



Piezotech, Polymères Fluorés Electroactifs

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Outline

- **Piezotech, History & Products**
- **Piezoelectric Ferroelectric Polymers PVDF and P(VDF-TrFE)
Properties and Applications**
- **Relaxor Ferroelectric Electrostrictive Polymers,
Recent Developments**



Piezotech

- Piezotech has been created in 1993, with a technology transfer from the ISL (French-German Research institute) to develop the “Bauer Gauge” (PVDF gauge for shock wave characterization).
- Piezotech becomes independent in 2006, directed by Dr F. Bauer
- Arkema acquires Piezotech in 2010
- Piezotech is specialized in the production and the development of piezoelectric and electroactive fluorinated-based polymers (EAP) :
 - PVDF and P(VDF-TrFE) piezoelectric and pyroelectric polymers, films, gauges and sensors
 - New Relaxor and electrostrictive terpolymers P(VDF-TrFE-CFE) and P(VDF-TrFE-CTFE) which presents multifunction and capabilities never achieved and offer a broad range of applications for actuators, capacitors, refrigeration, energy harvesting...

Piezotech Products

Polymers :

Patented Know-How for fluorinated Terpolymer synthesis

Piezoelectric Copolymers **P(VDF-TrFE)**

Relaxor Ferroelectric Terpolymers **P(VDF-TrFE-CFE/CTFE)**



Films :

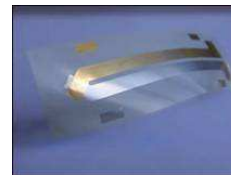
Material & unique know-how for the processing and poling of piezoelectric PVDF and copolymer films



20 x 60 cm Sheet

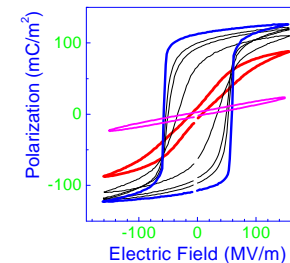
Gauges & Sensors :

Design of piezoelectric gauges & sensors based on PVDF & P(VDF-TrFE)
Metalization & Poling
Prototypes based on electrostrictive polymers



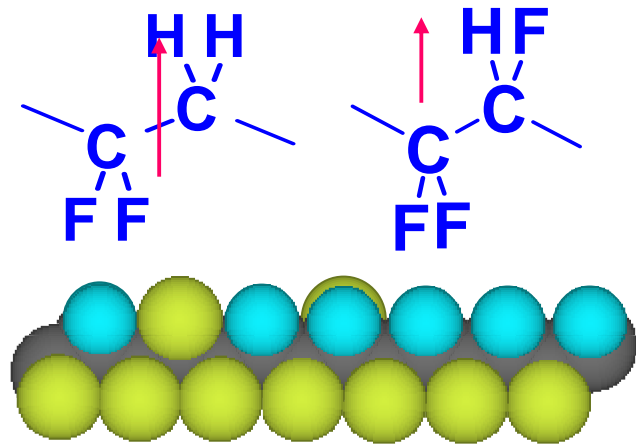
R&D Studies :

Characterization of piezoelectric, electrostrictive, ferroelectric polymer materials.
Sensor design
Prototypes design

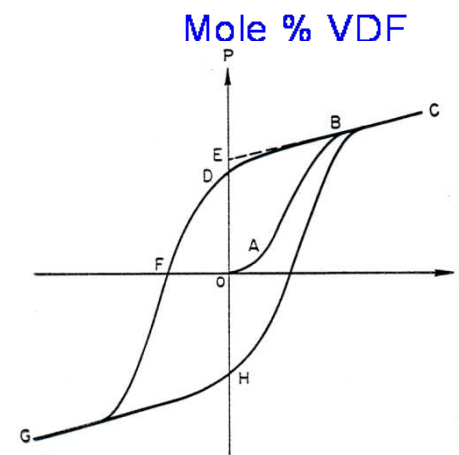
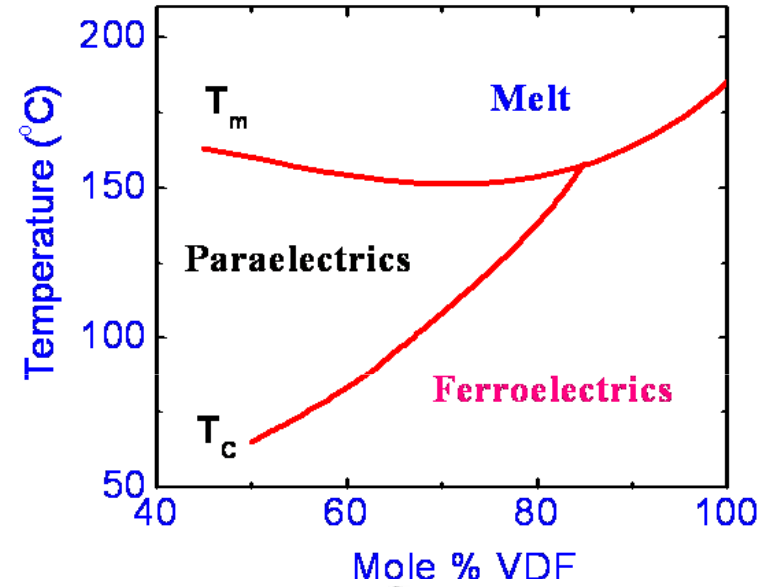
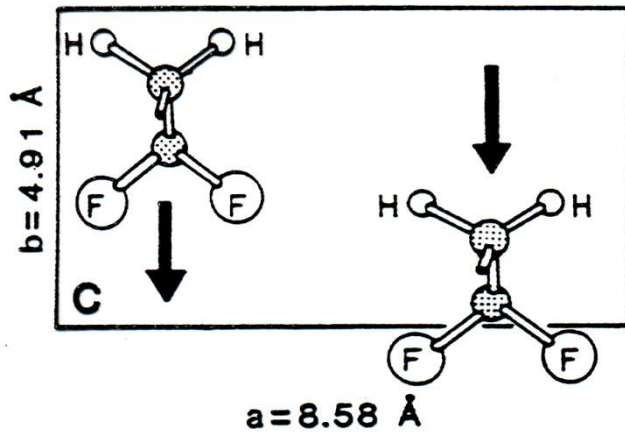


Piezoelectric fluorinated Polymers : P(VDF) & P(VDF-TrFE)

PVDF : Polar β phase when stretched ; P(VDF-TrFE) : Stable Polar β phase



β -phase

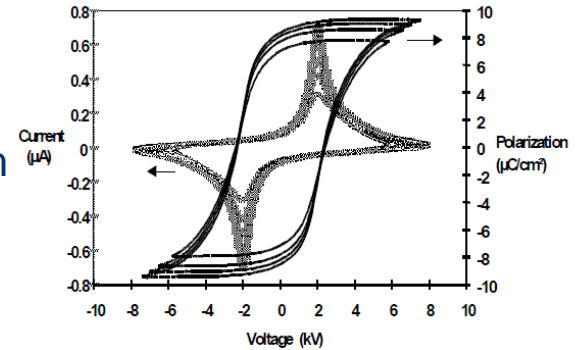




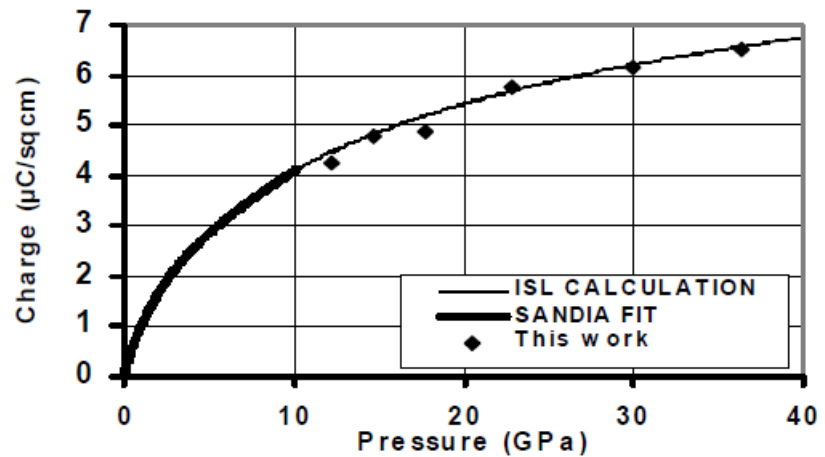
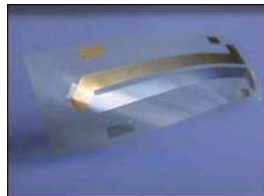
Piezoelectric Gauges & Sensors

Piezotech and Saint Louis Institute Bauers patented poling process

- Uniform poling procedure
- Eliminates the ions and space charges resident in the un-poled m
- Gauges, sensors with reproducible and calibrated response.



- Fast response (nanosecond)
- Large Stress Range (pa à tens Gpa)
- High noise/signal ratio
- Sensibility : $4\mu\text{C}/\text{cm}^2$ for 10 Gpa
- Easy to use



Developing applications

- Impact location using Cross Correlated Technique (CCT)
(Capsal et al. IEEE Sensors submitted January 2011 (CIRIMAT Institut Carnot, Toulouse))
- Vibration Damping
- Energy Harvesting
 - Energy recovery from structural vibrations
- Large area electro/transduction devices
- Artificial Skin, Printed sensors (PVDF-TrFE)
- Organic Electronic (ferroelectric memories) (PVDF-TRFE)



Piezoelectric polymers : Examples of Applications

- **Acoustic components:**

- - Ultrasonic detector
- - Hydrophones
- - Sonars

- **Electrical equipments:**

- Switches
- Miniature electric fans

- **Medical instrumentation:**

- Catheter
- Pedobarography
- Osteogenesis
- Medical echography
- Blood pressure detector

- **Robotics:**

- Artificial sensitive skin
- Pressure sensors

- **Security devices:**

- Intruder alarm
- IR alarms
- Vibration sensors

- **Optical devices:**

- Laser diameter measurement
- Variable mirrors

Transports:

- - Automotive detection on roads
- - Weighing vehicles

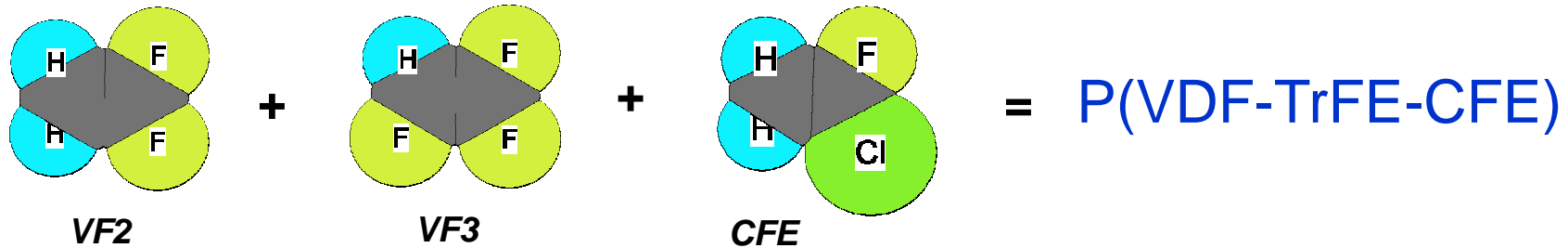
- **Pressure pick-ups:**

- Distribution of pressure on surfaces
- Localization of impacts
- Pick-ups for non destructive testing
- Accelerometer
- Keyboards

Sport and leisure:

- Tennis court line
- Display panel on sport grounds
- Impact detector if shooting targets

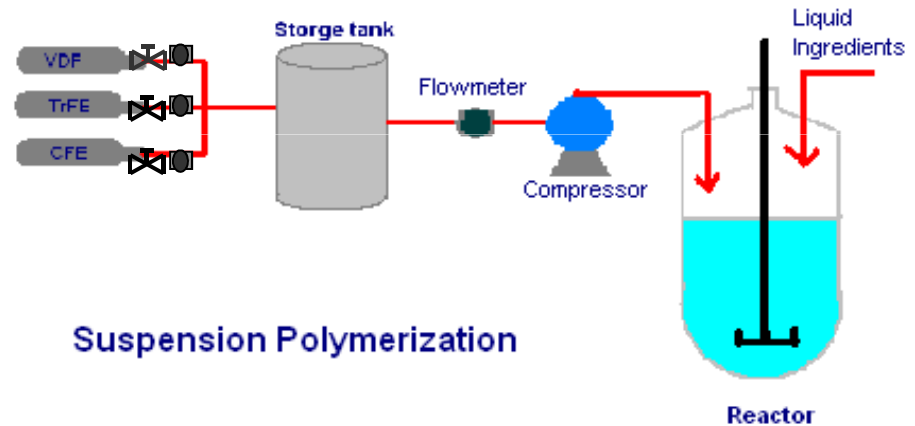
Fluorinated Electrostrictive Polymers



- Precise control of High pressure (50 up to 100 bars) and temperature (25°C – 50°C) during the process

- Homogeneous terpolymer composition distribution in taking into account the differences in monomer reactivities in the process

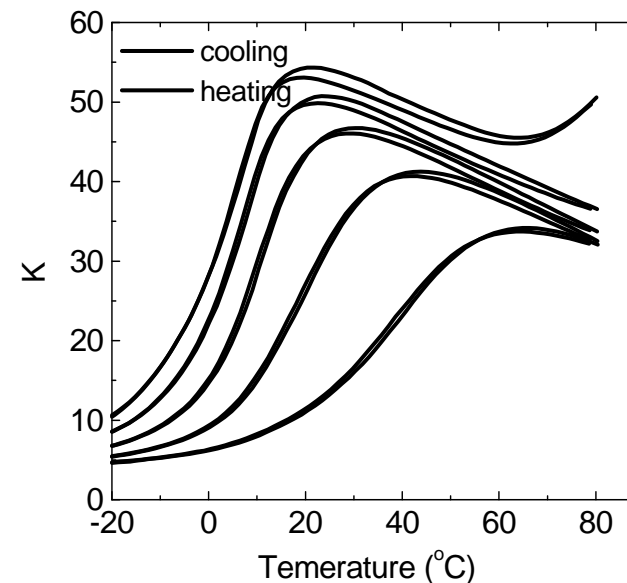
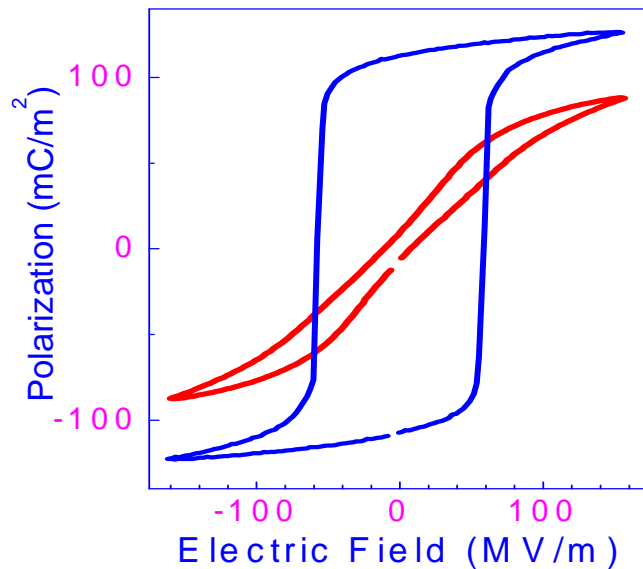
- Capacity : 2Kg/J



Materials Developed in strong scientific cooperation between ISL (Pr F. Bauer) and Pennstate University (Pr Q. Zhang)

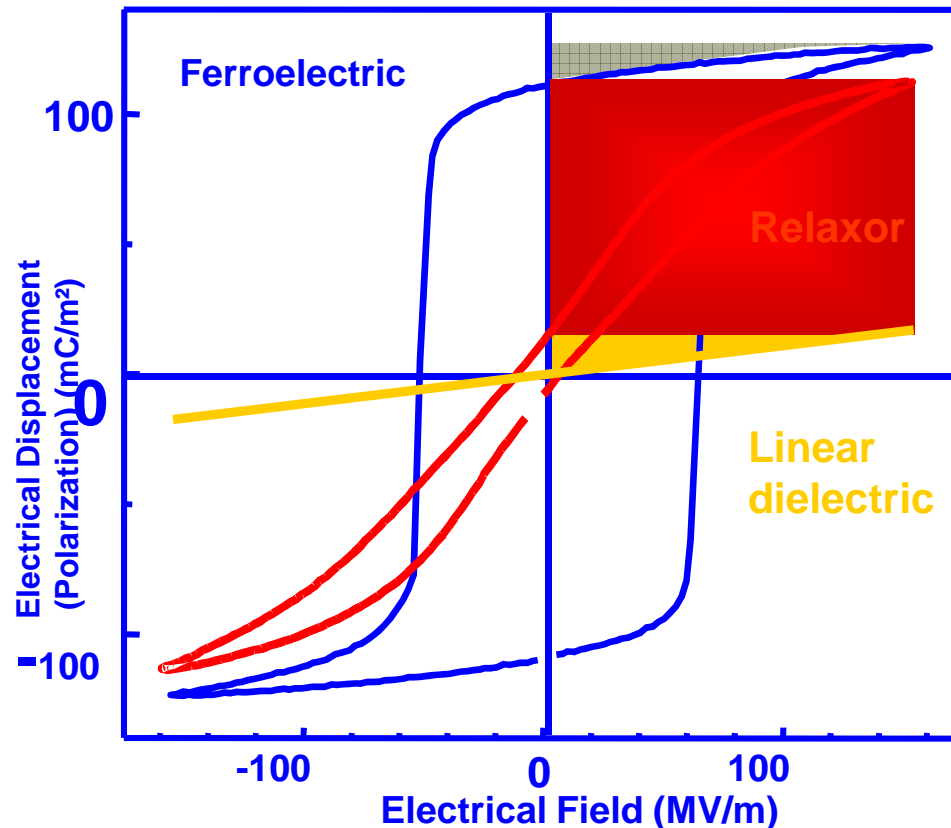
Terpolymers P(VDF-TrFE-CFE/CTFE)

- **The termonomer induce material defects :**
 - Reduce Ferroelectric domains size (less cooperativity in dipole orientation)
 - Lowers Ferro to Para transition zone
 - Enlarge Ferro-Para transition
- **P(VDF-TrFE-CFE) are ferroelectric relaxors :**
 - Poling hysteresis thinner.
 - Polarization is a function of applied electric field
 - Dielectric constant peak enlarged around T_{amb} and frequency dependent



Terpolymers & Electric energy storage

- High Dielectric constant at Tamb (~ 50, the highest for polymers)
- High induced polarization (~ 0.1 C/m²), High dielectric rigidity (>350 MV/m)
- Relaxor Behavior



Plastic Film	Dielectric Constant	Breakdown Field (MV/m)	Energy density (J/cm ³)
Polypropylene (PP)	2.2	640	1-2.5
Polyester (PET)	3.3	570	1-1.5
Polycarbonate (PC)	2.8	528	0.5-1
Polyvinylidene fluoride (PVDF)	12	590	2.4
Polyethylene-naphlate (PEN)	3.2	550	1-1.5
Polyphenylene-sulfide (PPS)	3.0	550	1-1.5
P(VDF-TrFE-CFE)	50 à 80	> 350	> 10

A Dielectric Polymer with High Electric Energy Density and Fast Discharge Speed, B.Chu, X. Zhou, K. Ren, B. Neese, M. Lin., Q. Wang, F. Bauer, Q. M. Zhang. 21 JULY 2006 VOL 313 SCIENCE

High induced polarisation (~ 0.1 C/m²), and high dielectric strength (>350 MV/m)

→ Large Discharged Energy Density (10J/Cm³)

Terpolymer & Energy Harvesting

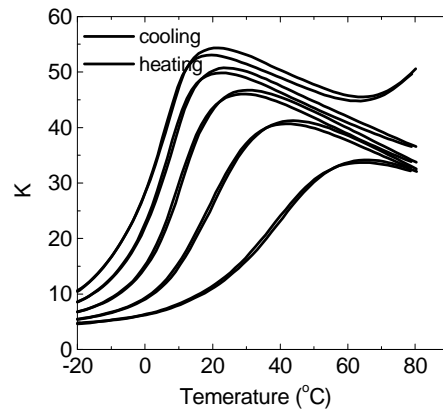
- **Mechanical Energy Harvesting**

Cottinet, P.-J. Guyomar, D. Guiffard, B. Putson, C. Lebrun, L., *IEE Trans Ultr. Ferroelect. and Freq Cont IEEE Transactions*, 57, 4, 774 - 784 (2010)

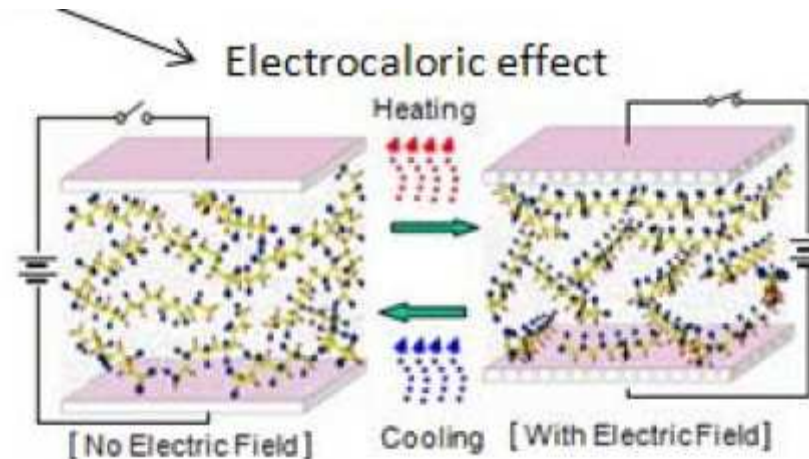
Ren, Y. Liu, H ; Hofmann, Q. M. Zhang, "An active energy harvesting scheme with an electroactive polymer," *Appl. Phys. Lett.*, Vol. 91, 132910, 2007. (Max Theoretical 0.9 J/cm³)

- **Thermal Energy Harvesting**

Energy harvesting by nonlinear capacitance variation for a relaxor ferroelectric poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) terpolymer , H. Zhu, S. Pruvost, P. J. Cottinet, and D. Guyomar (LGEF/INSA Lyon). *Appl. Phys. Lett.* **98**, 222901 (2011) (50mJ/cm³)



Terpolymers & Electro Caloric Effect (ECE)

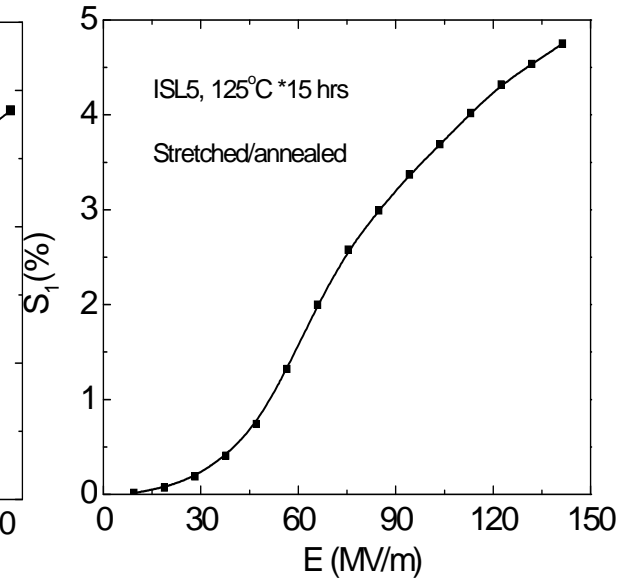
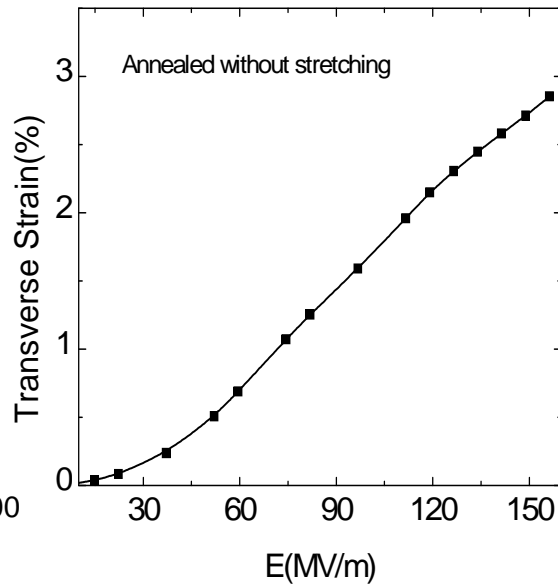
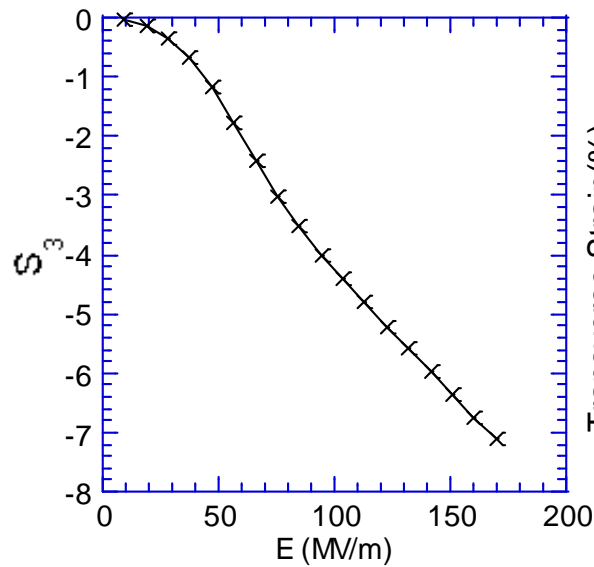


- Poor cooperativity of the terpolymers dipoles in the crystal structure
- Orientation/Disorientation induce variation of the entropy of the system
- Entropy & temperature variation $> 50\text{J}/(\text{KgK})$ of $\Delta T - 12$ à 17°C at room temperature

B. Neese, B. Chu, S-G. Lu, Y. Wang, E. Furman, Q.M. Zhang, "Large Electrocaloric Effect in Ferroelectric Polymers Near Room Temperature," *Science*, Vol 31, pp. 821-823, 2008

-S. G. Lu, B. Rožič, Q. M. Zhang, Z. Kutnjak, Xinyu Li, E. Furman, Lee J. Gorný, M. Lin, B. Malič, M. Kosec, R. Blinc, R. Pirc (APPLIED PHYSICS LETTERS **97**, 162904 2010)

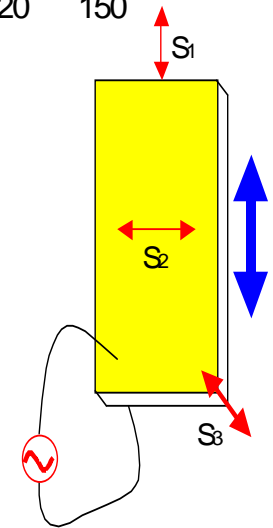
Terpolymers & Deformation



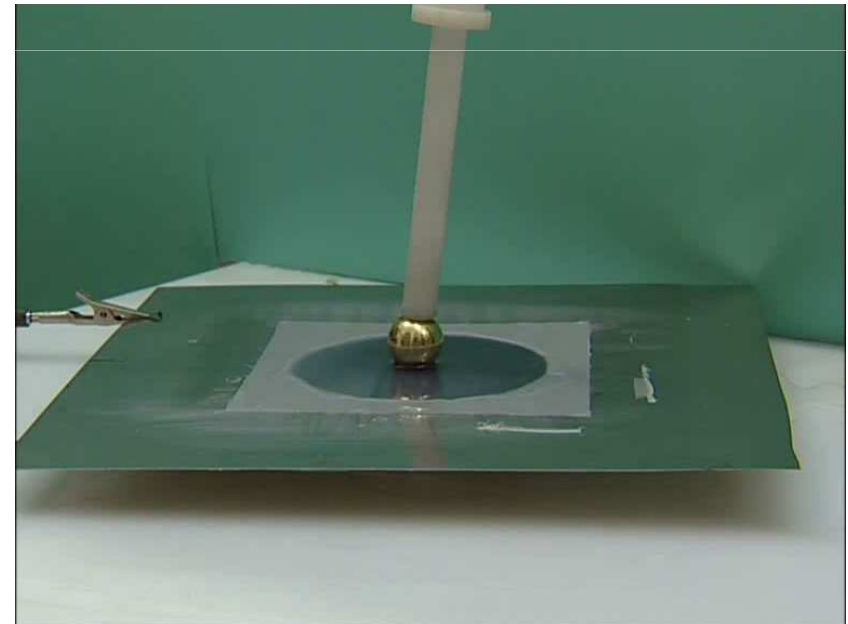
Electrostrictive behavior , Déformation >7%

Elastic energy density >1 J/cm³

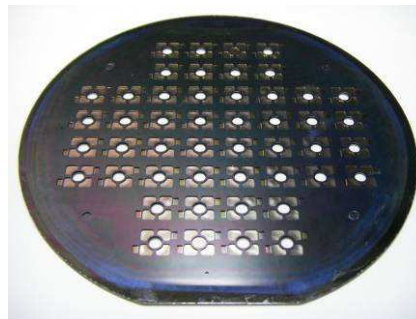
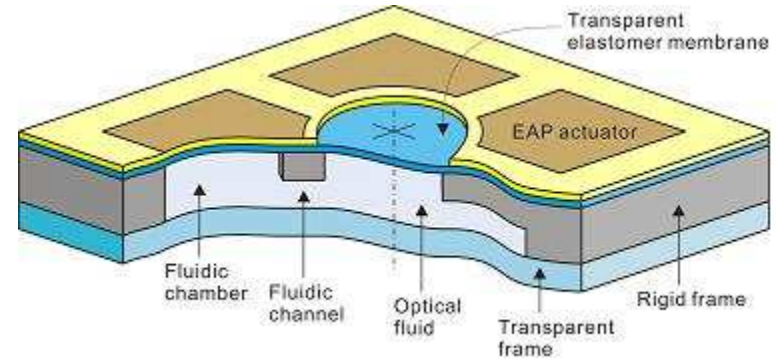
Elastic Modulus : films: 400 Mpa, Stretched films : 1 Gpa



Terpolymers & Deformation



Terpolymers & Deformation



*Varifocal Optical device
Choi et al, Samsung, US 7 819 637*

Actuators Development

Varifocal-Lens , Choi et al, Samsung, US 7 819 637

Braille Displays, Levard, Diglio, Lu, Gorny, Rahn, Zhang (Proc SPIE 2011, Vol 7976, 797611)

Micropumps, F. Xia, S. Tadigadapa, Q.M. Zhang, "Electroactive polymer based microfluidic pump," Sensors and Actuators A, Vol. 125, pp. 346-352, 2006.

Haptic devices, Microsteerable Catheters, Liu, Zellers, Anderson, Proc SPIE2011 7976, 797616

...



- Piezotech Produces Ferroelectric Fluorinated Polymers, films and devices
 - PVDF & P(VDF-TrFE) Ferroelectric Piezoelectric polymers
 - A new class of electroactive polymers P(VDF-TrFE-CFE) offers unique properties in comparison with other polymers.
 - These relaxor-ferroelectric terpolymers P(VDF-TrFE-CFE) are multifunctional i.e. electrostrictive material, dielectric for electric energy storage.
 - High electrostrictive strain leads to large actuation capability.
 - New properties are leading to new applications areas.
 - Energy Storage, Energy Harvesting, Actuators, Electrocaloric ...
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Merci

[www. Piezotech.eu](http://www.Piezotech.eu)


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Piezoelectric Polymers
ARKEMA