Polymeric dipole electrets and ferroelectric materials

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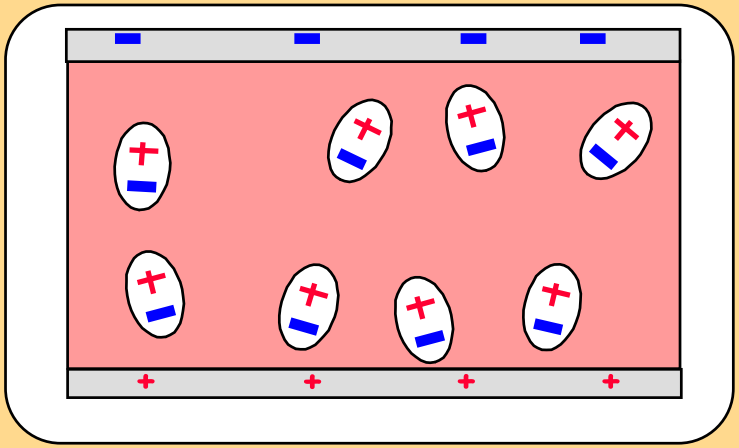
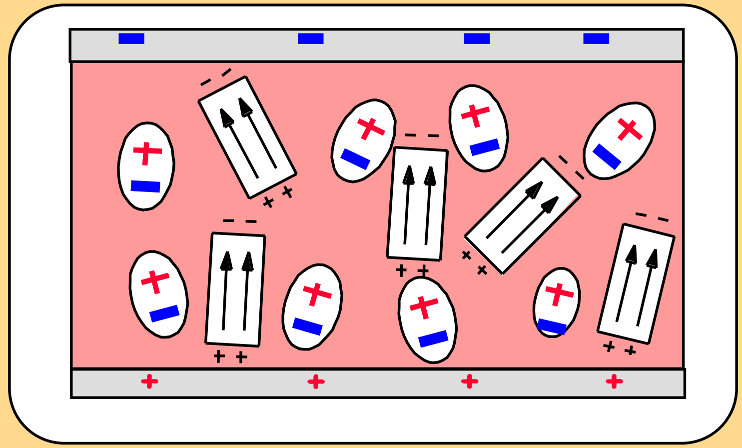
Amorphous dipole and semicrystalline ferroelectric polymer electrets

Frozen quasipermanent dipole orientation



Ferroelectric polarization + compensation charges

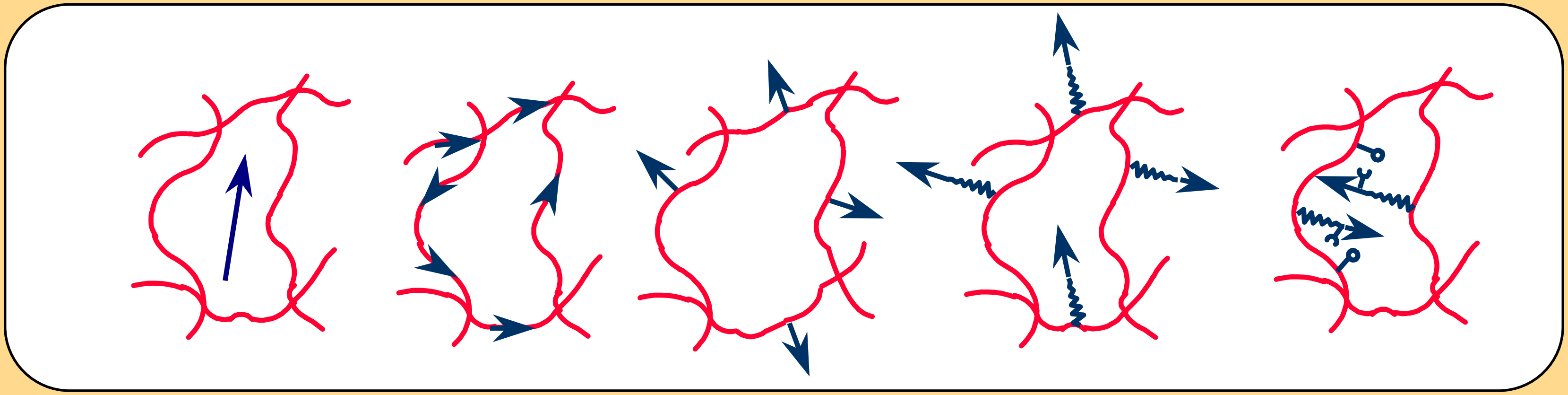


charges

polarization

ferroelectric polarization

Basic concepts for amorphous dipole electrets



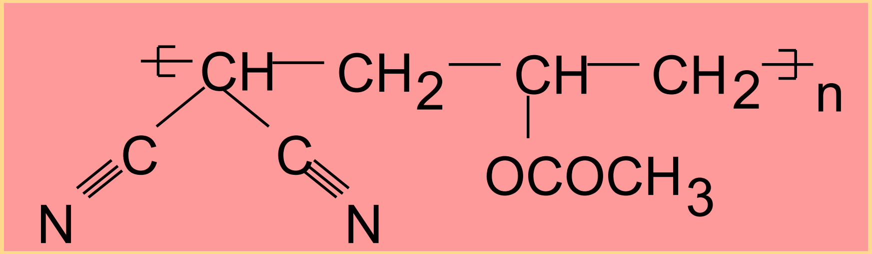
Guest-host | Type A | Type B | Type C | Network-forming

Main-chain | Side-chain

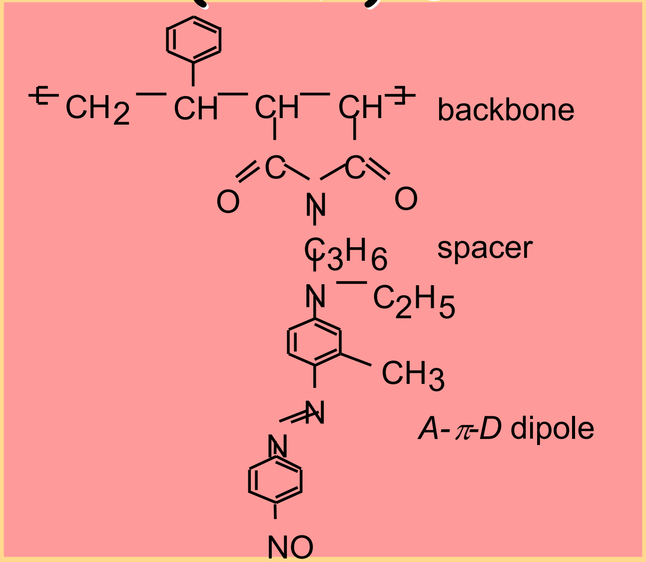
polymers

Amorphous piezo- and pyroelectric dipole electrets

P(VDCN-VAc)



P(S-MA)-DR1



	P(VDCN-VAc)	P(S-MA)-DR1
glass transition T_g	180°C	140°C
frozen polarization P_f	$55 mC/m^2$	$7.8 mC/m^2$
pyroelectric coefficient p	$20 \mu C/m^2K$	$1.3 \mu C/m^2K$
piezoelectric coefficient d_{33}	8pC/N	1.1pC/N

at a poling field of 50V/μm

Dielectric properties of amorphous dipole electrets I

α-relaxation

Dielectric function

$$\tilde{\varepsilon} = \varepsilon_\infty + \frac{\Delta\varepsilon}{\left[1 + \{i\omega\tau_\alpha(T)\}^p\right]^q}$$

ε_∞ : high-frequency dielectric constant

$\Delta\varepsilon \sim N\mu^2 / 3\varepsilon_0 kT$: dielectric relaxation strength

N : dipole density

μ : dipole moment

$\tau_\alpha(T)$: temperature-dependent relaxation time

p, q : shape parameter of the dielectric relaxation peak

Dielectric properties of amorphous dipole electrets II

α-relaxation

Temperature-dependent dielectric relaxation time

$$\tau_{\alpha}(T) = A\exp\left(\frac{B}{T\{1 - T_2/T_f\}}\right)$$

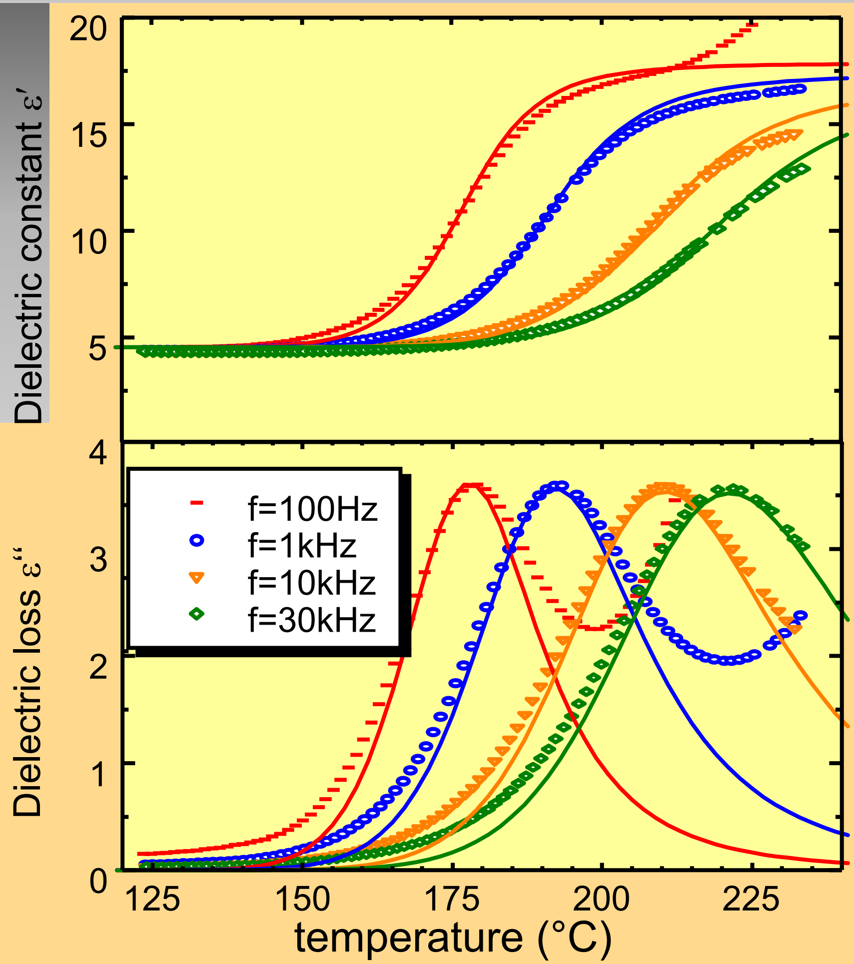
A : time factor

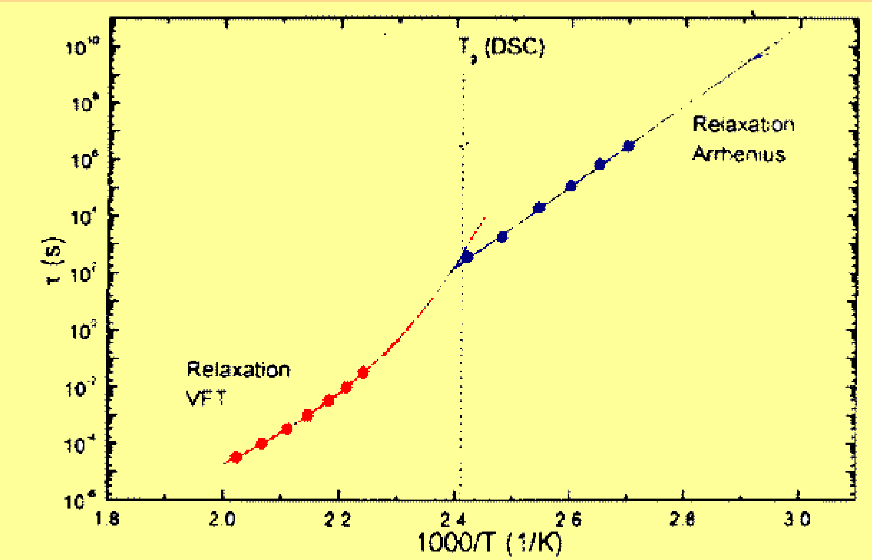
B : activation temperature

T_2 : glass transition temperature

T_f : fictive temperature

Dielectric properties of amorphous side-chain dipole electrets





Frozen polarization in amorphous dipole electrets

Polarization at T>Tg

$$P = \varepsilon_0(\varepsilon_\infty + \Delta\varepsilon)E_p$$

E_p: poling field

Polarization at T<Tg

$$P = \varepsilon_0\varepsilon_\infty E_p$$

Frozen polarization

$$P_f = \varepsilon_0\Delta\varepsilon E_p$$

Piezo- and pyroelectricity: Definition

$$d_{i\alpha} = \frac{\partial D_i}{\partial \sigma_\alpha} = \frac{\partial \varepsilon_\alpha}{\partial E_i}$$

$$p_i = \frac{\partial D_i}{\partial T}$$

D_i : dielectric displacement

E_i : electric field

ε_α : mechanical strain

σ_α : mechanical stress

SoMMaP

Piezo- and pyroelectricity in amorphous dipole electrets

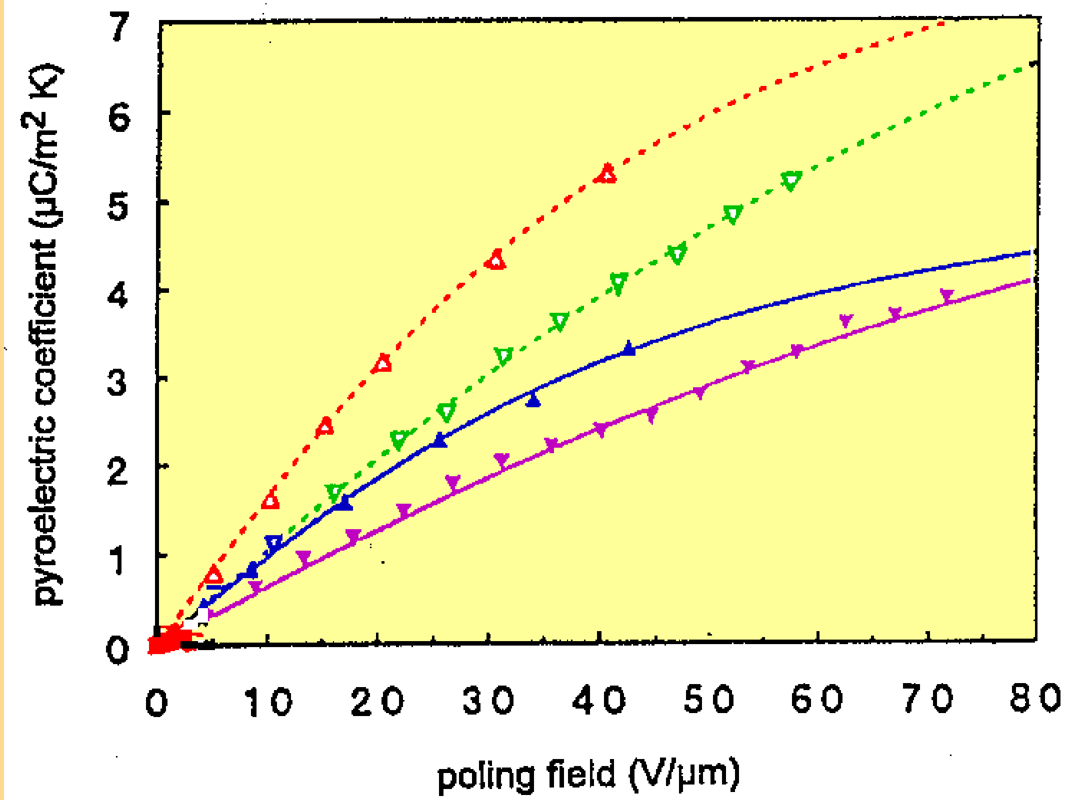
$$d_{33} = \frac{1+\nu}{1-\nu}\left(\frac{\varepsilon_\infty + 2}{3} - \frac{2}{5}\right)\beta_x P_f \qquad p_3 = \frac{1+\nu}{1-\nu}\left(\frac{\varepsilon_\infty + 2}{3} - \frac{2}{5}\right)\alpha_x P_f$$

ν : Poisson ratio

β_x : linear compressibility

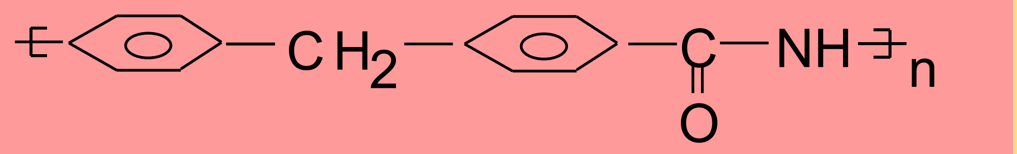
α_x : linear thermal expansion coefficient

Pyroelectric coefficient of an amorphous dipole electret vs. poling field



Fluorinated poly(2,3 bis tri fluoromethyl) norbornadiene

Semicrystalline dipole electrets

Nylon 7	Polyurea
$-[C(=O)-NH-C_{m-1}H_{2(m-1)}]_n-$	
PVDF	**P(VDF-TrFE)**
$-[CH_2-CF_2]_n-$	$-[(CH_2-CF_2)_{1-x}-(CHF-CF_2)_x]_n-$

remanent polarization

65 mC/m^2	up to 100 mC/m^2

pyroelectric coefficient

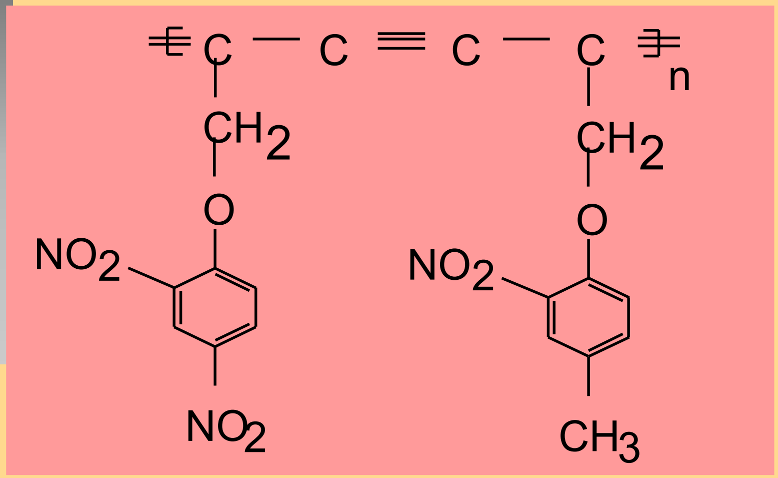
25 μC/m^{2}K	up to 40 μC/m^{2}K

piezoelectric coefficient

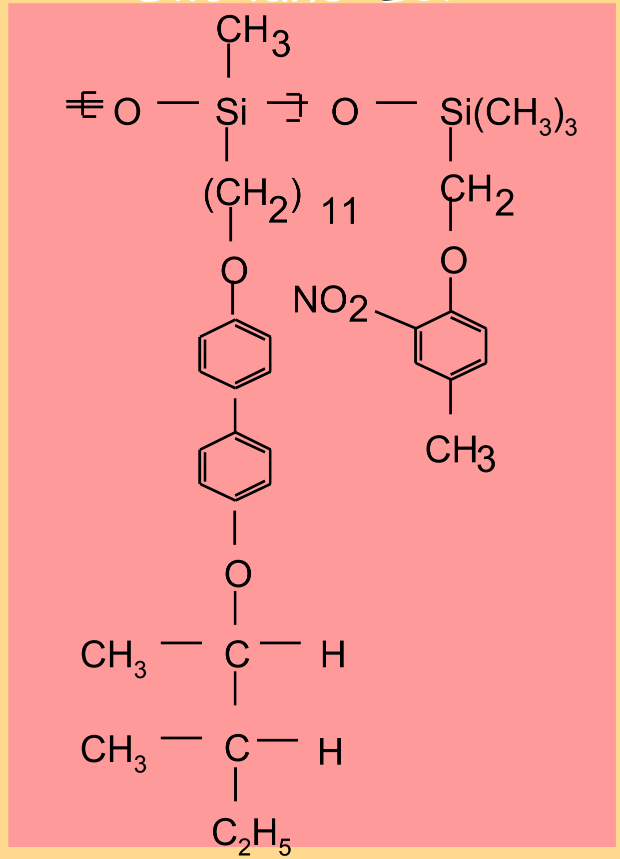
30pC/N	up to 35pC/N

Single-crystalline and liquid crystalline pyroelectric polymers

DNP-MNP



Siloxane-LCP

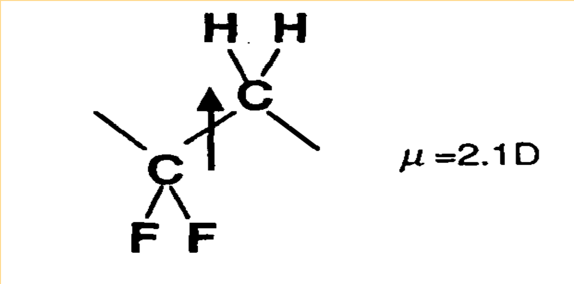


pyroelectric coefficient

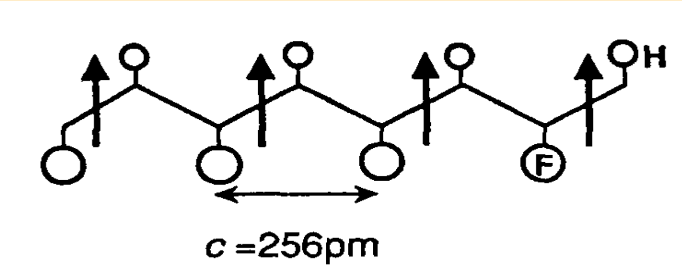
DNP-MNP	Siloxane-LCP
1.2-3.2 μC/m²K	50 μC/m²K

Molecular, chain and crystal structure of the ferroelectric ß-phase of PVDF

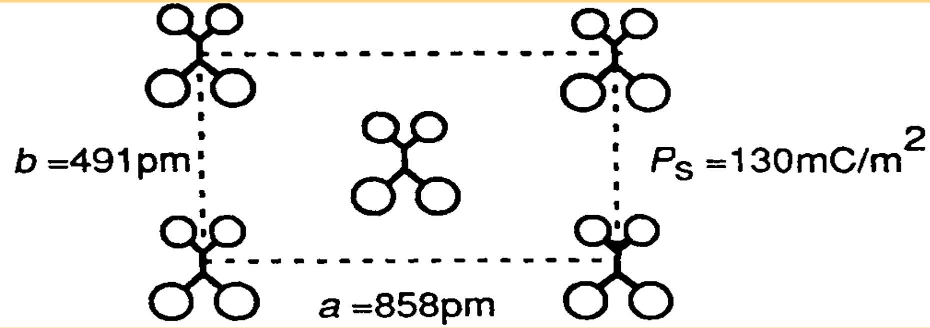
• Polyvinylidene fluoride (PVDF)



•molecular structure

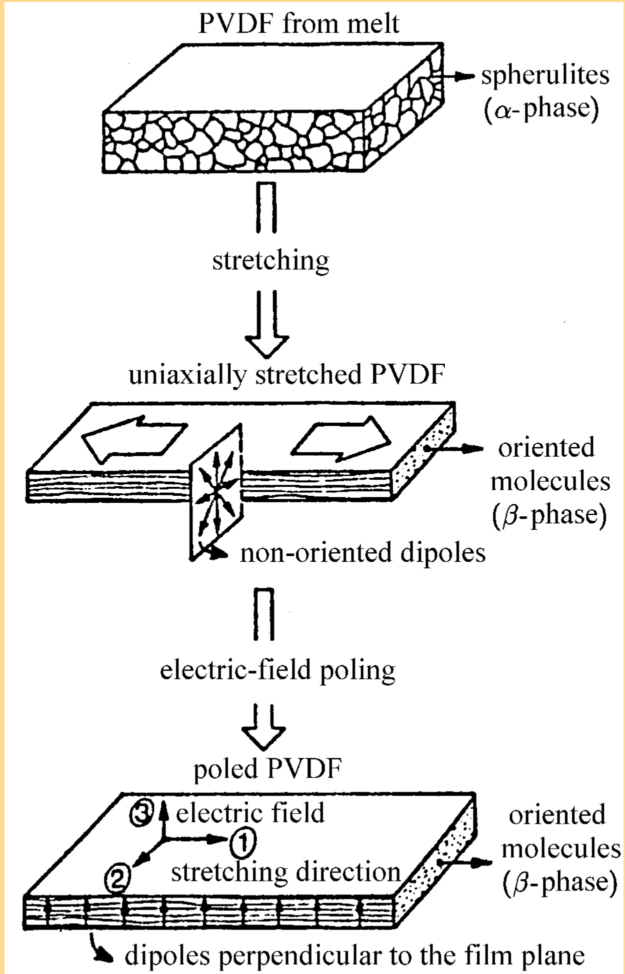


•chain structure

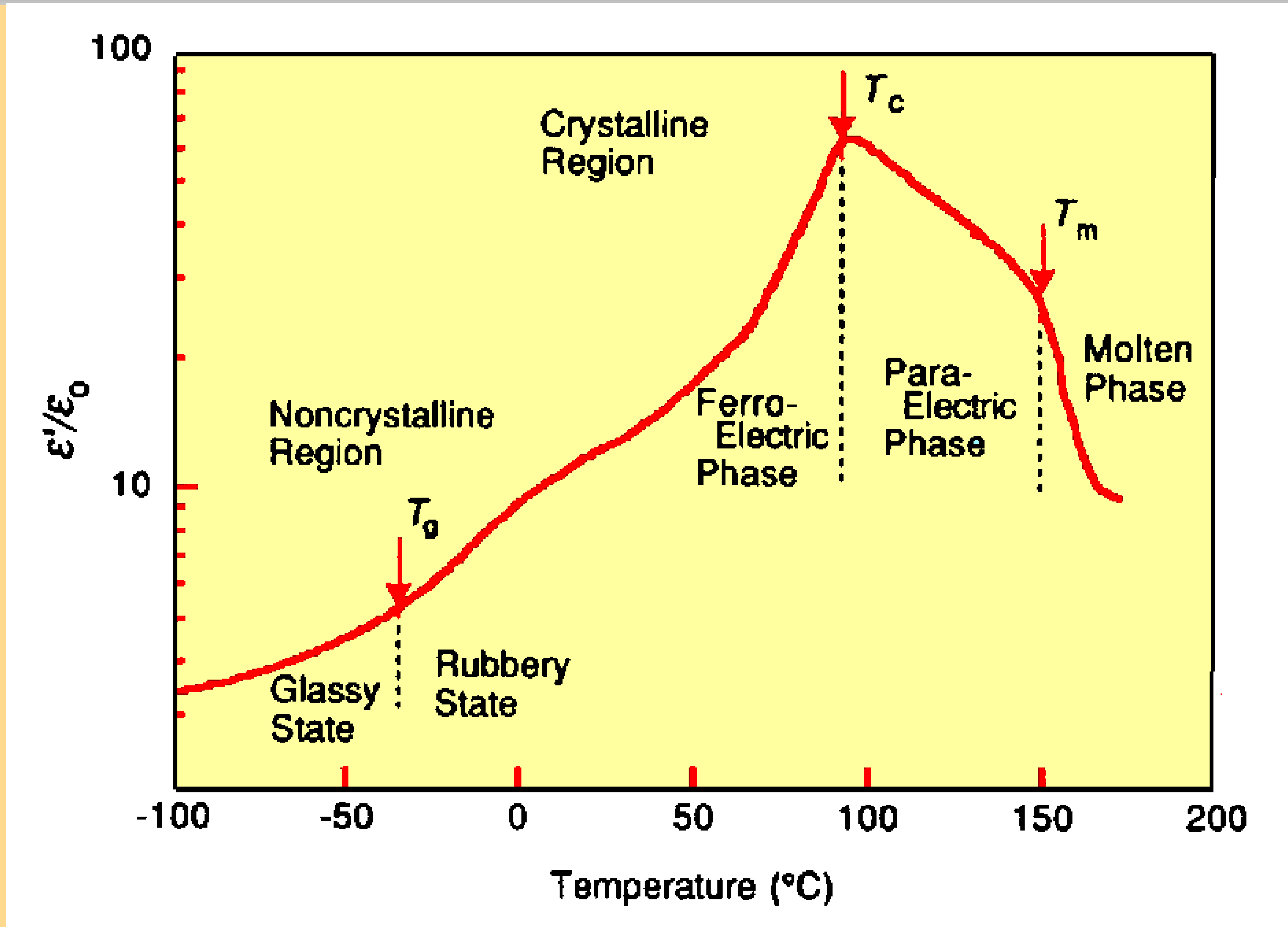


•crystal structure

Preparation of ferroelectric PVDF films

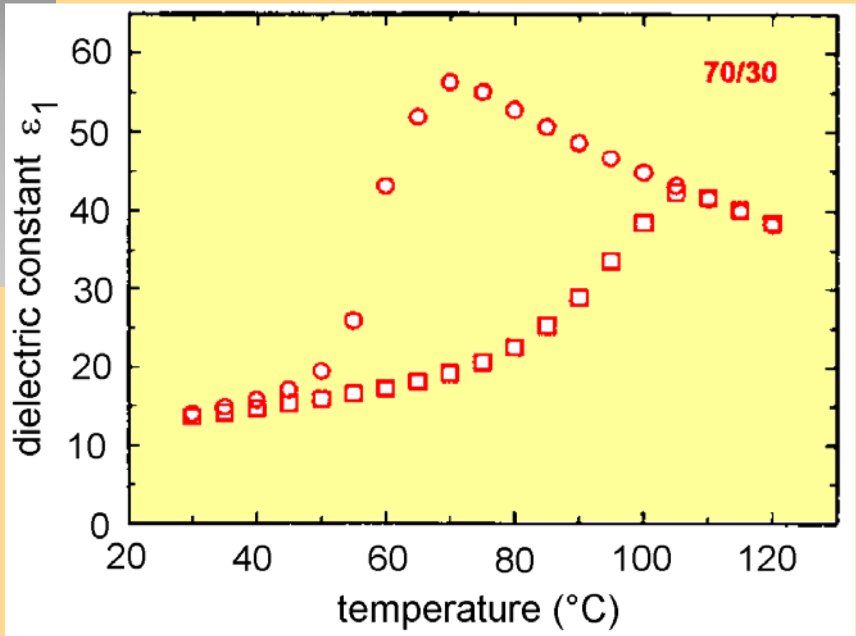


Temperature-dependent dielectric constant ε' of a 65/35 P(VDF-TrFE) copolymer

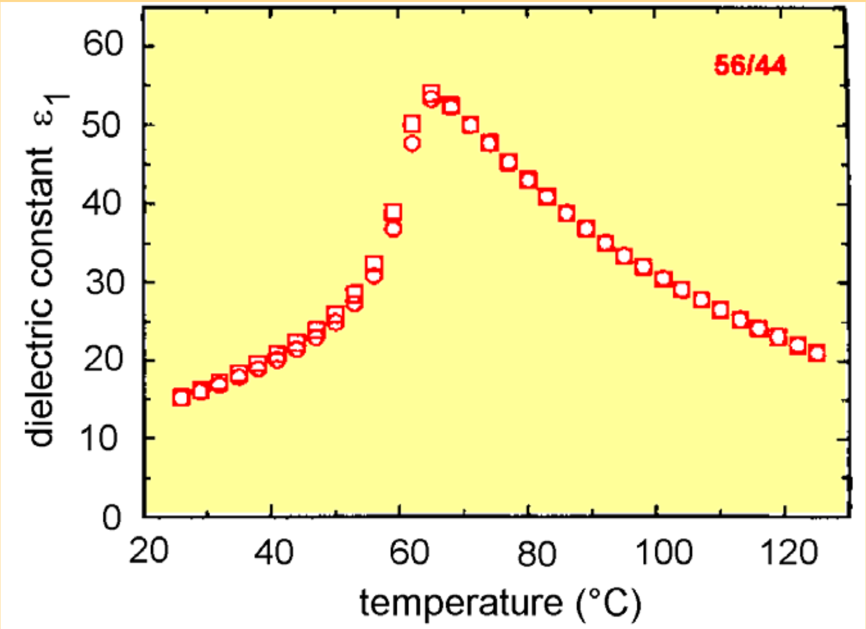


Dielectric constant ε' of 70/30 and 56/44 mol% P(VDF-TrFE) copolymers versus temperature

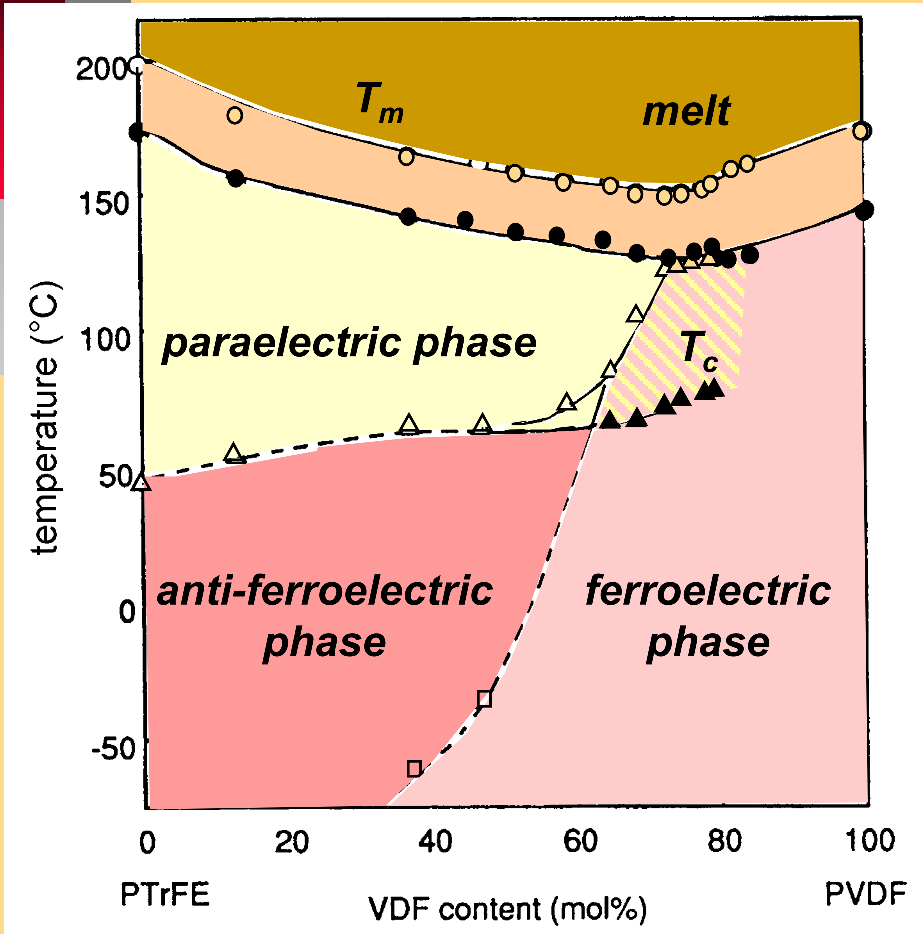
first-order phase transition



second-order phase transition



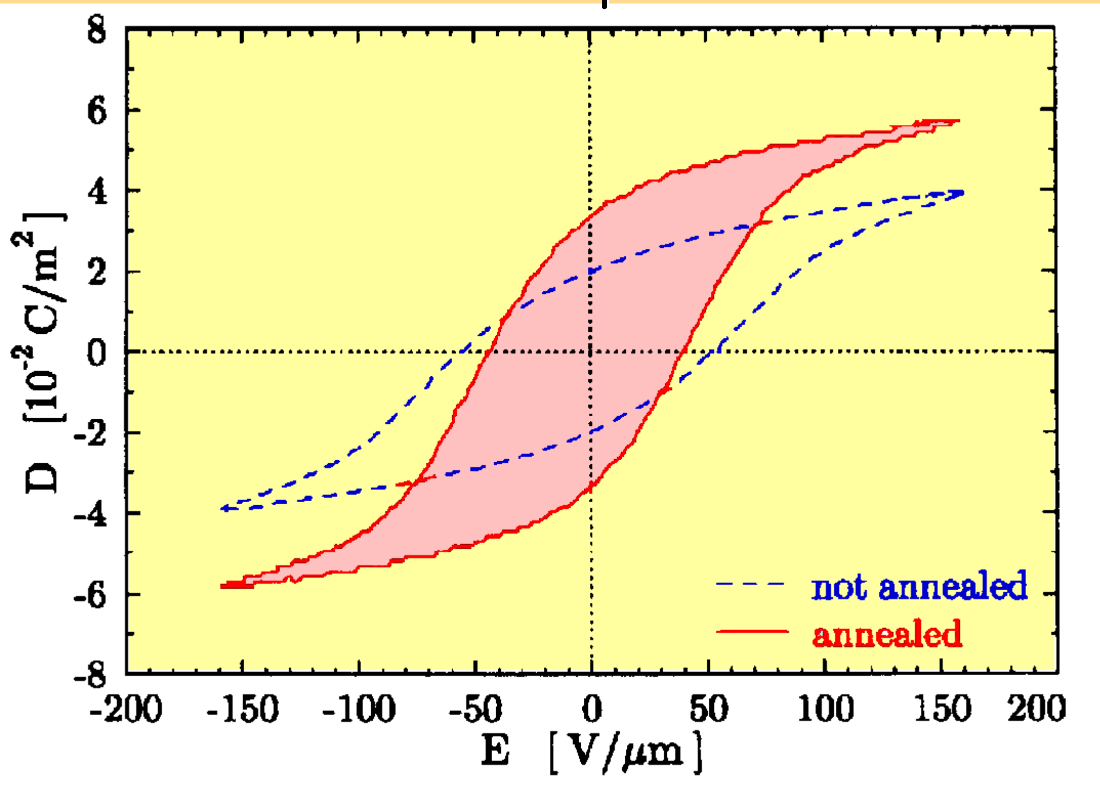
Phase diagram of (PVDF-TrFE) copolymers



- ○ : melting temperature
- ● : crystallization temperature
- △ : Curie temperature on heating
- ▲ : Curie temperature on cooling
- □ : ferroelectric-antiferroelectric transition

Ferroelectric hysteresis loop in as-cast and annealed 56/44 P(VDF-TrFE) films

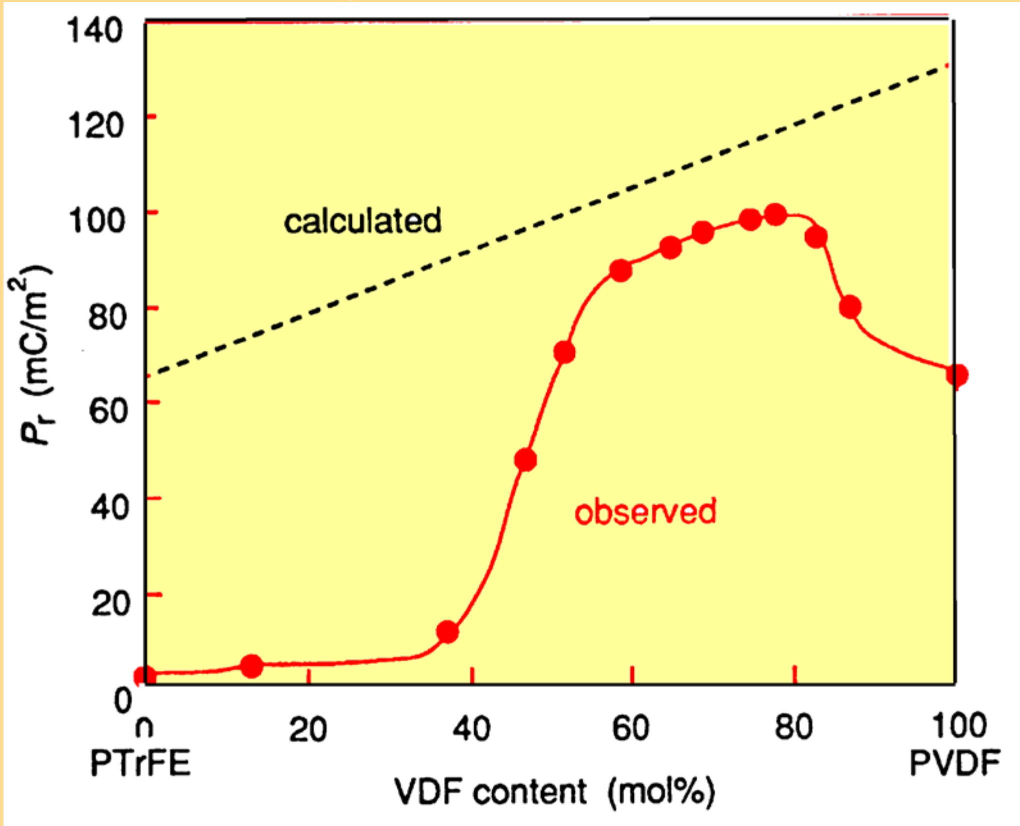
- Improved crystallinity in annealed films ⇨ increased remanent polarization



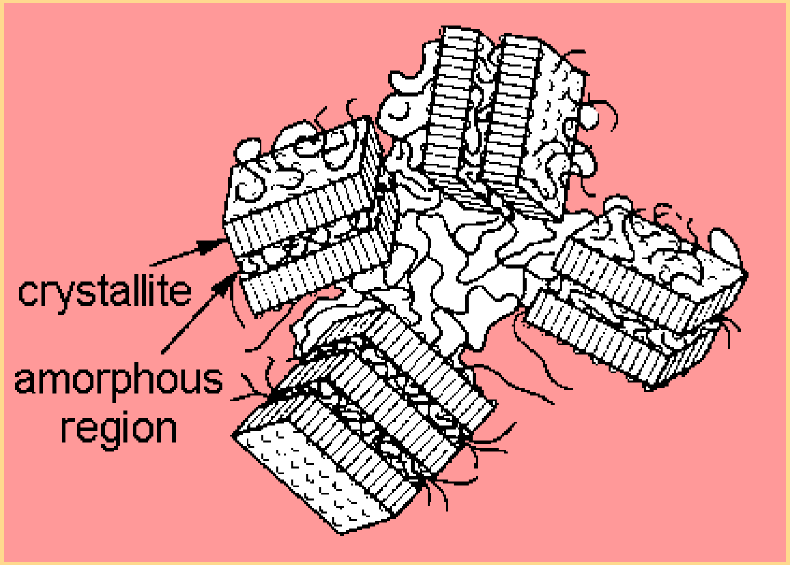
B. Ploss and B. Ploss, *IEEE Trans. Diel. Electr. Insul.* **5**, 91 (1998)

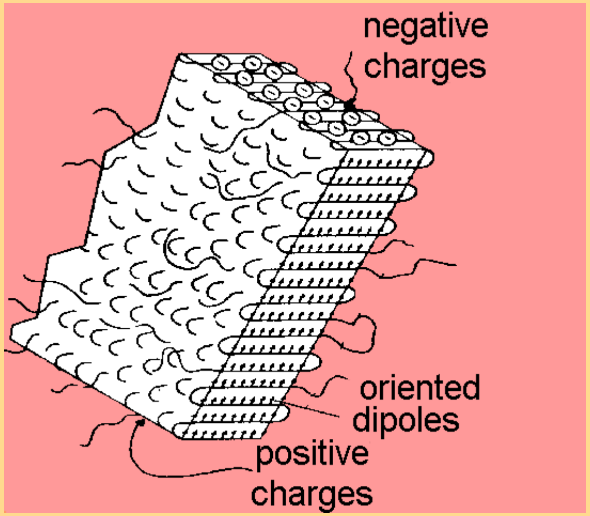
Composition dependence of the remanent polarization P_r for P(VDF-TrFE) copolymers

- Highest crystallinity between 60-80 mol% VDF ⇒ largest remanent polarization



Polymer structure with ferroelectric crystallites





semicrystalline polymer structure

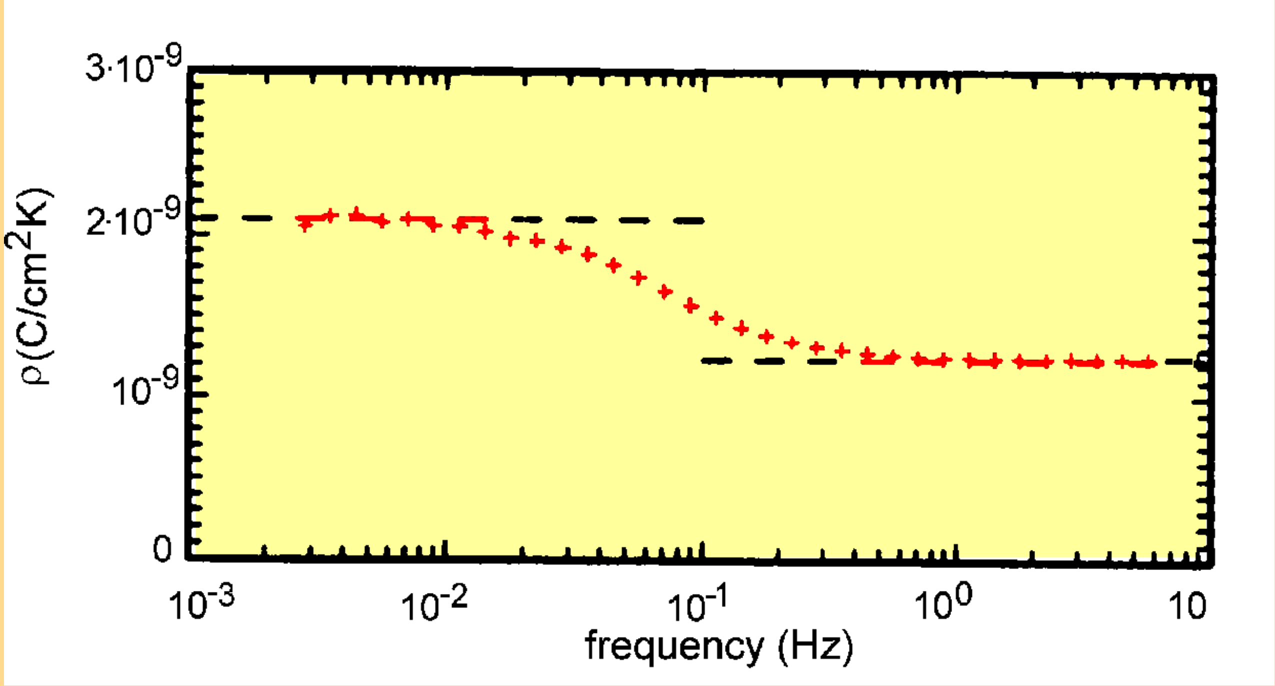
crystallite with compensation charges at the interfaces between amorphous and crystalline regions

symmetry class: ***mm∞* , *C*$_{\infty v}$**

piezo- and pyroelectricity in charged polymers?

Pyroelectric relaxation in PVDF

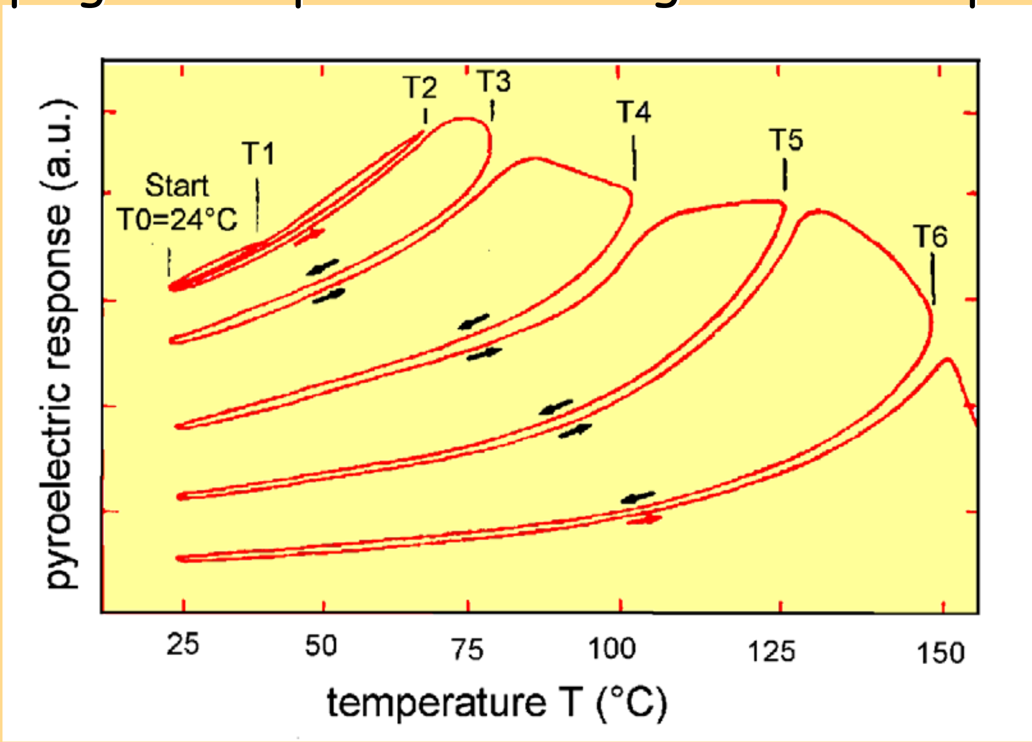
- Pyroelectric relaxation ⟹
  time- or frequency-dependent pyroelectric coefficient



B. Ploss and A. Domig, *Ferroelectrics* **159**, 263 (1994)

Thermal stability of pyroelectricity in PVDF under cyclic increase and decrease of the temperature

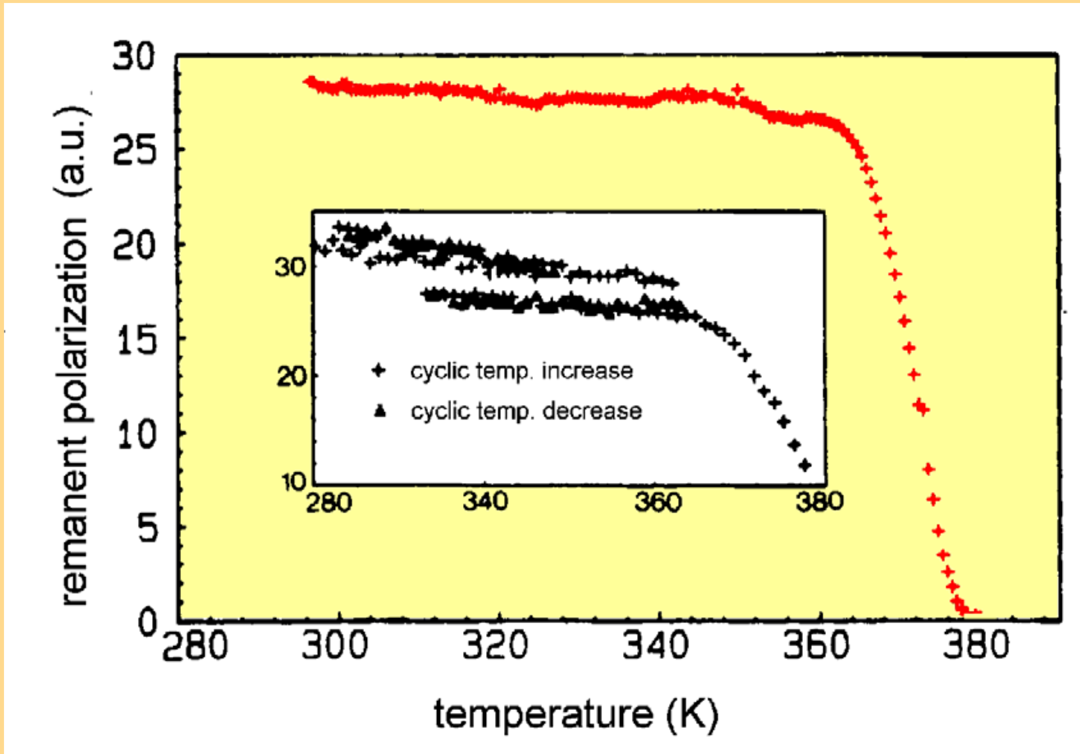
- Irreversible decrease of the pyroelectric response well below the Curie transition
- Detrapping of compensation charges reduces polarization



S. Bauer and S. Lang, *IEEE Trans. Diel. Electr. Insul.* **3**, 647 (1996)

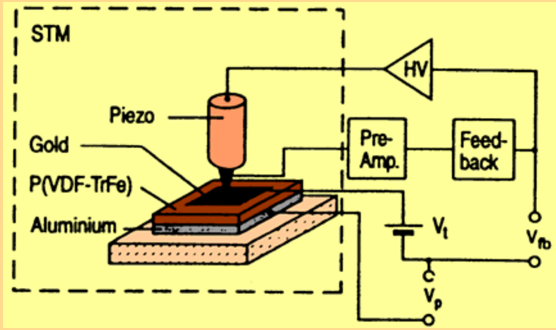
Thermal stability of the remanent polarization in a 70/30 P(VDF-TrFE) copolymer

• High crystallinity of the film ⟹ small irreversibilities of the pyroelectric response



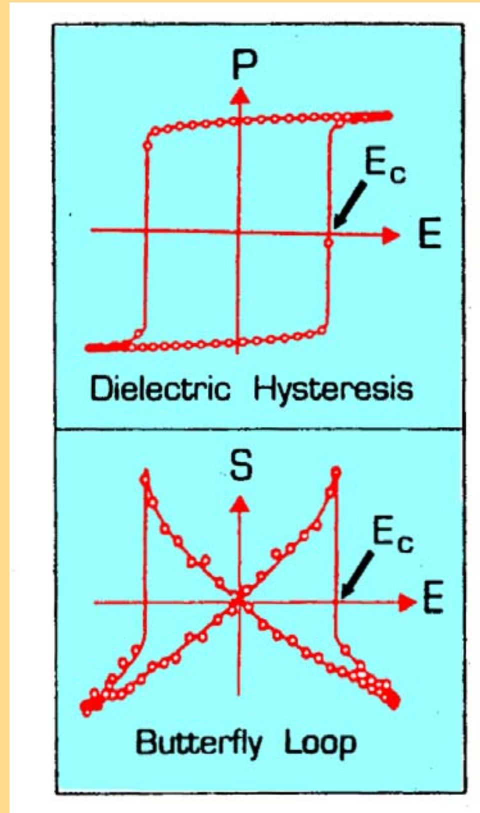
A. Wicker et al., *J. Appl. Phys.* **66**, 342 (1989)

Microscopic ferroelectric properties of P(VDF-TrFE)

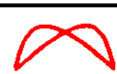


Experimental set-up for measuring the local strain in a ferroelectric polymer

Displacement D and strain S hysteresis loops

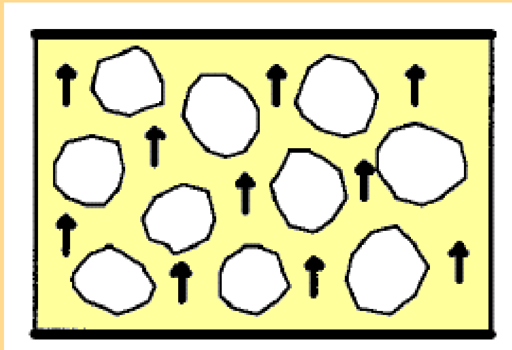


Microscopic hysteresis loops in films with different crystallinity

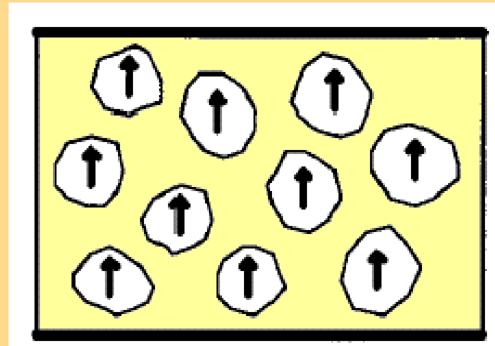
strain-field hysteresis	crystallinity
	>90%
	80%
	60%
	<10%

Li-Jie et al., *Physica B* **204**, 318 (1995)

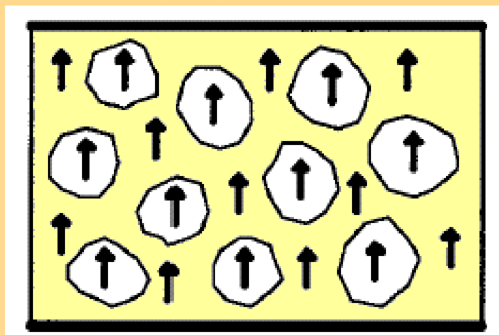
Composites of ferroelectric polymers and ferroelectric ceramics



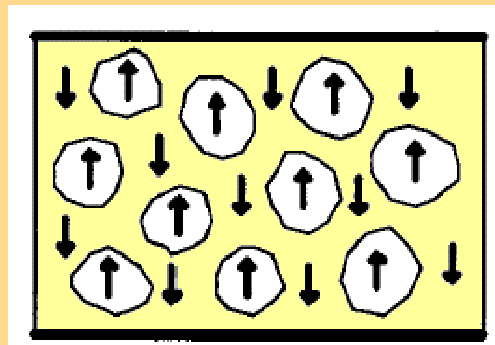
Poled polymer matrix



Poled ceramic inclusions



Both phases poled parallel

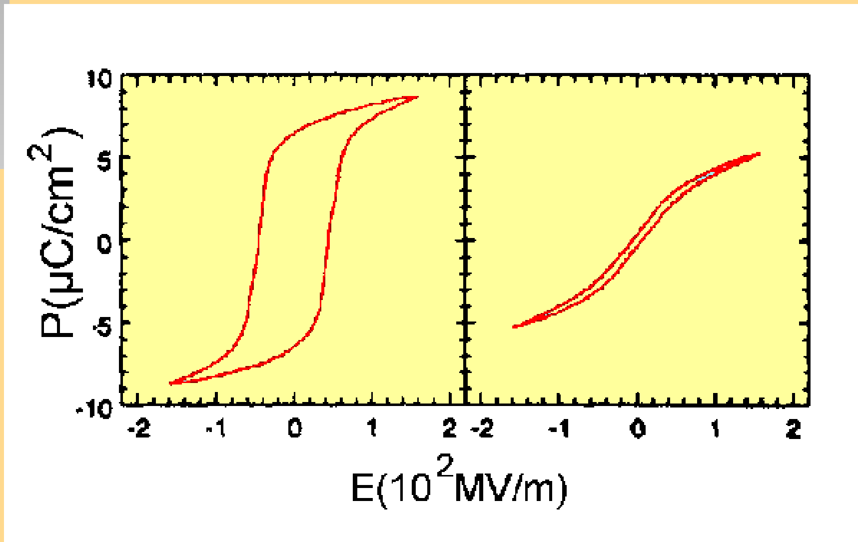


Both phases poled antiparallel

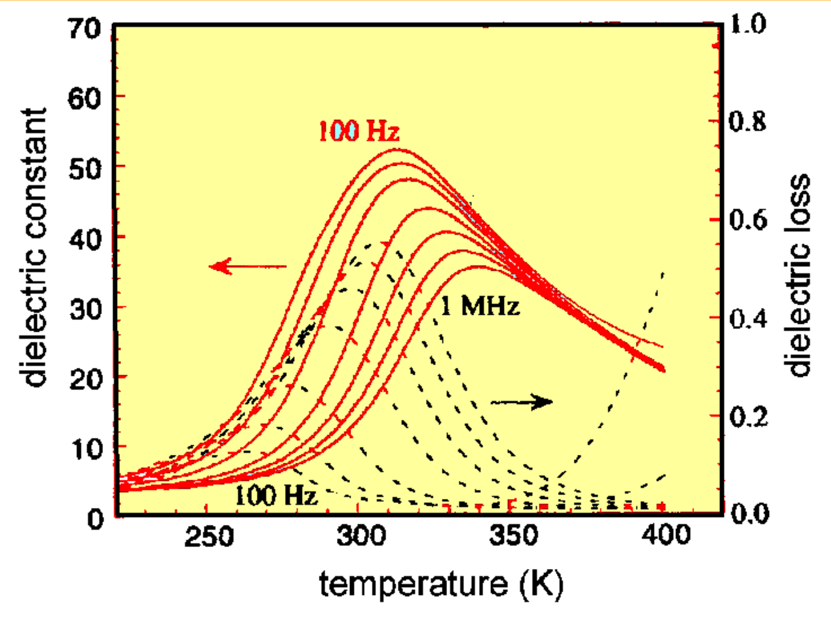
B. Ploss et al., *Applied Physics Letters* **76**, 2776 (2000)

Relaxor ferroelectric copolymers

- Hysteresis loop before and after irradiation with 3MeV electrons

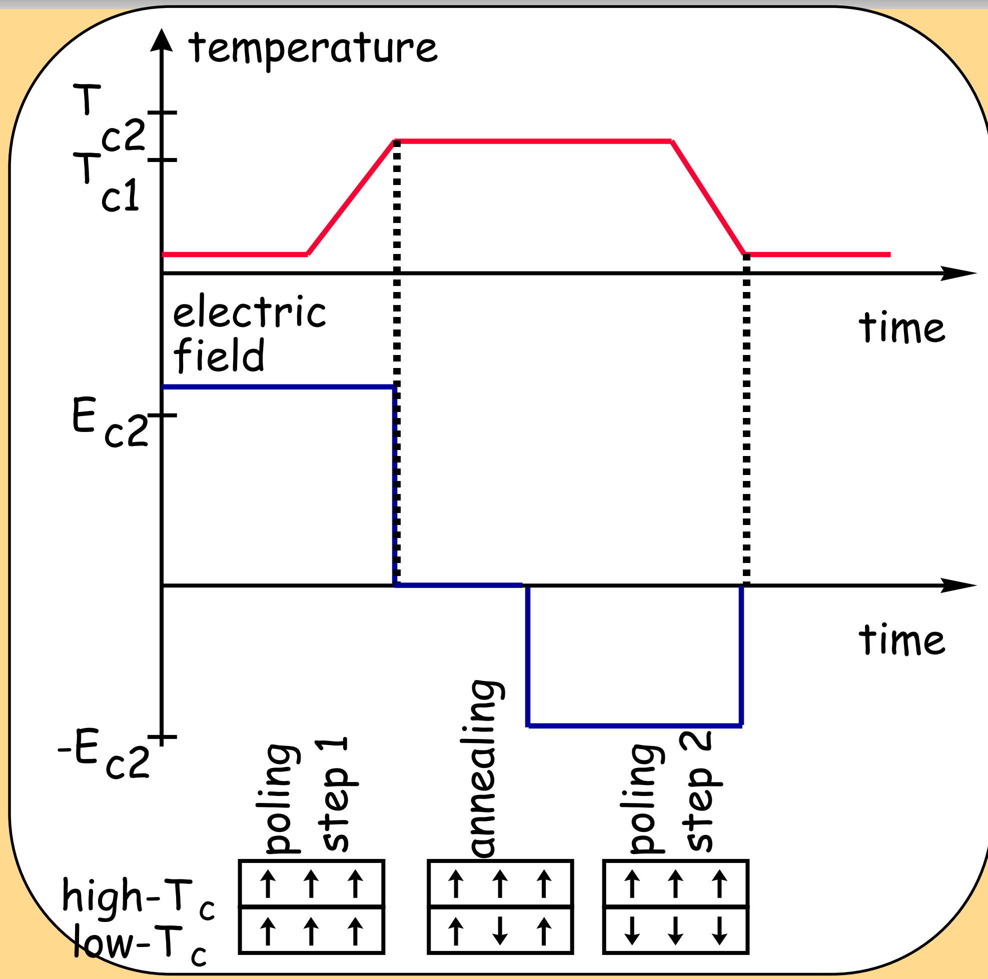


- Dielectric constant and loss of an irradiated film

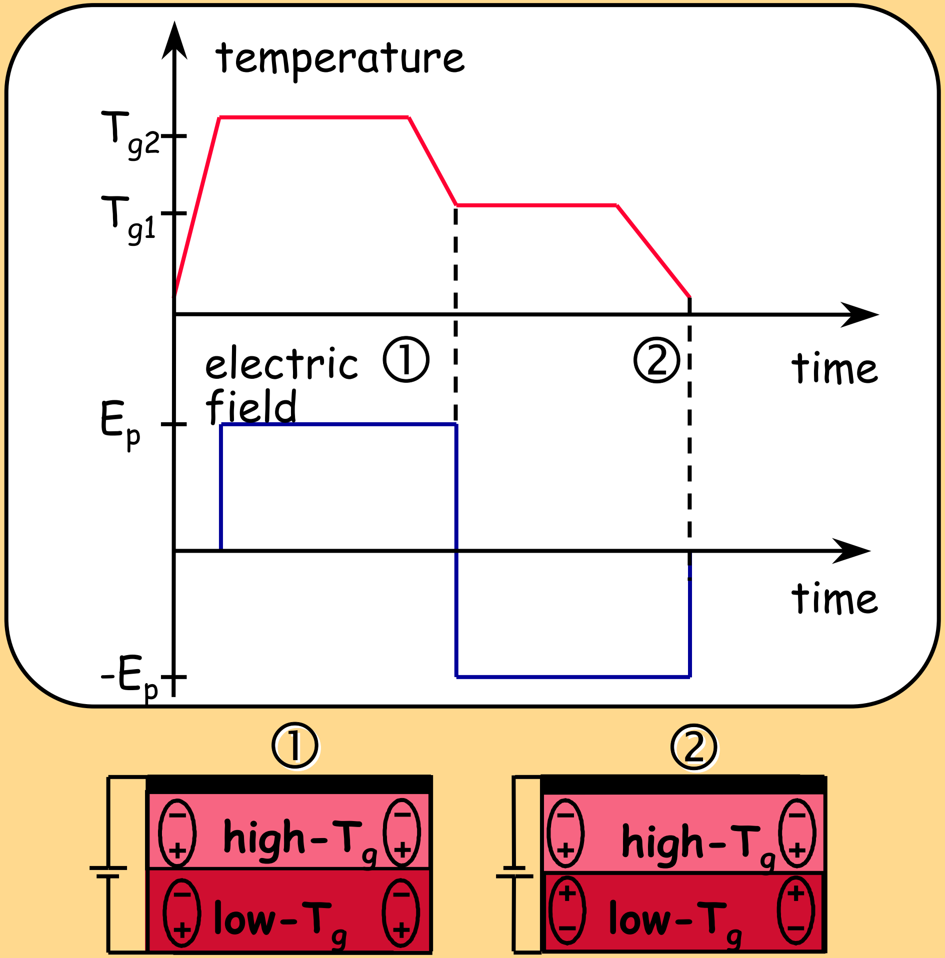


Q. M. Zhang et al., *Science*, **280**, 2101 (1998)

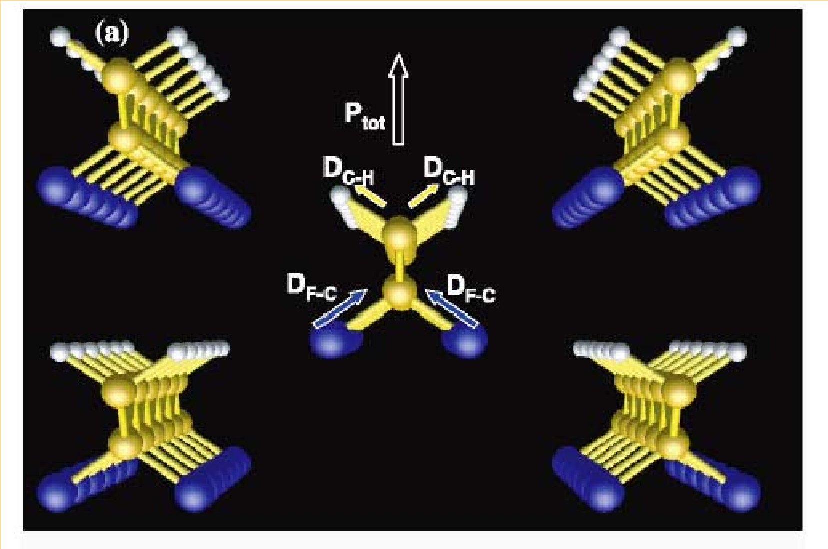
Preparation of ferroelectric polymer bimorphs by two-step poling

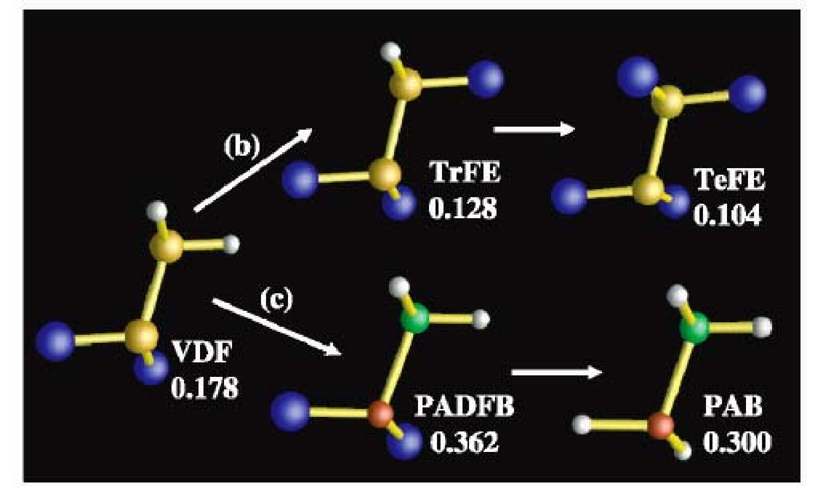


Two-step poling in amorphous polymer electrets



Improved ferroelectric polymers?





Replace C by B and N ⟹ increased piezoelectric coefficients

still awaits experimental verification

Summary

Amorphous dipole electrets

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- frozen quasipermanent polarization
- small piezo- and pyroelectric coefficients

Summary

Semicrystalline, ferroelectric dipole electrets

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- interplay between volume charges and ferroelectric polarization
- piezo- and pyroelectric relaxation

Relaxor ferroelectric polymers

↓

- large electrostrictive response

Acknowledgments