LIQUID CRYSTALLINE ACHIRAL FERROELECTRIC MATERIALS

E. A. Soto Bustamante*, **R. Vergara-Toloza, C. M. González Henriquez, G.A. Rodriguez Leyht, D. Saldaño Hurtado**

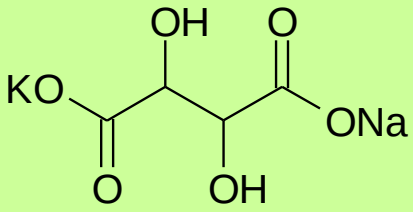
Universidad de Chile, Facultad de Ciencias Químicas y Farmacéuticas, Departamento de Química Orgánica y Físico Química

Ferroelectricity at the very beginning

Lyngourion or Tourmaline
(Na,Ca)(Li,Mg,Al)·(Al,Fe,Mn)6
Theophrastus, 2400 BC, Greek philosopher

1707, Curiöse Speculationen bey Schlaflosen Nächten
Curious Speculations during sleepless Nigths
Johann Georg Schmidt
Bring it to Europe from Ceylon 1703

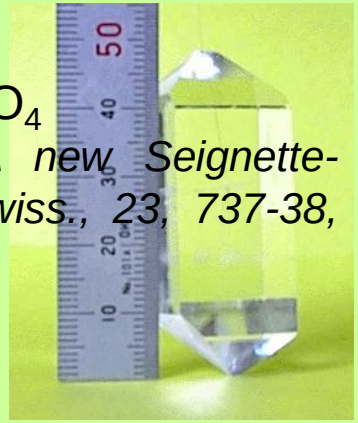
Attracts straw and bits of wood in fire



K Na ($C_4H_4O_6$) x 4 H_2O, 1675 (Elie Siegnette)
Town of La Rochelle, France.
D. Brewster, "Observation of Pyroelectricity of Minerals", Edinburgh, J. Sci., 1, 208-14 (1824)

KDP,KH_2PO_4

G. Busch, P Scherer, "A new Seignette-Electric Substance". Naturwiss., 23, 737-38, 1935.



TGS Triglycine sulphate $(H_2N\text{-}CH_2\text{-}CO_2H)_3$ H_2SO_4

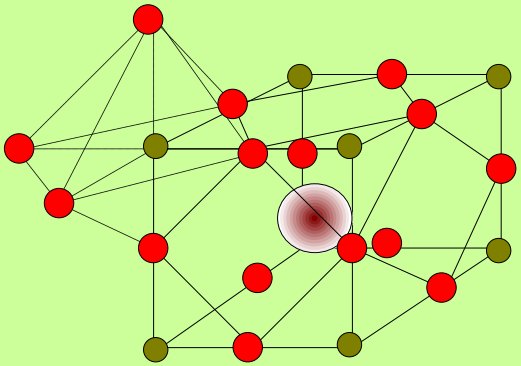
B.T. Matthias, C.E. Miller J.R. Remeika, Phys. Rev., 104, 849, 1956.

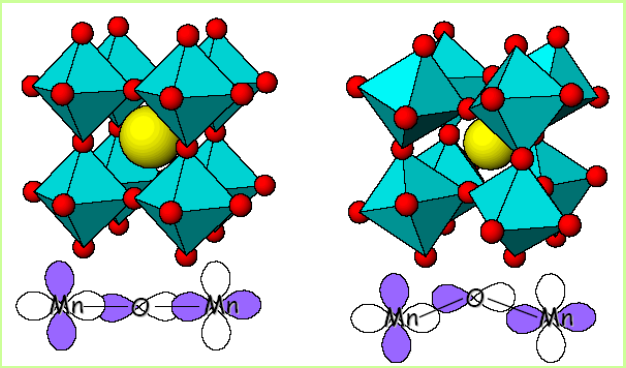
1830, Gustav Rose CaTiO3

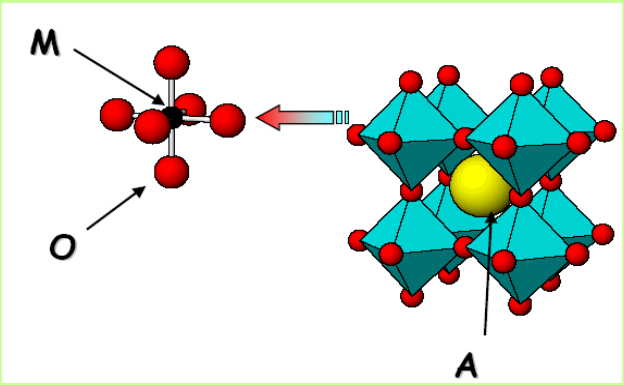
Count Lev Aleksevich von Perovski

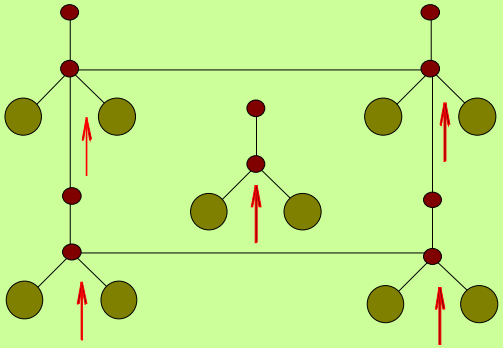
E. Wainer, N. Salomon, Electrical report Titanium Alloys Manufacturing Division Nantional Lead Co. 1938-1943

A. Von Hippel 1945

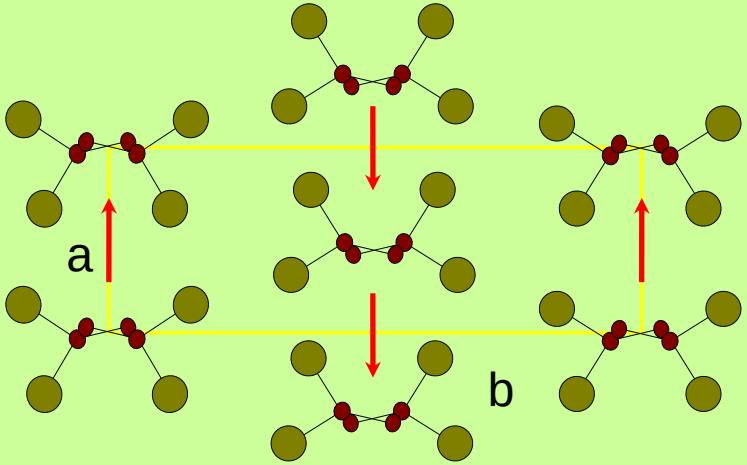








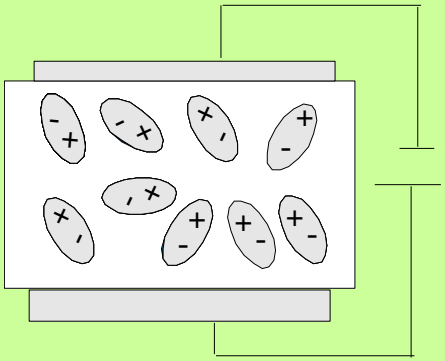
β-fase



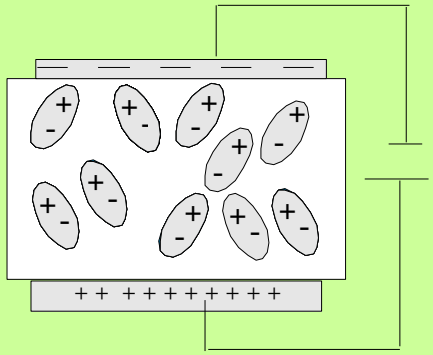
α-fase antiparallel dipoles

In 1969, induced piezoelectric effects were reported in fluorinated polymers due to strong applied electric field

PVDF



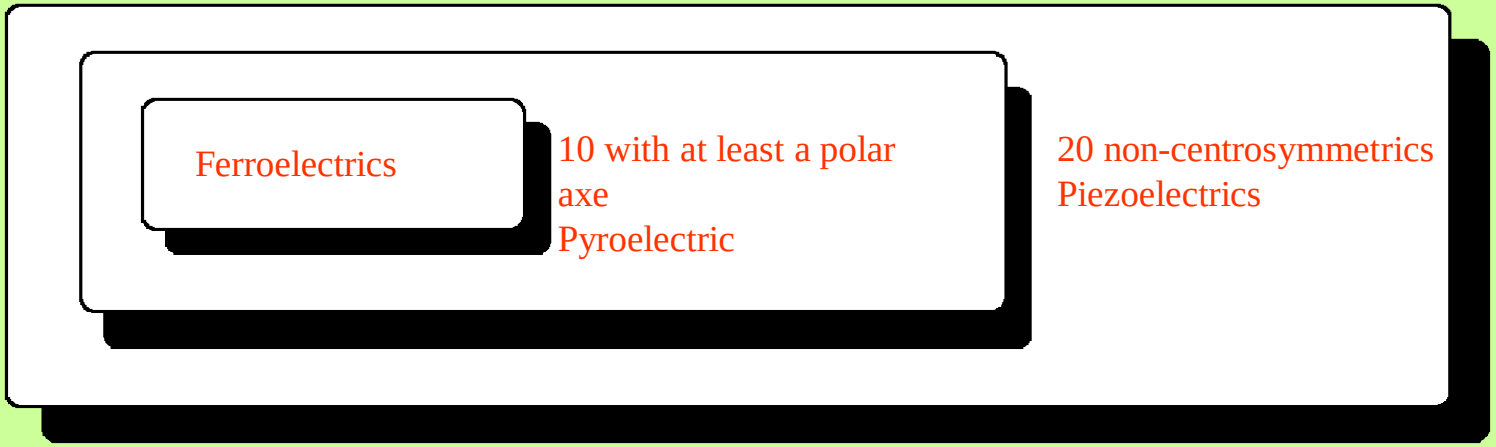
Poled



un-poled

Ferroelectricity

32 Crystal Classes where 11 are Centrosymmetrics

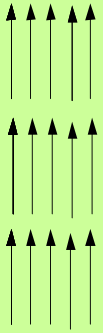


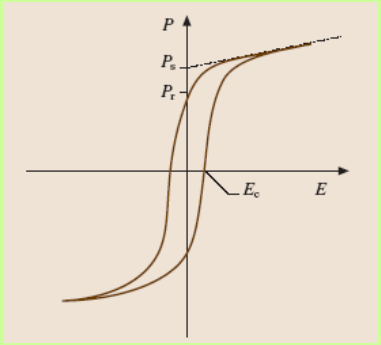
Thermodynamic equilibrium where a material can be organized in two different directions

Boths directions posses similar energy

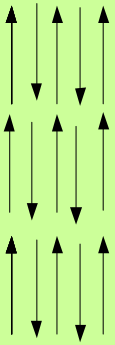
The ferroelectric state must be defined empirically

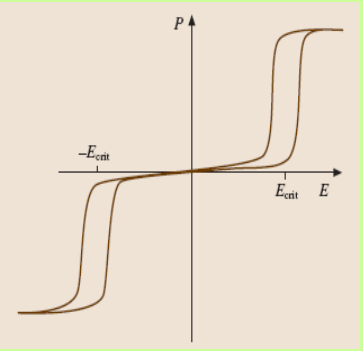
Ferroelectricity





Antiferroelectricity

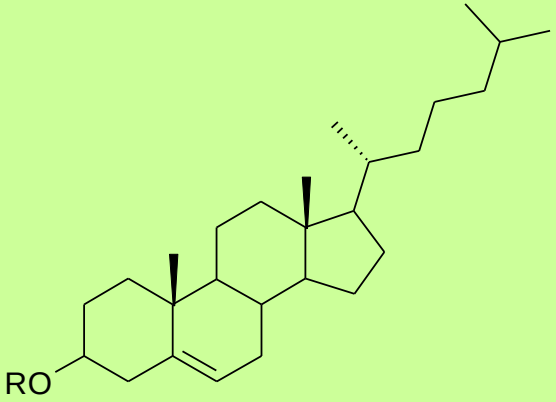




LIQUID CRYSTALS, THE BEGINNING 1888-1935

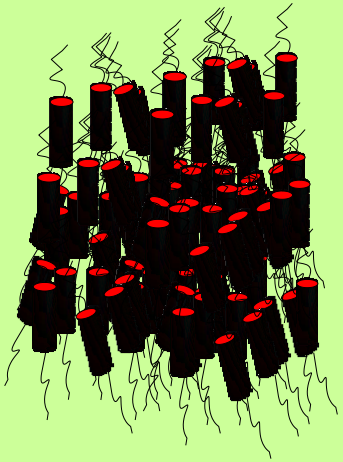
Friedrich Reinitzer
1888, Uni Prage

Cholesteryl Chloride and benzoate



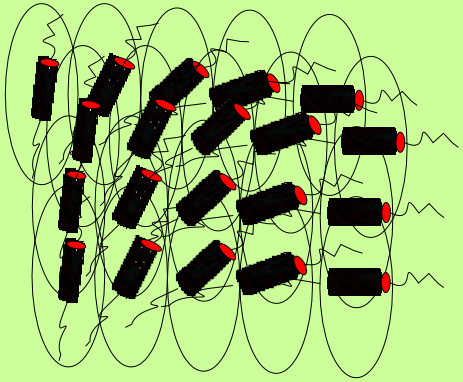
Otto Lehmann
Uni Aachen

George Friedel 1922

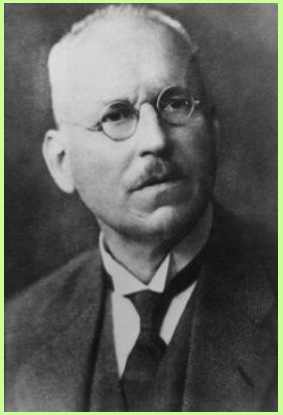


Nematic:
thread like (nema, greek)

Smectic: Soapy
(smegma, greek)

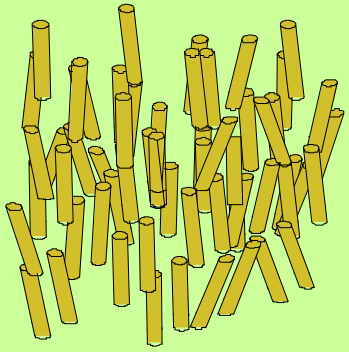


Cholesteric:
from cholesteryl derivatives



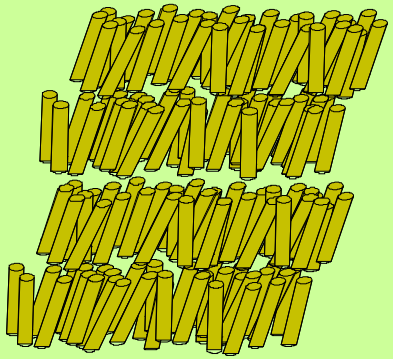
Daniel Vorländer
Uni. Halle

Nematic



Smectic A

Smectic C

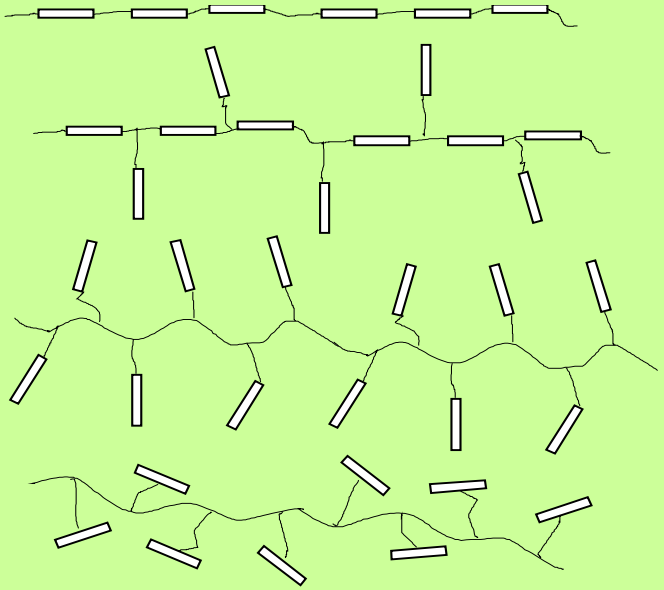


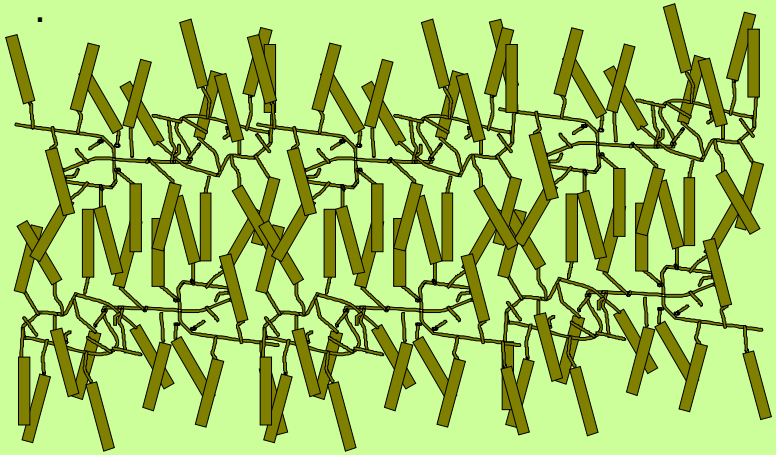
Side Chain liquid crystalline polymer

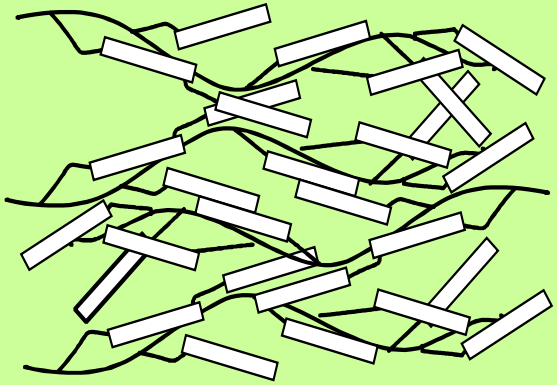
Mesogenic units incorporated in the main chain MCLCP

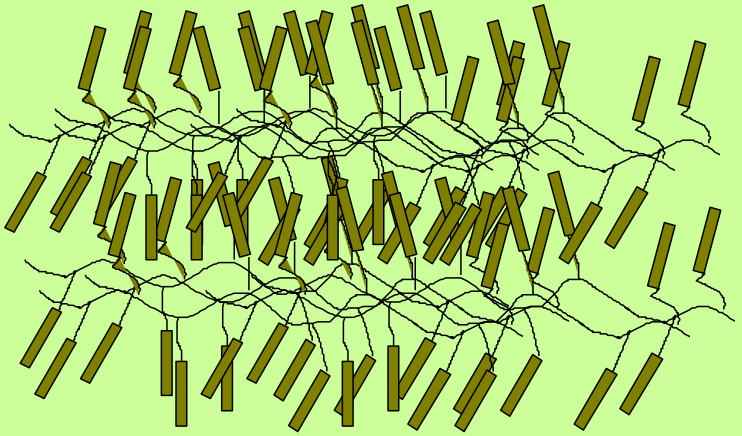
Through aliphatic spacers as side chain liquid crystal polymers SCLCP

.









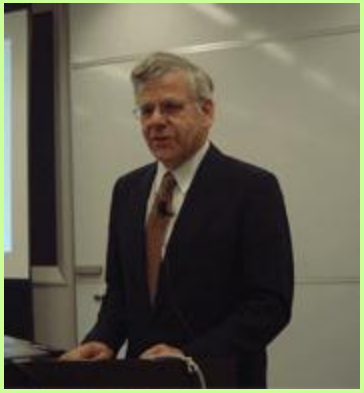
Technological applications, nematics 1960-1975

George Heilmeier. 1967 Radio Corp. Of America and
James Fergason at Westinghouse Corp.
Working temp: 80 °C p,p'-dialcoxybenzoates

Hans Kelker, Hoechst, 1969 synthesized MBBA
p-methyl-oxybenzilidene-p'-butoxyaniline:
Nematic between 20 and 41 °C

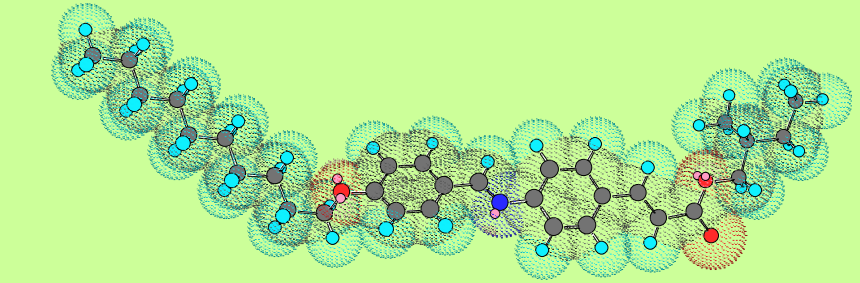
1971 Symmetrically and asymmetrically substituted
Phenylbenzoates (University of Halle and Merck)
p-methoxy-p'-n-butylazoxybenzene.

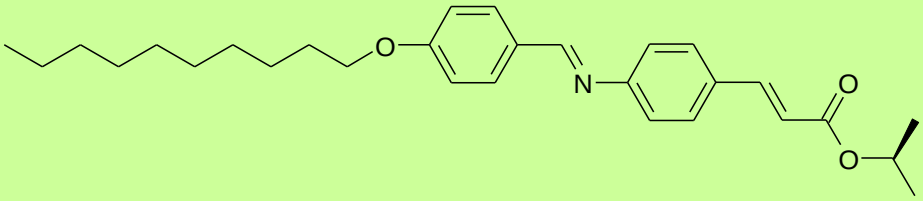
Non-stable material ligth sensitive

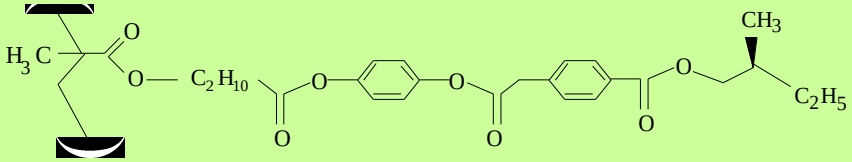


1971 James Fergason (Kent State University)
Martin Schadt, Wolfgang Helfrich, Switzerland
TN Cell or twisted nematic cell
1973 George W. Gray, University of Hull, GB
Ciano-biphenyls and –terphenyls
Stable nematic untill room temperatures
Realibel molecules

In 1974, the first FLC (ferroelectric liquid crystal) was reported by Mayer y col. Later on, tousands of new materials appeared

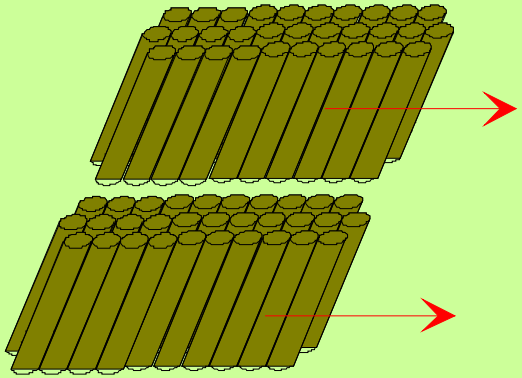




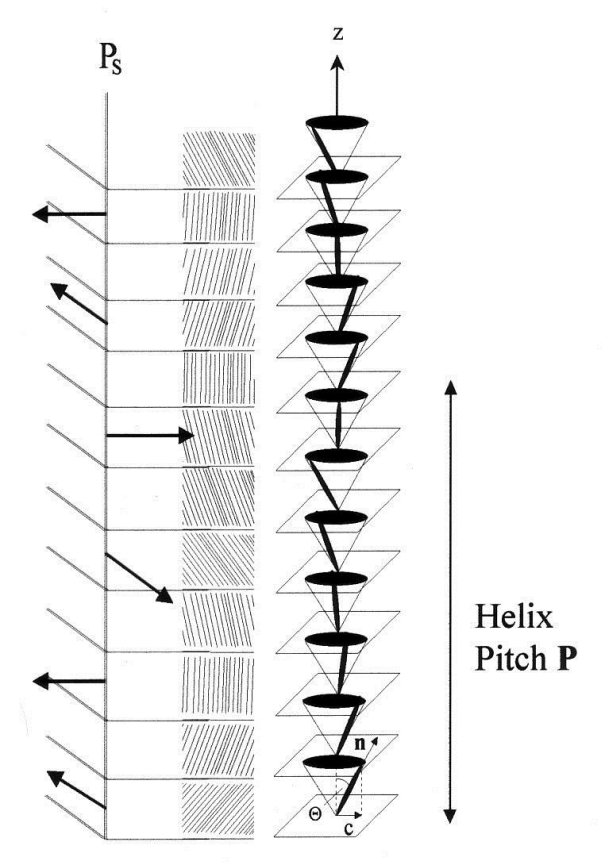


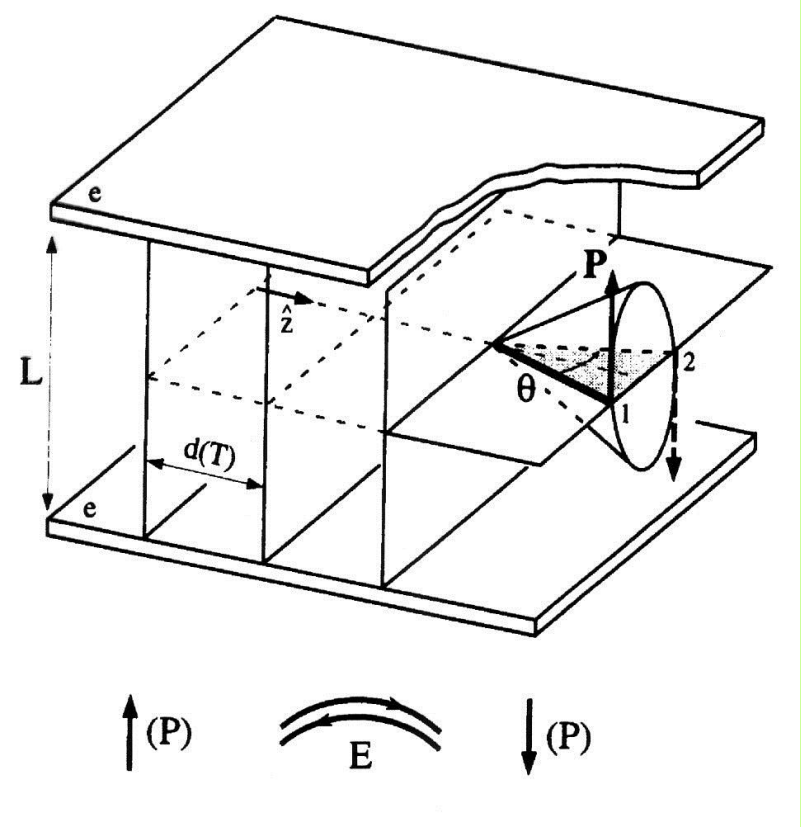
Polymeric materials were firstly reported on 1984 by Shibaev et al. It combines the FLC approach in a SCLCP.

After the discovery of the Bistable switching in surface stabilized liquid crystal cells in the 80's by Clark and Lagerwall and other electrooptics, effects a new brand for technological applications of LC begun.



Pseudoferroelectric Sc

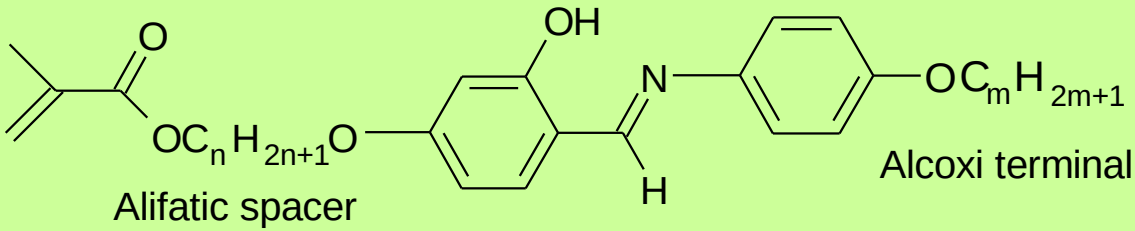




In 1996 we informed for the first time about a liquid crystalline system without chirality and exhibiting unusual electrical properties based on a low molecular weigth methacrylic monomer mixed in a 1:2 ratio with its polymer

Monomer

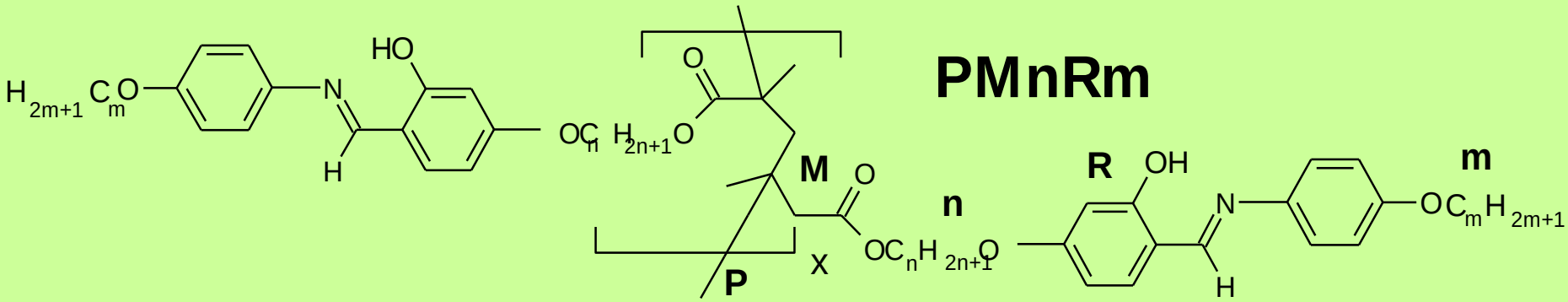
Aromatic rigid core



Alifatic spacer

Alcoxi terminal chain

Polymer



PMnRm

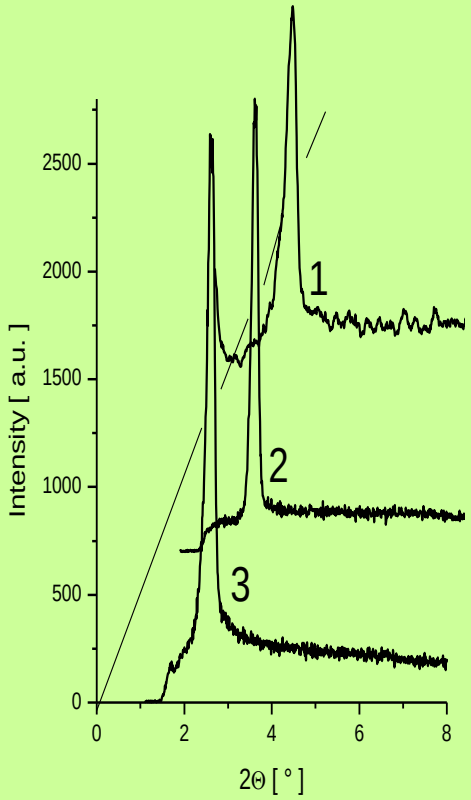
Liquid crystal laboratory

MLP

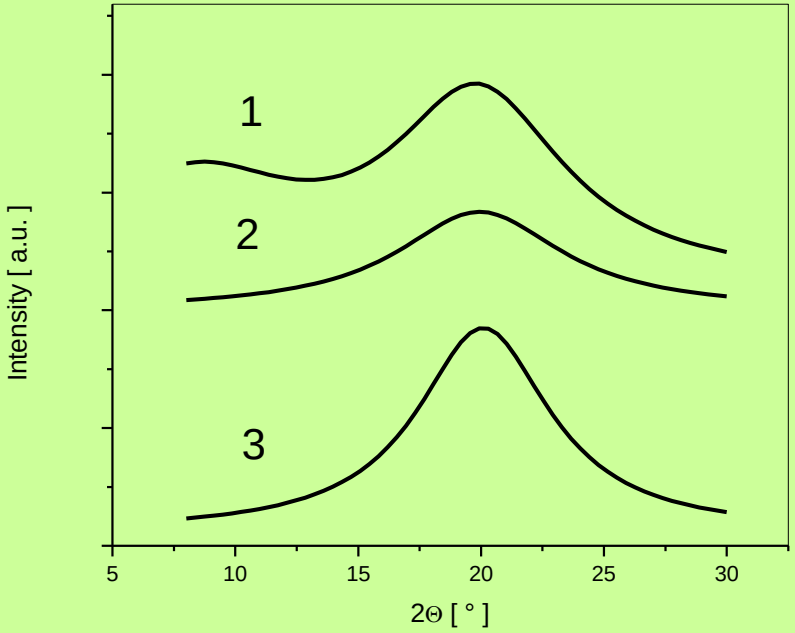
DTA

X-Ray Diffraction

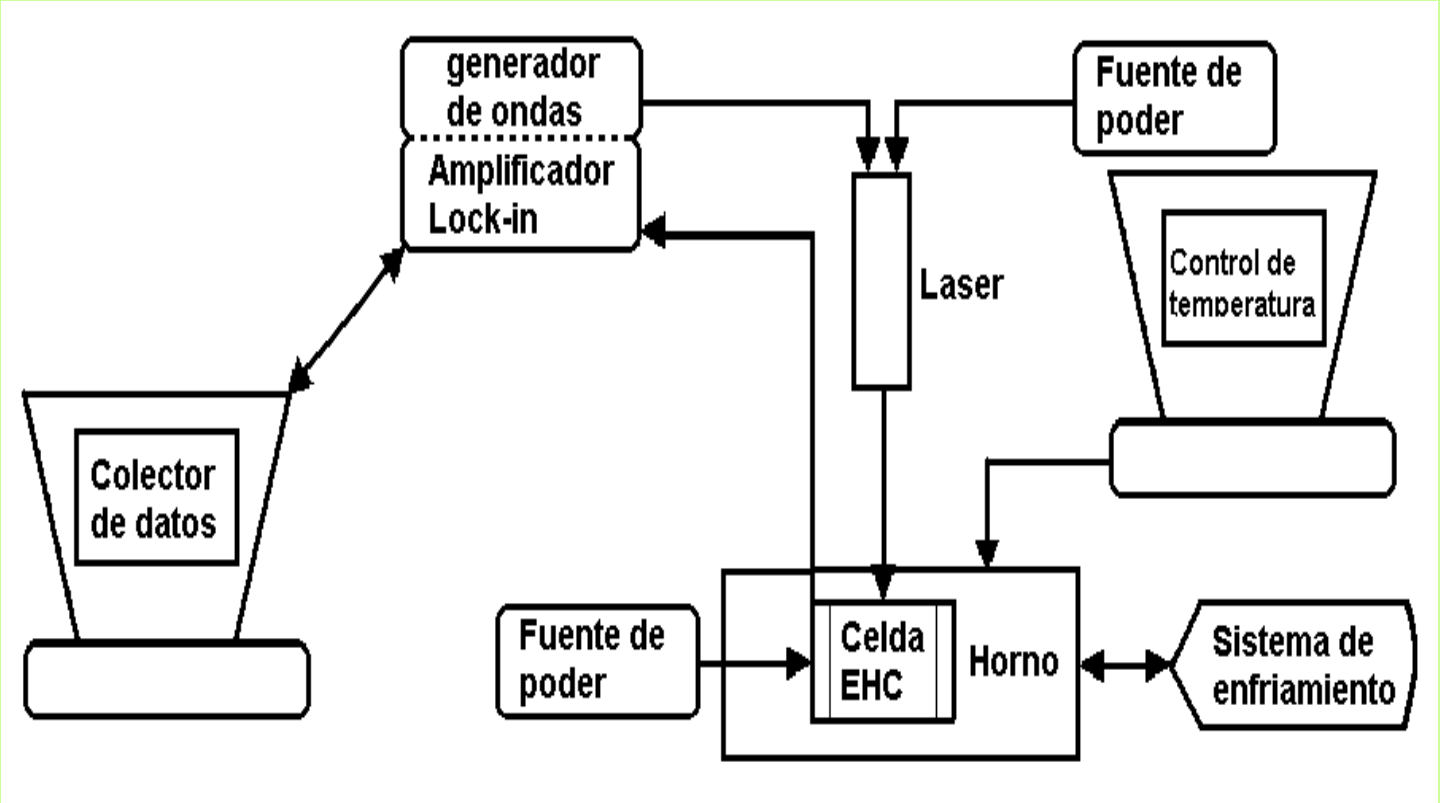
Small angles region
the smectic A or C phase



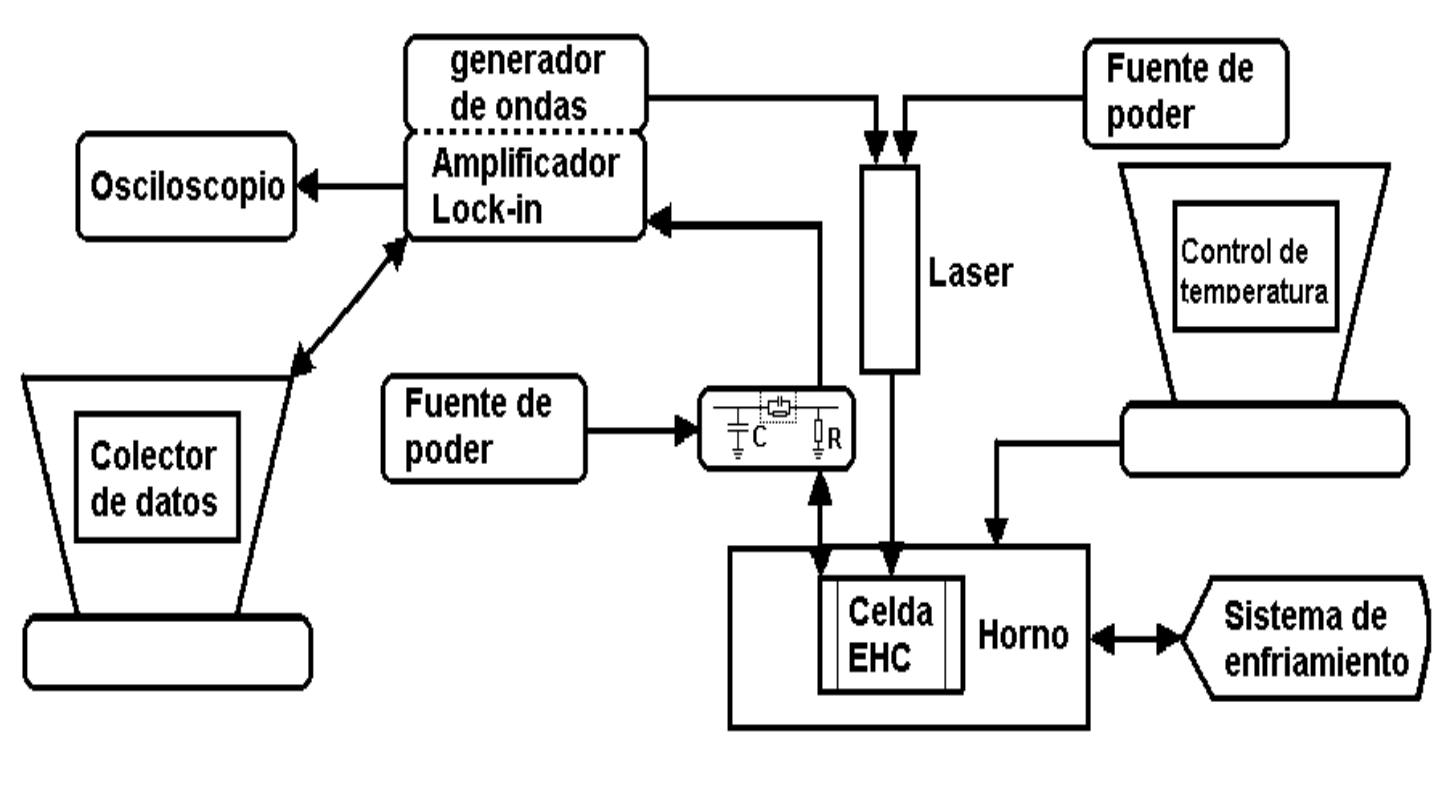
Wide angle region
Liquid ot crystal like behaviour



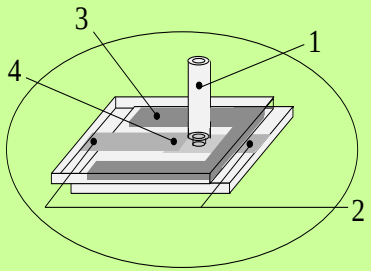
Modulated Pyroelectric Technique
Poled samples
By cooling without electric field

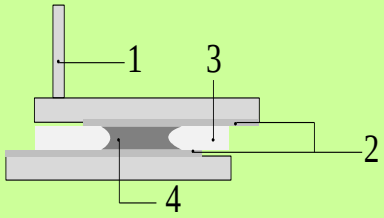


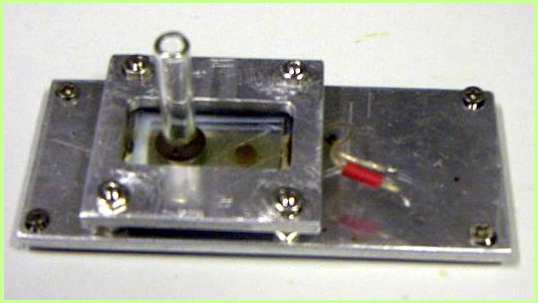
With applied electric field
By cooling and heating

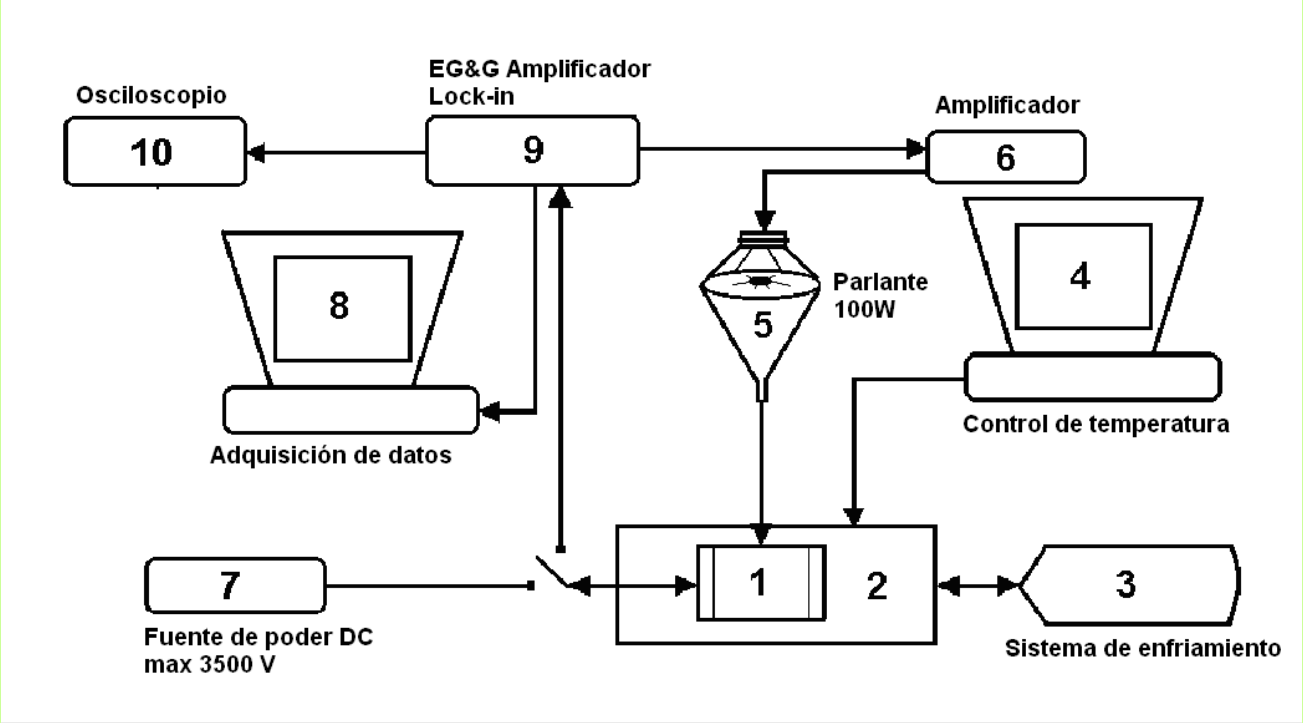


Piezoelectric technique

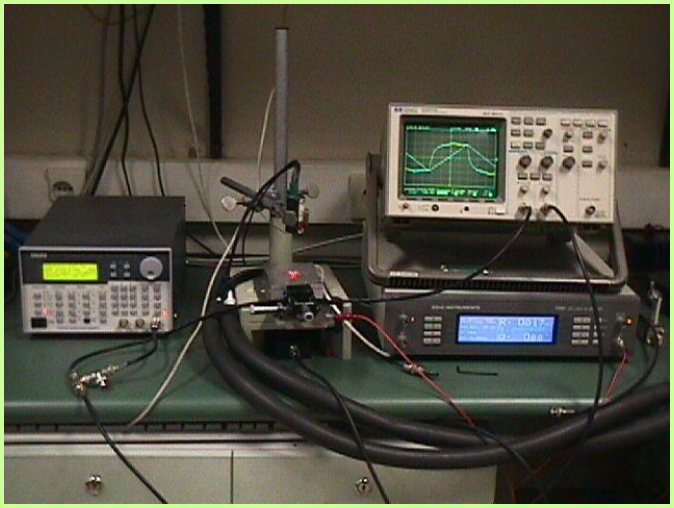


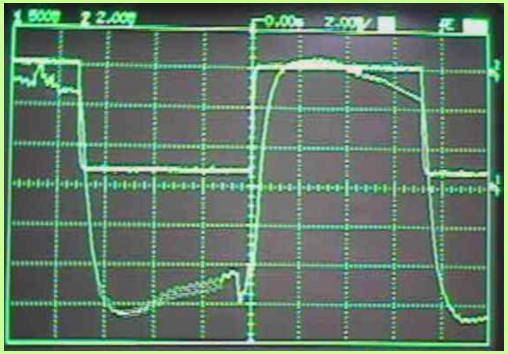


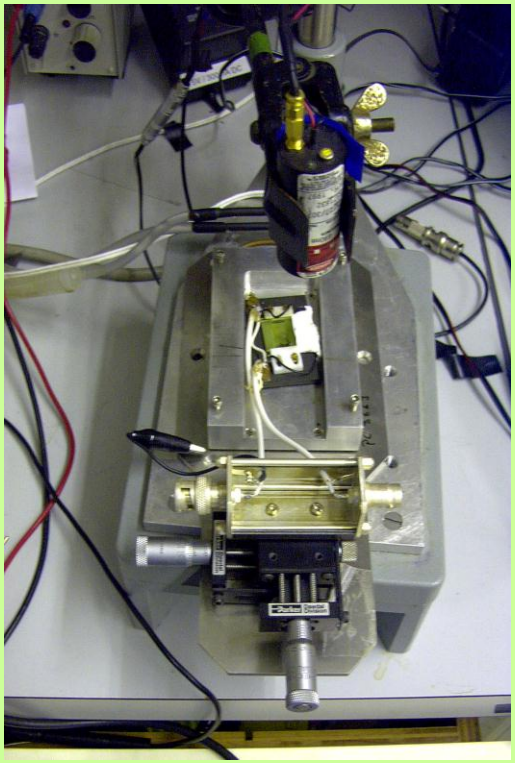




Pyroelectric modulated technique



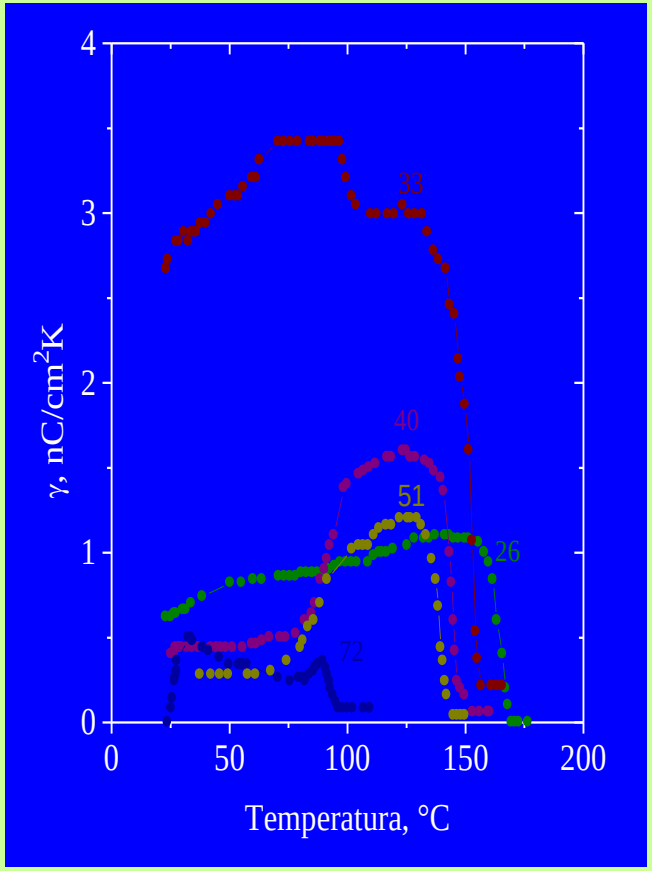




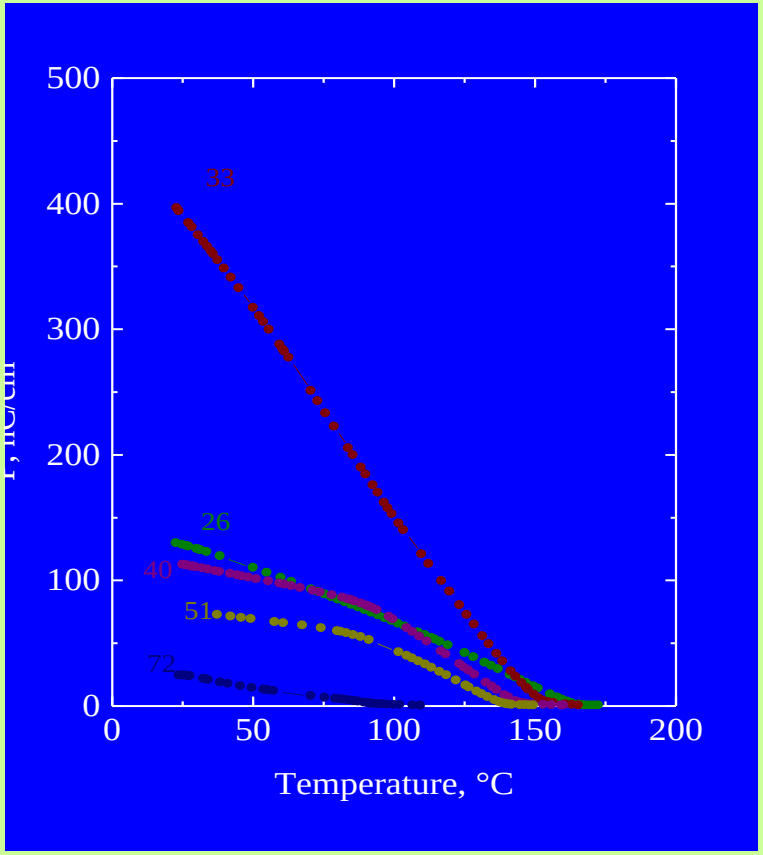
Pyroelectric measurements in PM6R8 mixtures

By cooling under an applied electric field

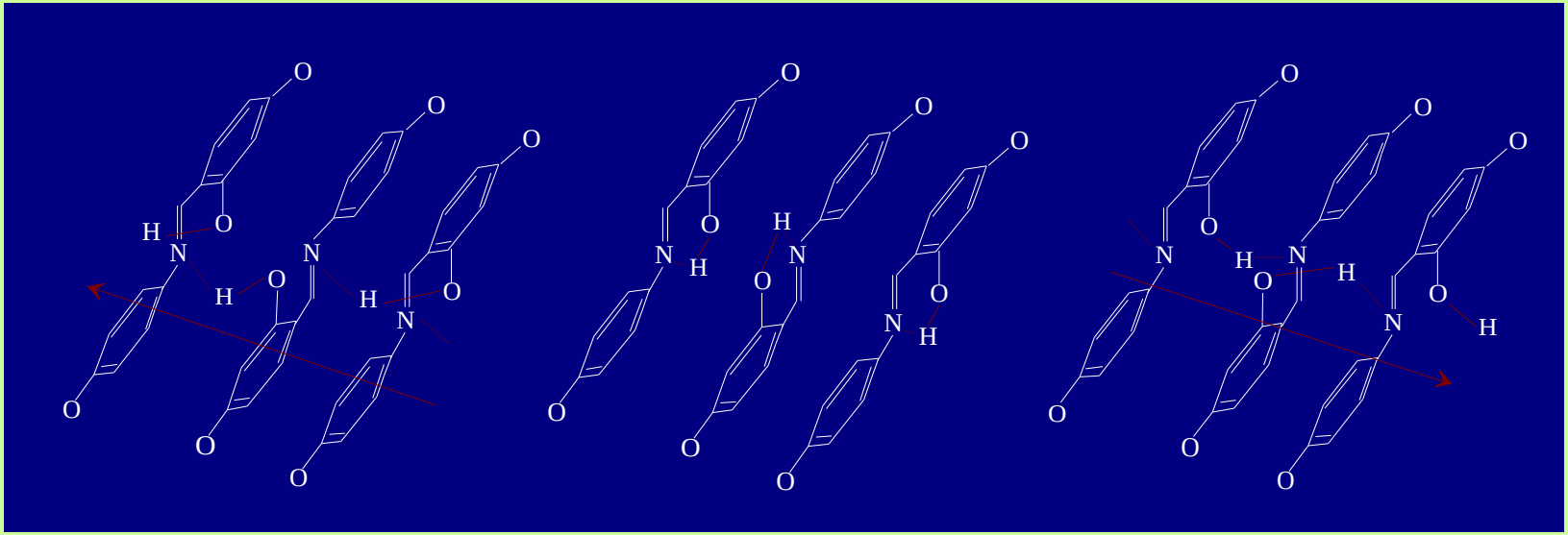
Pyroelectric curve



Macroscopic polarization



Electric field influence



-E E=0 +E

Mesofase structure