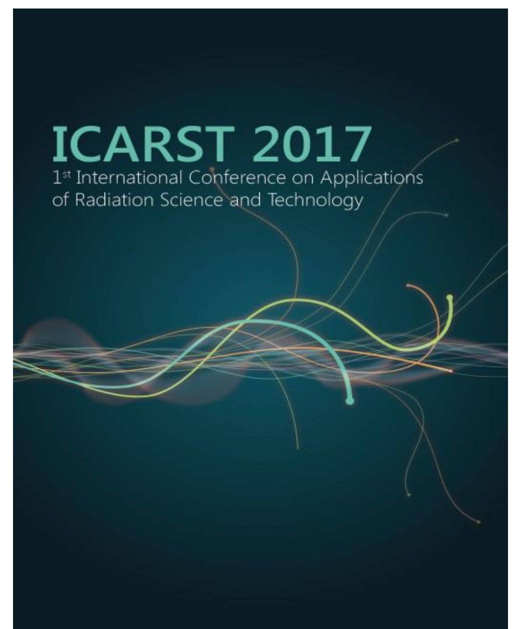
DE LA RECHERCHE À L'INDUSTRIE

24/04/17

Conservation of the piezoelectric response of PVDF films under irradiation

G. Melilli, D. Lairez, D. Gorse, E. Garcia-Caurel, A. Peinado, O. Cavani, B. Boizot, M-C Clochard



Context

-Renewable harvesting energy → **Polymer piezoelectricity**

-Actual demand: development of piezogenerator flexible for portable devices

Material of interest: **Poly(vinylidene fluoride) (PVDF)**

piezoelectric PVDF membrane has experienced a resurgence of interest for **energy harvesting**.

•decrease of energy consumption
•Robustness and flexibility allows an easier integration respect to conventional piezoelectric materials such as PZT ceramics

How to enhance piezoelectric properties in miniaturized objects?

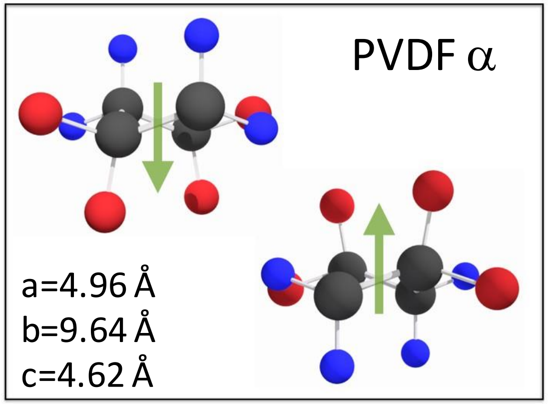
- Multilayers or nanostructuration

- Structural modification : SHI irradiation and e-beam*,**

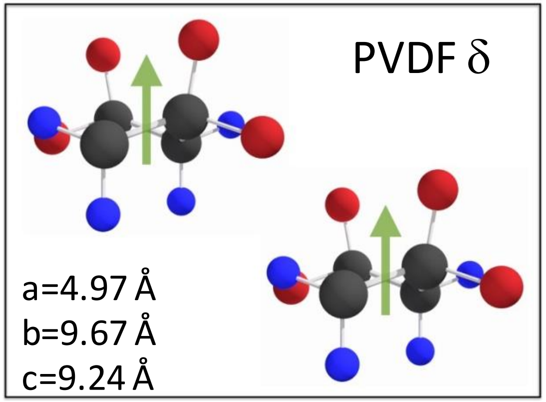
** Zhang et al, Science 280 (1998) 2101-2104 ; ** Giegerich et al, IEEE Trans., 7, 3 (2000) 353-359*

PVDF

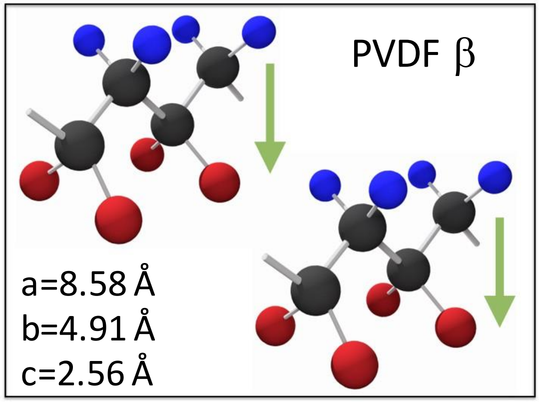
PVDF polymorphism: crystalline phases α, β, δ and γ phases.



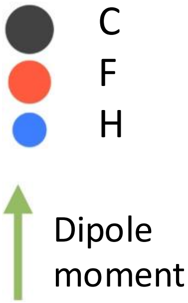
Monoclinic cell
Non net dipole moment

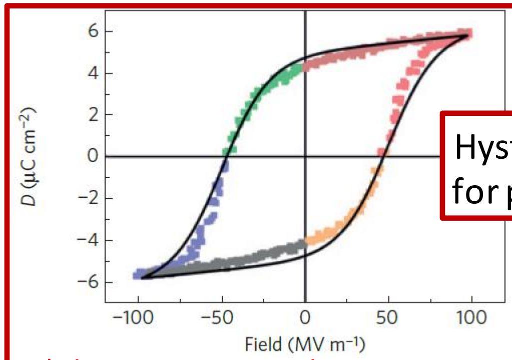


Orthorombic cell
net dipole moment



Orthorombic cell
net dipole moment





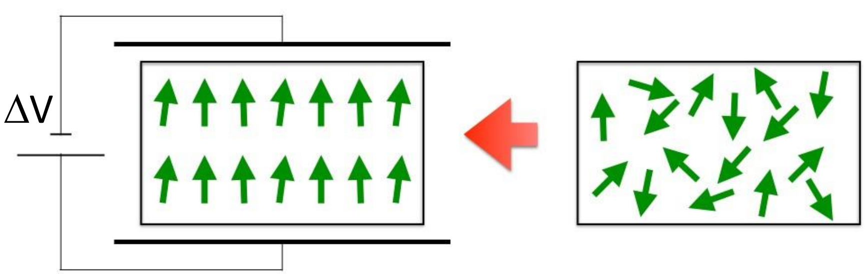
Hysteresis loop for piezo- PVDF

* Ilias Katsouras *et al.* Nature Materials 15, 78–84 (2016)

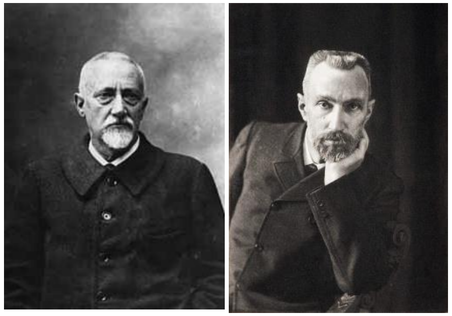
Poling process

(T≈ 95°C , ΔV=50 ÷ 100 MV.m^{-1})

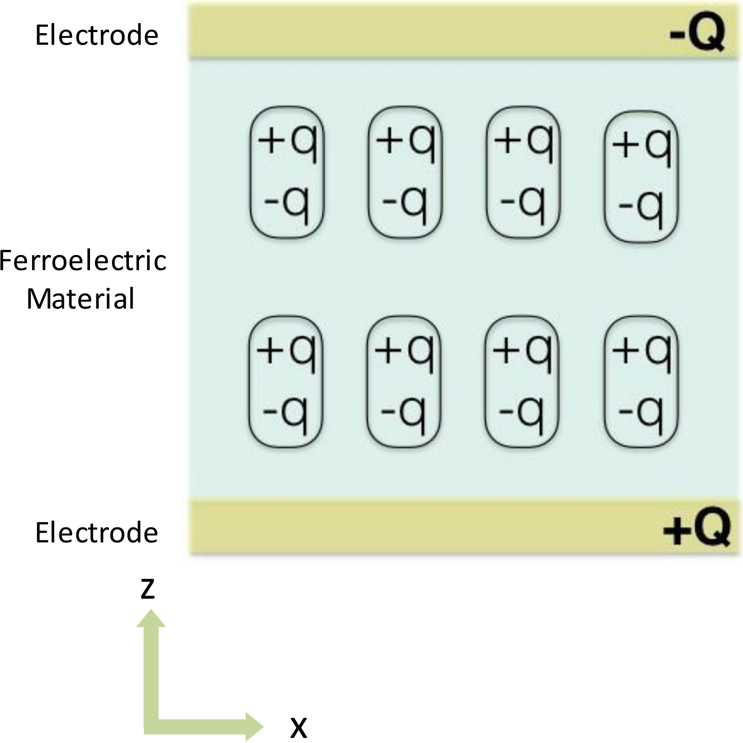
Dipole moments are randomly oriented (β and δ phase)



Piezoelectric effect



Curie Brothers
Direct piezoelectric effect
1880



Piezoelectricity is defined as the aptitude to convert mechanical strain in electrical charge and vice versa.

Constitutive equations

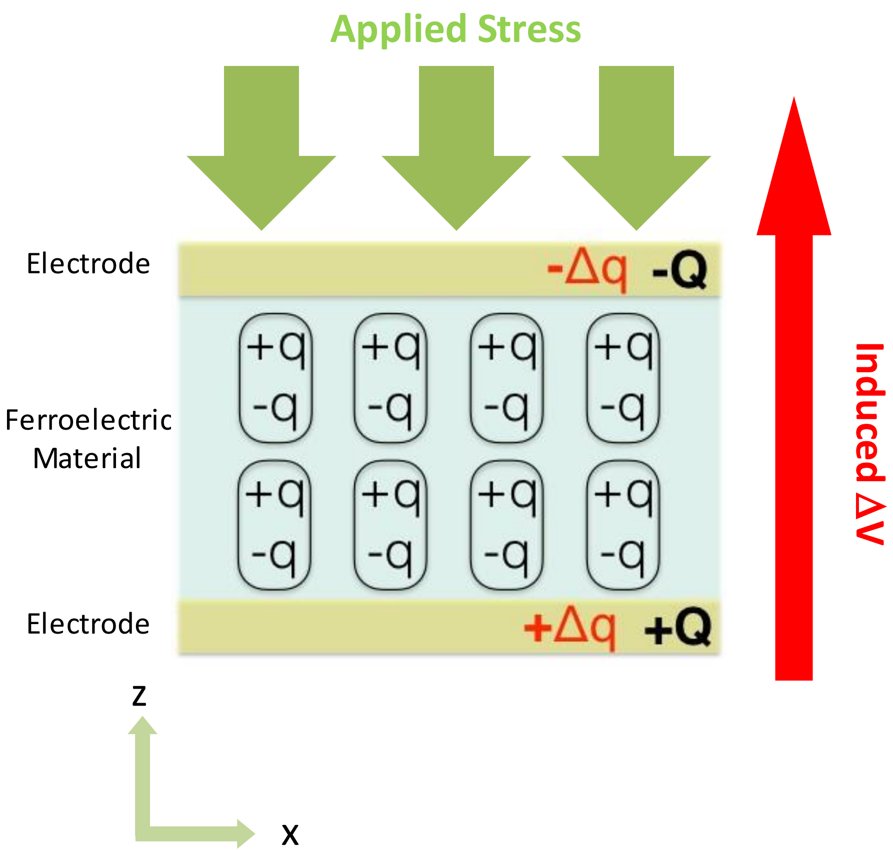
$$D = \varepsilon^T E + d_{33} T$$

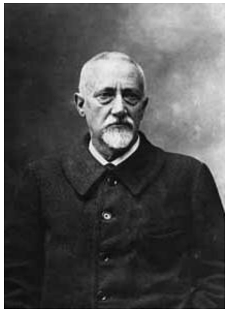
$$S = d_{33} E + s^E T$$

D : electric displacement ($C.m^{-2}$)
E : electric field ($V.m^{-1}$)
T : stress ($N.m^{-2}$)
S : strain
ε^T : dielectric constant
s^E : compliance (inverse of the young's modulus)
d_{33} : piezoelectric constant ($m.V^{-1}$ or $C.N^{-1}$) in z direction

Piezoelectric effect

Direct piezoelectric effect (sensors)






Curie Brothers
Direct piezoelectric effect
1880

Piezoelectricity is defined as the aptitude to convert mechanical strain in electrical charge and vice versa.

Constitutive equations

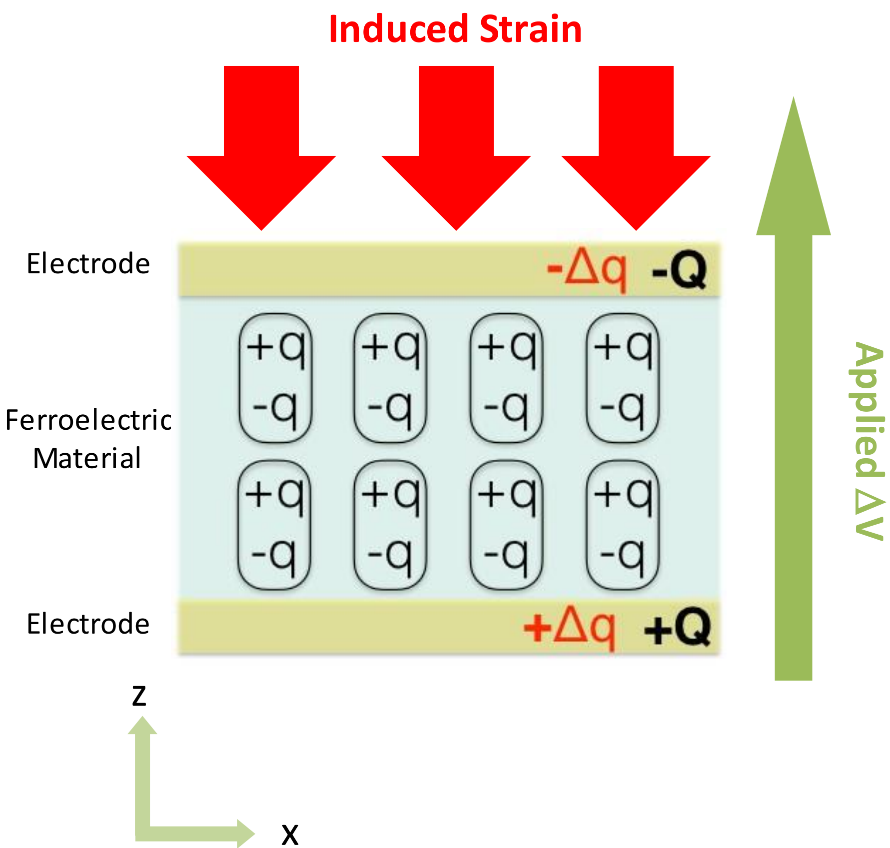
$$D = \varepsilon^T E + d_{33} T$$

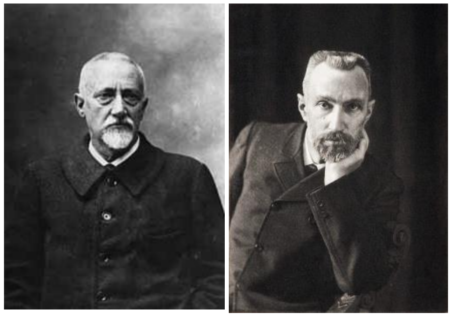
$$S = d_{33} E + s^E T$$

D : electric displacement ($C.m^{-2}$)
E : electric field ($V.m^{-1}$)
T : stress ($N.m^{-2}$)
S : strain
ε^T : dielectric constant
s^E : compliance (inverse of the young's modulus)
d_{33} : piezoelectric constant ($m.V^{-1}$ or $C.N^{-1}$) in z direction

Piezoelectric effect

Inverse piezoelectric effect (Actuators)





Curie Brothers
Direct piezoelectric effect
1880

Piezoelectricity is defined as the aptitude to convert mechanical strain in electrical charge and vice versa.

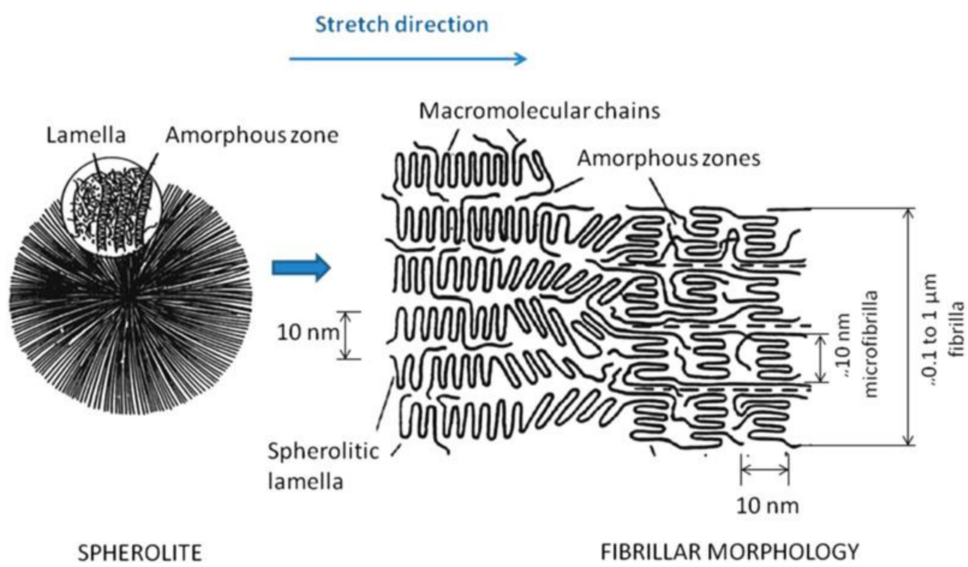
Constitutive equations

$$D = \varepsilon^T E + d_{33} T$$

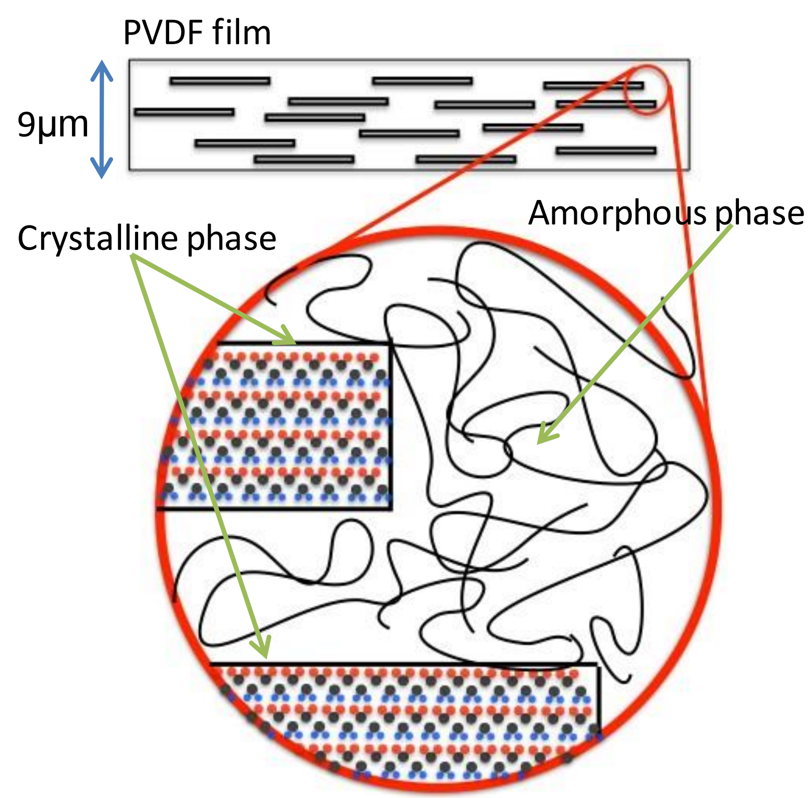
$$S = d_{33} E + s^E T$$

D : electric displacement ($C.m^{-2}$)
E : electric field ($V.m^{-1}$)
T : stress ($N.m^{-2}$)
S : strain
ε^T : dielectric constant
s^E : compliance (inverse of the young's modulus)
d_{33} : piezoelectric constant ($m.V^{-1}$ or $C.N^{-1}$) in z direction

Bi-oriented PVDF film : an easy way to obtain β-PVDF



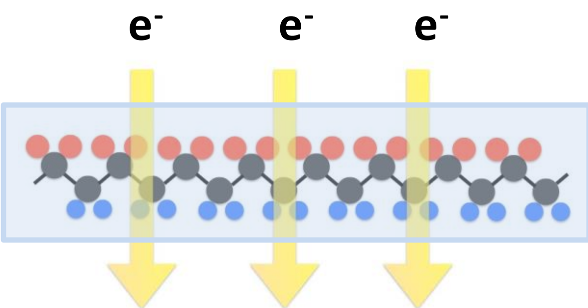
- ❑ Mechanical stretching allows to transform α phase (**spherulite**) in β phase (**fibrillar**).



- ❑ The bi-oriented piezo PVDF film is an anisotropic system with majority β phase

Nominal Thickness (um)	9 µm
Electromechanical coupling factor K_T (%)	10 to 15
d_{33} (pC/N)	27 ± 20%
Young's modulus (GPa)	2.5
Crystallinity content (%)	36±2

E-beam and SHI irradiation



2.5MeV

Investigated doses for SHI irradiation:
0.076 kGy, 0.76 kGy and 7.6 kGy

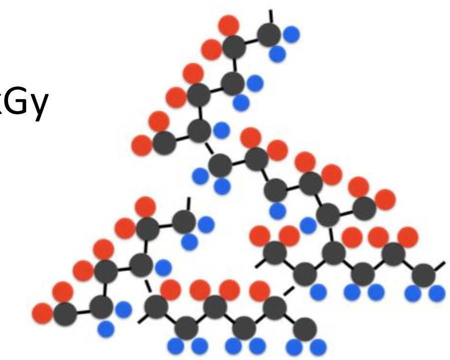
Grand Accélérateur National d'Ions Lourds
GANIL
Laboratoire commun CEA / DSM - CNRS / IN2P3

$_{136}Xe^{48+}$
$7.46 MeV.amu^{-1}$

Primary beam interacts with valence electrons generating defects.

Gel dose ≈ 10kGy

Crosslinking

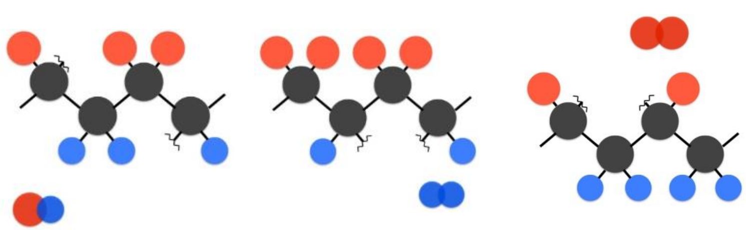


Investigated e-beam range doses: 5, 10, 25, 50 and 100 kGy
(***Gy** absorption of one joule of radiation energy per kilogram of matter)

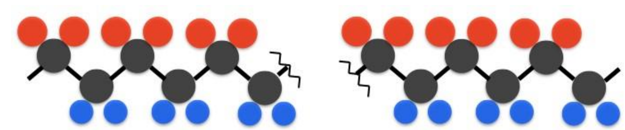
Irradiations were performed under He atmosphere

Defects in PVDF:

Radicals + gas release



Chain scission

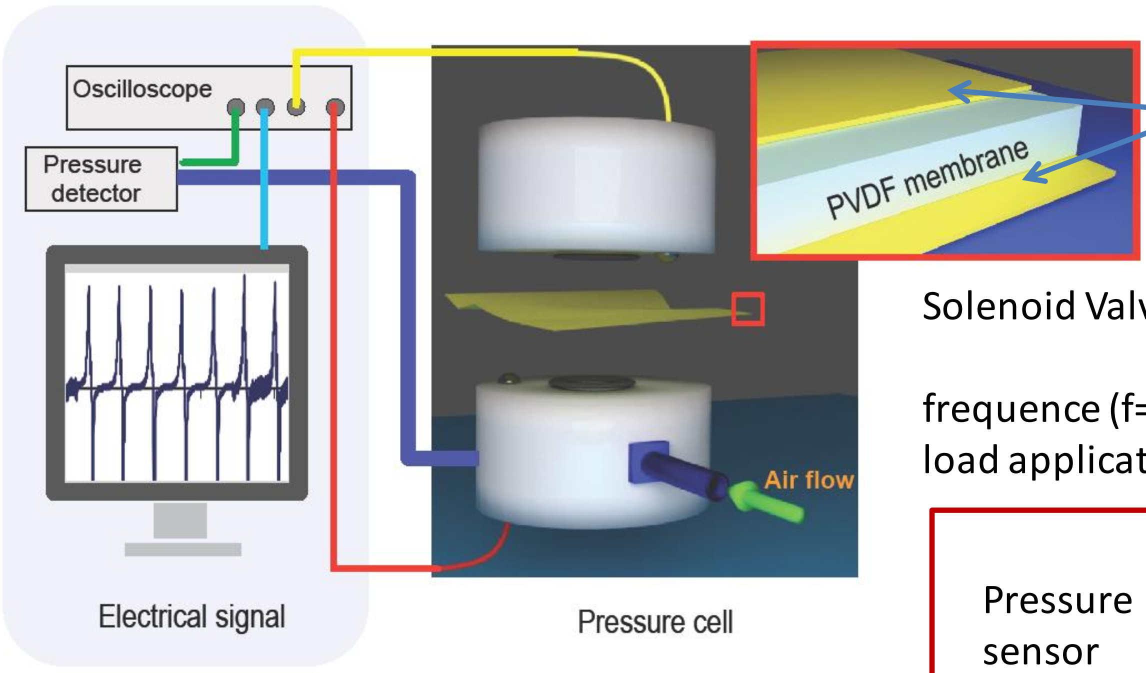


low doses range, leads mainly to main-chain scission → higher molecular mobility.

DE LA RECHERCHE À L'INDUSTRIE

- Electrical measurements
- Characterisations

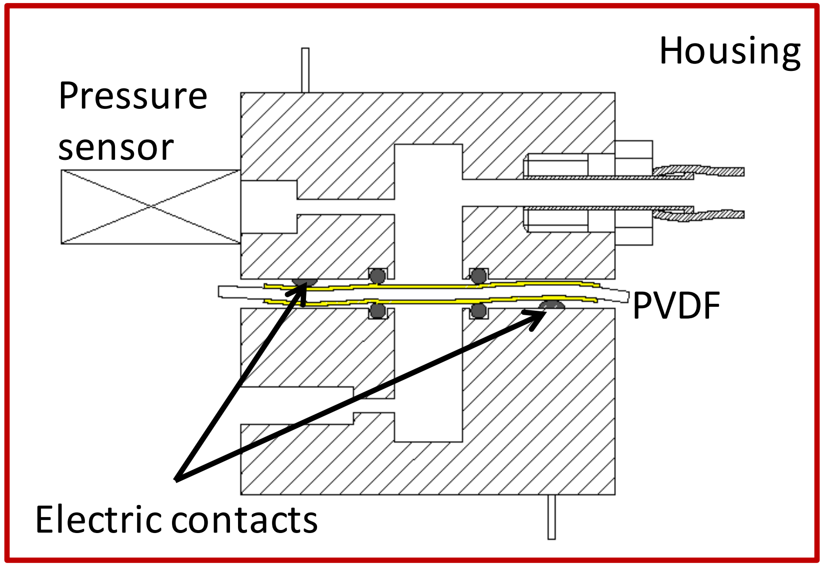
Home-made experimental set-up



Gold electrodes sputtered on both sides (100 nm)

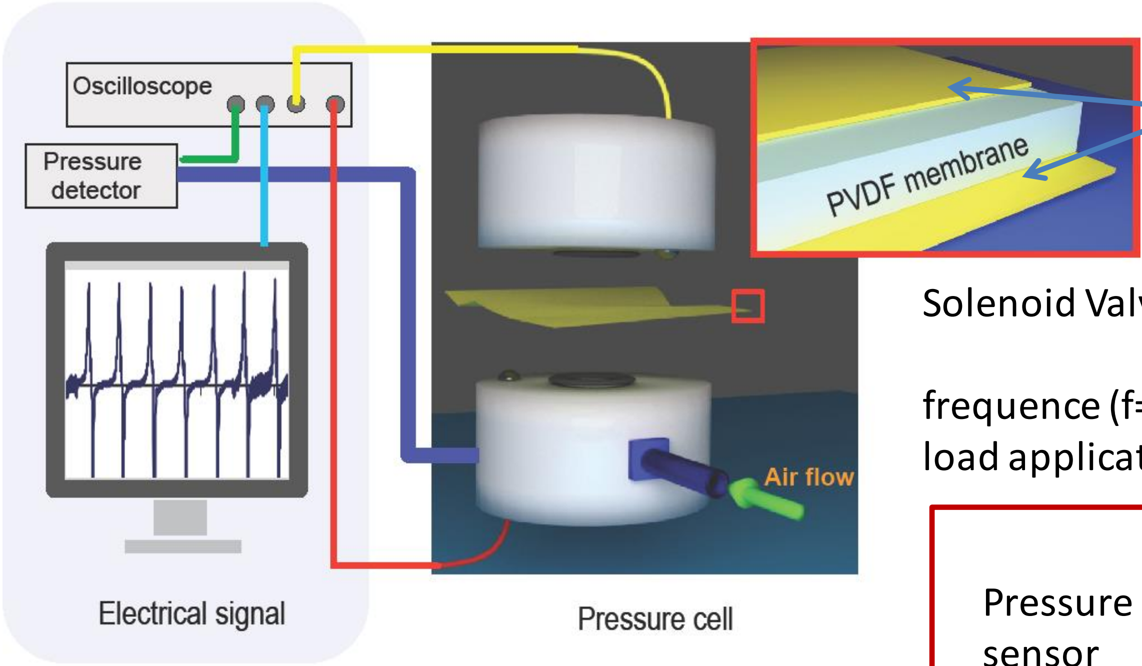
Solenoid Valve controls the pressure:

frequence (f=1 ÷ 10Hz)
load application time (T =20ms ÷ 1.25s)



- ❑Simultaneous registration of pressure and V_{output}
- ❑Clamped membrane under **bending** stress
- ❑Testing area: 0.785 cm^2

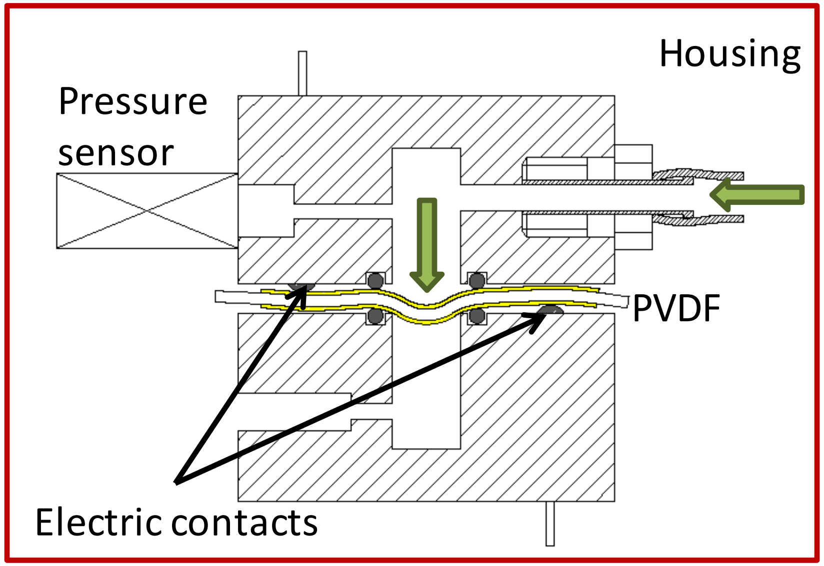
Home-made experimental set-up



Gold electrodes sputtered on both sides (100 nm)

Solenoid Valve controls the pressure:

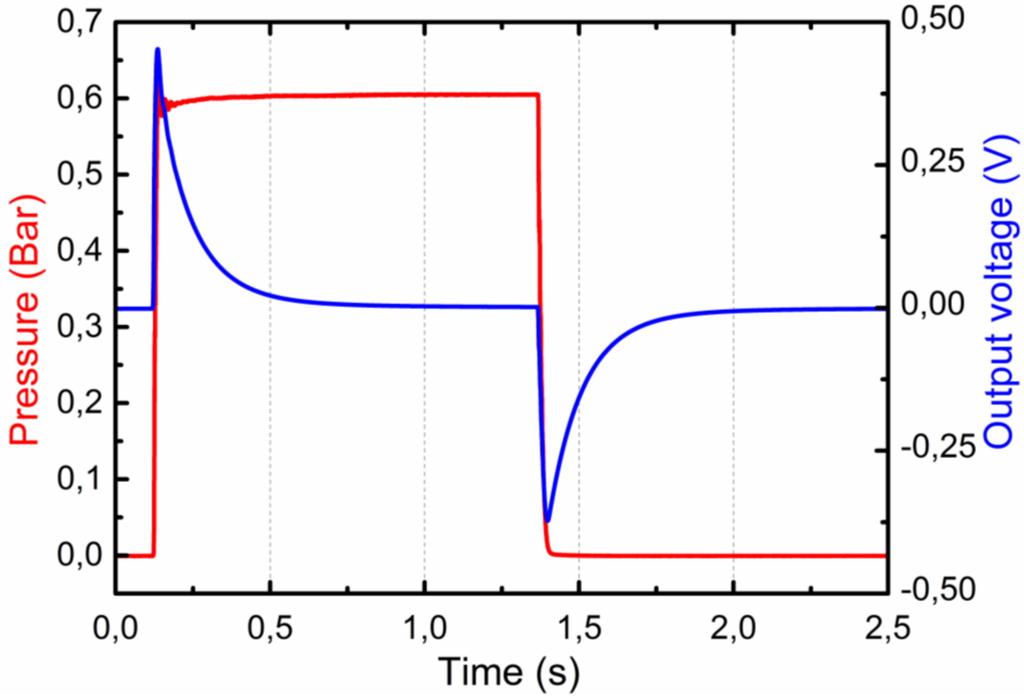
frequence (f=1 ÷ 10Hz)
load application time (T =20ms ÷ 1.25s)



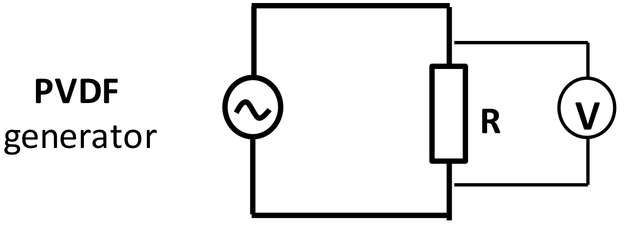
- ❑Simultaneous registration of pressure and V_{output}
- ❑Clamped membrane under **bending** stress
- ❑Testing area: 0.785 cm^2

Output voltage *versus* pressure

Output voltage under cycling bending stress condition



Electrical circuit:

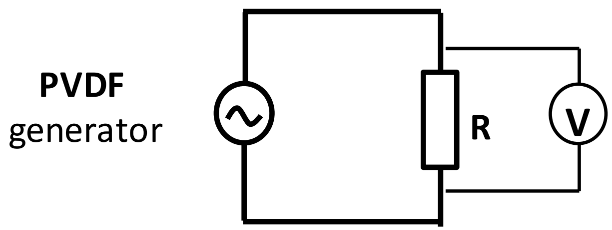


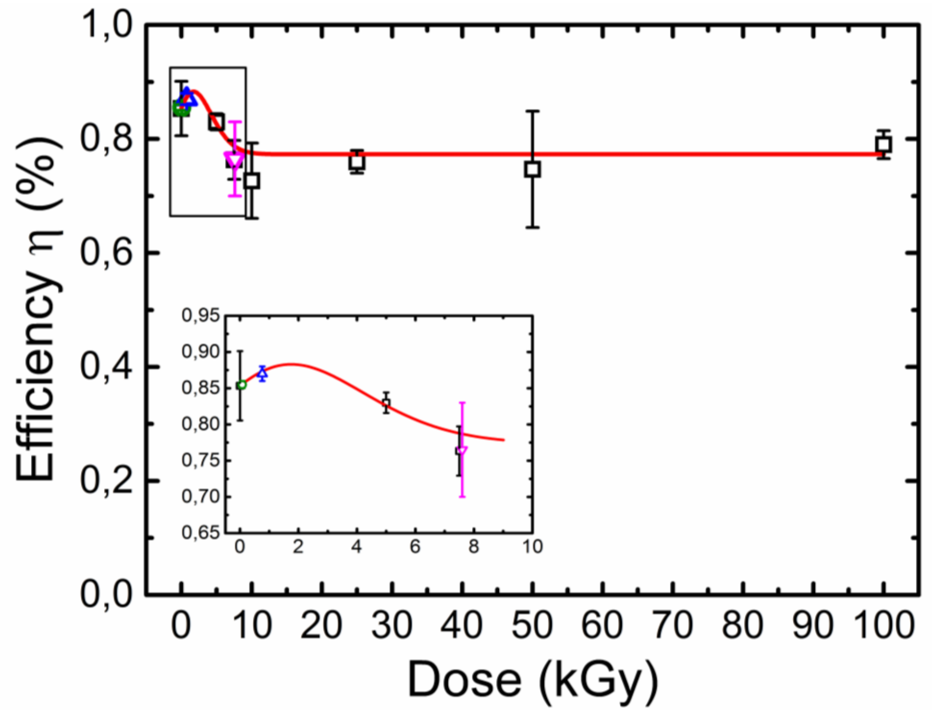
Piezoelectric PVDF is considered as capacitor with a *RC time constant τ*

Results

- ❑ The energy conversion efficiency is the ratio between the total electrical energy (W_e) and the total mechanical energy (W_m).

- ❑The conversion efficiency was found to be around 0.8%





Electrical efficiency:

Load=0.6Bar, f=0.4Hz, R = 1MΩ, tested volume=5.73E-10m^3

$$\eta(\%) = \frac{W_e}{W_m}100 \quad \begin{cases} W_e = \int \frac{V^2}{R} dt \\ W_m = \frac{1}{T}\int PV\, dt \end{cases}$$

DE LA RECHERCHE À L'INDUSTRIE

- Electrical measurements
- Characterisations

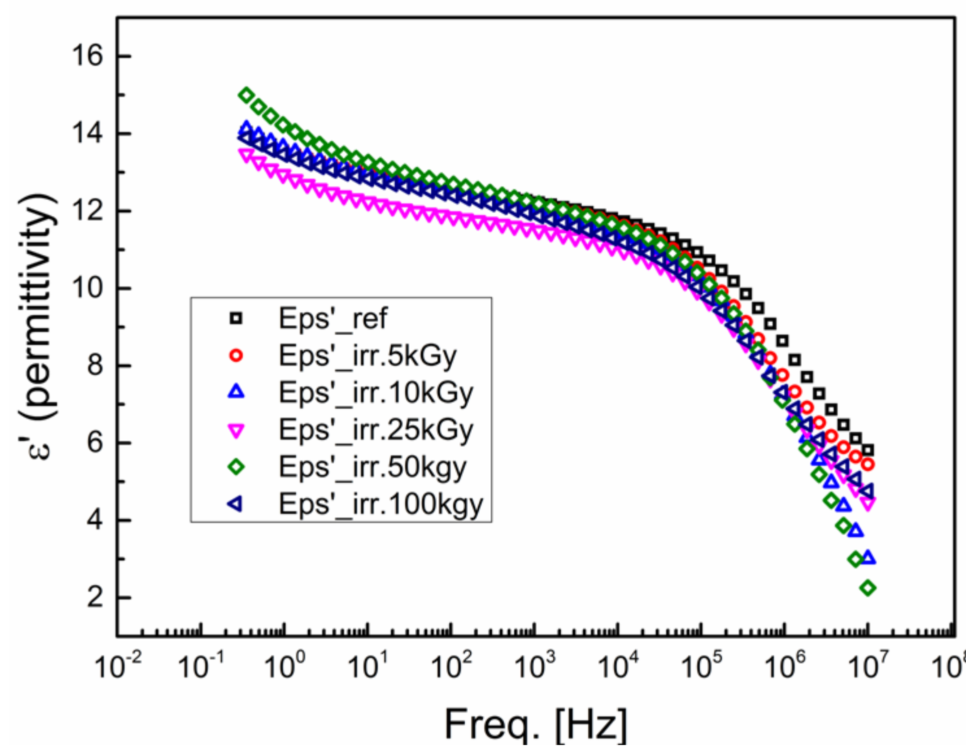
Dielectric measurement

- Permettivity is directly linked with the dipole moment density of the sample:

$$D = \varepsilon_r \varepsilon_0 E$$

- No variation of the permittivity with the doses.

The density of the dipoles not changes with the range doses investigated



Freq. [kHz]	ε_r PVDF ref	ε_r PVDF irr. 5kGy	ε_r PVDF irr. 10kGy	ε_r PVDF irr. 25kGy	ε_r PVDF irr. 50kGy	ε_r PVDF irr. 50kGy
0,108	12,578	12,587	12,538	11,846	12,692	12,398
1,134	12,224	12,182	12,029	11,498	12,184	11,871
11.952	11,732	11,62	11,419	10,966	11,551	11,182

Elastic Modulus

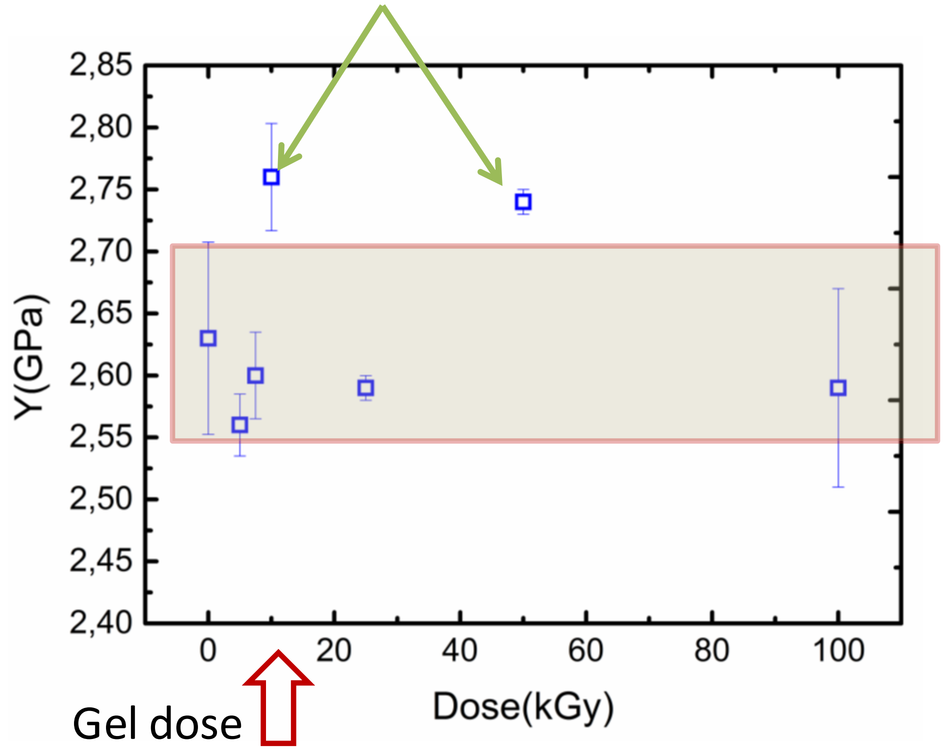
- The polymer is stressed in the eleastic regime.

- The polarization generated at applied stress T is proportional to the piezoelectric coefficient d_{33}:

$$D = d_{33} T$$

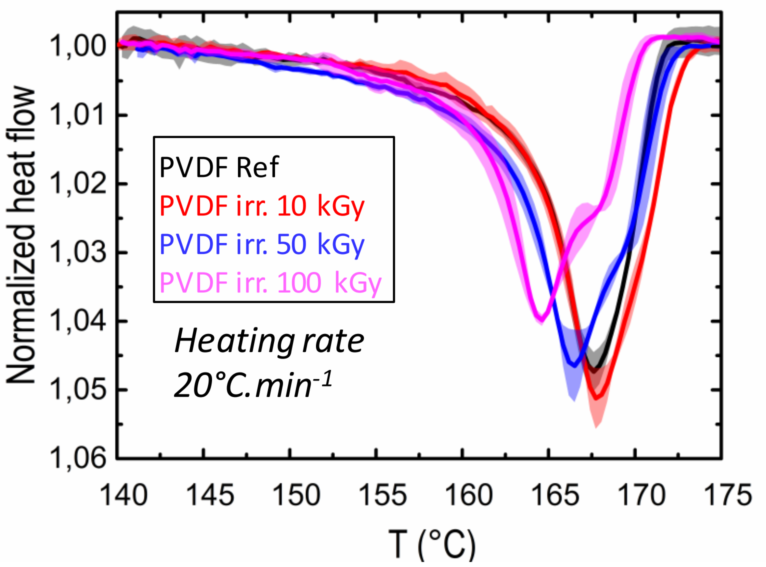
$$d_{33} \propto \sqrt{\frac{\varepsilon_{33}^{T}}{Y_{33}^{E}}}$$

- The young's modulus is not affect by the irradiation, except for 10 and 50kGy



Combined effect of crosslinking and chain scissions lead to increase the young's modulus at 10 and 50 kGy

Crystallinity content by DSC

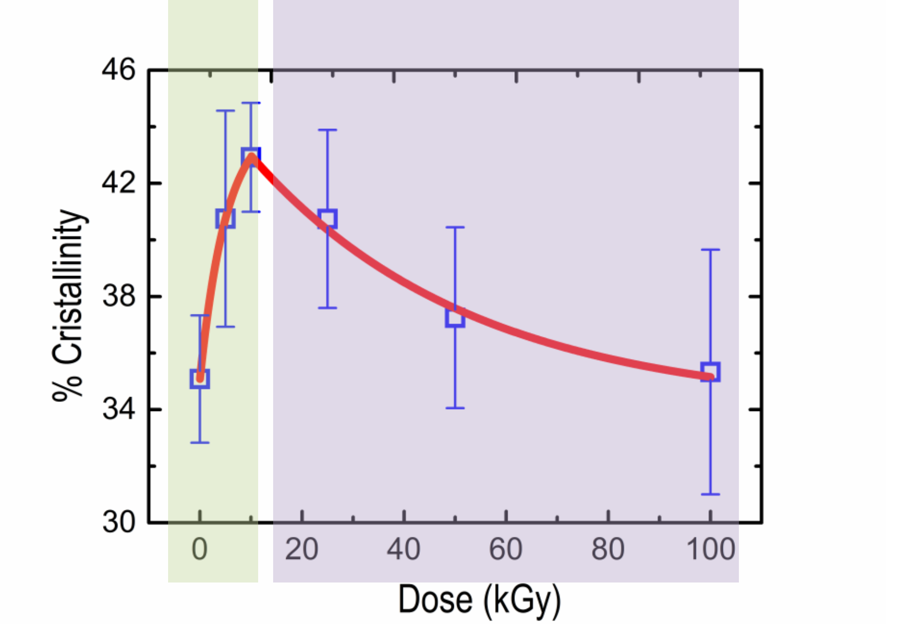


$$X_c(\%) = \frac{H_f}{H_{0f}} \cdot 100$$

*$\mathbf{H_f}$ is the heat of fusion for the tested sample
*$\mathbf{H_{0f}}$ =104.7 J/g (Nakagawa and Ishida, 1973), the heat of fusion for the 100% crystalline sample.

- ❑ shift of the melting peak with irradiation dose increase meaning creation of smaller crystallites

- ❑The crystalline content reaches the maximum at 10 kGy. At higher irradiation dose (10-20kGy **gel dose**) Competition crosslinkings/chain scissions



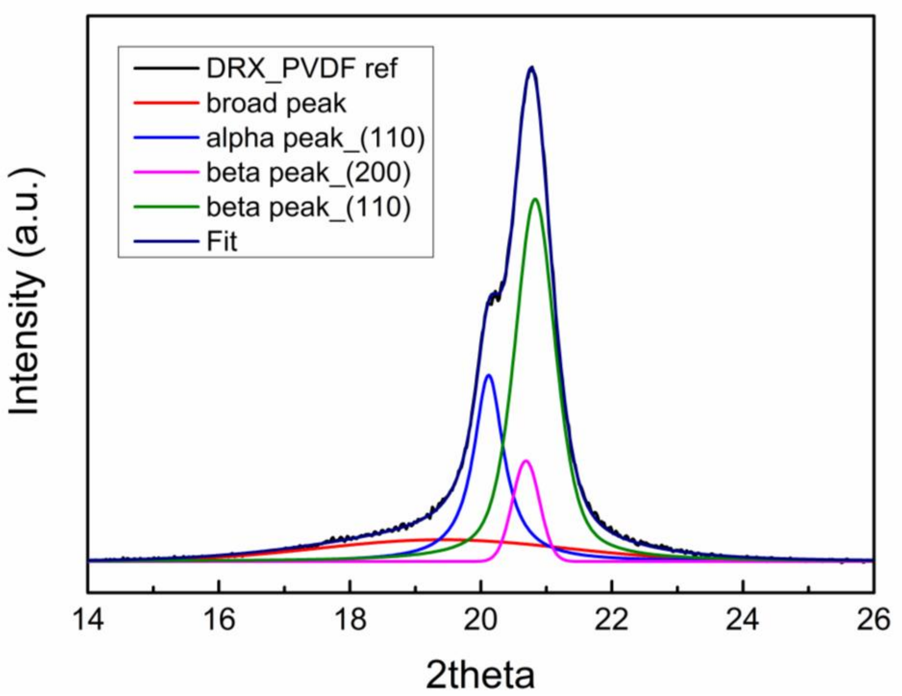
X-ray diffraction

- Comparison of the area of the crystallintes peak fits for different doses.

$$\beta\ Fraction\ (\%) = \left(\frac{A_\beta}{A_\beta + A_\alpha}\right) * 100$$

- Referring to DSC data the degree of crystallinity of the α and β phases

Dose [kGy]	Degree XX from DSC (%)	% α phase	% β phase
0	35,08	10,07952	25,00048
5	40,75	9,68688	31,06312
10	42,92	10,56043	32,35957
25	40,74	11,05309	29,68691
50	37,25	10,10486	27,14514
100	35,33	8,99655	26,33345



phase	(hkl)	2Θ
β	(200) (110)	20.668 20.828
α	(110)	20.119

Conclusion

❑SHI and e-beam irradiation not affect the electrical efficiency of the PVDF in a range between 0 and 100kGy. The dipoles density is maintained under relative strong doses (100kGy) and the elastic modulus not shows relevant variation in that range doses.

❑Chain scissions are responsable to increase the crystallization and in particular between 5 and 10kGy (before the **gel dose**). XRD technique combined with the DSC shows that the increase of crystallinity correspond to the increase of the β phase.

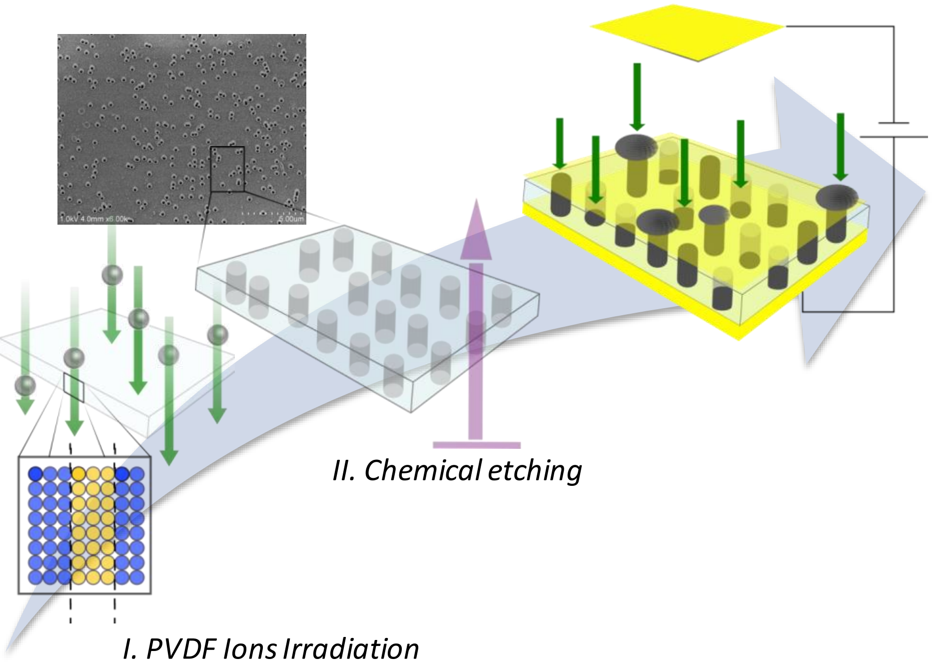
❑The increase of the β phase not correspond with an increase of the piezoelectric response.

The sensitivity of the instrument is not enough to detect the variation of the
piezo-response of the irradiated PVDF.

High electric field needs to polarized the additional β phase: Hysteresis loops will be performed.

Perspective

Exploiting SHI irradiation…



Nanostructuration to enhance piezoresponse

- ❑ Exploiting interfacial polarization between filler (nanowire) and matrix (PVDF)

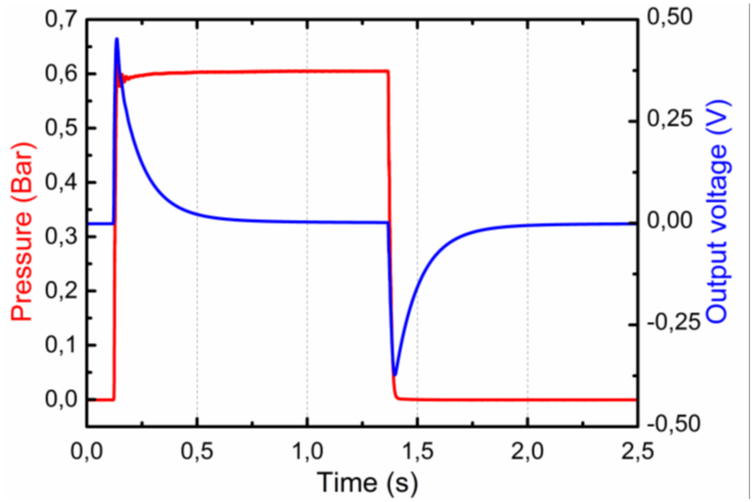
⇩

Increase piezoelectric response

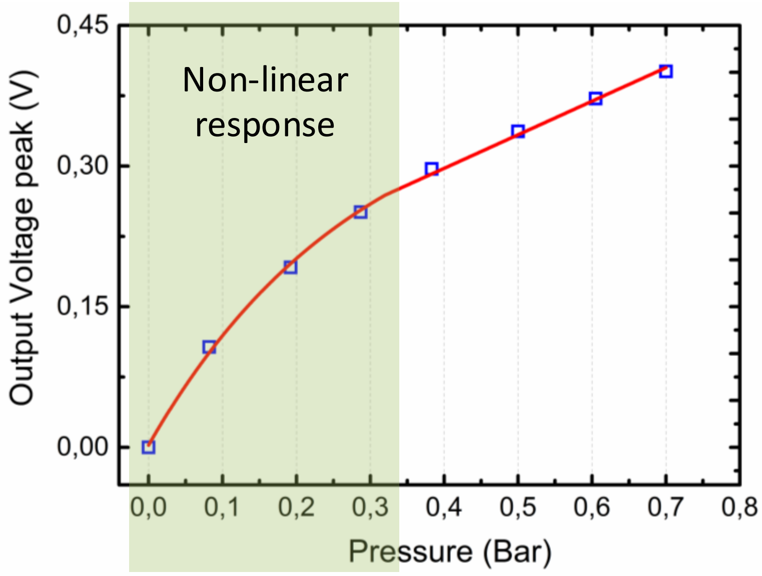
Thank you for the attention

Output voltage *versus* pressure

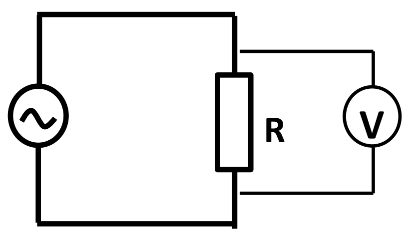
Output voltage under cycling bending stress condition



Output voltage peak vs Pressure



PVDF generator

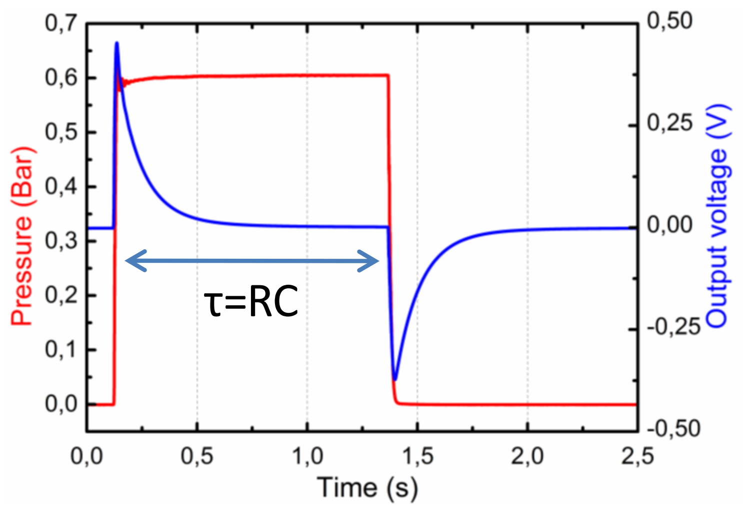


Piezoelectric PVDF is considered as capacitor with a *RC time constant τ*

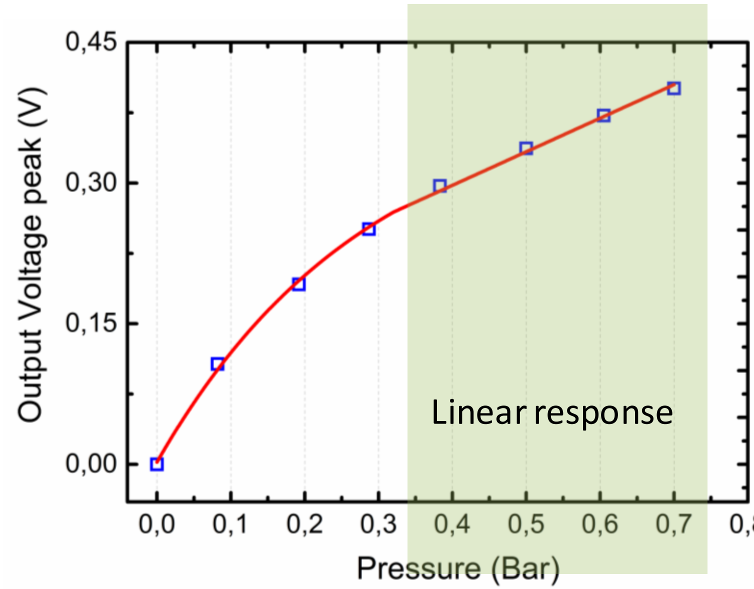
Local curvature not allowed a complete extention of the membrane.

Output voltage *versus* pressure

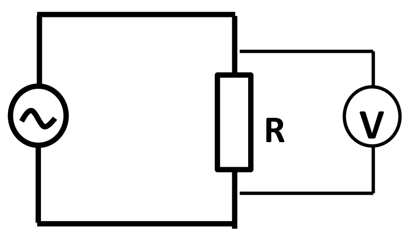
Output voltage under cycling bending stress condition



Output voltage peak vs Pressure



PVDF generator



Piezoelectric PVDF is considered as capacitor with a *RC time constant τ*

PVDF

The pressure extends the membrane to the shape of a spherical cap.