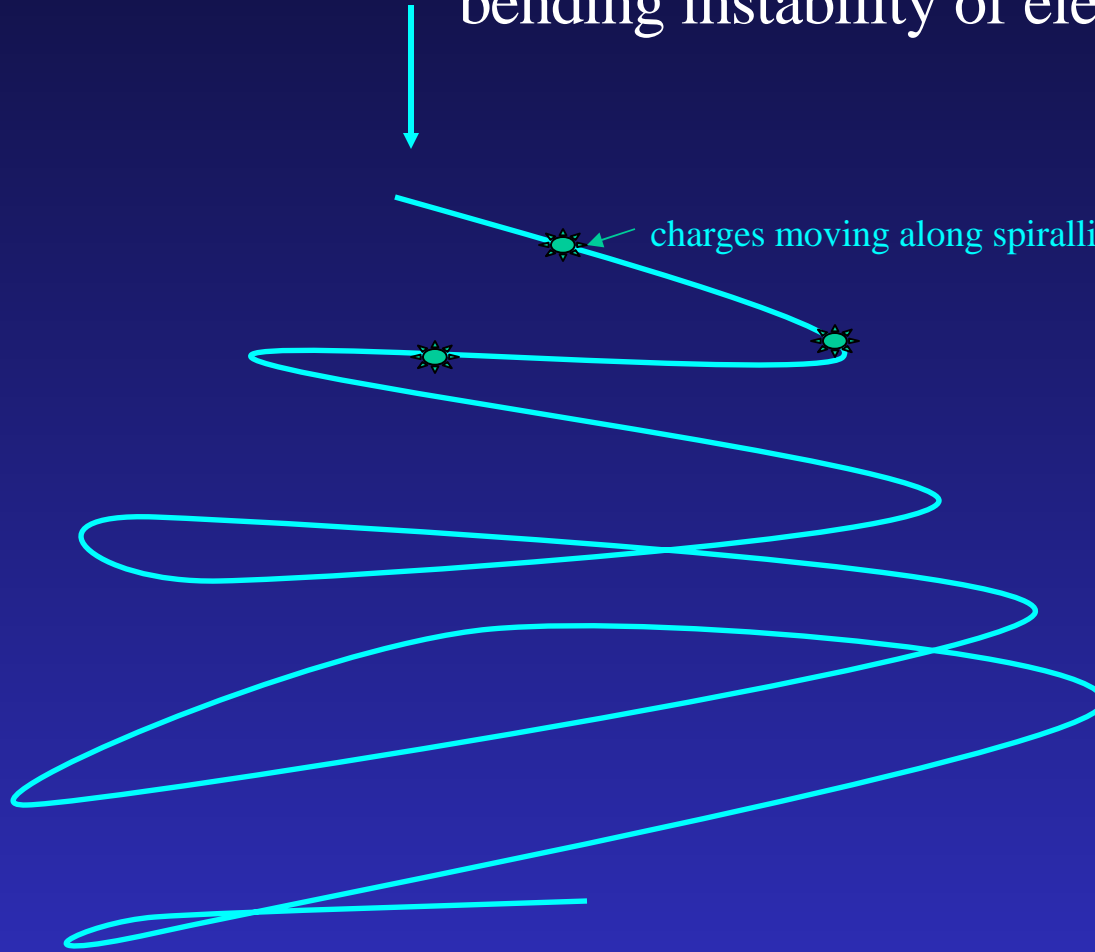


# Electro-spinning

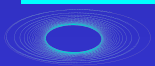
bending instability of electro-spun jet

charges moving along spiralling path

$E \sim 10^5 \text{V/m}$



Bending instability enormously increases path of the jet, allowing to solve problem: how to decrease jet diameter 1000 times or more without increasing distance to tenths of kilometres



# Electro-spinning

## Simple model for elongating viscoelastic thread

$$\frac{d\sigma}{dt} = G \frac{dl}{l dt} - \frac{G}{\mu} \sigma$$

*Stress balance:*  $\mu$  - viscosity,  $G$  – elastic modulus stress,  $\sigma$  stress tensor,  $dl/dt$  – thread elongation

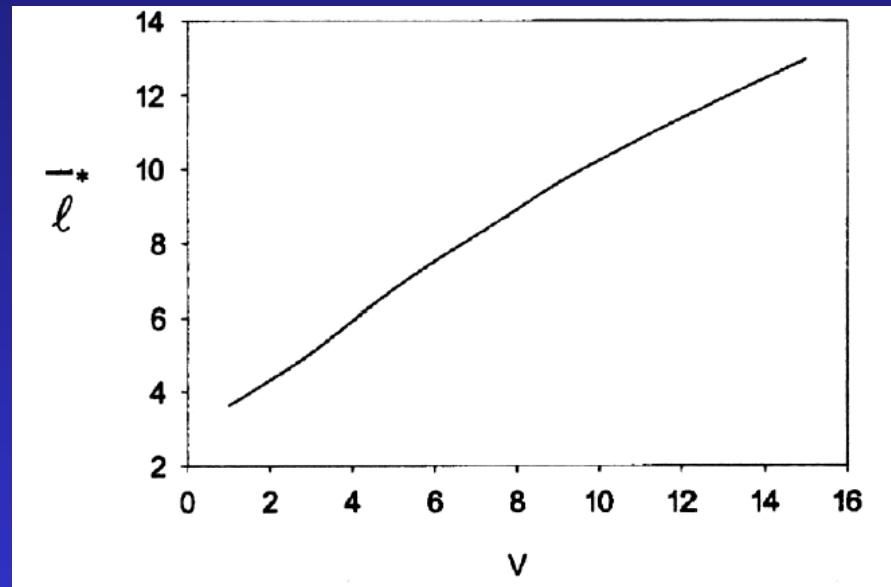
$$m \frac{dv}{dt} = -\frac{e^2}{l^2} - \frac{eV_0}{h} + \pi a^2 \sigma$$

*Momentum balance:*  $V_0$  – voltage,  $e$  – charge,  $a$  – thread radius,  $h$  - distance pipette-collector

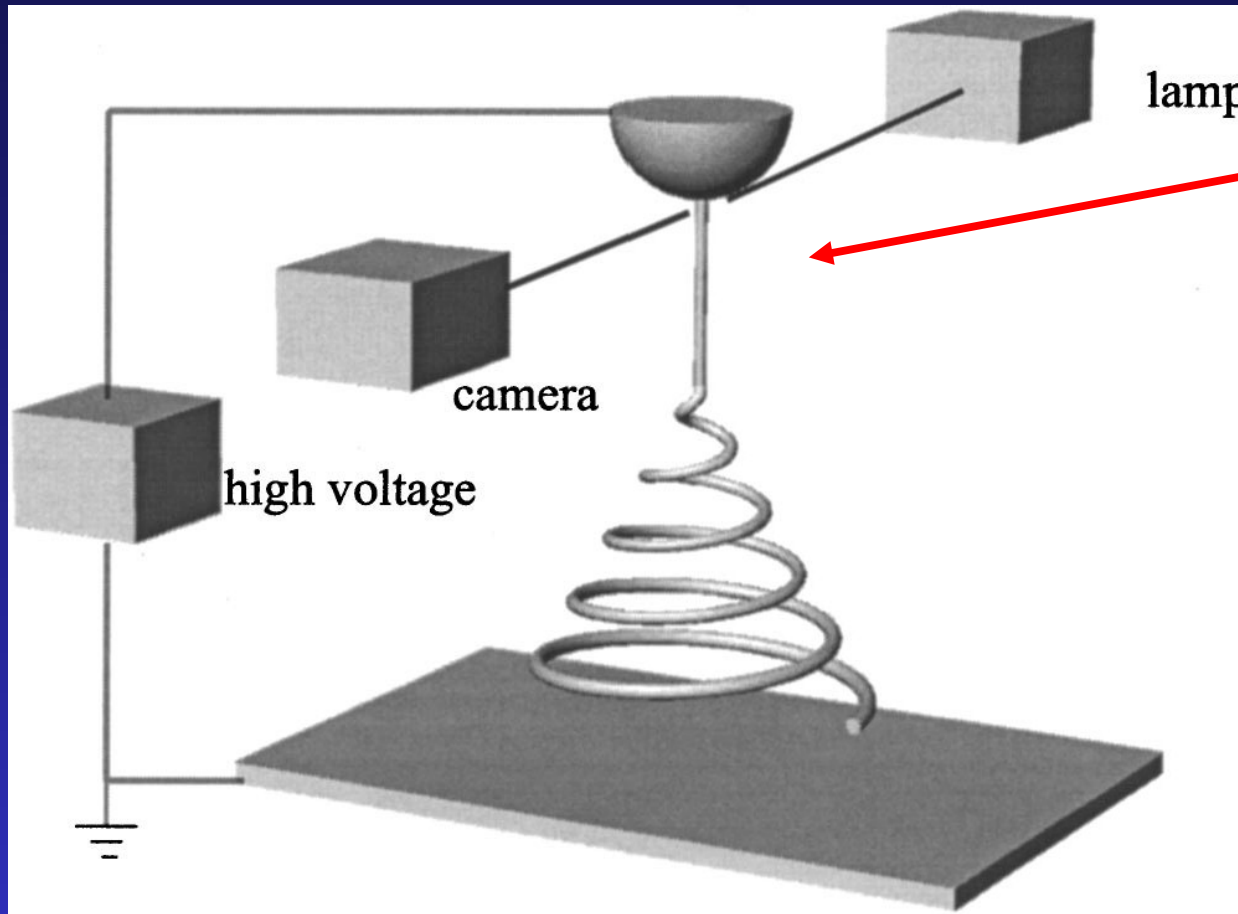
$$\frac{dl}{dt} = -v$$

*Kinematic condition for thread velocity  $v$*

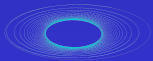
Non-dimensional length of the thread as a function of electrostatic potential



# Nanofibres – basic setup



$5 \text{ Volt/m}10 \sim$



# Nanofibres – howto?

## 1. Viscoelastic fluid:

Dilute solution (4 – 6)% of polyethylene oxide (molar weight  $4 \cdot 10^5$  g/mol), in 40% ethanol –water solvent

## 2. Electrostatic field

high voltage power supply (5-30kV)

plastic syringe

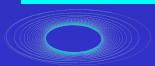
metal grid to collect fibres

## 3. Visualization

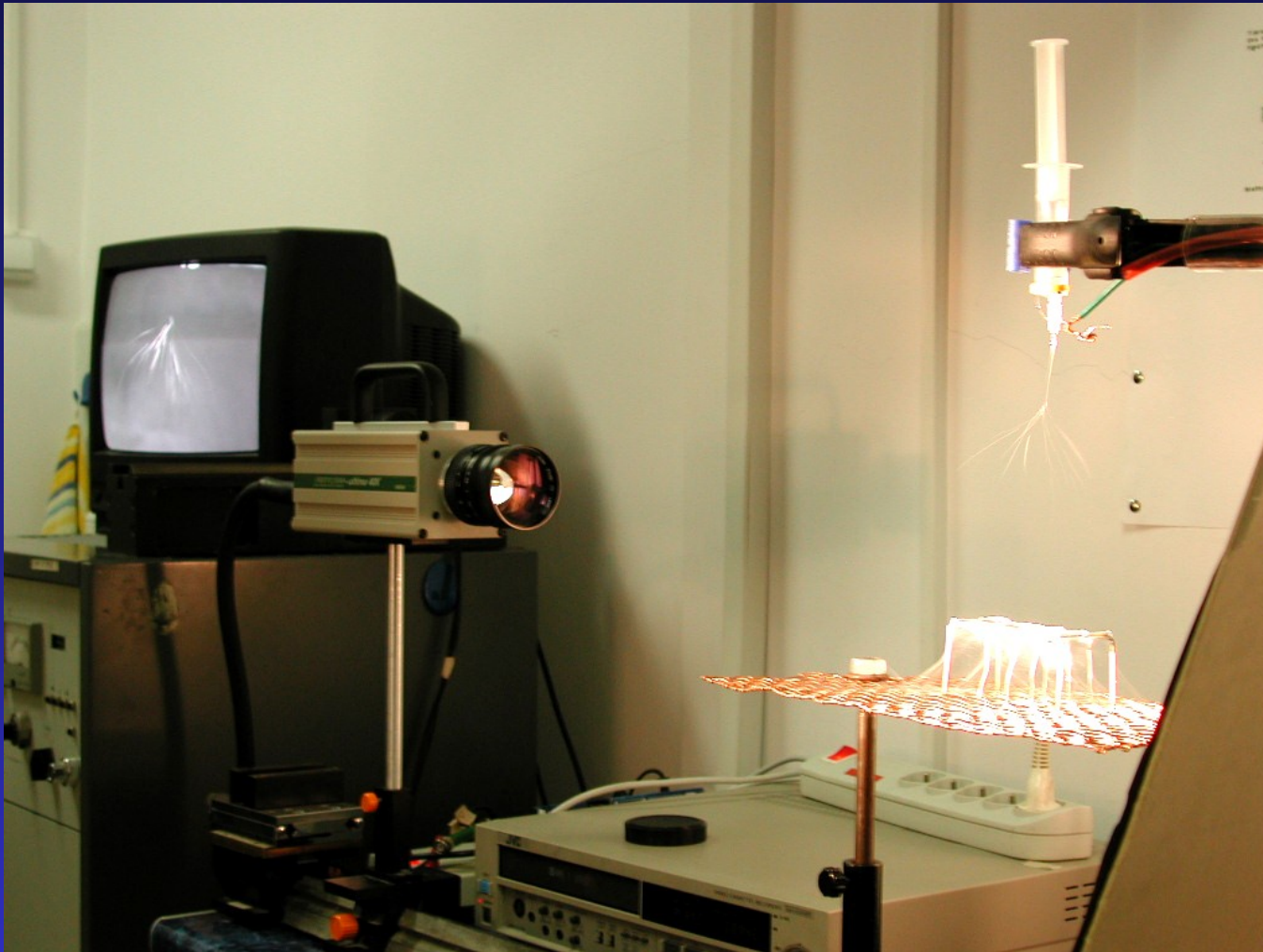
high speed camera (4000 – 40000 fps)

high resolution „PIV” camera (1280x1024pixels)

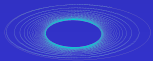
CW Argon laser, double pulse Nd:Yag laser, projection lens



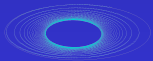
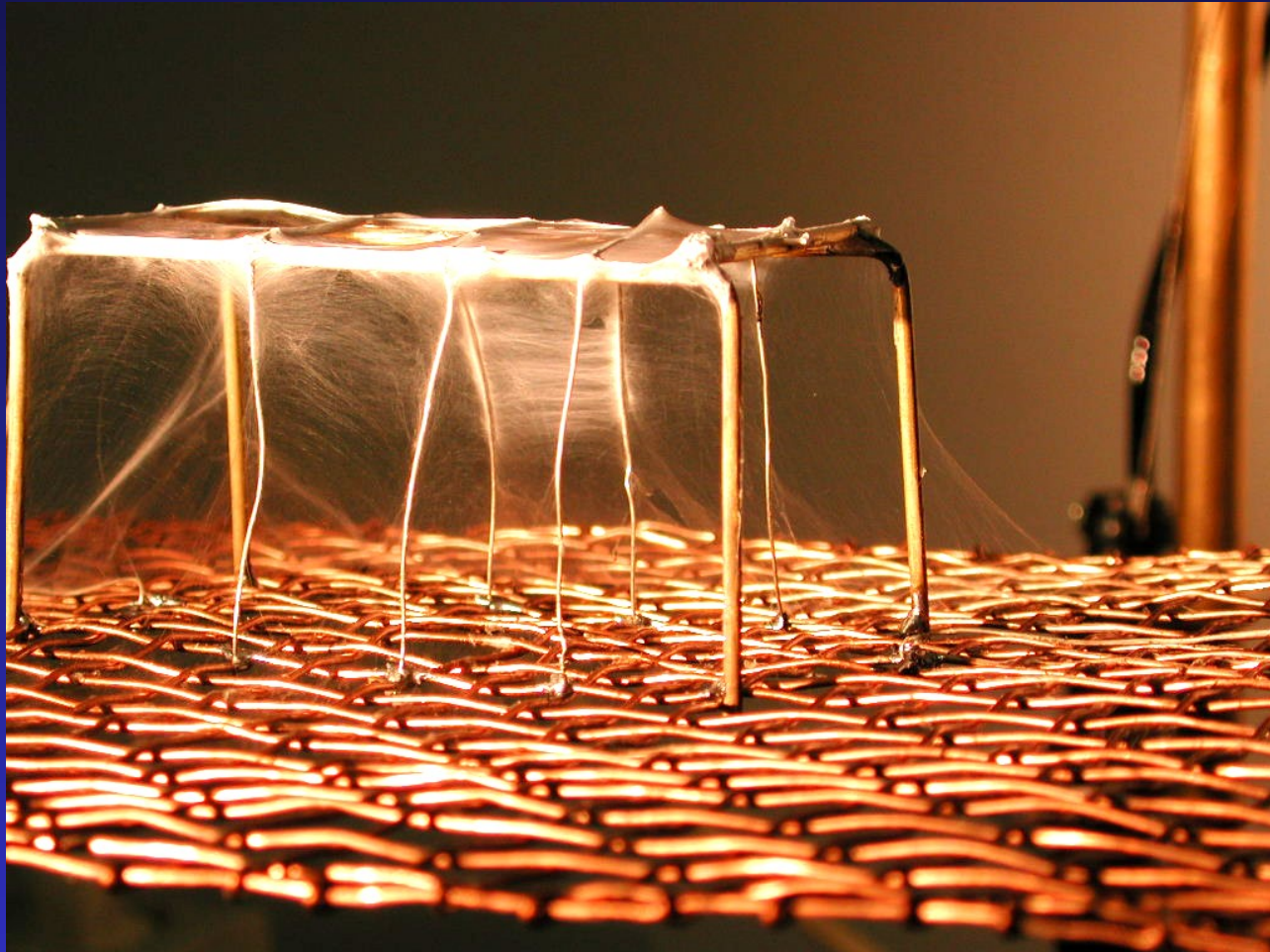
# Nanofibres – basic setup



# Nanofibres collection

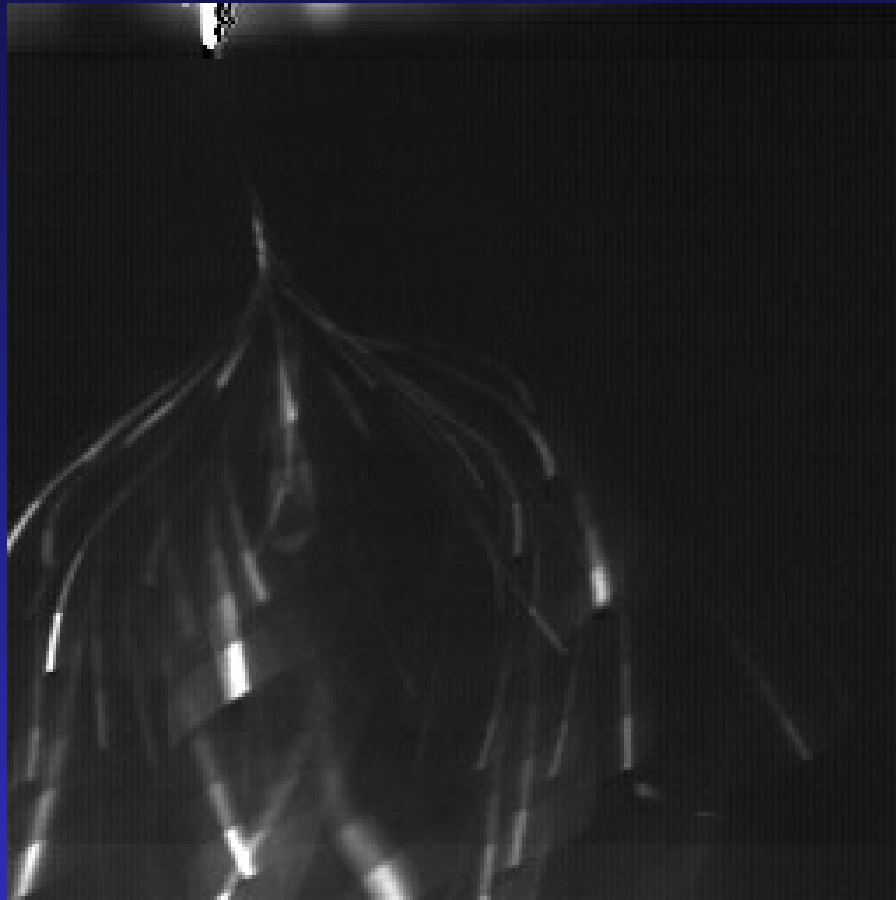


# Nanofibres collection

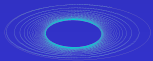


# Electrospinning observed at 30fps

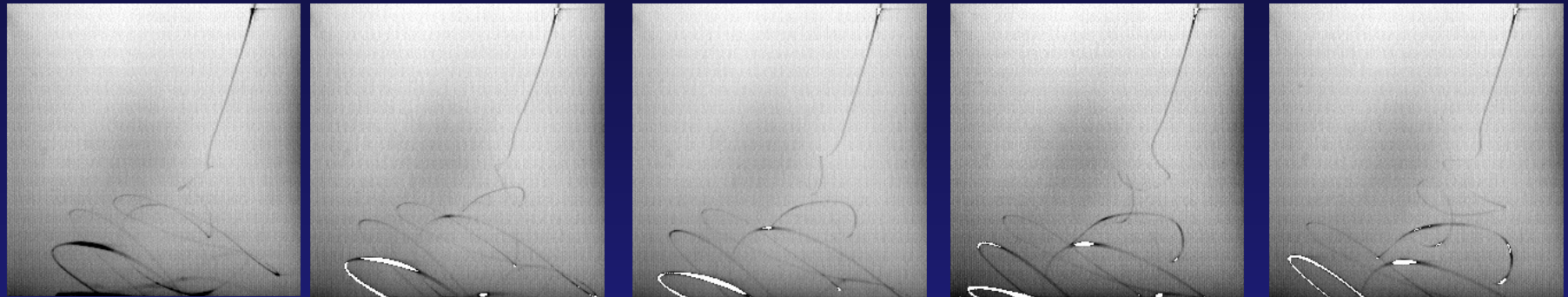
5 cm



Average  
velocity of the  
fibres: 2 m/s



# Electrospinning observed at 4500fps



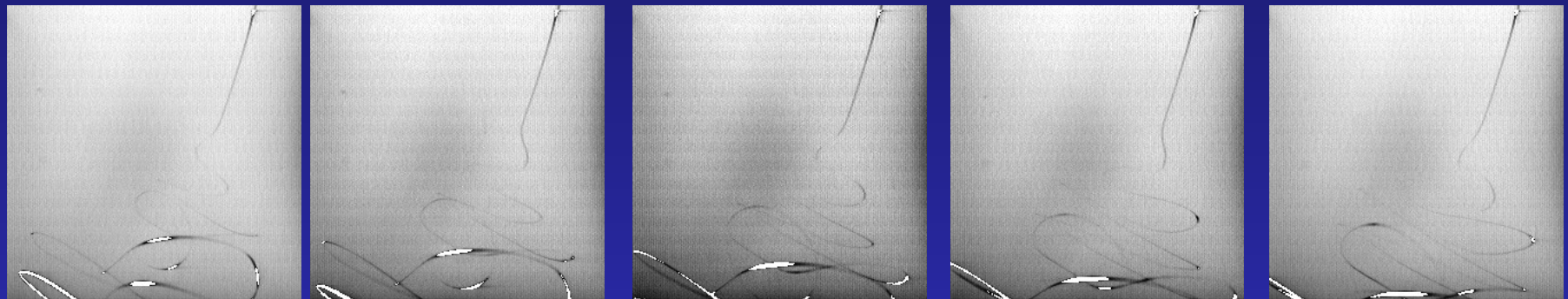
0.0 ms

8.9 ms

17.8 ms

26.7 ms

35.6 ms



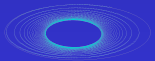
44.4 ms

53.3 ms

62.2 ms

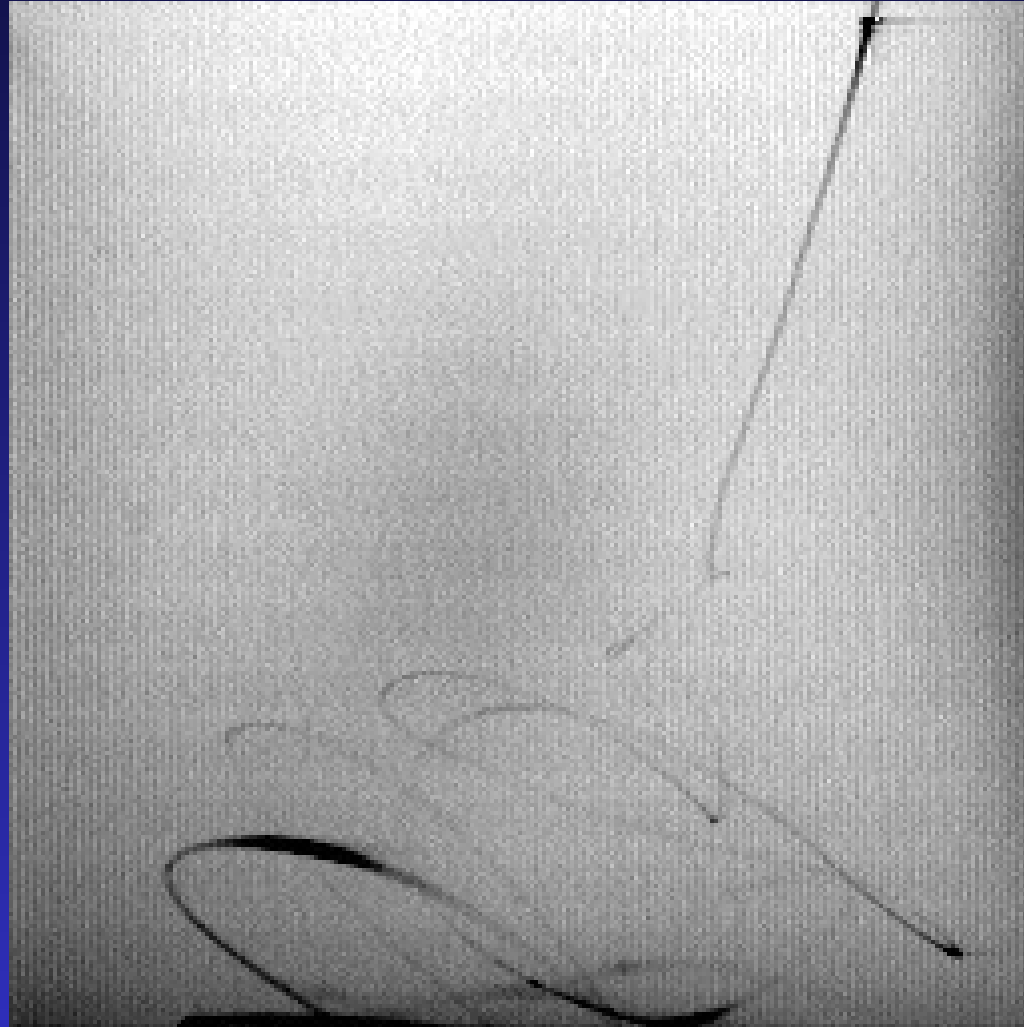
71.1 ms

80.0 ms

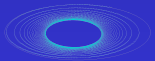


# Electrospinning observed at 4500fps

5 cm

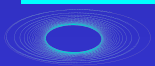
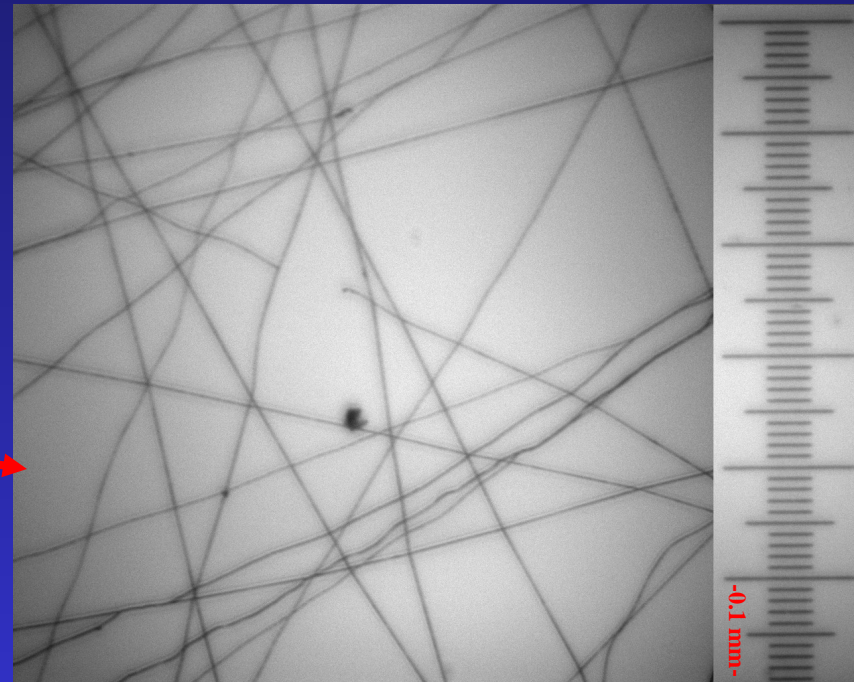
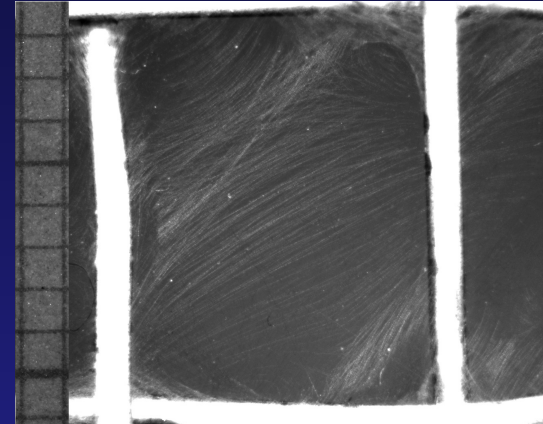
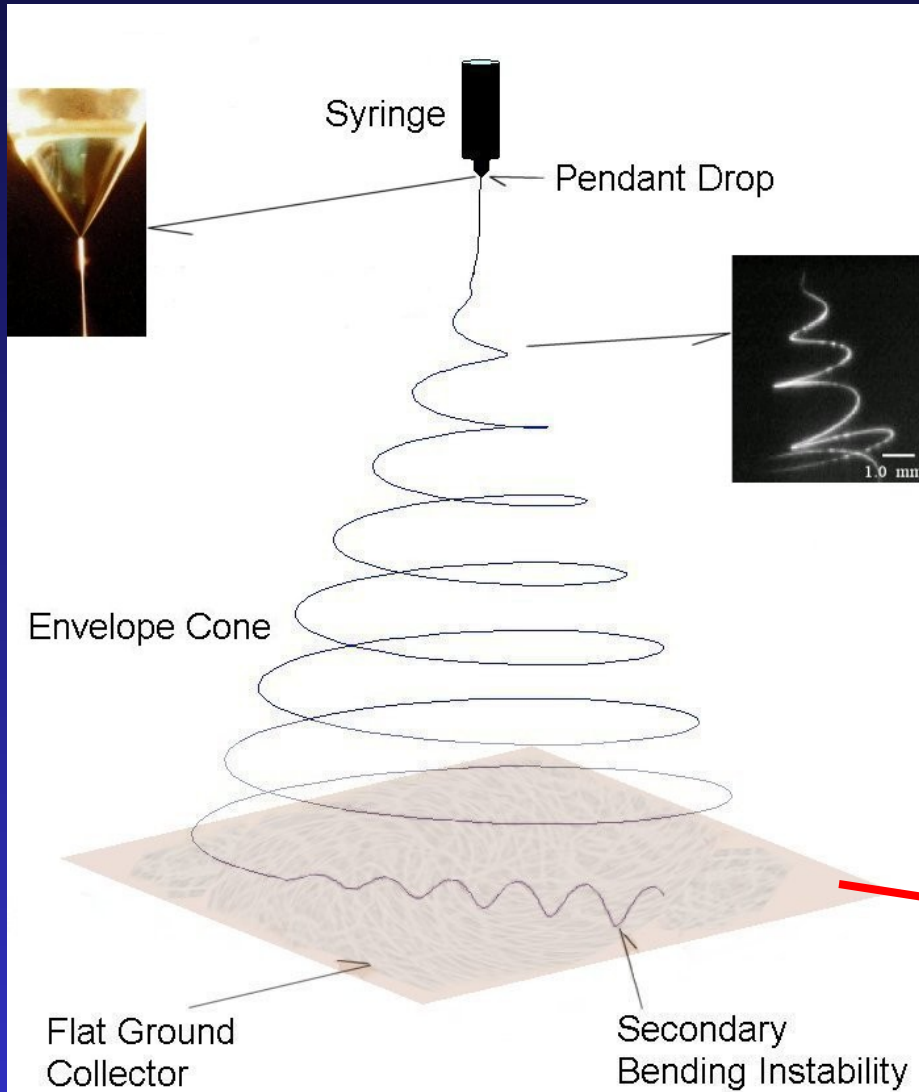


Average  
velocity of the  
fibre: 2 m/s



# Electrospinning

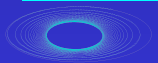
## Collected nanofibres



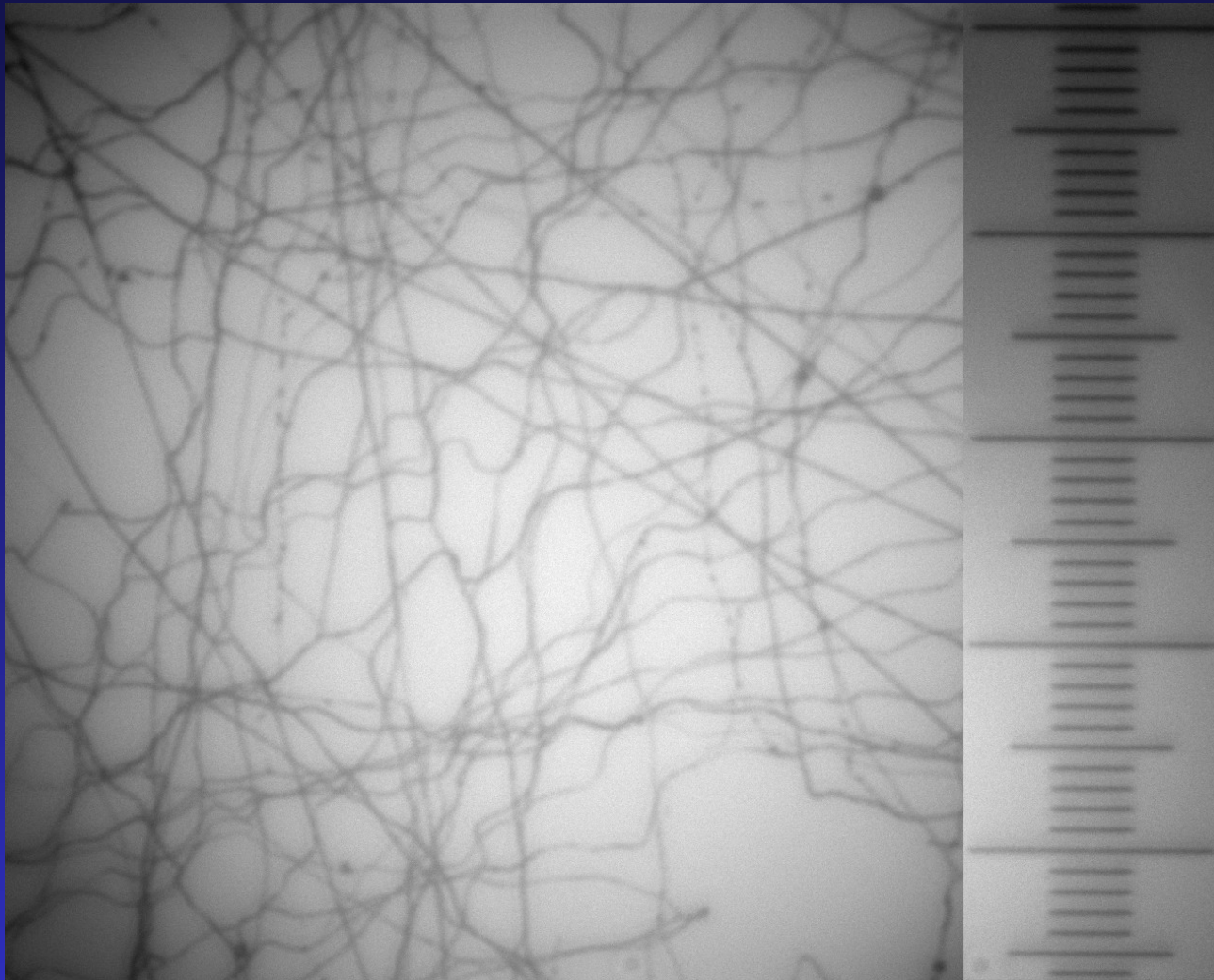
# Electron microscopy



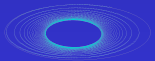
PEO nanofibres



# Failure modes



0.5 mm



# Parametric study

Model validation varying following parameters:

$L$  – length of the rectilinear part

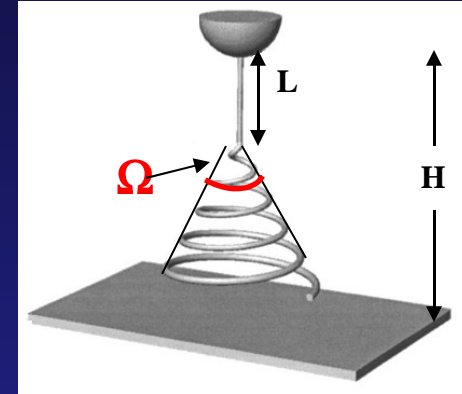
$\Omega$  – angle of the envelope cone (image analysis)

$U$  – velocity of the fibre by PIV method

$a$  – fibre diameter (image analysis)

structure of collected woven (failure modes)

elongation strength of single fibre measured by air jet



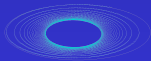
Effect of

Electrostatic potential  $V$

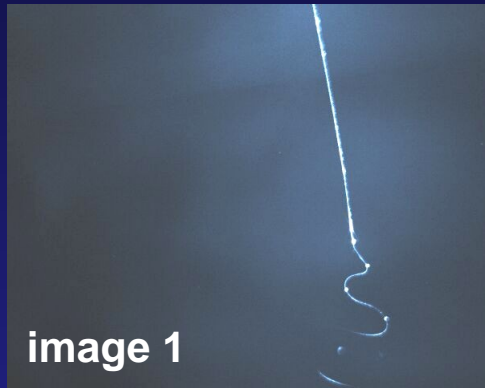
Distance pipette-collector  $H$

Solution concentration  $c$

Distance from the pipette  $x$



# Parametric study

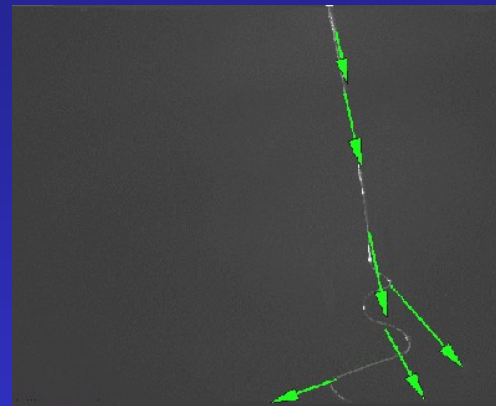


PIV

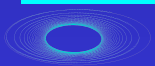
cross – correlation

$\Delta t = 500 \mu s$

- concentration of PEO: 3%
- Voltage: 8 kV
- $H = 215 \text{ mm}$
- polymer solution with the addition of fluorescent particles (0.3 $\mu\text{m}$  polymer microspheres)
- light source: Nd:Yag laser



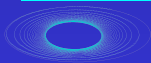
Average  
velocity of the  
fibres: 2 m/s



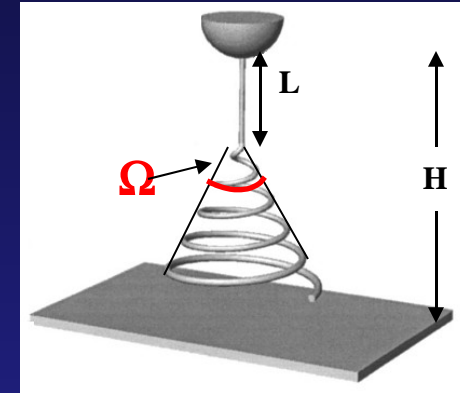
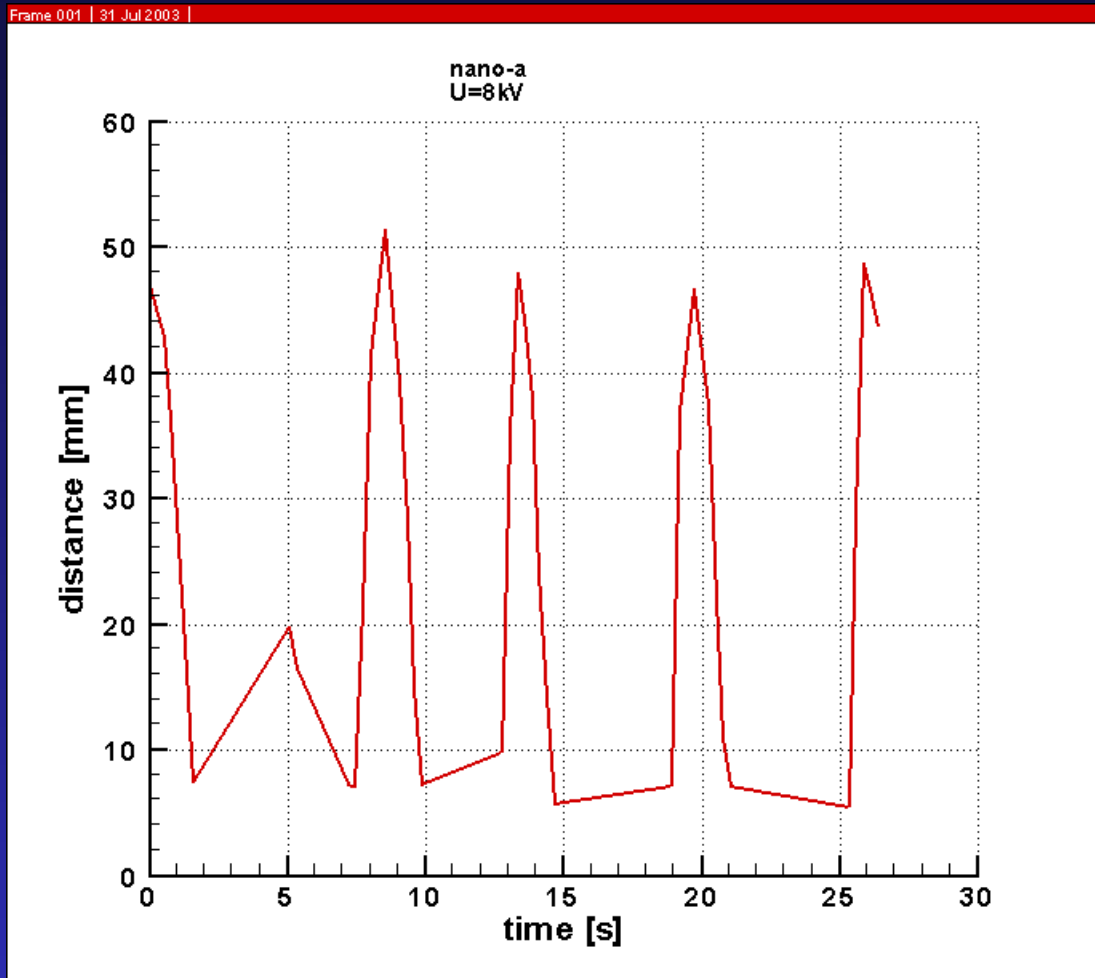
# Tested polymers

Test	Polymer	Solvent	Concentration	Voltage [kV]	Electrospinning
I	<b>PEO</b> Polyethylene-oxide	40% water – ethanol solution	3 – 4 %	3 – 12	good and stable process for voltage up to 10kV
II	<b>DBC*</b>	Ethanol	2-29%	6 – 16	fairly good
III	<b>TAC*</b>	Ethanol	7-30 %	3 – 30	polymer too viscous
			1-7 %	10 – 30	difficult
IV	<b>PAN*</b>	DMF	1-25 %	5 – 25	very good

*\*Prepared at Technical University of Łódź by dr Anna Błasińska*



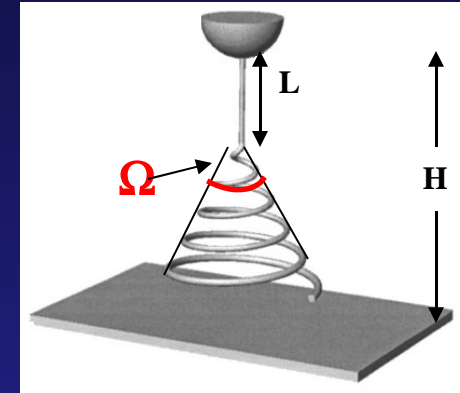
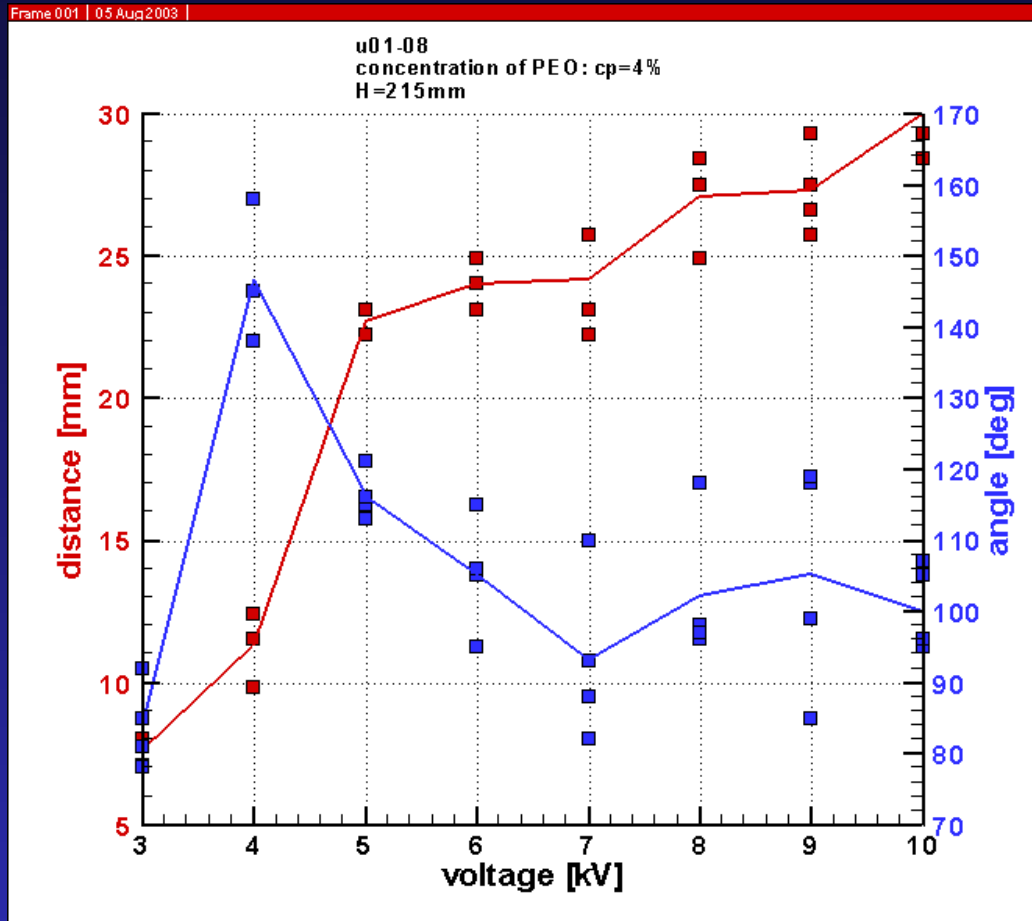
# Parametric study



- Polymer: PEO
- Concentration:  $c=3\%$
- Solvent: 40% water-ethanol solution
- $H=215\text{mm}$
- $V=8\text{kV}$

$L(t)$  – instability of length of the rectilinear part

# Parametric study

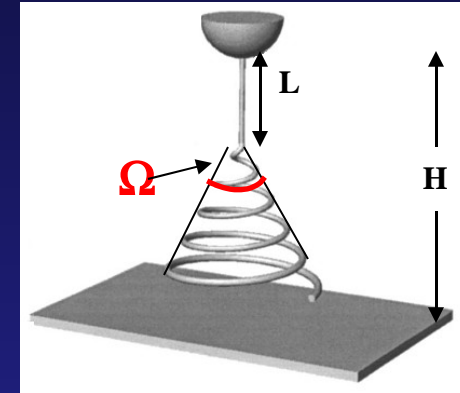
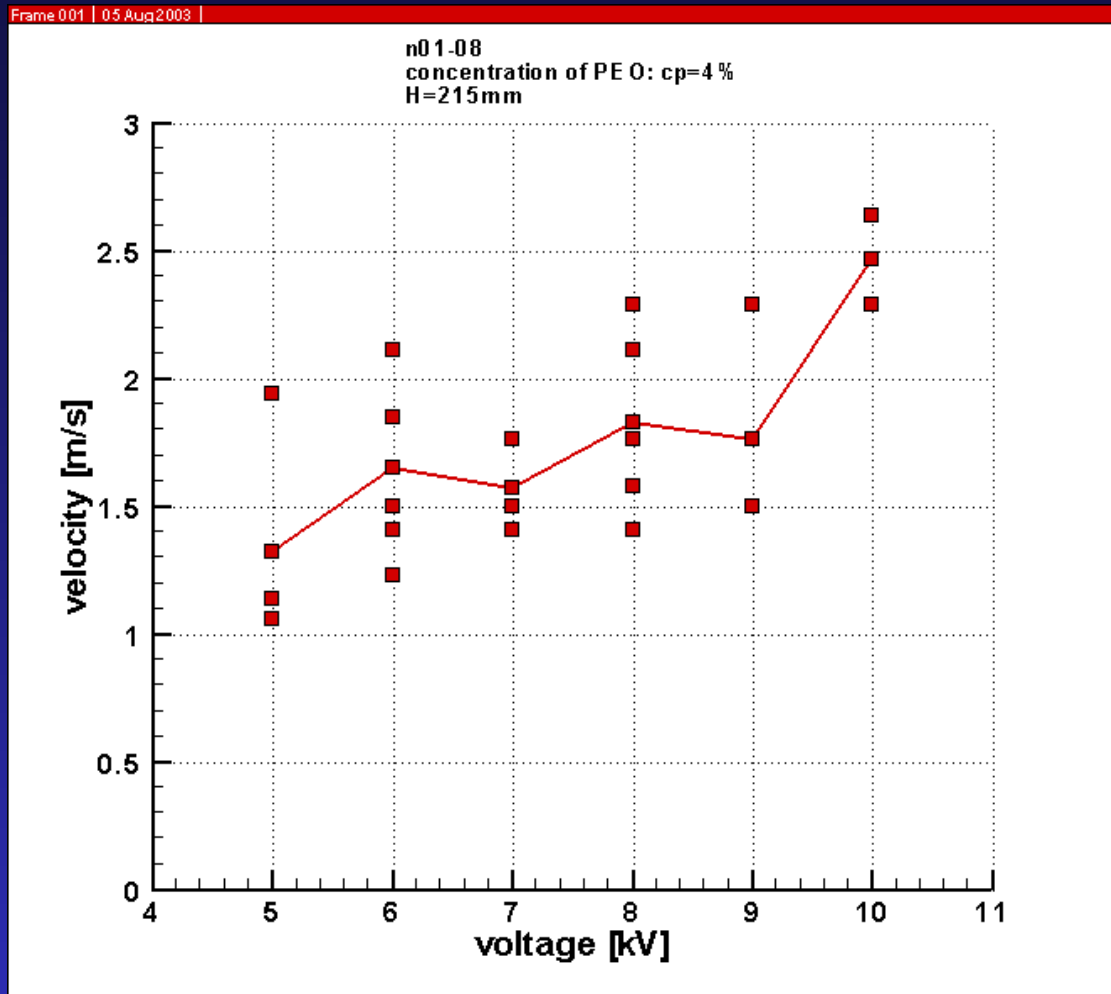


- Polymer: PEO
- Concentration: c=4%
- Solvent: 40% water-ethanol solution
- H=215mm

L (V) – length of the rectilinear part

$\Omega$  (V) – angle of the envelope cone

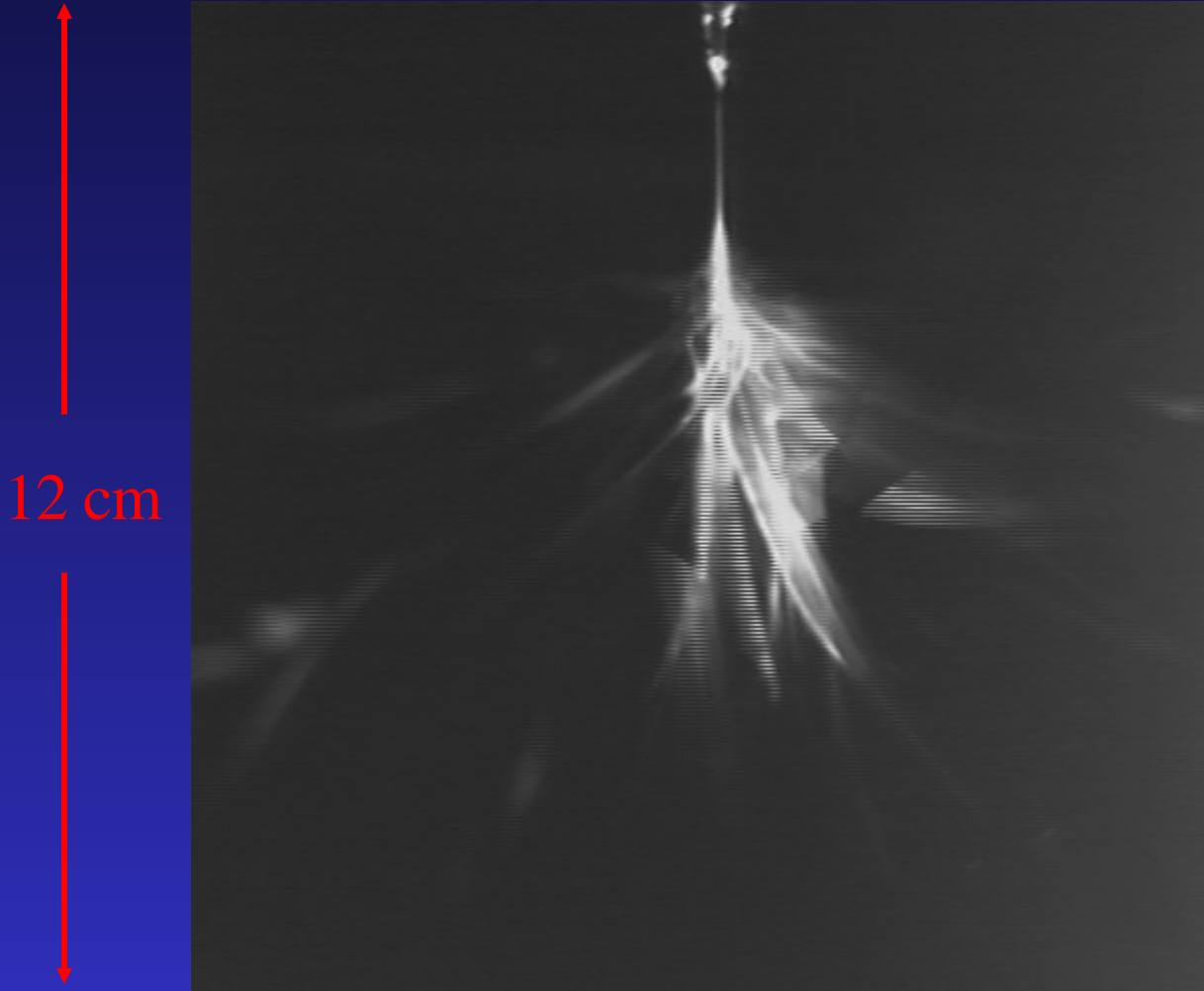
# Parametric study



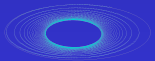
- Polymer: PEO
- Concentration: c=4%
- Solvent: 40% water-ethanol solution
- H=215mm

**U(V) – velocity of the fibre at the rectilinear part**

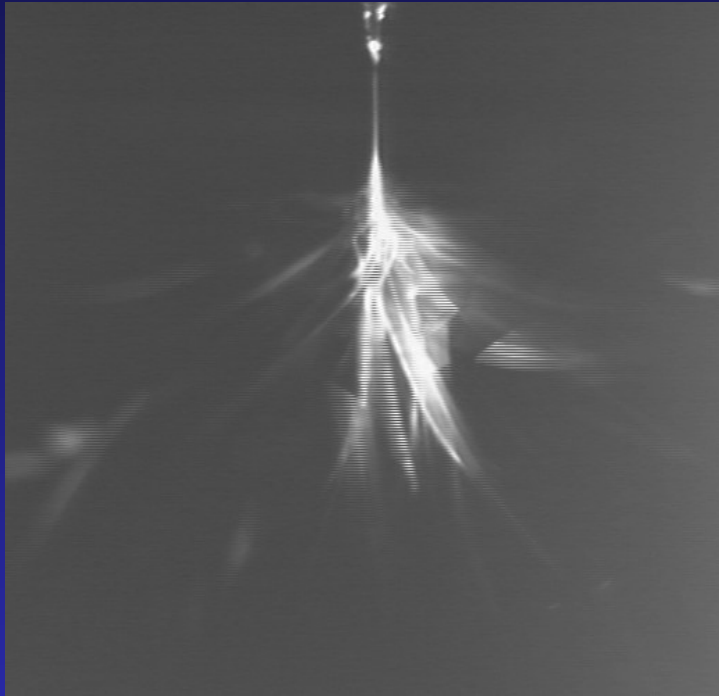
# Electrospinning observed at 25fps



- Polymer: DBC
- Concentration:  $c=9\%$
- Solvent: ethanol
- $H=215\text{mm}$
- $V=6\text{kV}$



# Different structure of spinning fibres for DBC polymer

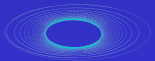


U=6kV

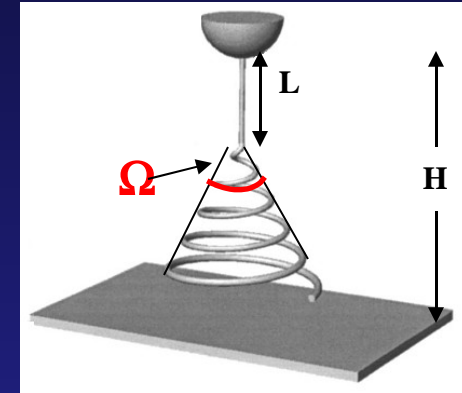
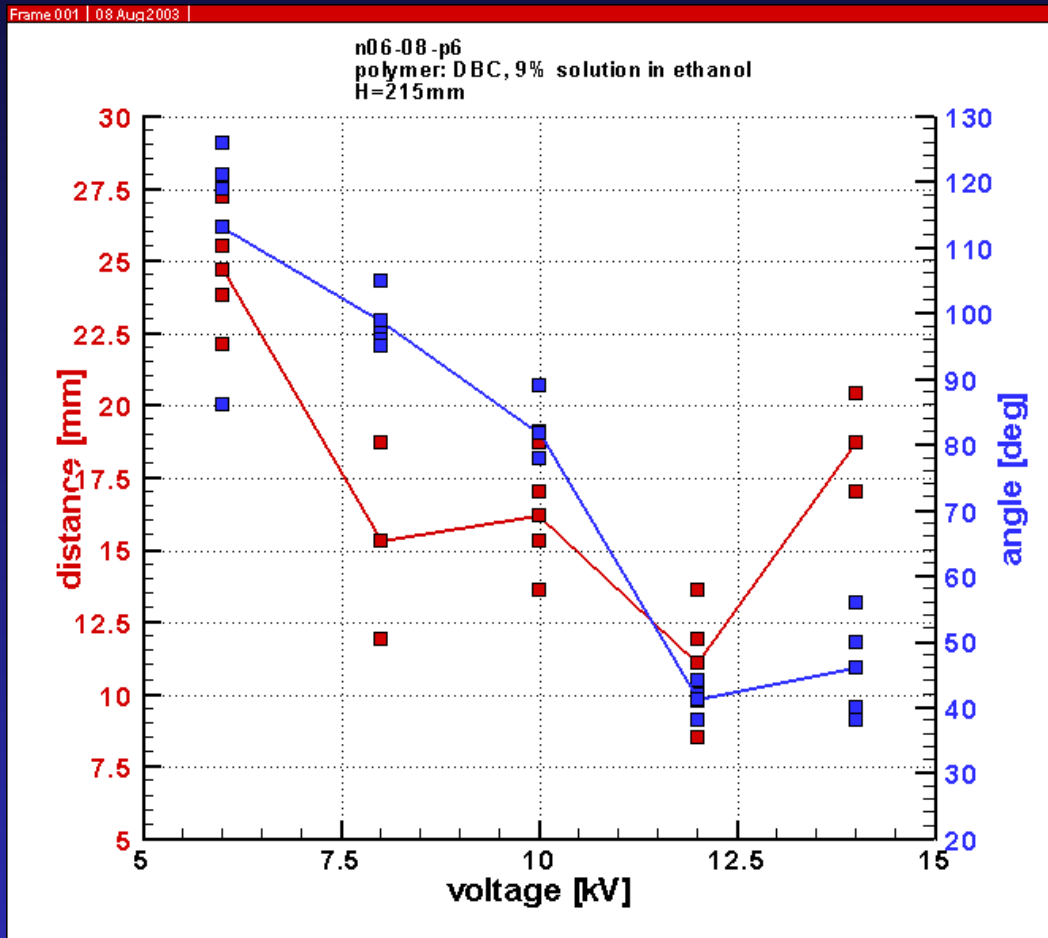


U=12kV

DBC: c=9% H=215mm



# Parametric study



- Polymer: DBC
- Concentration: c=9%
- Solvent: ethanol
- H=215mm

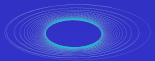
L (V) – length of the rectilinear part

$\Omega$  (V) – angle of the envelope cone

# Electrospinning observed at 25fps



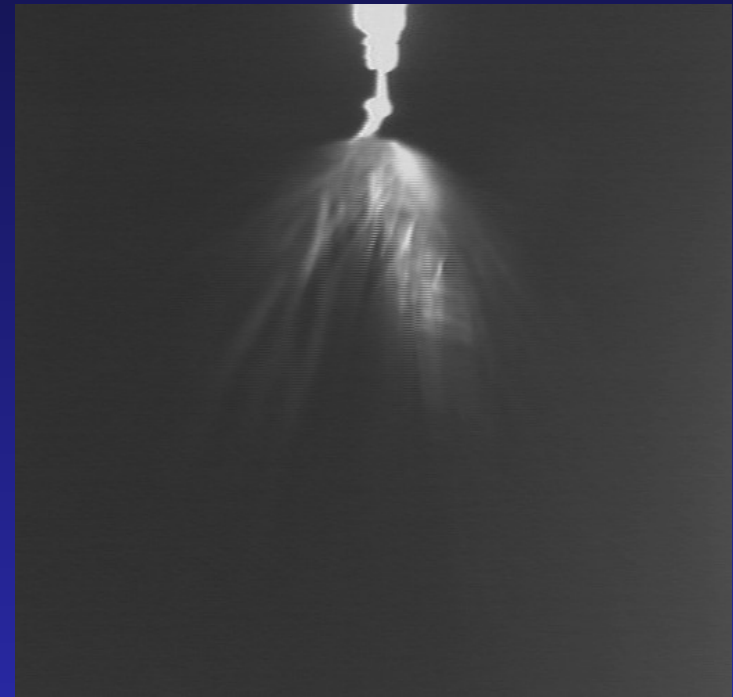
- Polymer: PAN
- Concentration:  $c=15\%$
- Solvent: DMF
- $H=215\text{mm}$
- $V=13\text{kV}$



# Different structure of spinning fibres for PAN polymer

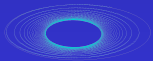


U=13kV

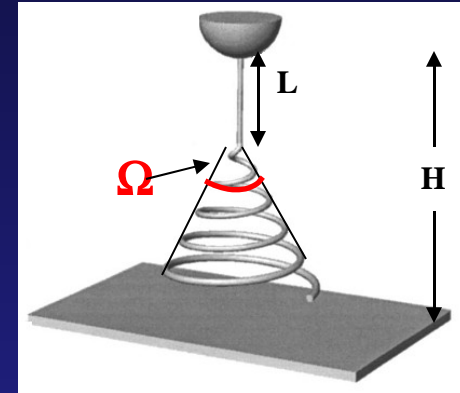
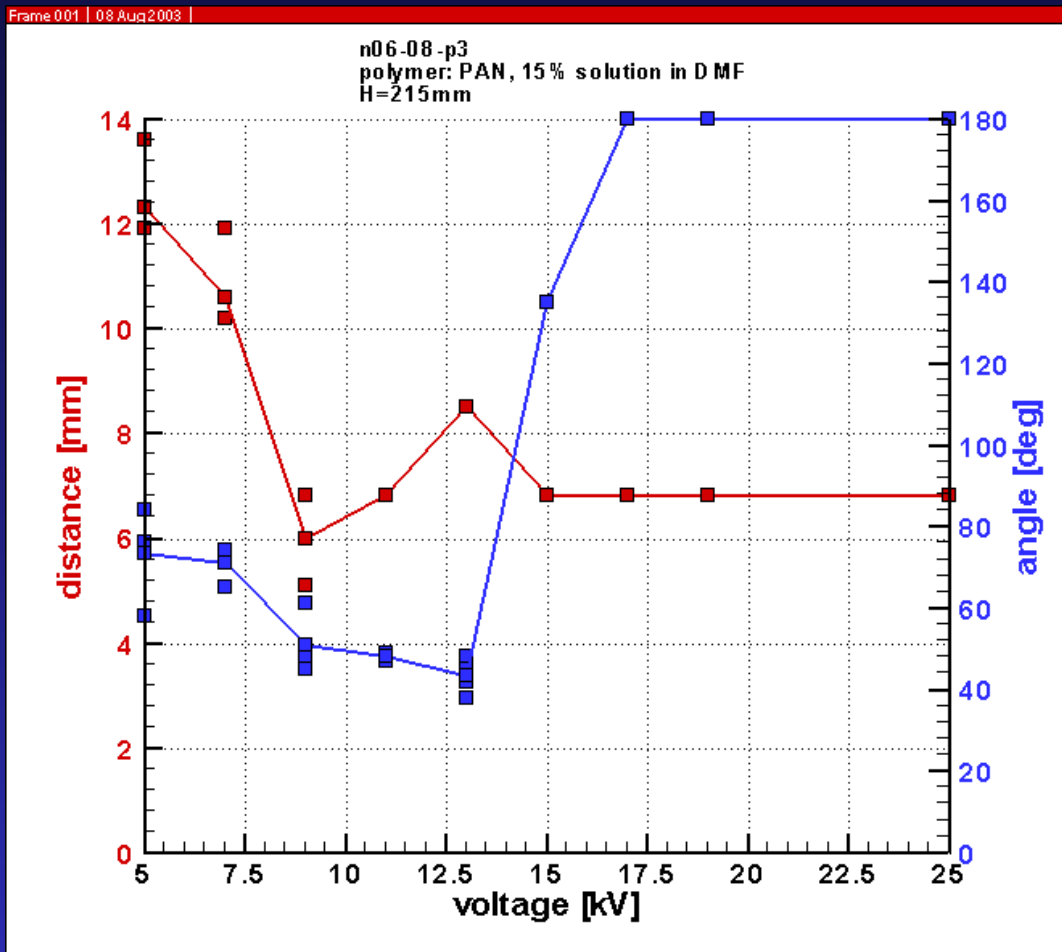


U=19kV

PAN: c=15% H=215mm



# Parametric study

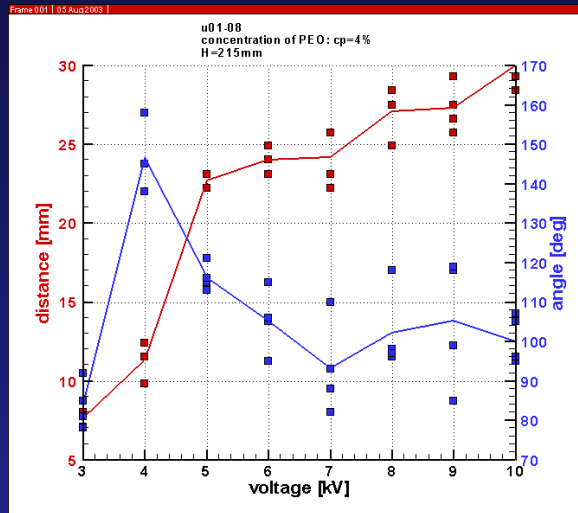


- Polymer: PAN
- Concentration: c=15%
- Solvent: DMF
- H=215mm

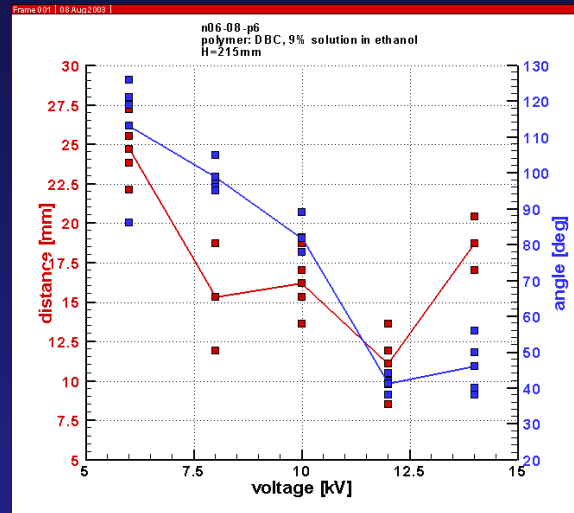
L (V) – length of the rectilinear part

$\Omega$  (V) – angle of the envelope cone

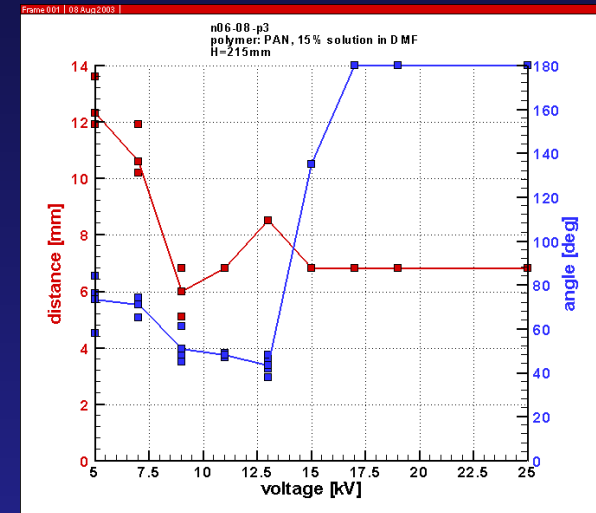
# Comparison of PEO & DBC & PAN polymers



PEO



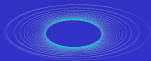
DBC



PAN

L (V) – length of the rectilinear part

$\Omega$  (V) – angle of the envelope cone

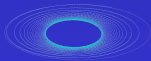


# Conclusions

**Electrostatic elongation of polymer threads allows to produce relatively easily fibres in nano range diameters**

**Collection of nano-woven of bio-active polymers, e.g.. chitin may have practical application for tissue growth**

**Electrospinning of polymer solutions still lacks detailed mathematical model, necessary to perform process optimisation**



# Acknowledgements

**We would like to acknowledge the valuable contribution of dr Anna Błasińska from TU of Łódź and Anna Blim from IPPT PAN in the work presented.**

**The work was partly supported by the Centre of Excellence AMAS of the IPPT PAN**

