

Ferroelectric Polymers and Composites for Actuators and Sensors

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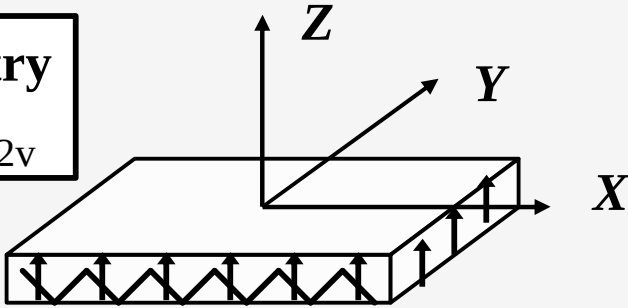
Tokyo, Japan

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Classification of Piezoelectric Polymers

1. *Poled Polar Polymers*

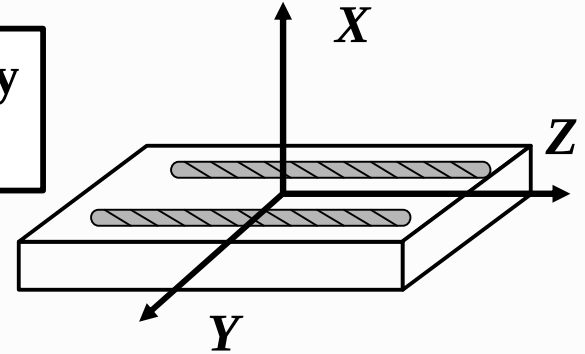
Symmetry

$$\mathbf{C}_{\infty v}, \mathbf{C}_{2v}$$


$$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ p_3 \end{pmatrix}$$

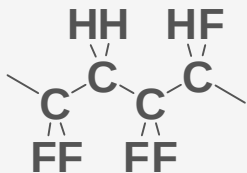
2.Oriented Chiral Polymers

Symmetry

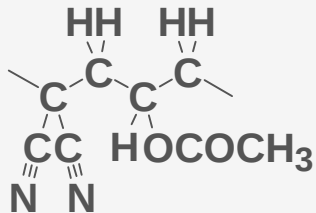
$$\mathbf{D}_{\mathbb{Y}}, \mathbf{D}_2$$


$$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

VDF/TrFE



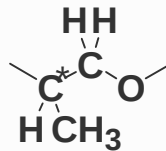
VDCN/VAc



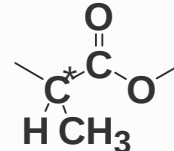
Odd Nylon

PZT/Polymer Composite

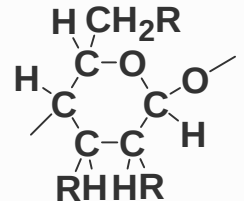
PPO



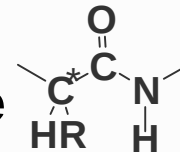
PLA



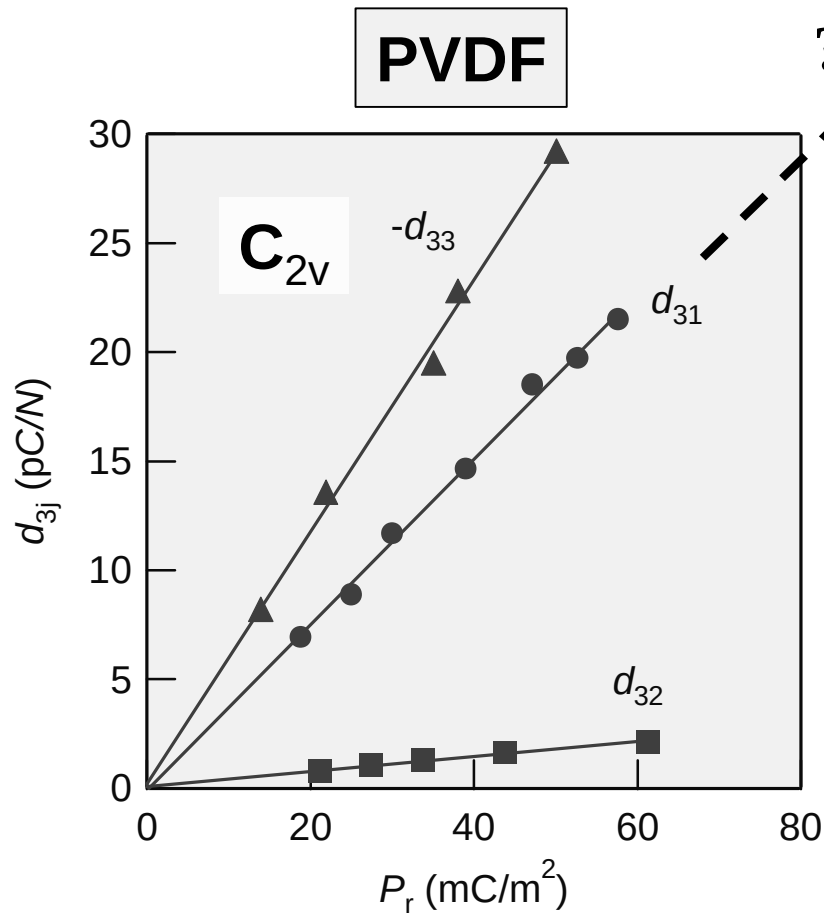
Cellulose



Polypeptide

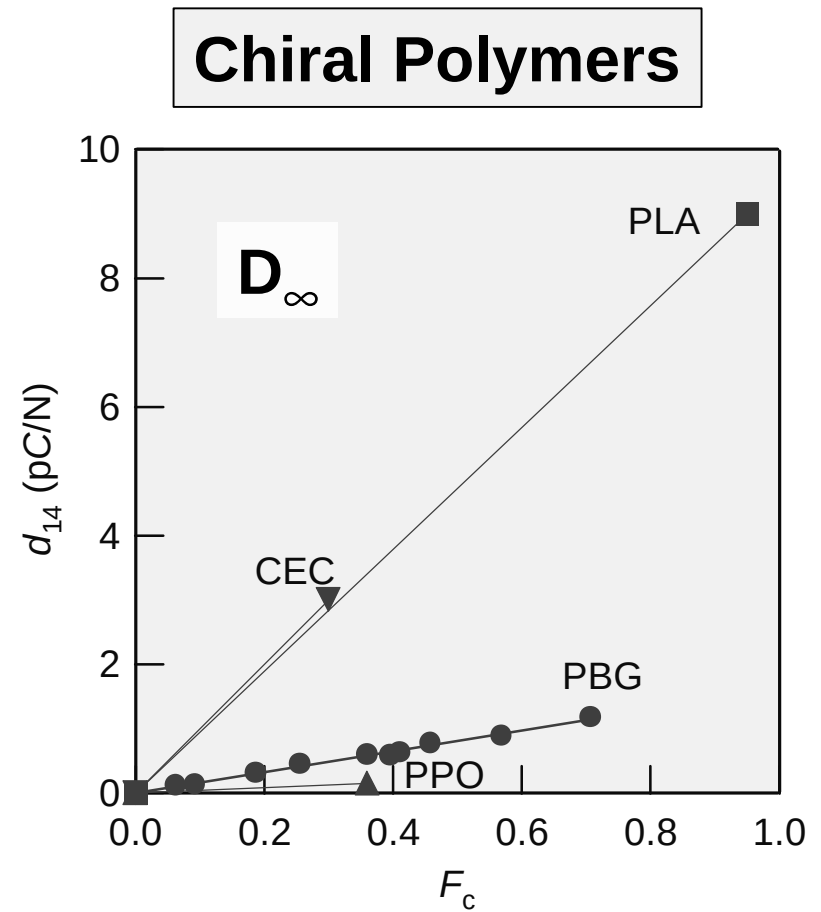


Structure-Dependent Piezoelectric Constants of Oriented Polymer Films



$$P_1 = \langle \cos q \rangle$$

Dipole orientation

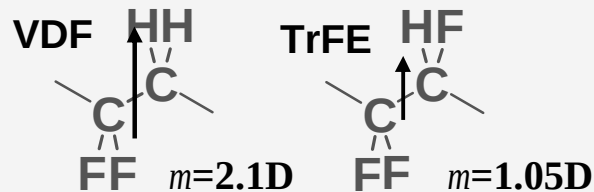


$$P_2 = \frac{1}{2} (3 \langle \cos^2 q \rangle - 1)$$

Chain orientation

VDF / TrFE Copolymer

A. Monomer

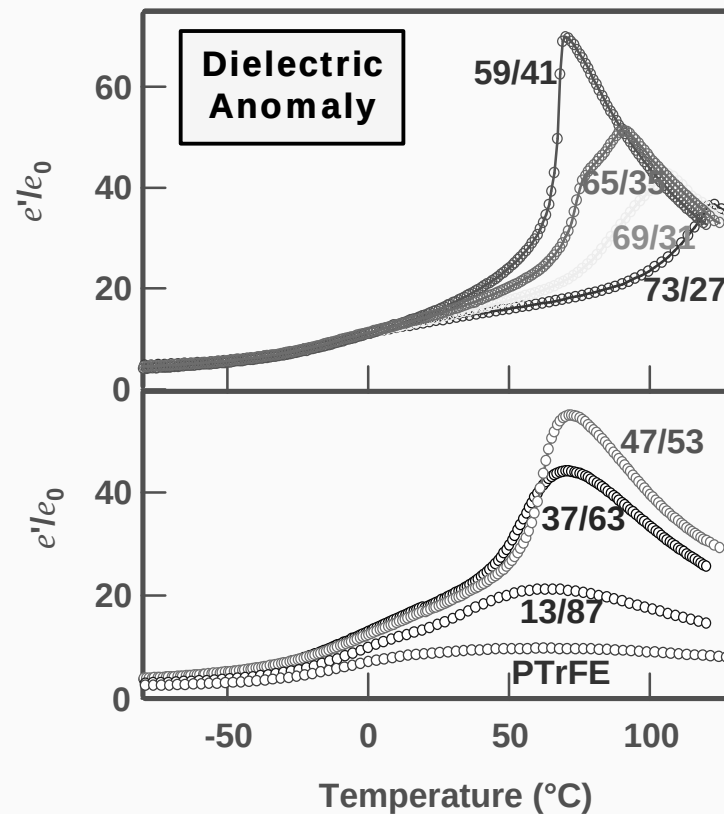
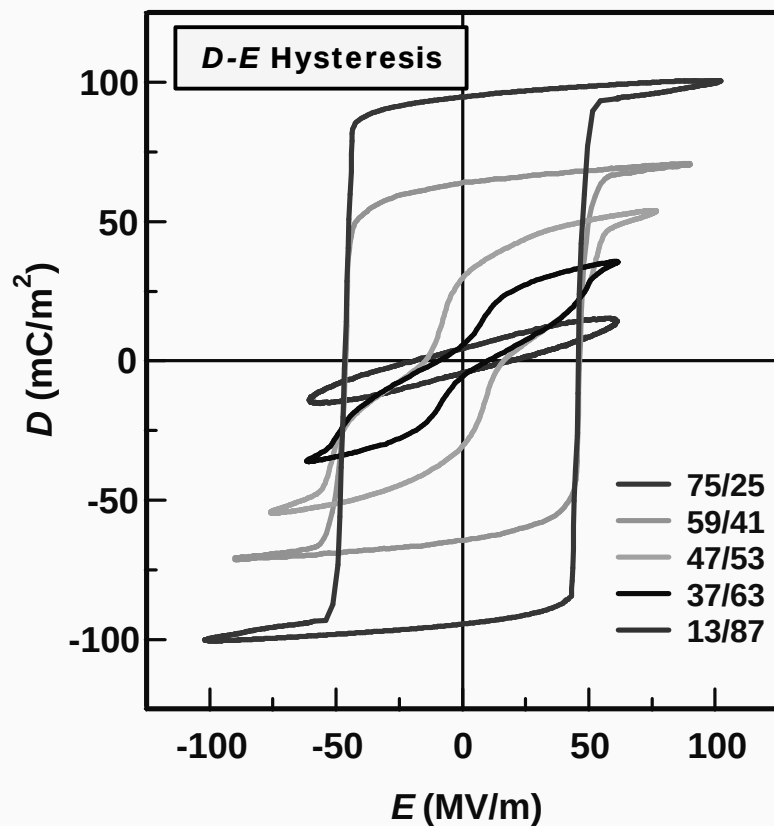
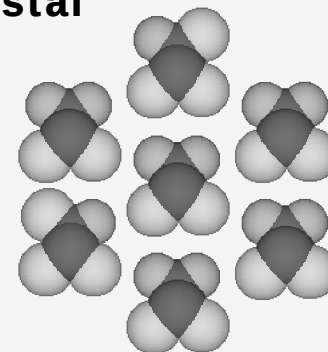


B. Chain

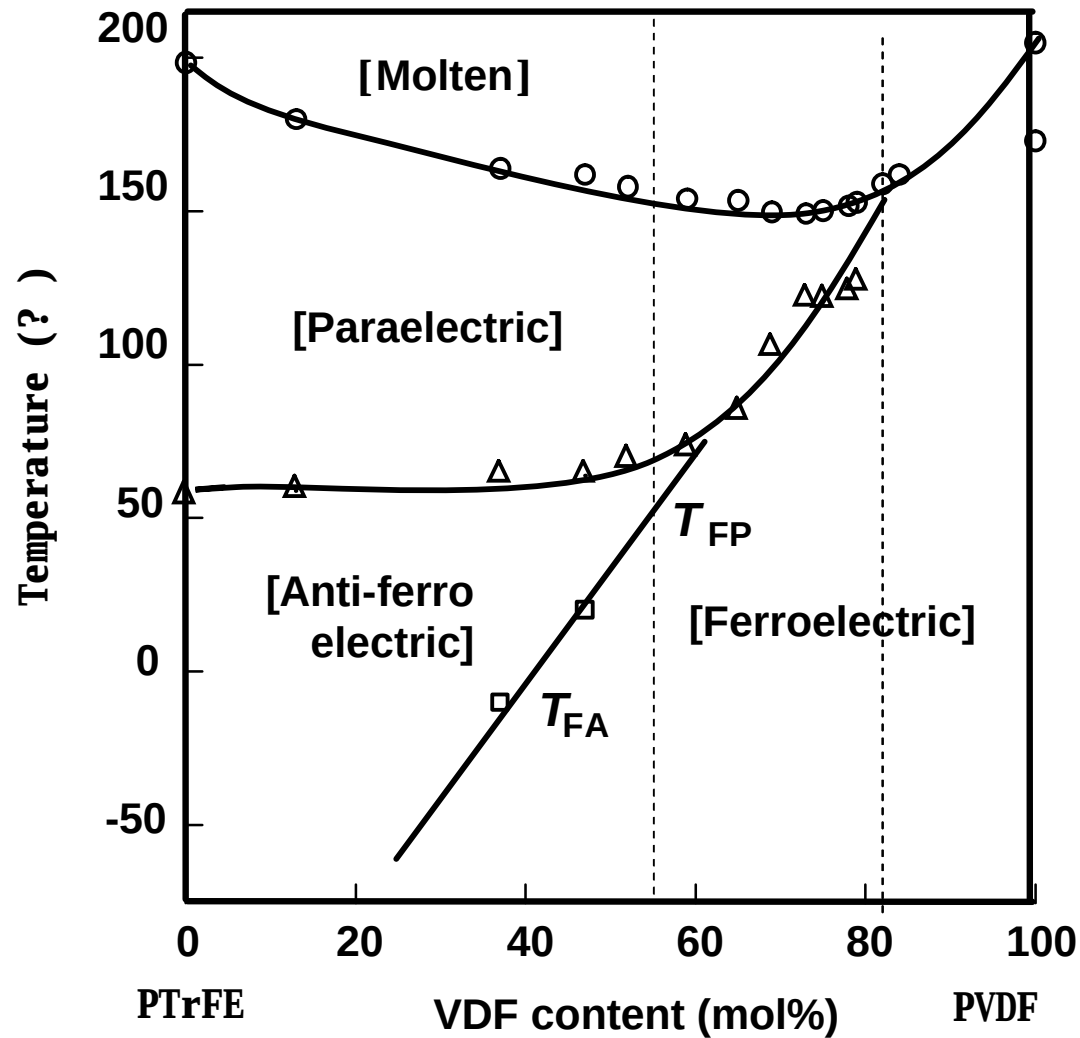


C. Crystal

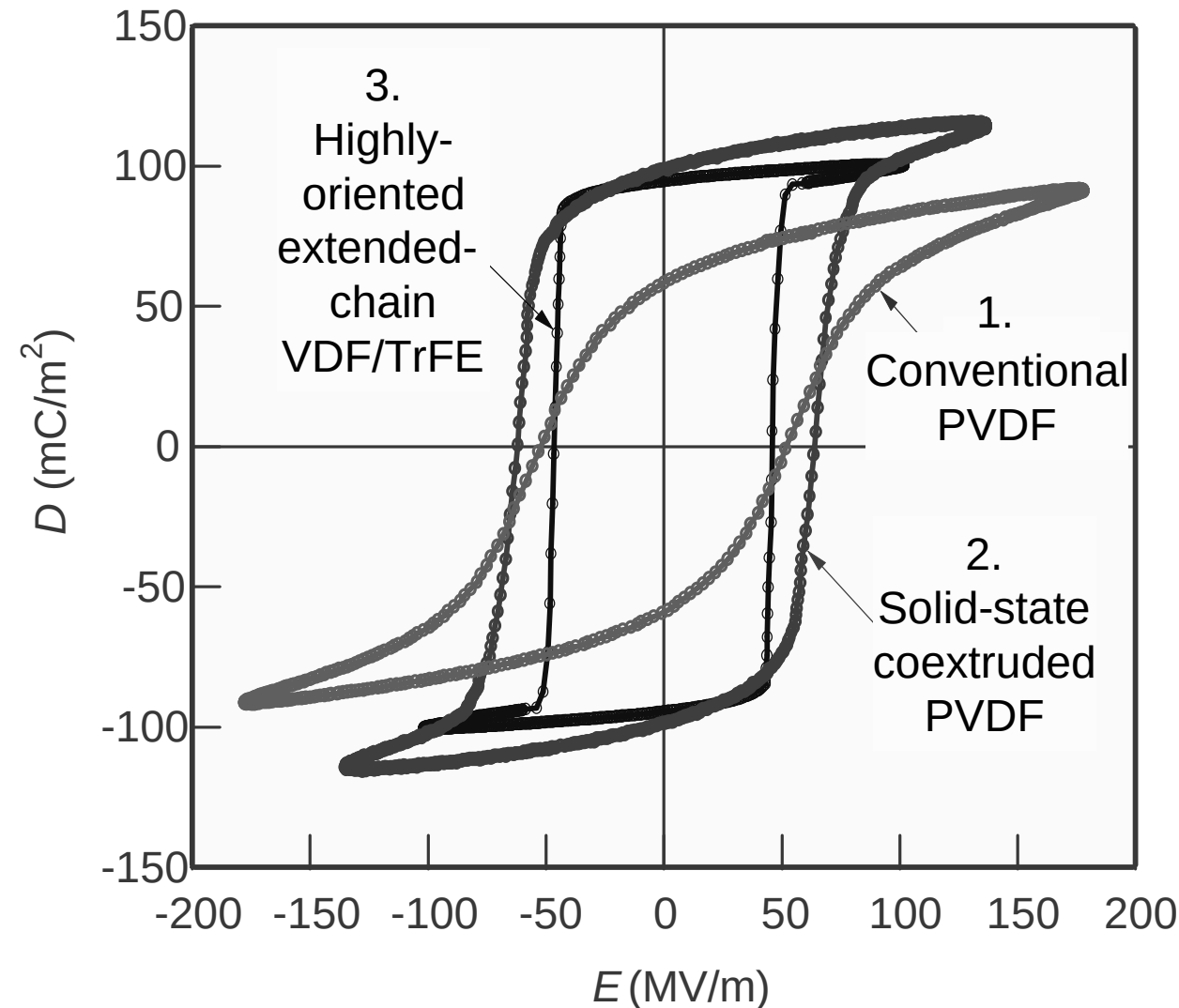
$$P_s = 130 \text{ mC/m}^2$$



Phase Diagram of VDF/TrFE Copolymers



Improved-Performance of PVDF and VDF/TrFE Copolymer



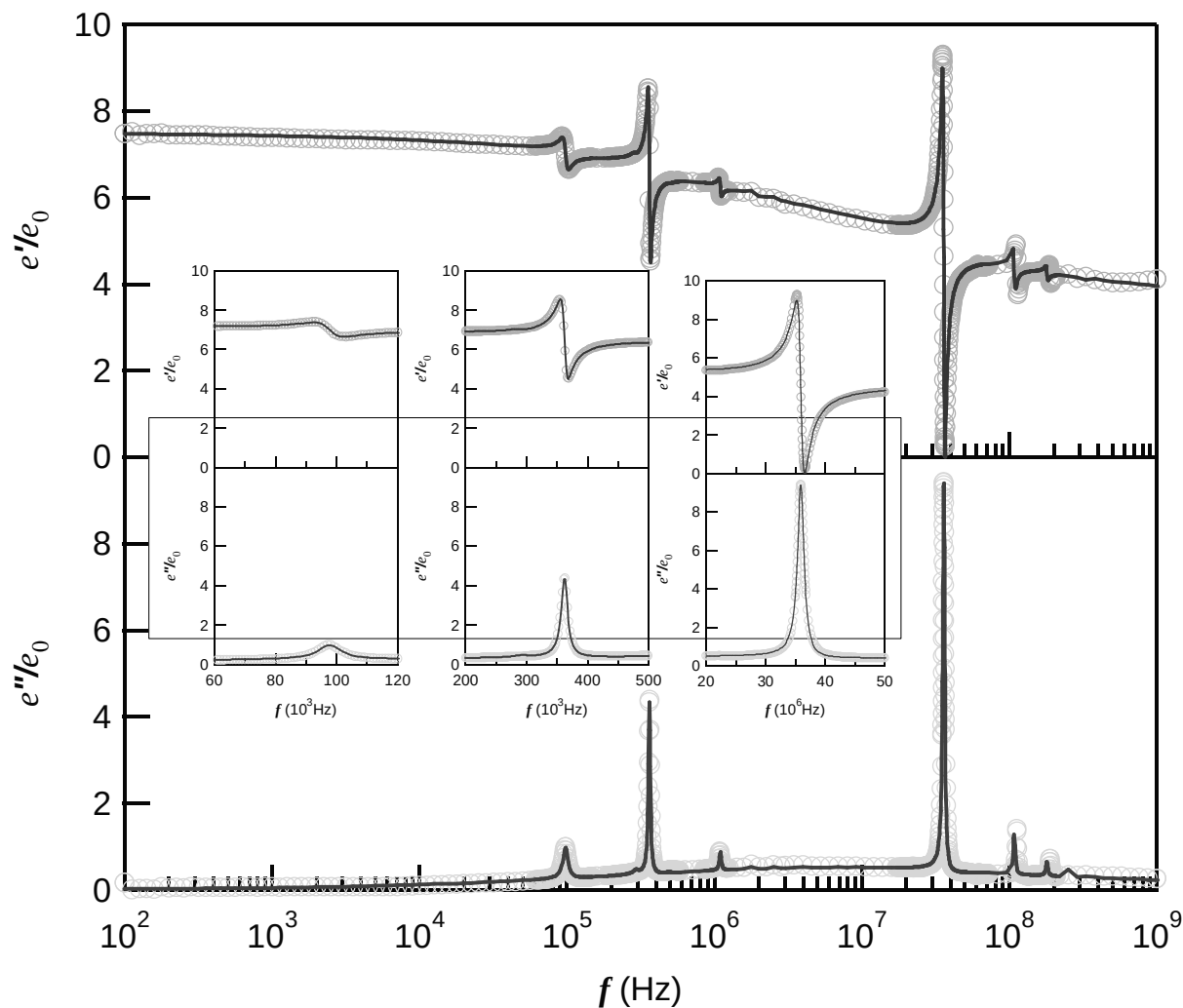
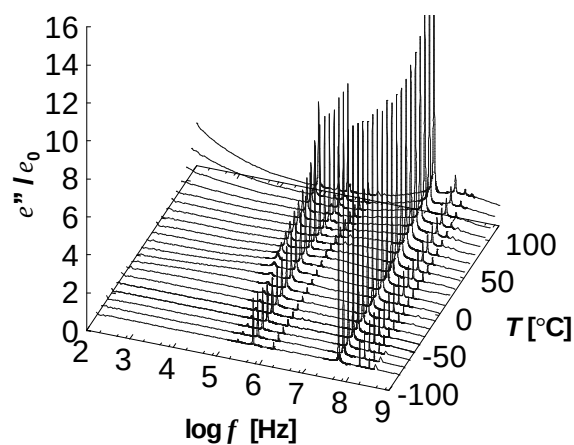
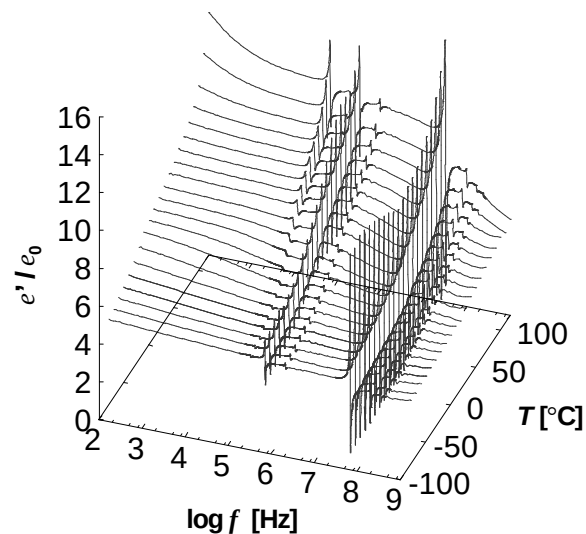
1. Conventional PVDF
Uniaxial-drawn 4 times
 $P_r=60\text{mC/m}^2$
 $k_{33}=0.14$

2. High Performance PVDF
Solid-state coextruded
 $P_r=100\text{mC/m}^2$
 $k_{33}=0.27$

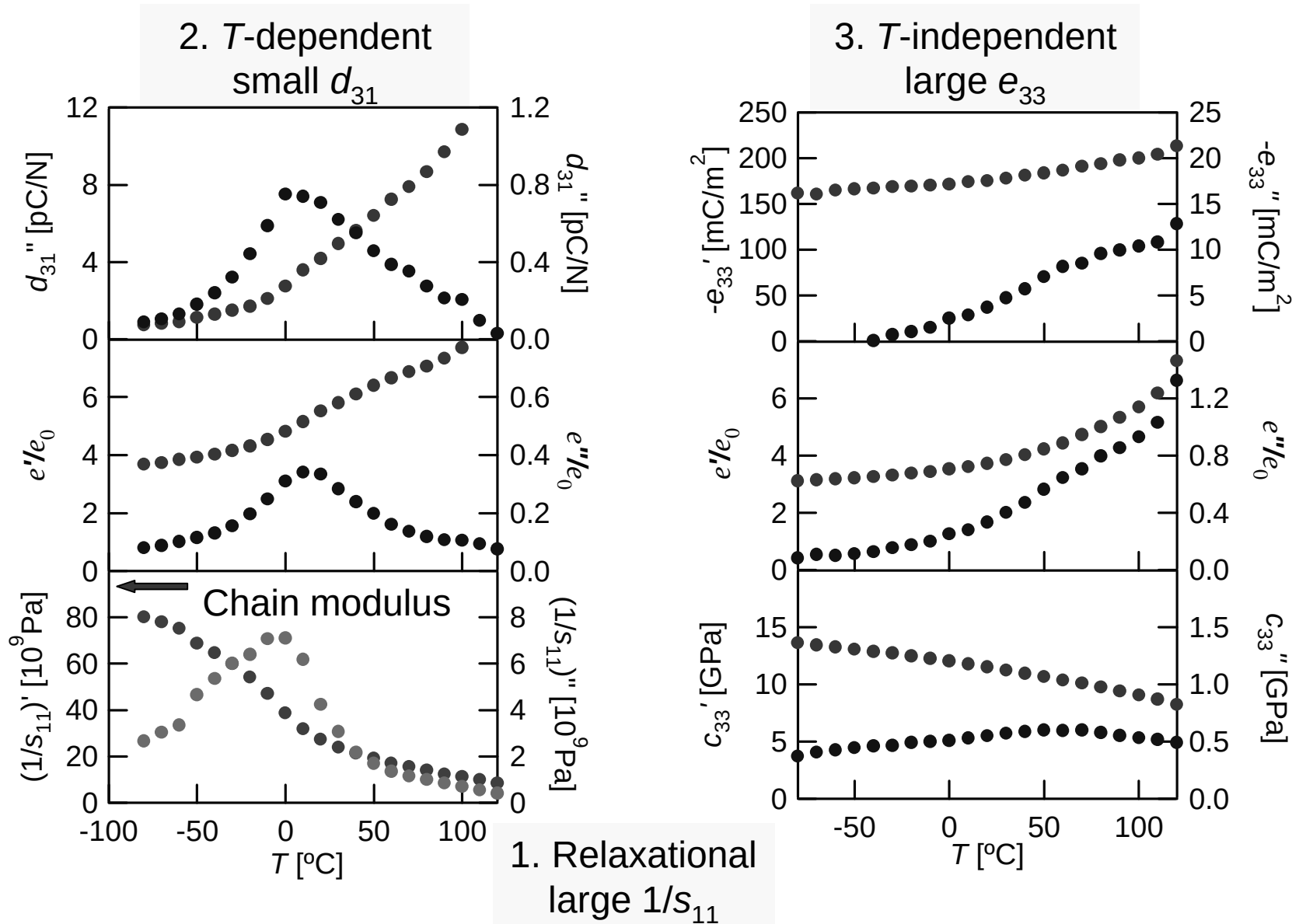
3. VDF(75)/TrFE(25)
Uniaxially-drawn
and annealed
Highly-oriented
extended-chain crystals
 $P_r=100\text{mC/m}^2$
 $k_{33}=0.27$

Piezoelectric Resonance in VDF/Tr FE Copolymer

$$e^* = e^S \frac{\left(1 + \frac{k_l^2}{1 - k_l^2} \frac{\tan a_l f}{a_l}\right) \left(1 + \frac{k_w^2}{1 - k_w^2} \frac{\tan a_w f}{a_w}\right)}{1 - k_t^2 \frac{\tan a_t f}{a_t}}$$



Temperature Spectra of Elastic, Piezoelectric and Dielectric Constants of Extended-Chain-Crystal VDF(75) / TrFE(25) Film

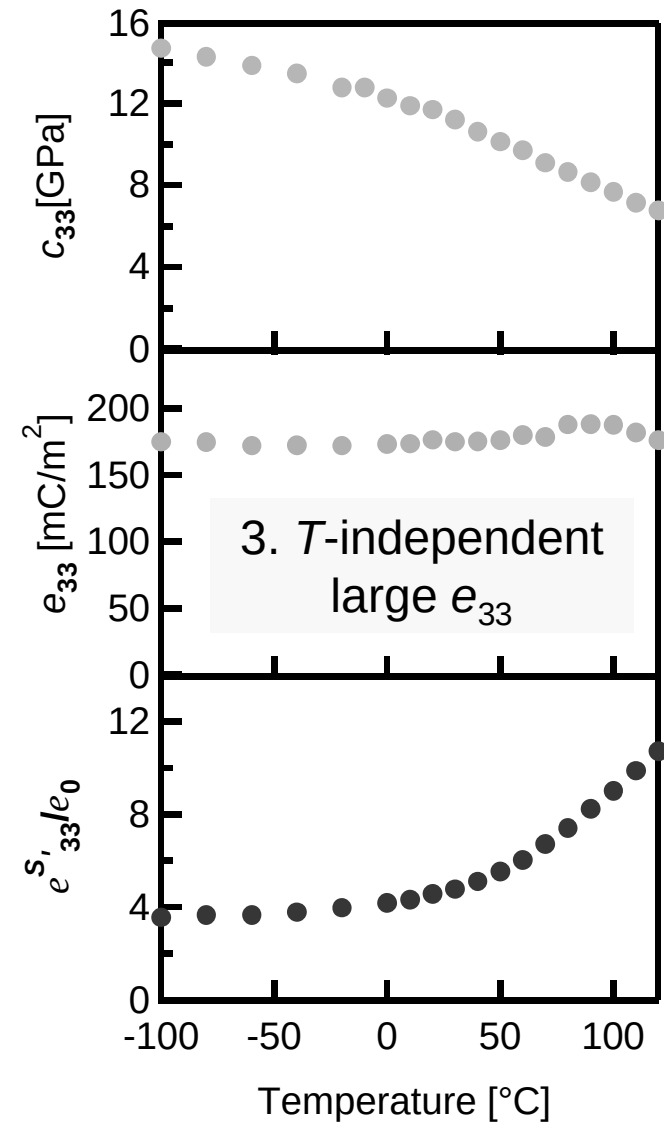
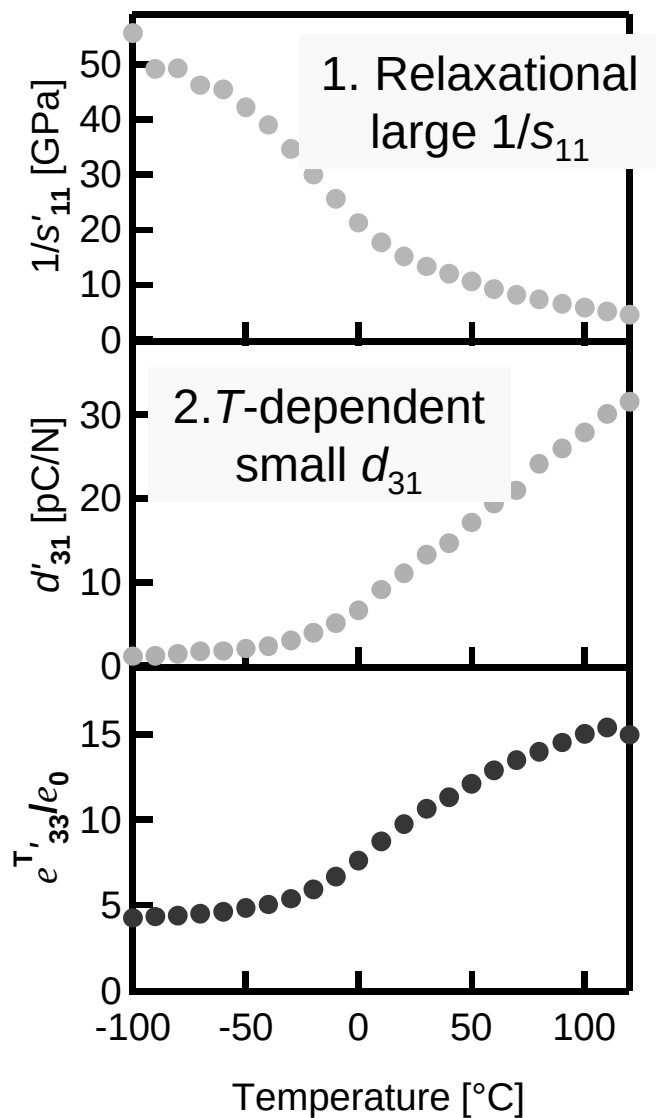


Thermo-Electro-Mechanical 22 Matrix Components of Highly-Oriented VDF(75)/TrFE(25) Copolymer Films with C_{2v} Symmetry at 20?

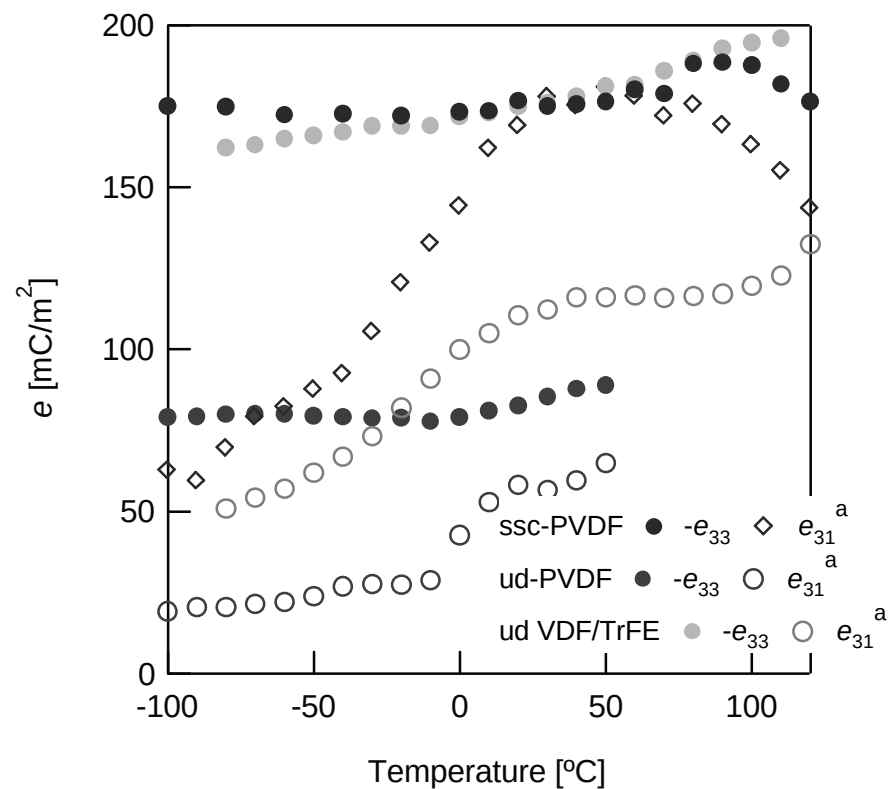
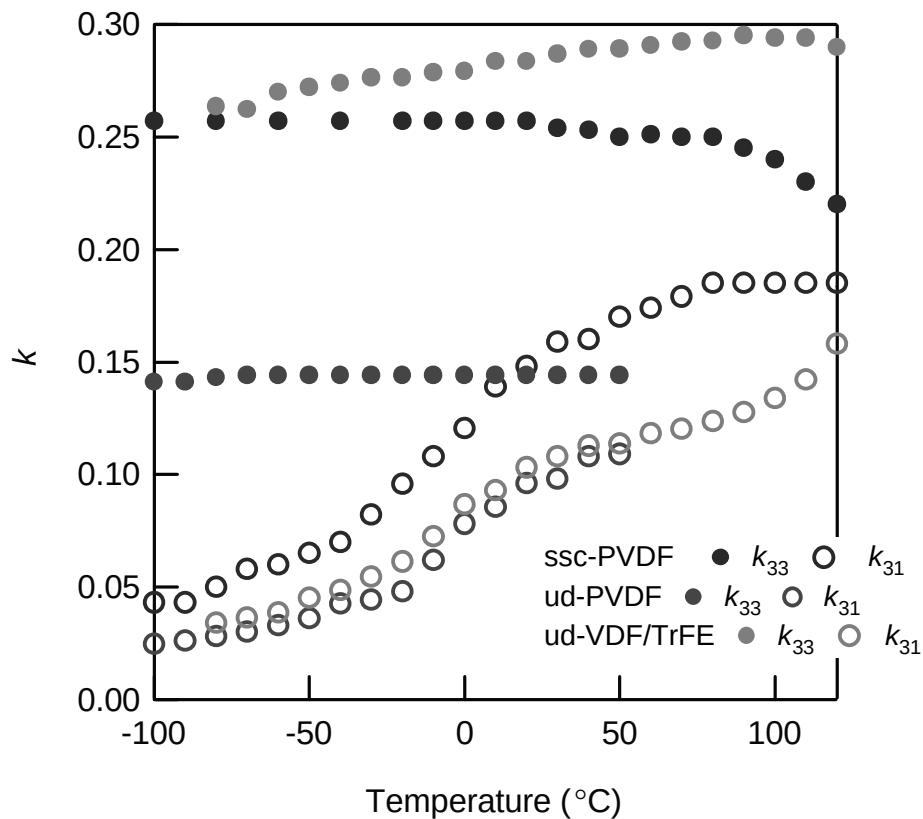
	X_1	X_2	X_3	X_4	X_5	X_6	E_1	E_2	E_3	T
x_1	40	-6	-21						4	50
x_2		15	-62						12	130
x_3		0	150						-29	90
x_4				400				-50		
x_5					450		-31			
x_6	s_{ij}					71				
D_1					d_{15}	0	5			
D_2				d_{24}				7		
D_3	d_{31}	d_{32}	d_{33}				e_{ik}/e_0		10	25
S	a_1	a_2	a_3						p_3	2.3

s_{jl} (nPa⁻¹), e_{ik}/e_0 , C (MJ/m³K), d_{ij} (pC/N), p_i (μC/m²K), a_j (μK⁻¹)

Temperature Spectra of Elastic, Piezoelectric and Dielectric Constants of Coextruded PVDF



Temperature Dependence of Electromechanical Coupling Coefficients and Piezoelectric Constants for PVDF and VDF/TrFE

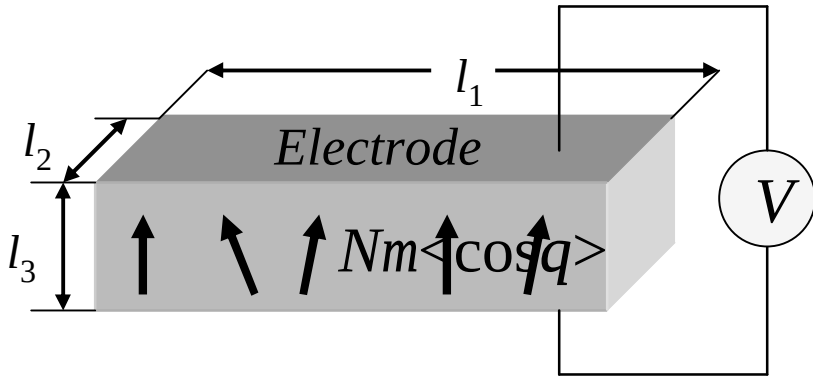


Electromechanical Properties of Coextruded PVDF and Highly-Oriented VDF/TrFE at 20?

Materials	d_{31} (pC/N) k_{31}	$1/s_{11}^E$ (GPa) e_3^X/e_0	e_{33} (mC/m ²) k_{33}	c_{33}^D (GPa) e_3^X/e_0	p_3 (μC/m ² K) P_r (mC/m ²)
PVDF Conventional	16 0.10	4 10	-90 0.14	12 5	25 60
PVDF Coextruded	11 0.16	16 10	-180 0.27	12 5	25 100
VDF(75)/TrFE(25) Highly-Oriented	4 0.11	28 7	-185 0.29	12 4	25 95

- ? T -independent large k_{33} and e_{33}
associated with thickness change
- ? T -dependent small d_{31} originated in $e_{33} s_{31}$
- ? Large but relaxational Young's modulus
reflecting extended-chain stiffness and chain motion
- ? Quantitative understanding of basic mechanisms

Mechanisms of Piezoelectricity in Ferroelectric Polymers



Experimental Data

$$P_r = 100 \text{ mC/m}^2$$

$$e_{33} = -200 \text{ mC/m}^2$$

Polarization

$$P_r = \frac{Nm \langle \cos q \rangle}{l_1 l_2 l_3}$$

Charge on the Electrode

$$Q = \frac{Nm \langle \cos q \rangle}{l_3}$$

Piezoelectric
e-constant

$$e_{33} = \frac{l_3}{l_1 l_2} \left(\frac{\partial Q}{\partial l_3} \right)_{V=0} = -P_r \left(1 - \frac{\partial \ln m}{\partial \ln l_3} - \frac{\partial \ln \langle \cos q \rangle}{\partial \ln l_3} \right)$$

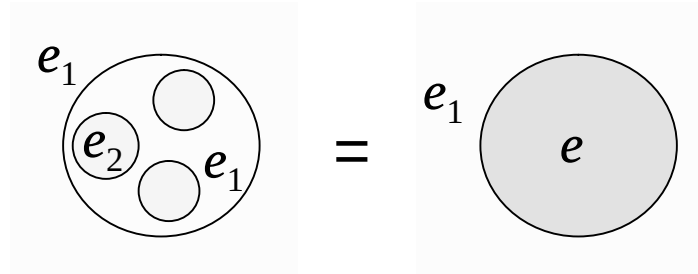
Dimensional
effect

$$\left(-\frac{\partial \ln(1/l_3)}{\partial \ln l_3} = 1 \right)$$

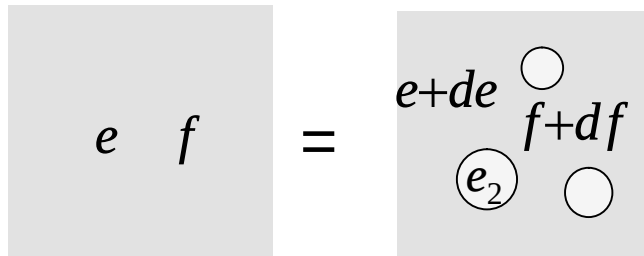
Remaining=1

(local field
dipole orientation)

Two-Phase Spherical Dispersion System

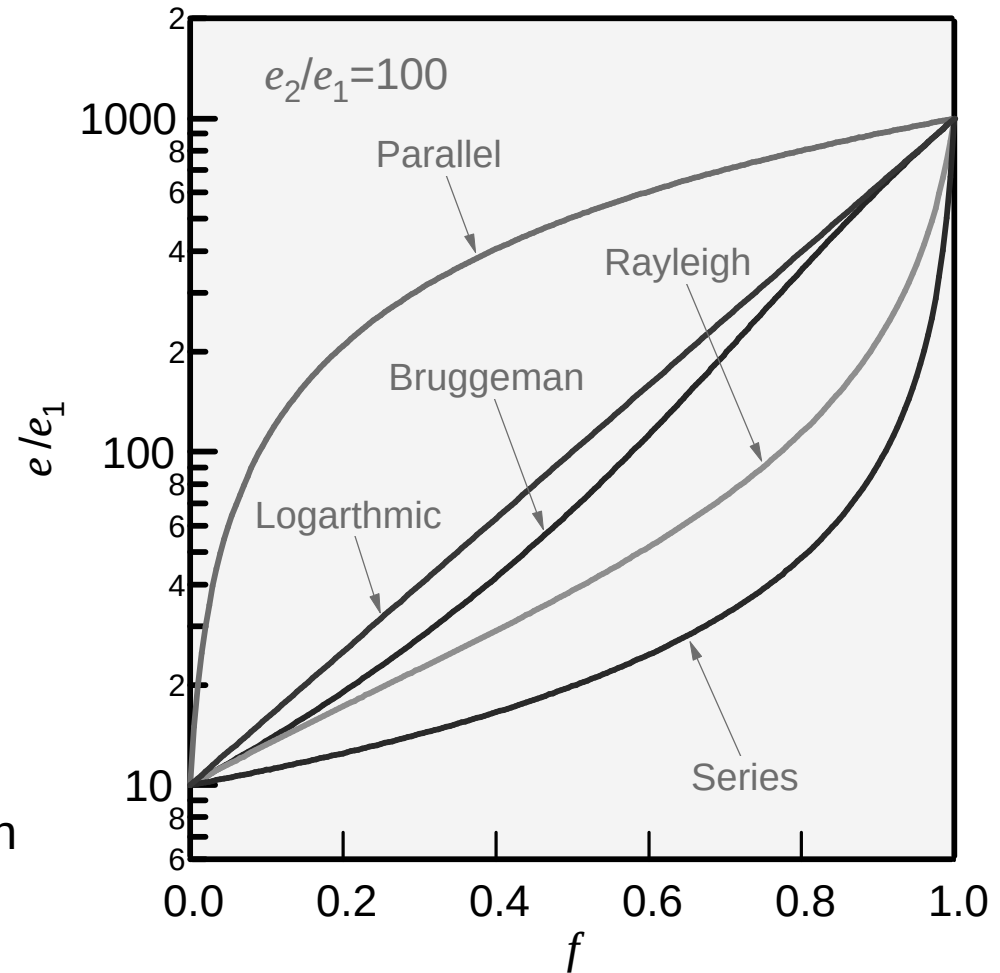


$$\frac{e - e_1}{e + 2e_1} = f \frac{e_2 - e_1}{e_2 + 2e_1} \quad \text{Rayleigh (1892)}$$



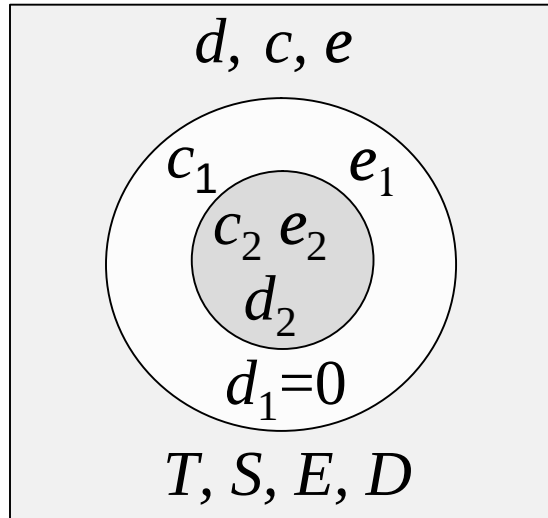
$$de = \frac{df}{1-f} \frac{e_2 - e}{e_2 + 2e} 3e \quad \text{Bruggeman (1935)}$$

$$(1-f) \left(\frac{e}{e_1} \right)^{1/3} = \frac{e_2 - e}{e_2 - e_1}$$



Piezoelectric Mixing Law

Piezoelectric spherical inclusion in non-piezoelectric matrix



Piezoelectric
constants

$$d = fL_E L_T d_2$$

$$e = fL_E L_S e_2$$

$$g = fL_D L_T g_2$$

$$h = fL_D L_S h_2$$

Local field coefficients

Stress

$$L_T = \frac{T_2}{T} = \frac{c_2(c - c_1)}{fc(c_2 - c_1)}$$

Strain

$$L_S = \frac{S_2}{S} = \frac{(c - c_1)}{f(c_2 - c_1)}$$

Electric
field

$$L_E = \frac{E_2}{E} = \frac{e - e_1}{f(e_2 - e_1)}$$

Electric
displacement

$$L_D = \frac{D_2}{D} = \frac{e_2(e - e_1)}{fe(e_2 - e_1)}$$

Dielectric permittivity

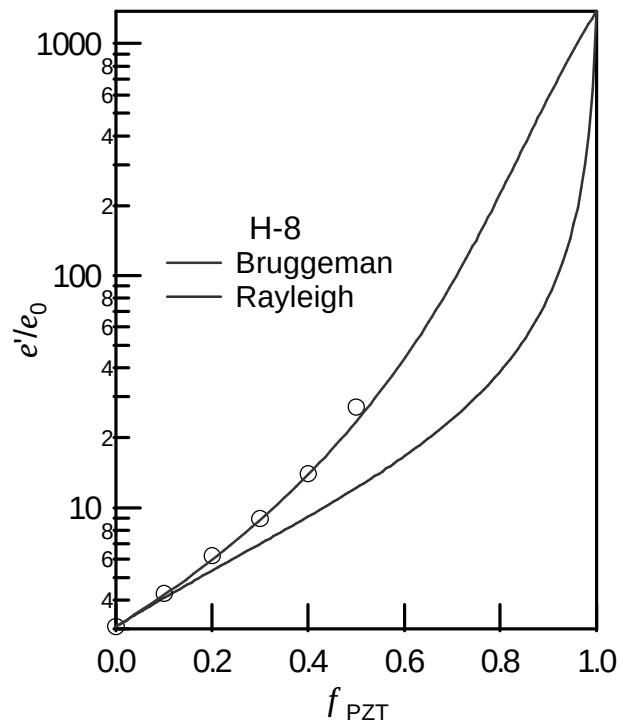
$$(1 - f) = \frac{e_2 - e}{e_2 - e_1} \left(\frac{e}{e_1} \right)^{-1/3}$$

Elastic constant

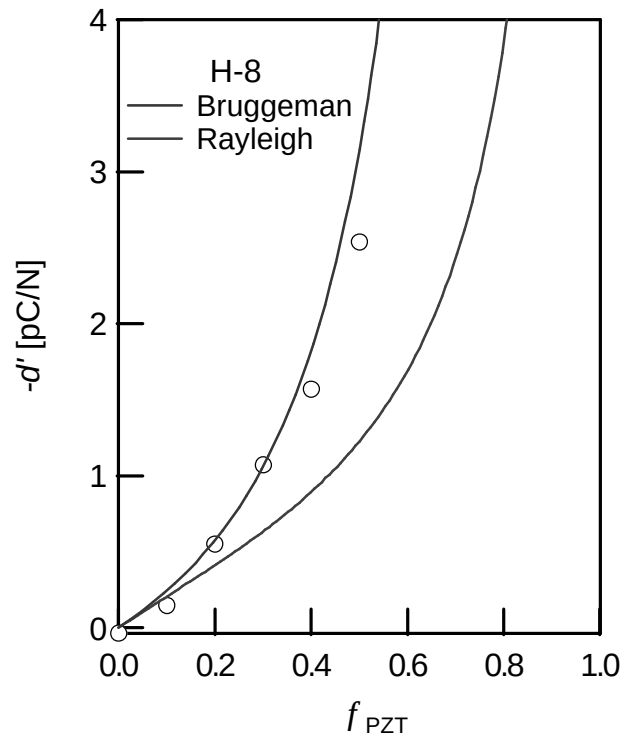
$$(1 - f) = \frac{c_2 - c}{c_2 - c_1} \left(\frac{c}{c_1} \right)^{-2/5}$$

PZT / PVC Composite

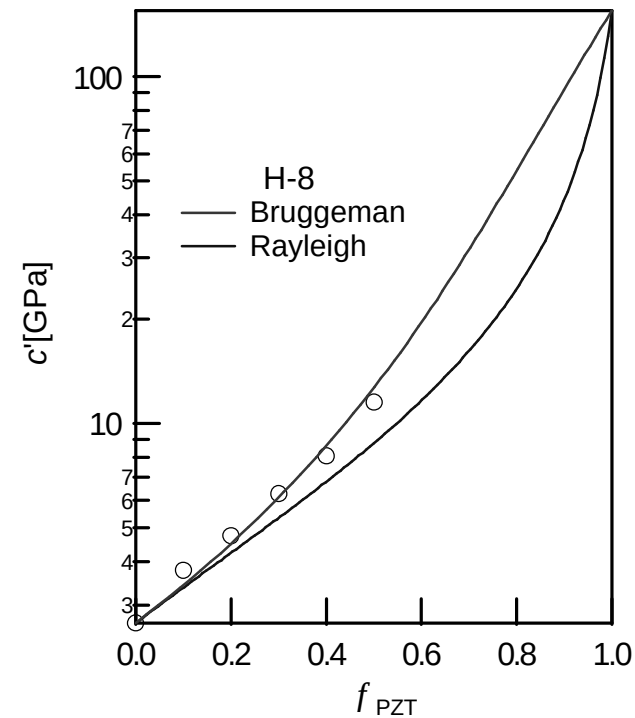
dielectric



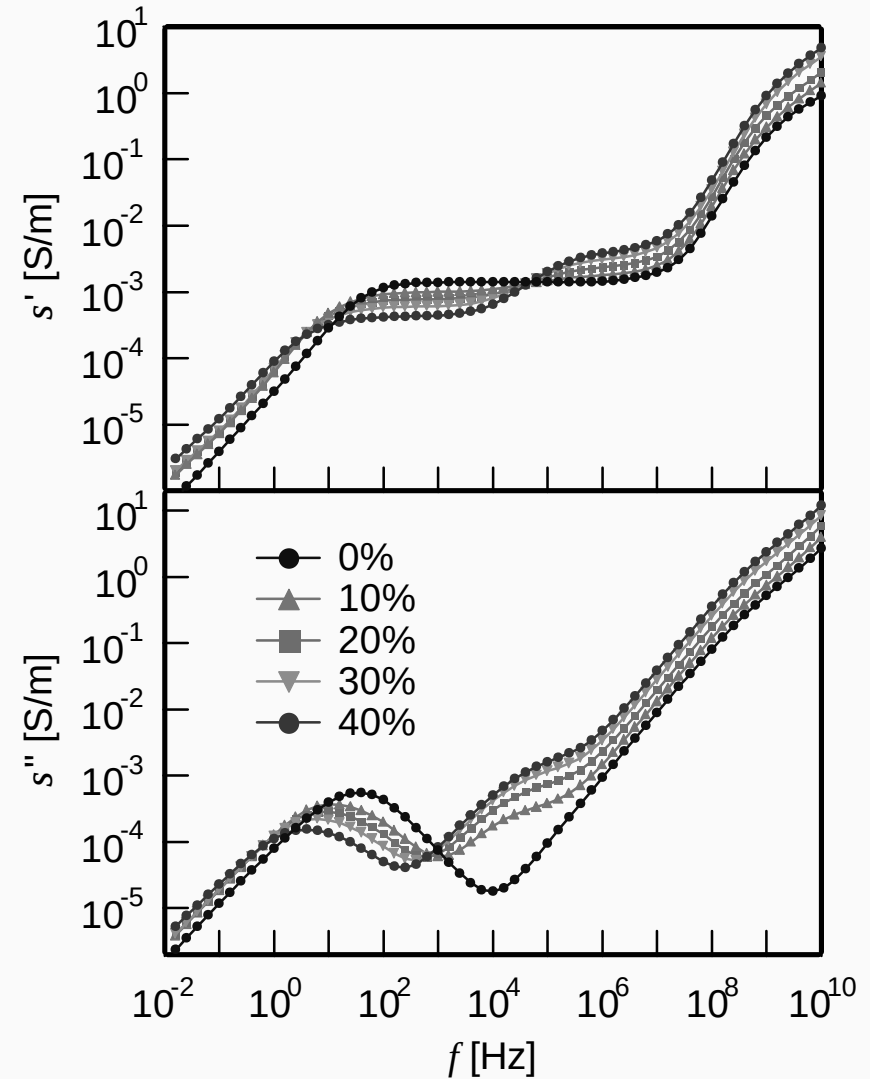
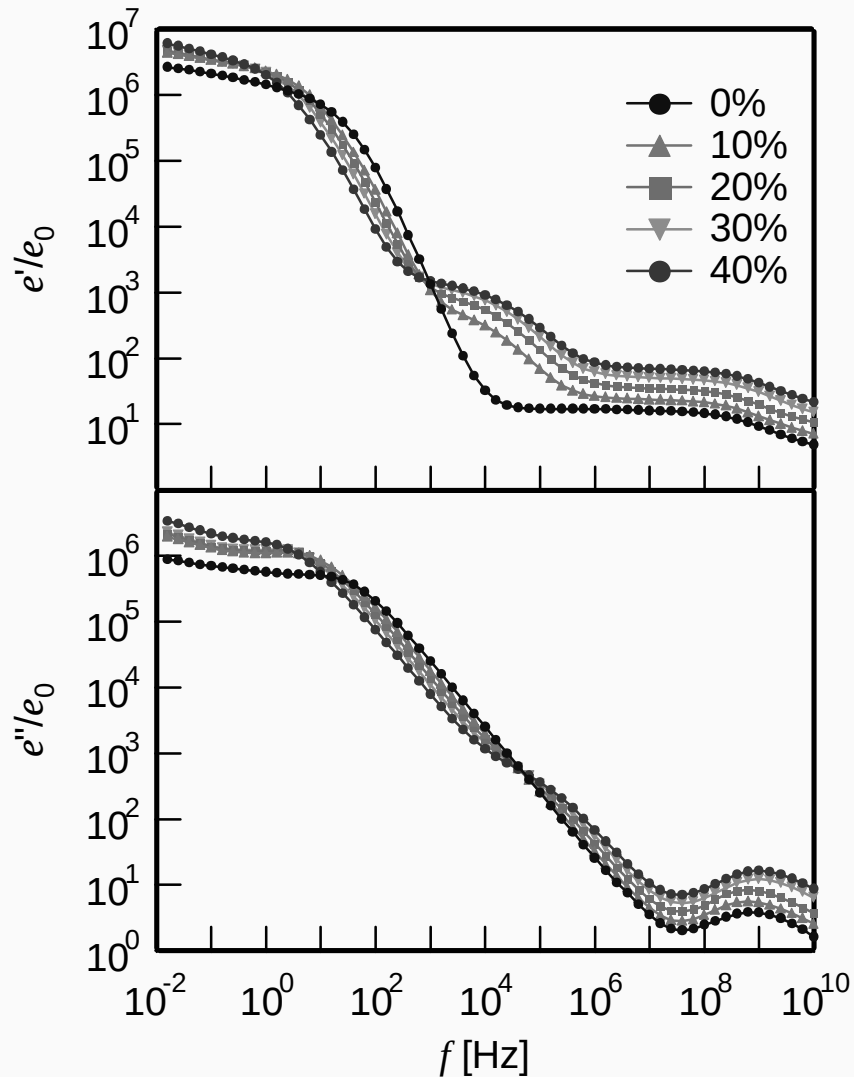
piezoelectric



elastic

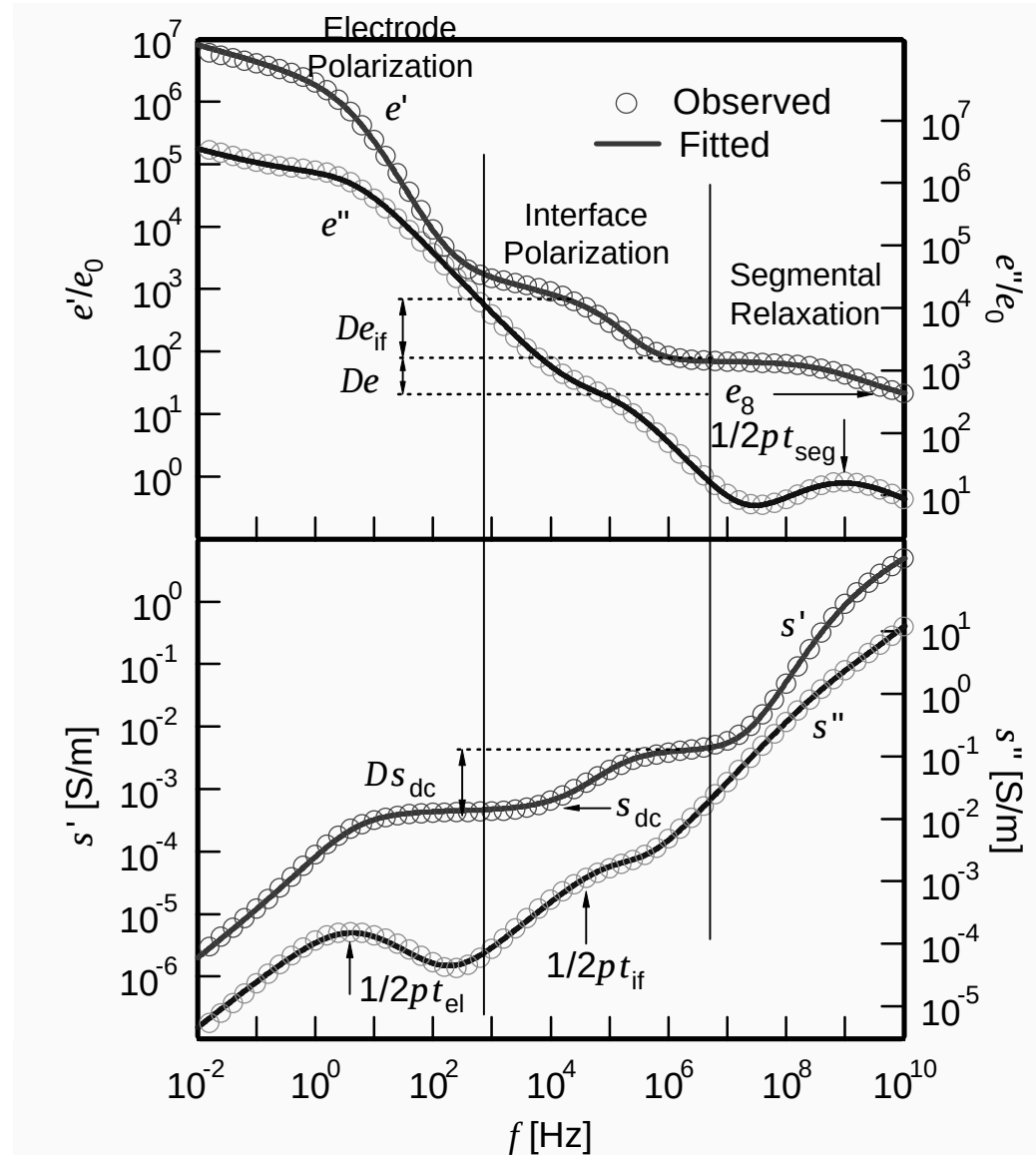
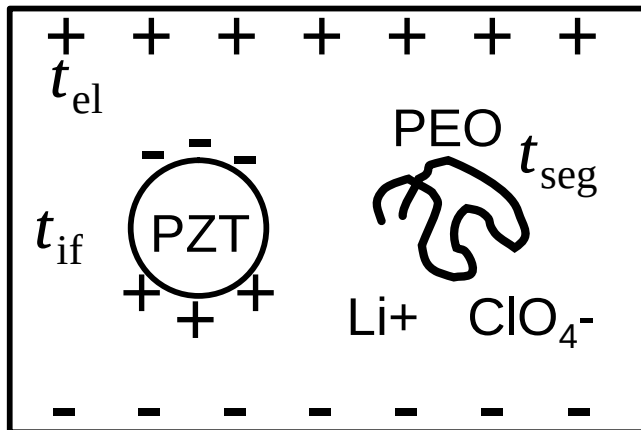


Dielectric and Conductive Frequency Spectra for $\text{BaTiO}_3(3\text{mm}) / \text{PEO400} (0.1\% \text{LiClO}_4)$ Composites

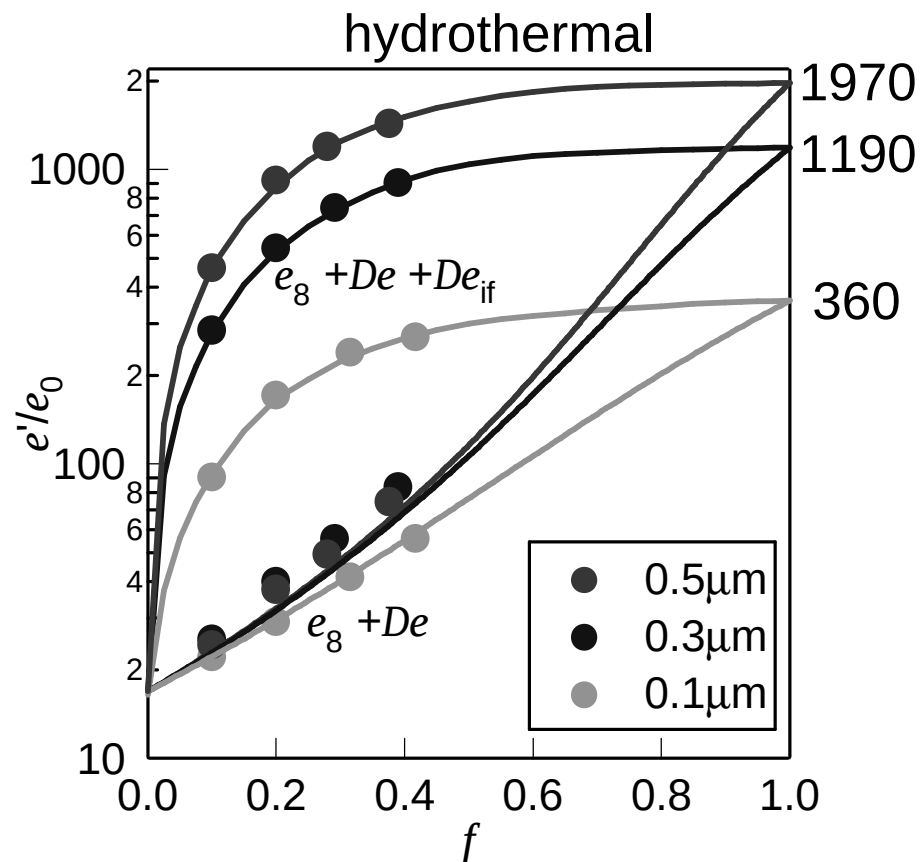
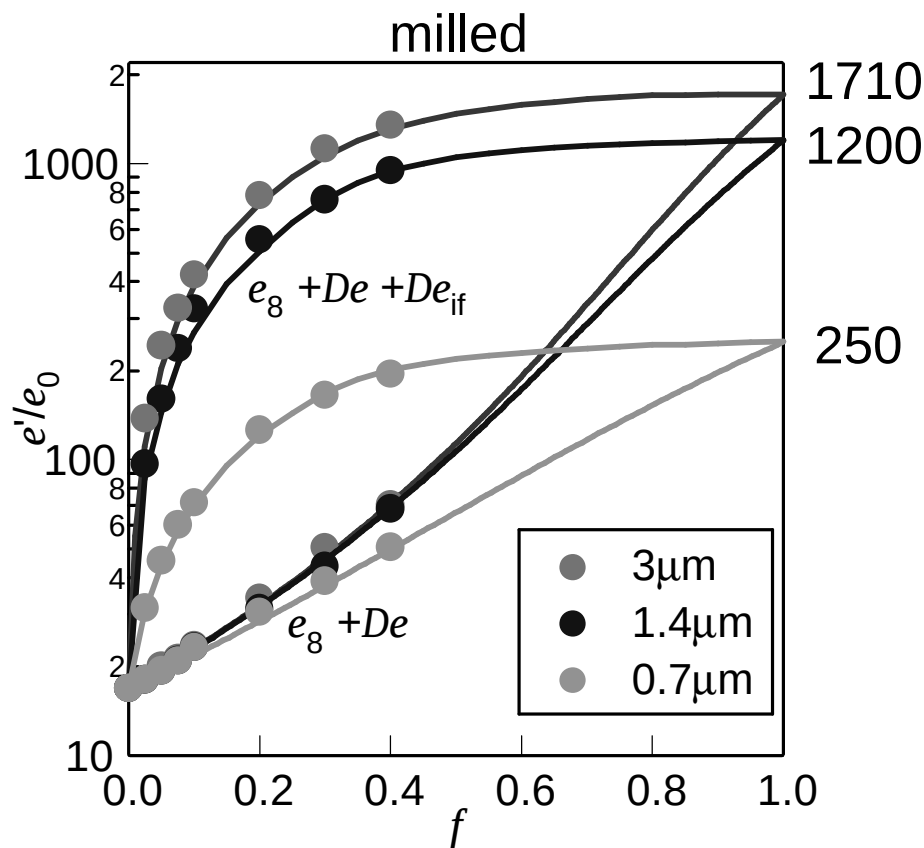


Dielectric and Conductive Processes in BaTiO₃ / Li-PEO Composites

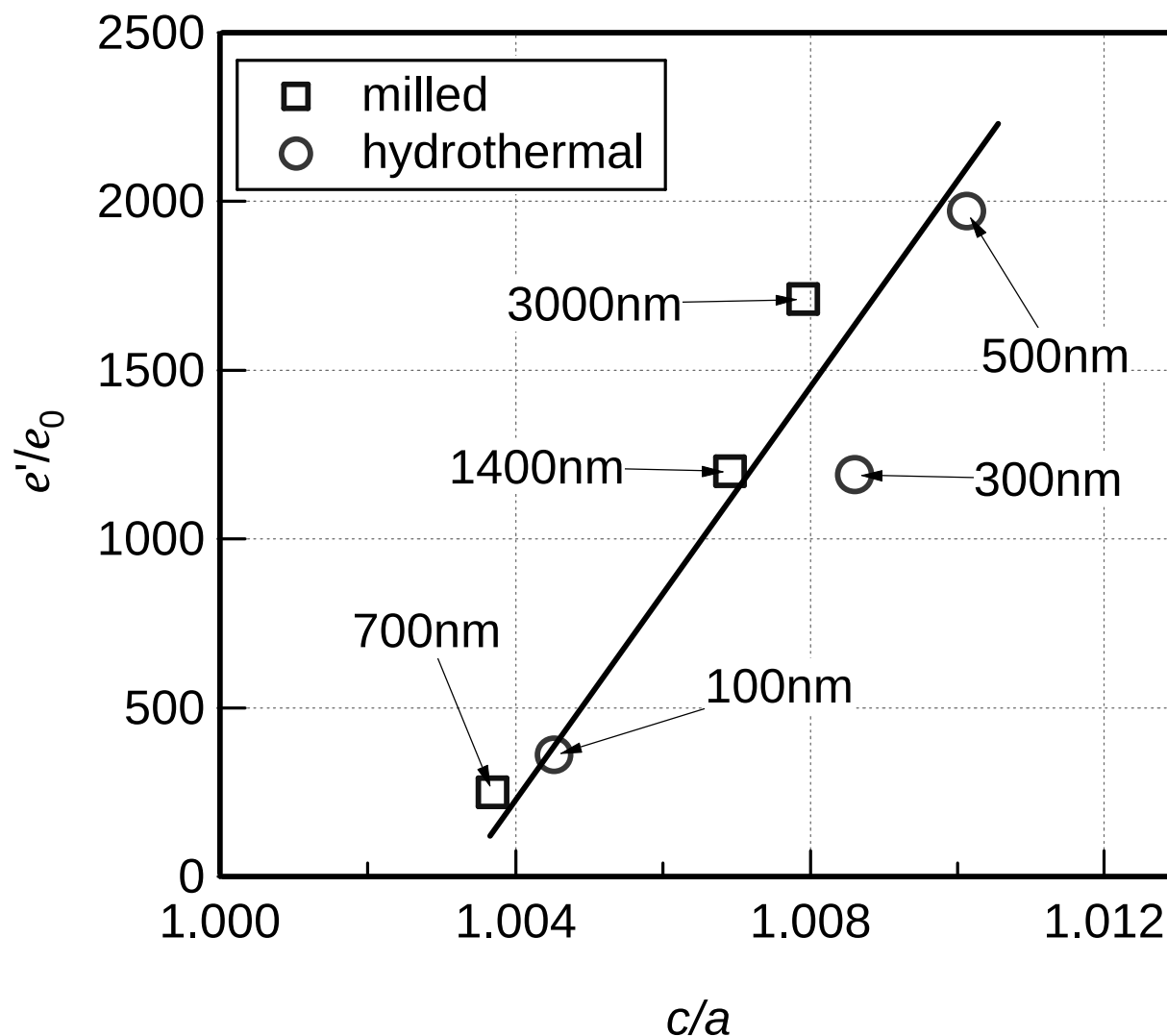
$$\begin{aligned}
 e = e_{\infty} &+ \frac{\Delta e}{(1 + (i\omega t_{\text{seg}})^b)^a} \\
 &\quad \text{Segmental-mode Relaxation} \\
 &+ \frac{\Delta s_{\text{dc}}}{i\omega} \left(1 - \frac{1}{1 + (i\omega t_{\text{if}})^{g_{\text{if}}}} \right) \\
 &\quad \text{Interface Polarization} \\
 &+ \frac{s_{\text{dc}}}{i\omega} \left(1 - \frac{1}{1 + (i\omega t_{\text{el}})^{g_{\text{el}}}} \right) \\
 &\quad \text{Electrode Polarization}
 \end{aligned}$$



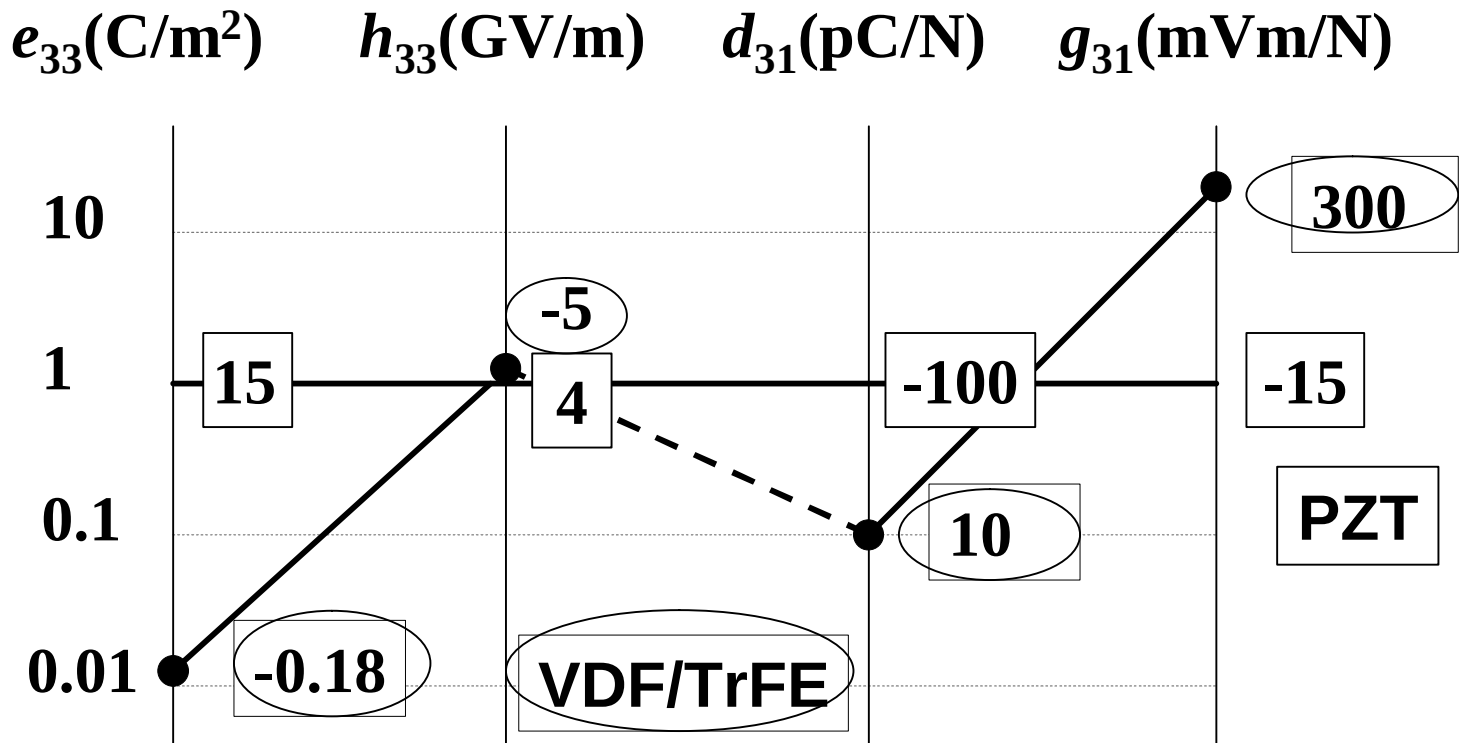
Dependence of observed and predicted permittivities on the volume fraction of BaTiO₃ with varying particle size



Relation between permittivity and c/a ratio for BaTiO_3 powder



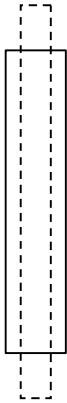
Comparison of Piezoelectric Constants of VDF/TrFE Copolymer and PZT Ceramics



Piezoelectric polymers are suited for sensors and soft actuators because of their low permittivity and high compliance.

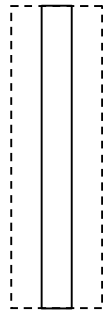
Deformation of Piezoelectric Polymers and Related Applications

Large Deformation, Low Power



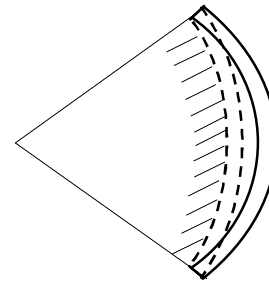
(A) Transverse Effect

Inch Worm



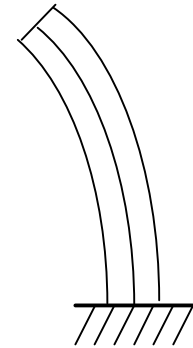
(B) Longitudinal Effect

Ultrasonic Transducer



(C) Longitudinal-Transverse Conversion

Speaker Headphone



(D) Bimorph

Fan Display