LIQUID CRYSTALLINE ACHIRAL FERROELECTRIC MATERIALS

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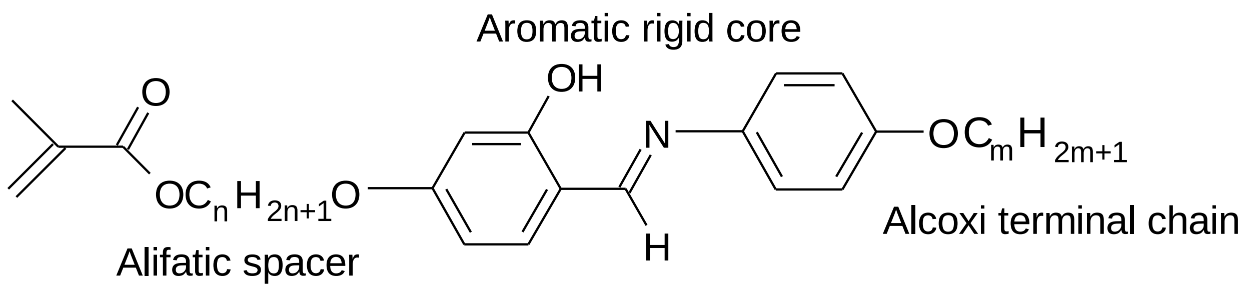
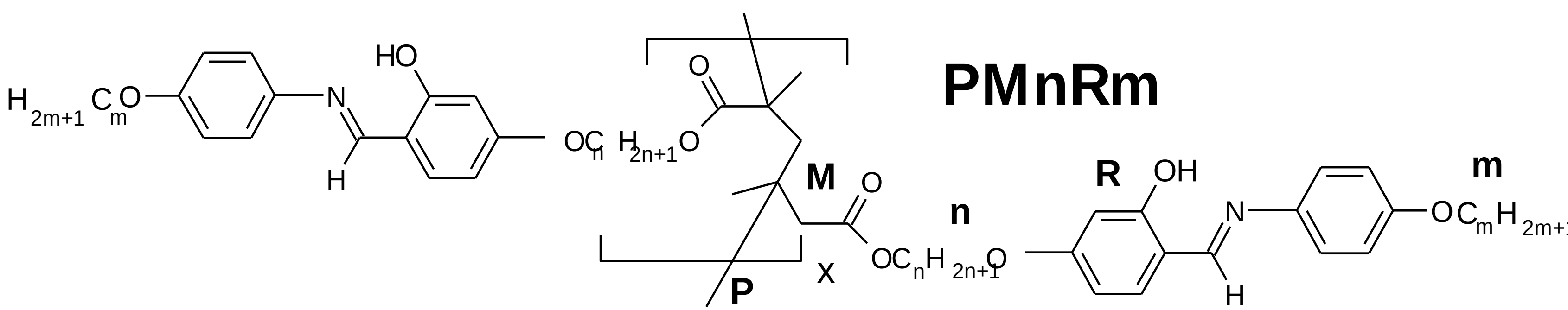
In 1996 we informed for the first time about a liquid crystalline system without chirality and exhibiting unusual electrical properties

A 2:1 ratio polymer-monomer composite

Monomer



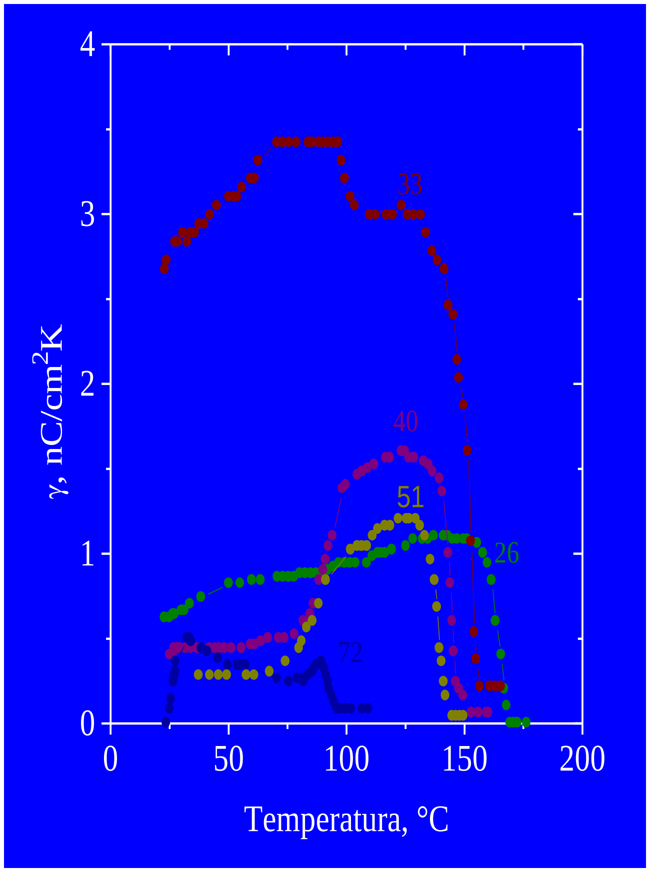
Polymer



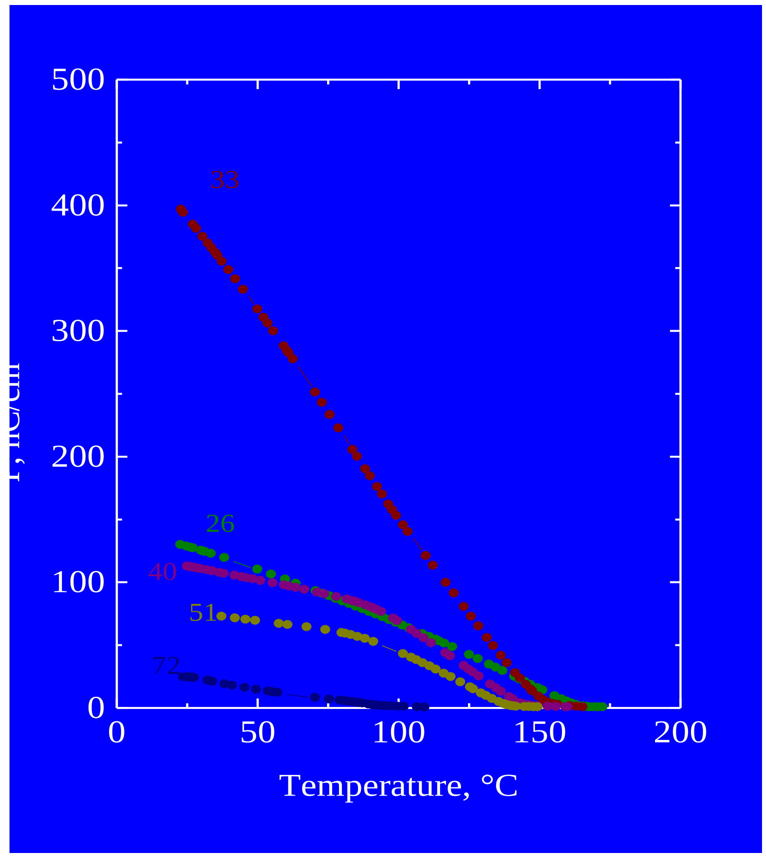
Pyroelectric measurements in PM6R8 mixtures

By cooling under an applied electric field

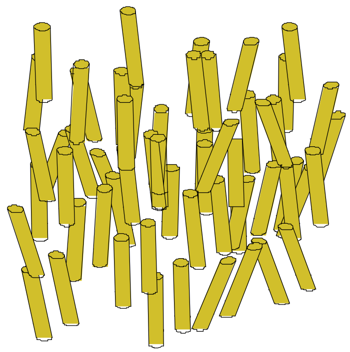
Pyroelectric curve



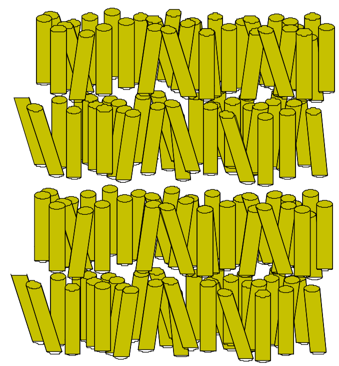
Macroscopic polarization



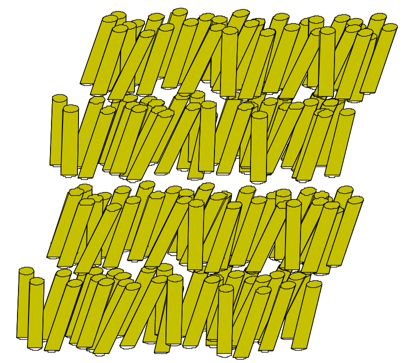
Nematic



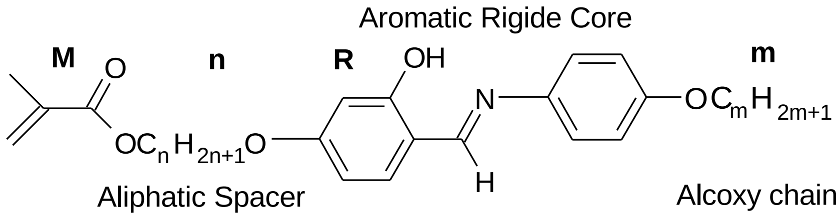
Smectic A



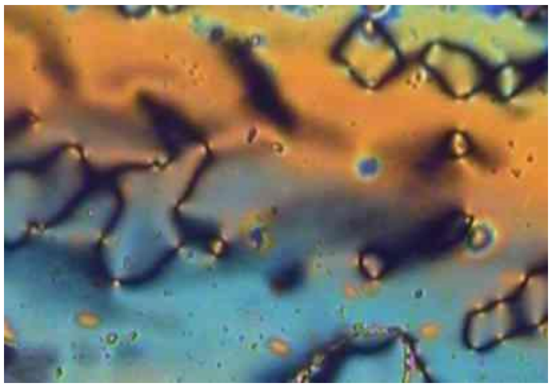
Smectic C

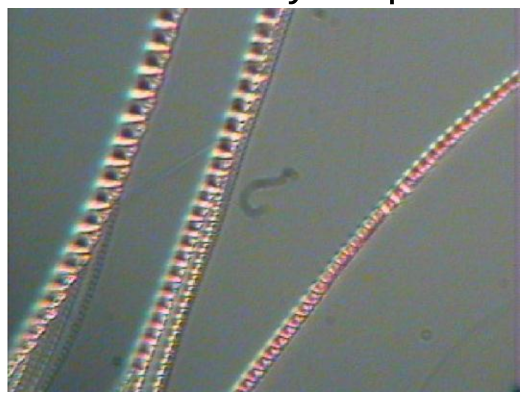


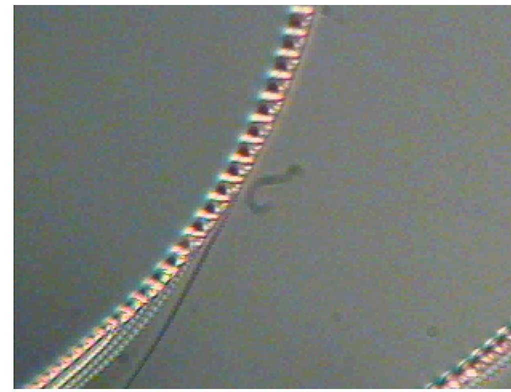
Monomer Characterization



Observed Textures in freely suspended films







Nematic phase (M4R5, T=88.1 °C)

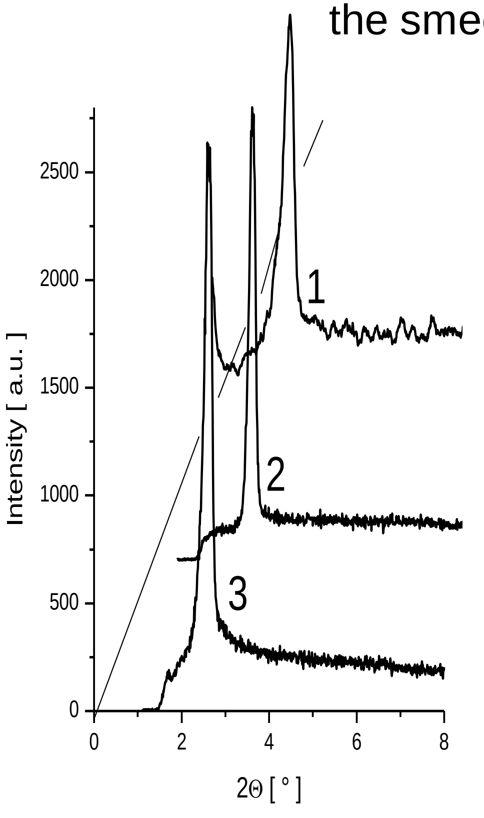
Smectic A phase (M4R6, T=72.5 °C)

Smectic C phase (M4R6, T=66.5 °C).

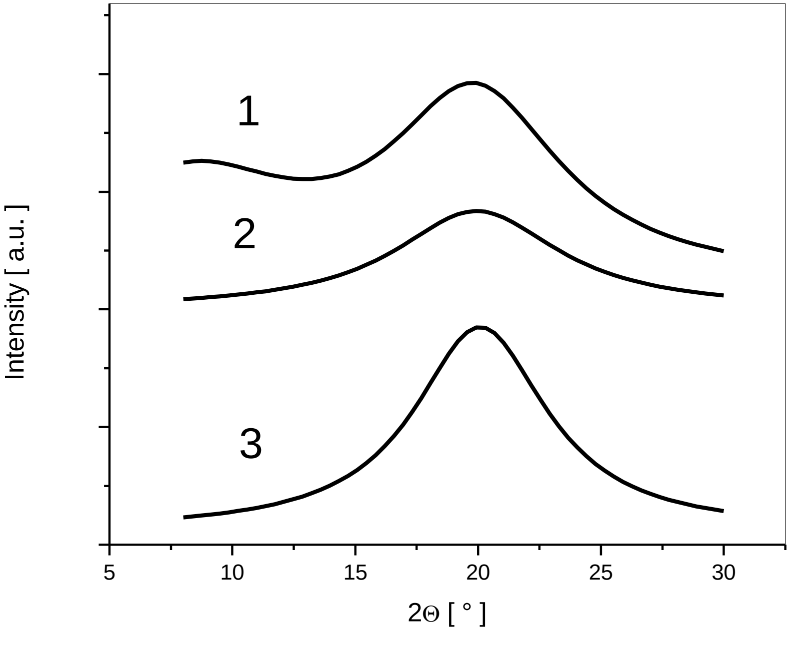
Shorter monomers (M4R4, M4R5 y M4R6) developped a nematic phase
SA - SC are second order phase transitions.

X-Ray Diffraction for monomers

Small angles region at 80 °C: (1) M4R5, (2) M4R6 and (3) M4R8 in the smectic A phase.



Wide angle region showing diffues halos. The solid lines corresponds to the statistic correlation.



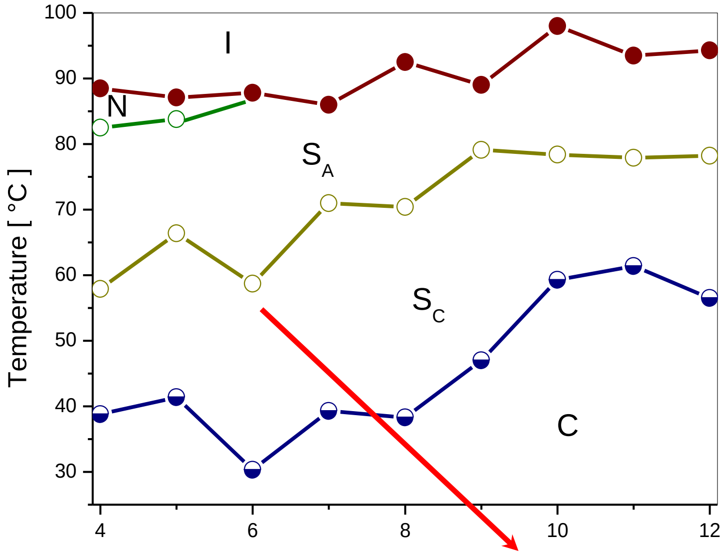
Phase transitions and enthalpy for monomers

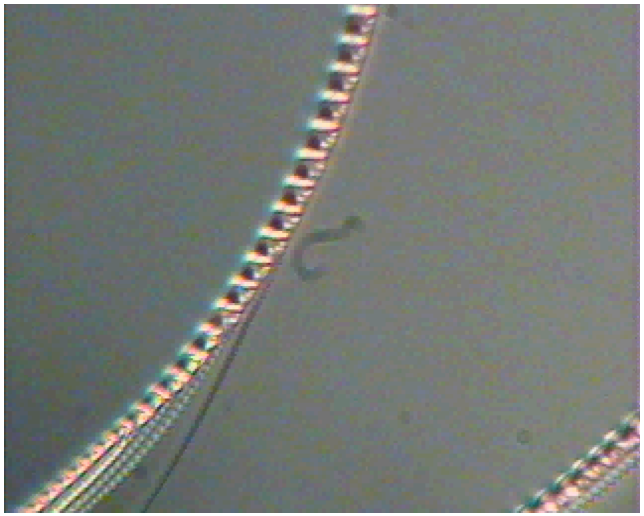
Sample	Mesophase	Enthalpy [KJ/mol]
M4R4	C – 38.8 – S_C – 57.9 – S_A – 82.5 – N – 88.5 – I	30.25 – n.d. – 2.08 – 4.76
M4R5	C – 41.4 – S_C – 66.4 – S_A – 83.8 – N – 87.1 – I	45.00 – n.d. – 2.50 – 1.54
M4R6	C – 30.3 – S_C – 58.7 – S_A – 87.8 – I	45.66 – n.d. – 5.12
M4R7	C – 39.3 – S_C – 71.0 – S_A – 86.0 – I	48.52 – n.d. – 6.63
M4R8	C – 38.3 – S_C – 70.4 – S_A – 92.5 – I	50.26 – n.d. – 6.83
M4R9	C – 47.0 – S_C – 79.1 – S_A – 89.0 – I	50.84 – n.d. – 7.03
M4R10	C – 59.3 – S_C – 78.4 – S_A – 98.0 – I	56.09 – n.d. – 7.23
M4R11	C – 61.4 – S_C – 77.9 – S_A – 93.5 – I	60.25 – n.d. – 6.90
M4R12	C – 56.5 – S_C – 78.2 – S_A – 94.3 – I	59.12 – n.d. – 7.95
M6R6	C – 60.0 – S_C – 69.0 – S_A – 96.4 – I	38.72 – n.d. – 5.53
M6R7	C – 51.4 – S_C – 69.8 – S_A – 91.4 – I	27.72 – n.d. – 5.00
M6R8	C – 54.7 – S_C – 80.0 – S_A – 97.9 – I	39.38 – n.d. – 5.80
M6R9	C – 55.2 – S_C – 70.2 – S_A – 91.3 – I	29.29 – n.d. – 6.01
M6R10	C – 48.3 – S_C – 83.3 – S_A – 96.6 – I	30.02 – n.d. – 6.82
M6R11	C – 58.1 – S_C – 74.6 – S_A – 92.0 – I	41.99 – n.d. – 7.27
M6R12	C – 46.1 – S_C – 87.9 – S_A – 96.6 – I	33.28 – n.d. – 7.12

n.d. : Non determined

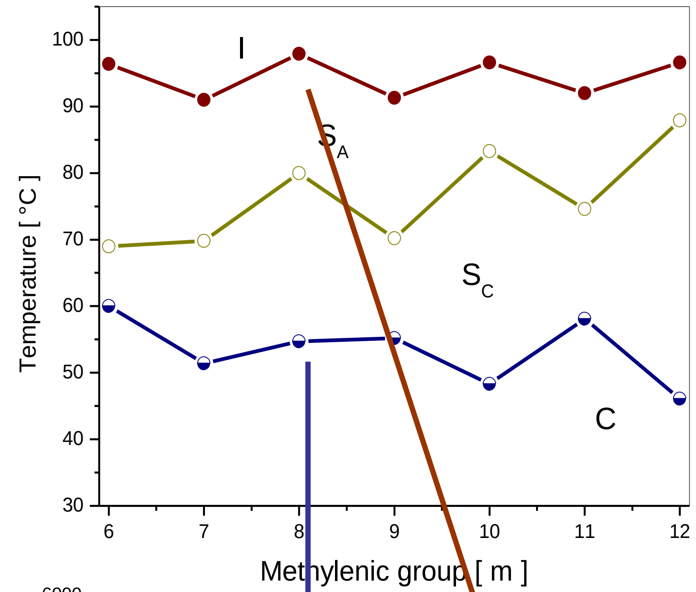
Phase diagrams by cooling

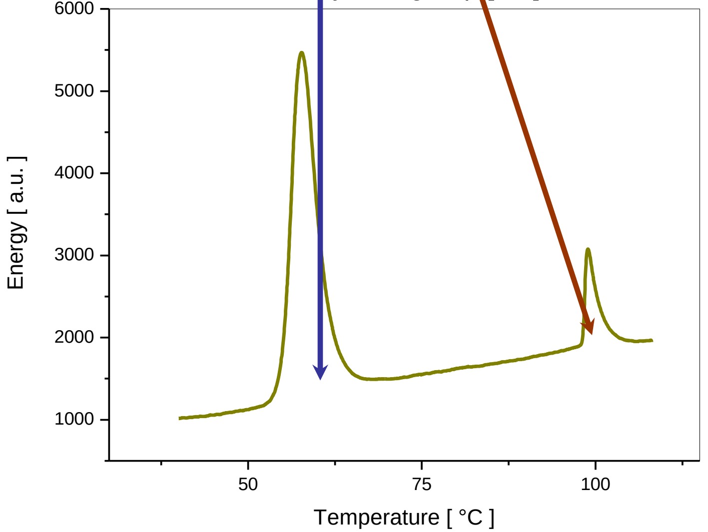
M4 Serie





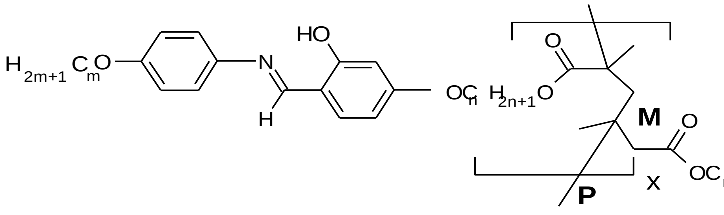
M6 Serie





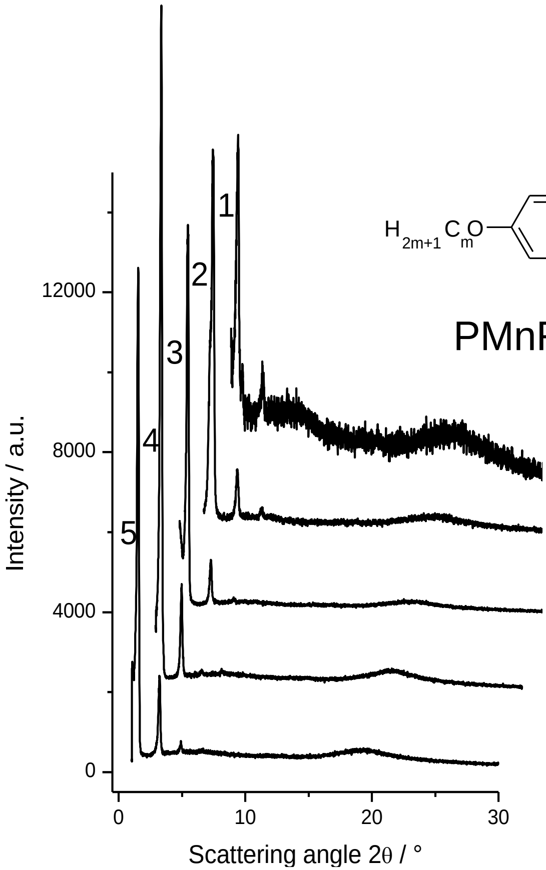
Polymer Characterization

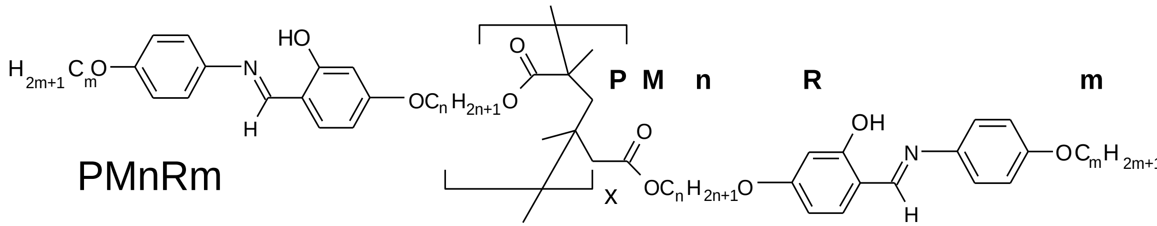
Phase transition Temperature, entalpy and molecular weigth characterization Mw and Mn



Sample	Mesophase	Entalpy [J/g]	$\overline{M}_w$ [g / mol]	*DI*	*Pw*
PM4R5	g – 50.8 – S_{C2} – 187.1 – I	21.97	124,813	1.703	284
PM4R6	g – 58.7 – S_{C2} – 191.3 – I	13.80	86,229	1.786	190
PM4R8	g – 57.8 – S_{C2} – 201.3 – I	15.62	129,607	1.193	269
PM6R6[7]	g – 82.0 – S_{C2} – 157.0 – S_{Ad} – 173.0 – I	10.30/ 4.32	77,575	1.756	161
PM6R7	g – 83.4 – S_{C2} – 162.7 – S_{Ad} – 176.7 – I	7.78/2.70	55,126	1.313	111
PM6R8[12]	g – 82.0 – S_{C2} – 180.0 – I	16.40	81,500	2.100	160
PM6R9	g – 62.2 – S_{C2} – 183.6 – I	18.55	115,209	1.313	220
PM6R10[9]	g – 64.2 – S_{C2} – 190.3 – I	19.02	104,300	2.370	194
PM6R11	g – 70.6 – S_{C2} – 195.3 – I	19.45	102,016	1.587	185
PM6R12[9]	g – n.d. – S_{C2} – 190.5 – I	21.20	108,100	2.609	191

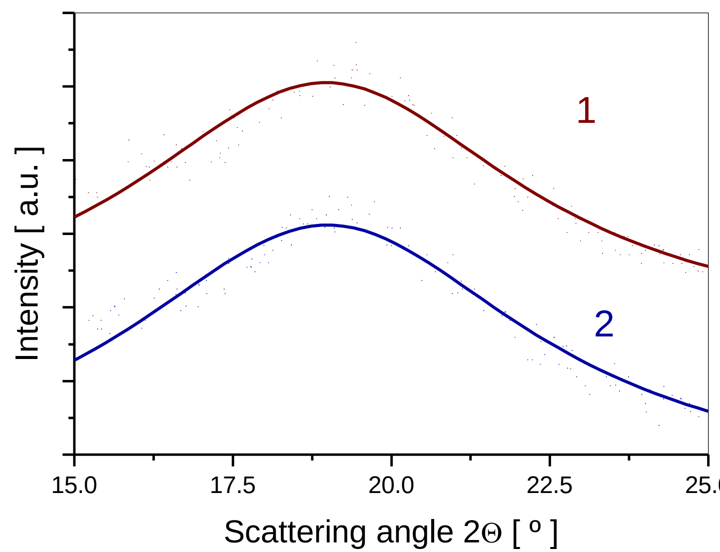
X-Ray Diffraction



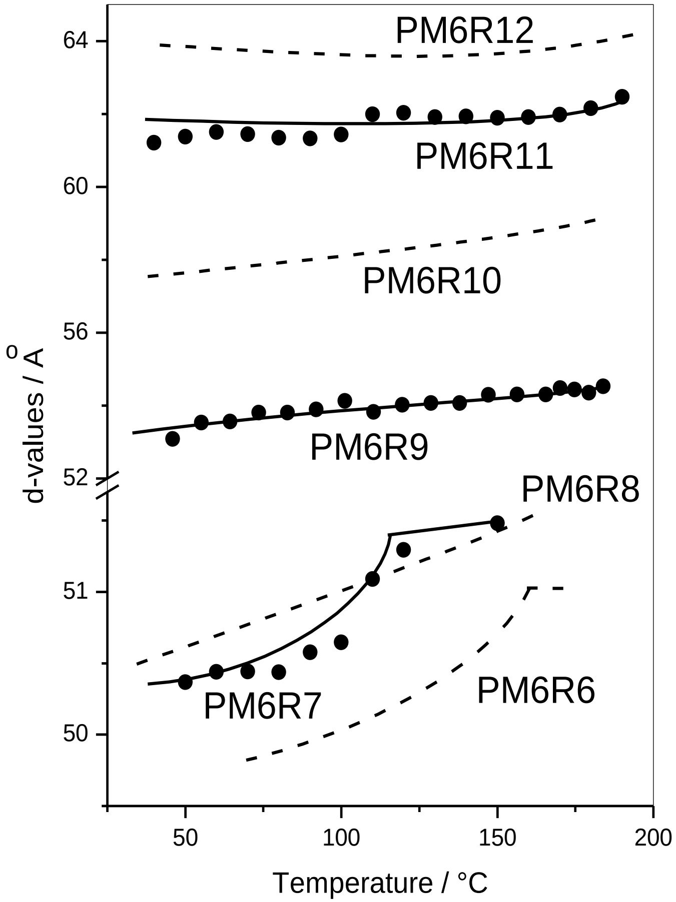


(1) PM4R5 at 190 °C, (2) PM4R6 at 160 °C, (3) PM4R8 at 120°C, (4) PM6R9 at 125 °C and (5) PM6R11 at 170 °C. The (001) reflex position corresponds to a bilayer structure.

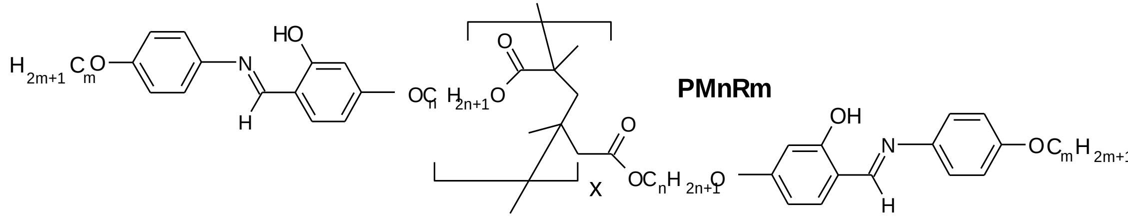
Difuse halos correspond to the distance average for the intermolecular distance D in the smectic phase, showing a liquid like packing.



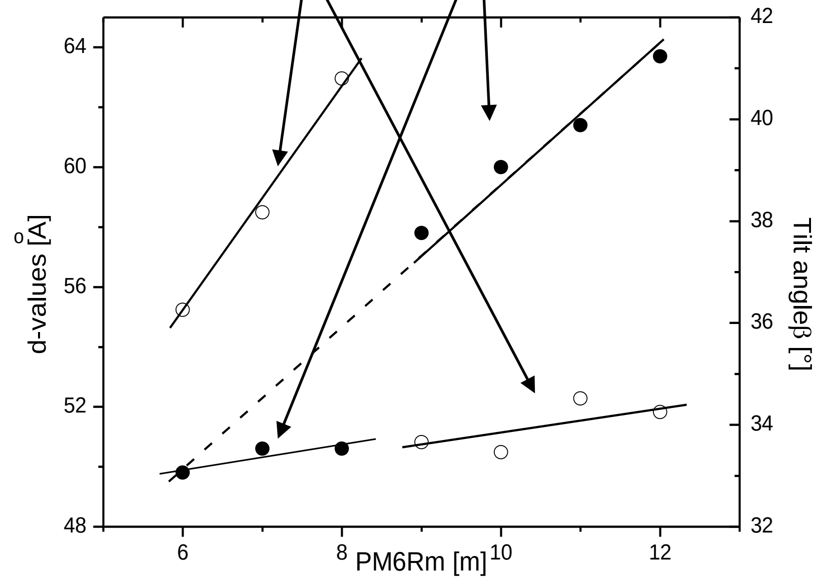
Interlayer distance temperature dependence



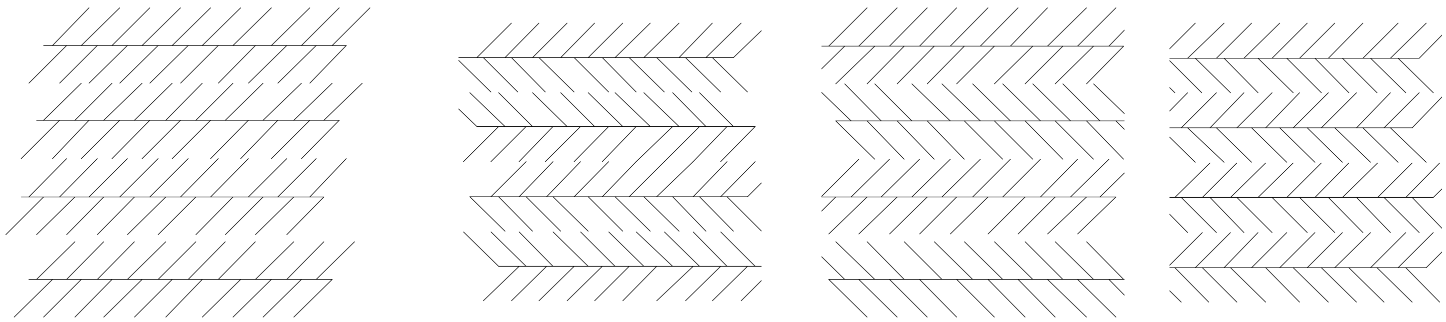
Interlayer distance temperature dependance by cooling

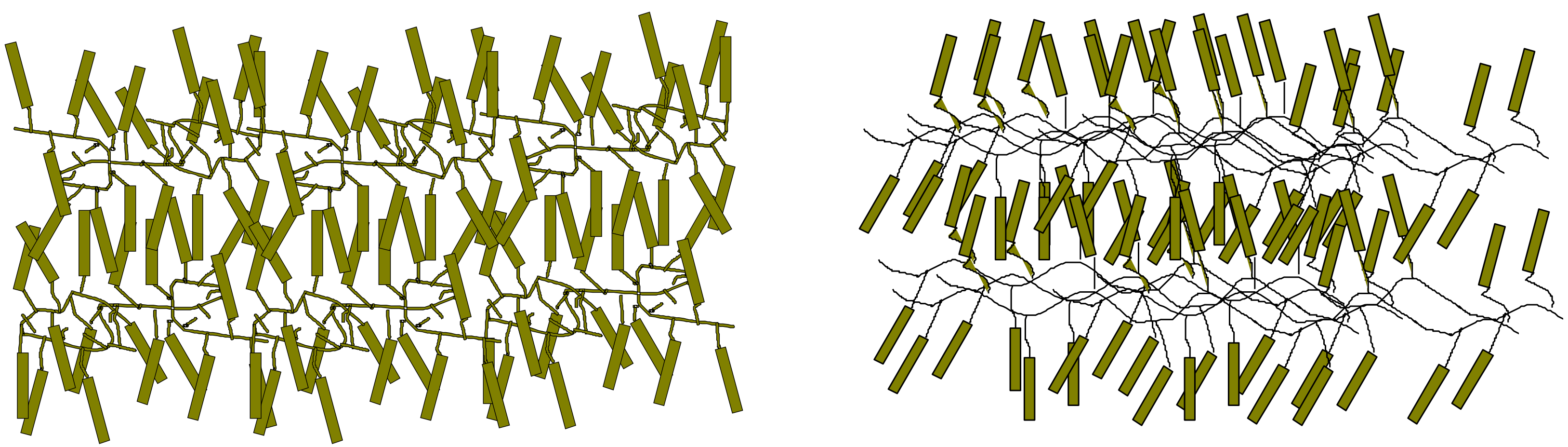


Interlayer distance *d* (full circle) and tilt angle *β* (open circles) in the smectic C2 phase at 80 °C against the mesogenic group length.

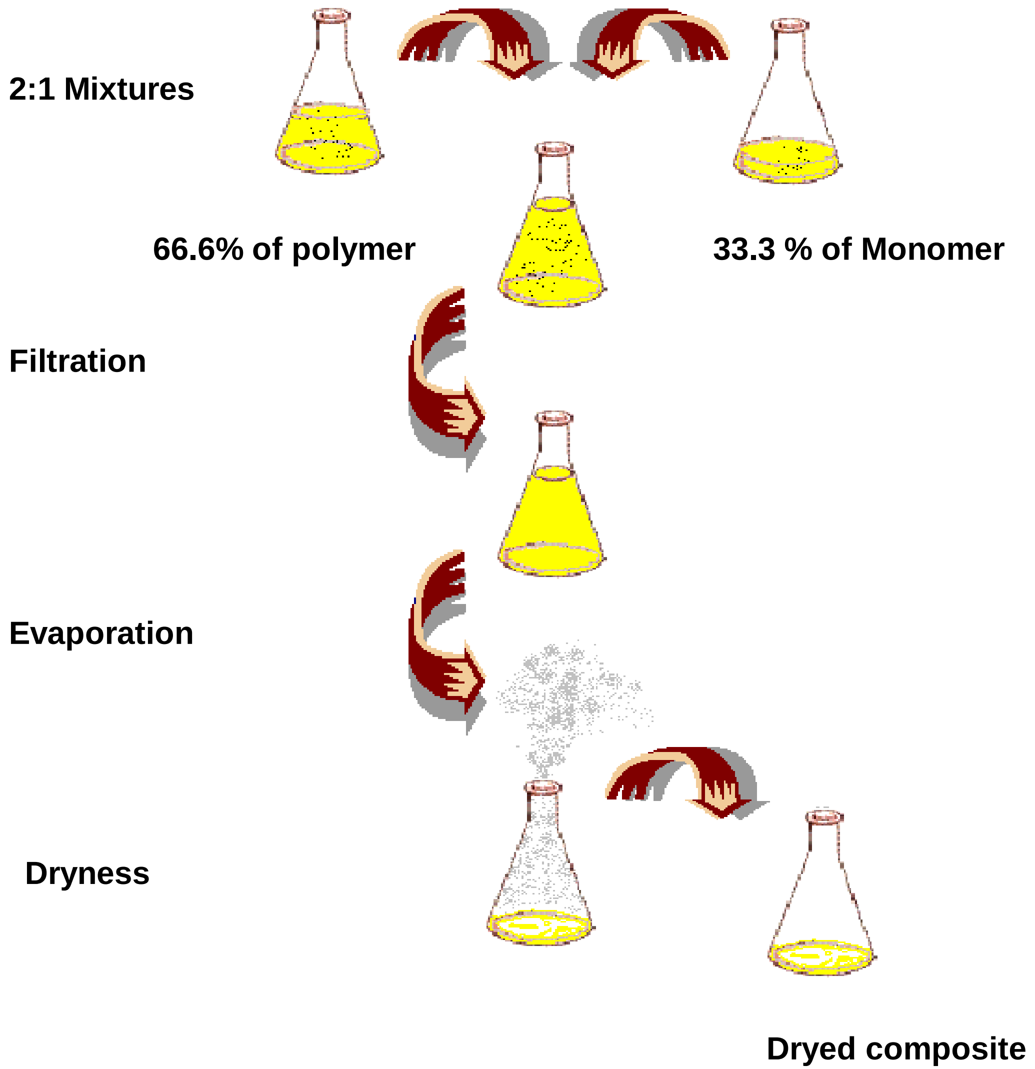


Smectic C2 phase in a polymer

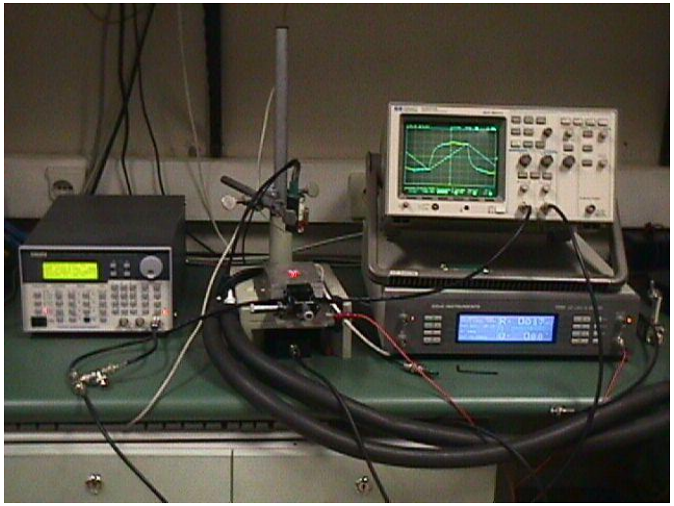


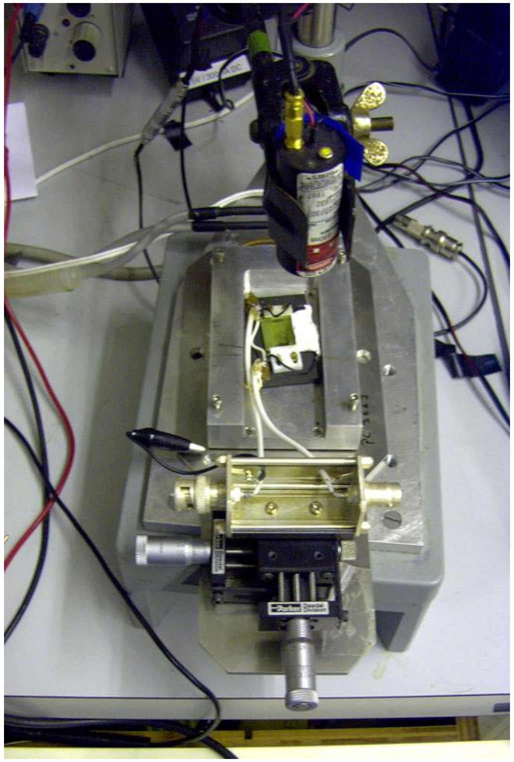


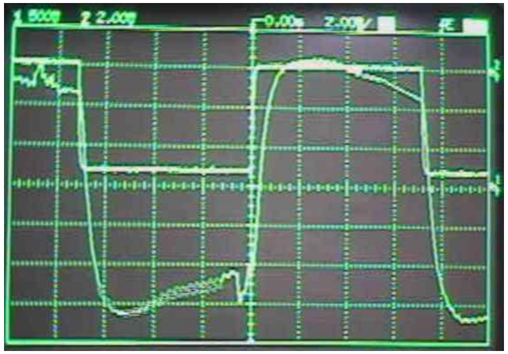
Composites Preparation



Pyroelectric modulated technique

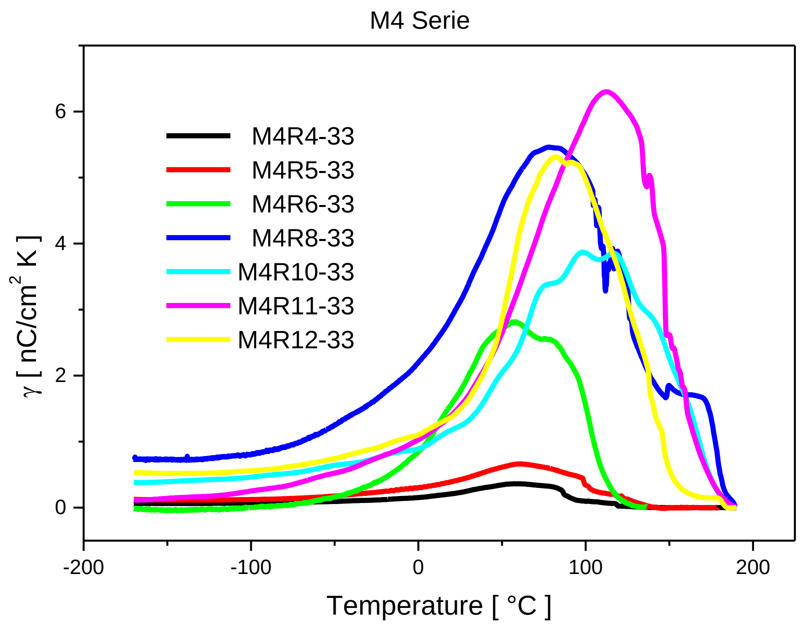


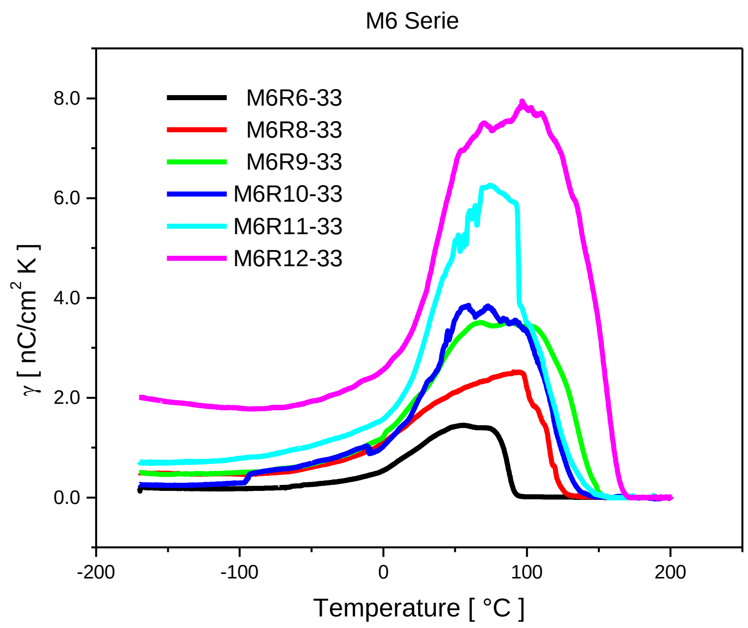




Pyroelectric studies

In previously poled samples: from -170 °C until the isotropic state. (10 V/µm).

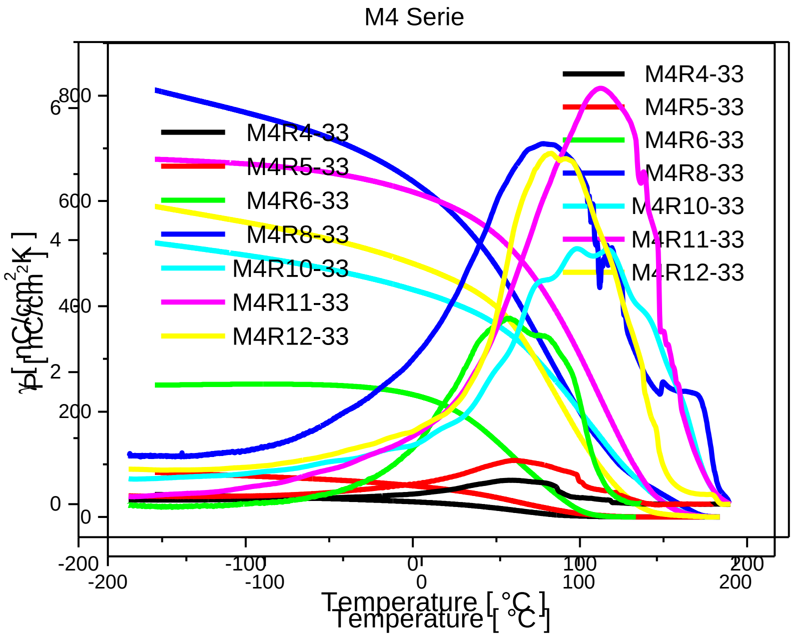


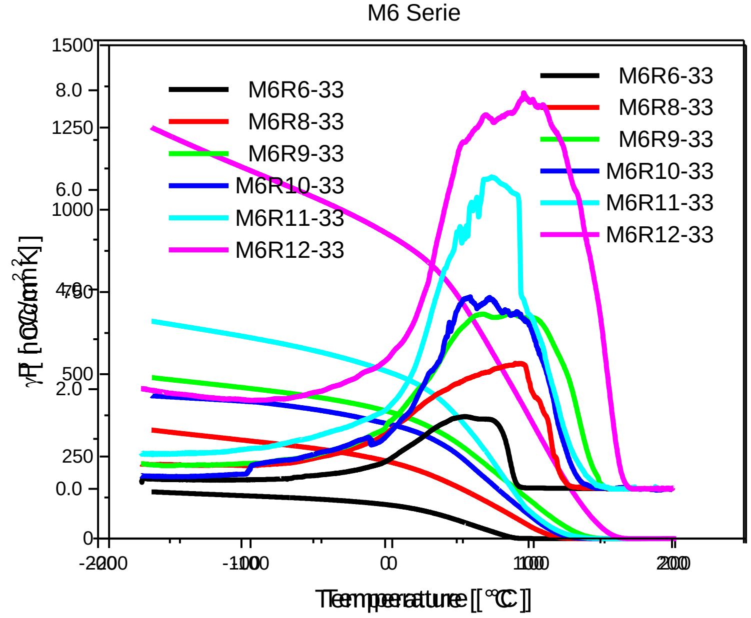


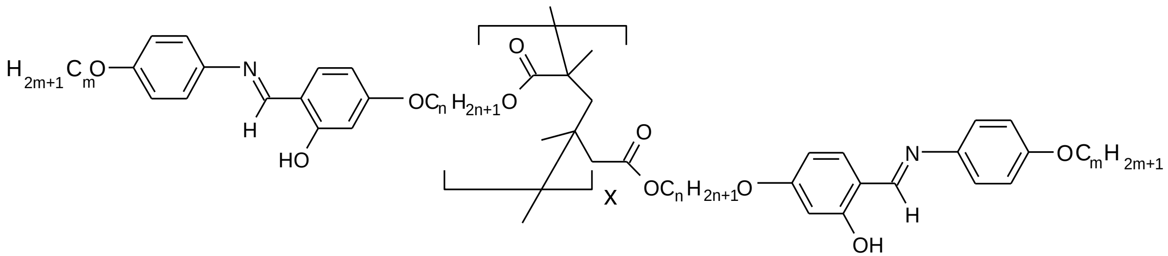
Pyroelectric answer for M4Rn-33 and PM6Rn-33 Serie

Composite Polarization

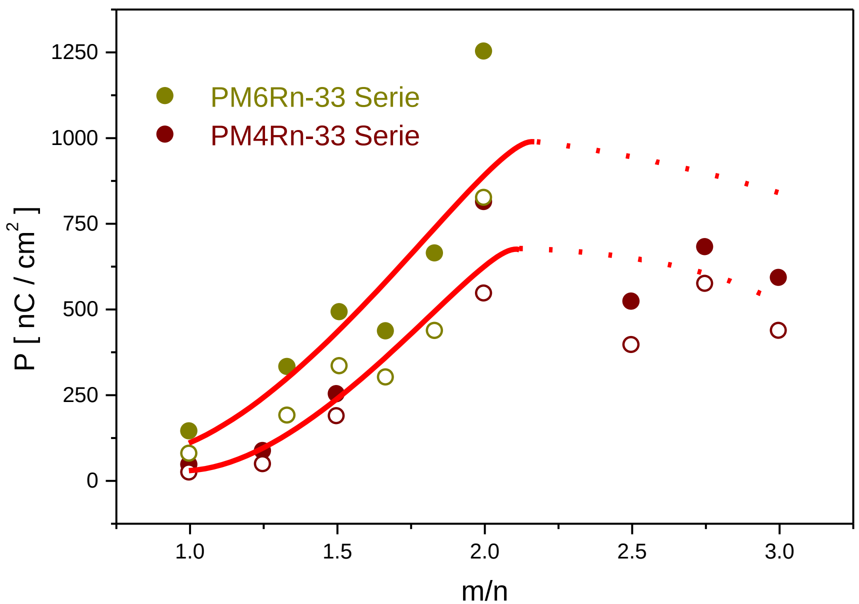
If we consider the equation *γs(T)= dPs(T)/dT*, the polarization will arise from the integrated pyroelectric curves.







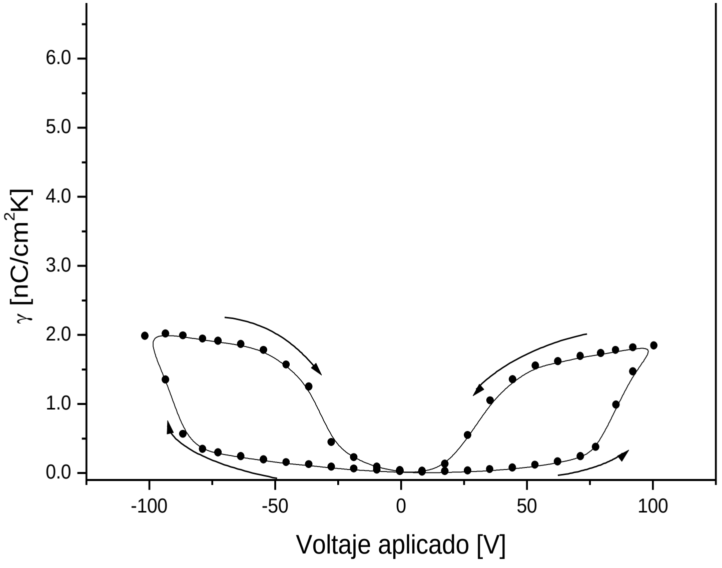
The pyroelectric response obtained focused our attention on an interesting relationship between the estimated polarization and the aliphatic chain to spacer ratio (m/n). This is reproducible for both of the homologous series, showing the largest value for PM6R12-33 in the PM6Rn-33 Serie and for PM4R8-33 in the PM4Rn-33 serie.



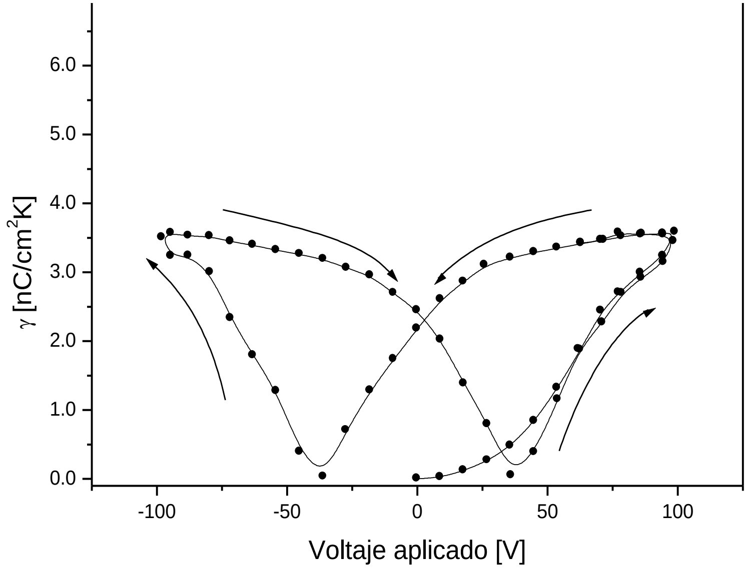
Polarisation vs alkyl chain to spacer ratio for both Series.
Open circles at 30 °C; solid circles at -170 °C.

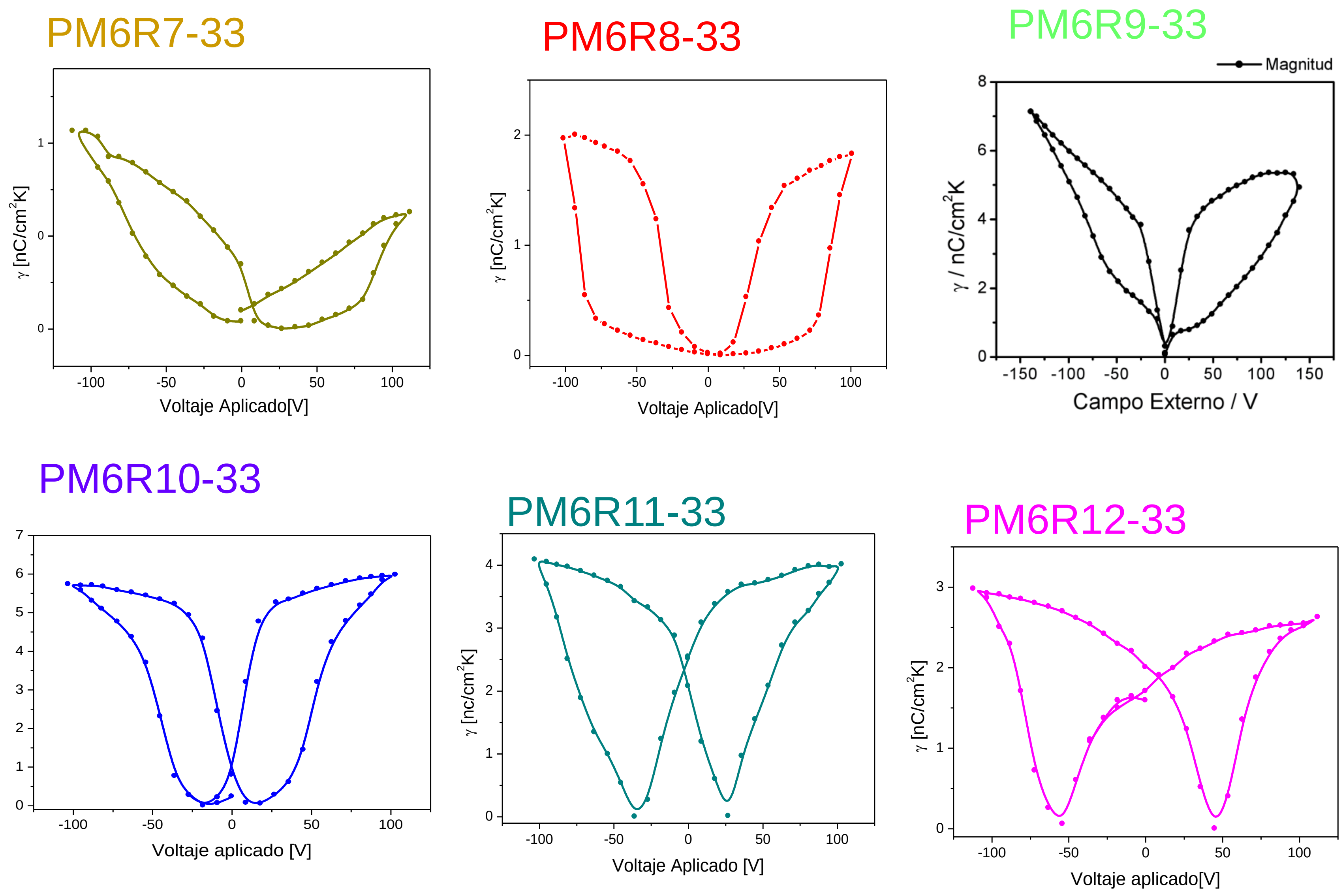
Hysteresis loops at T= 150°C

PM6R8-33

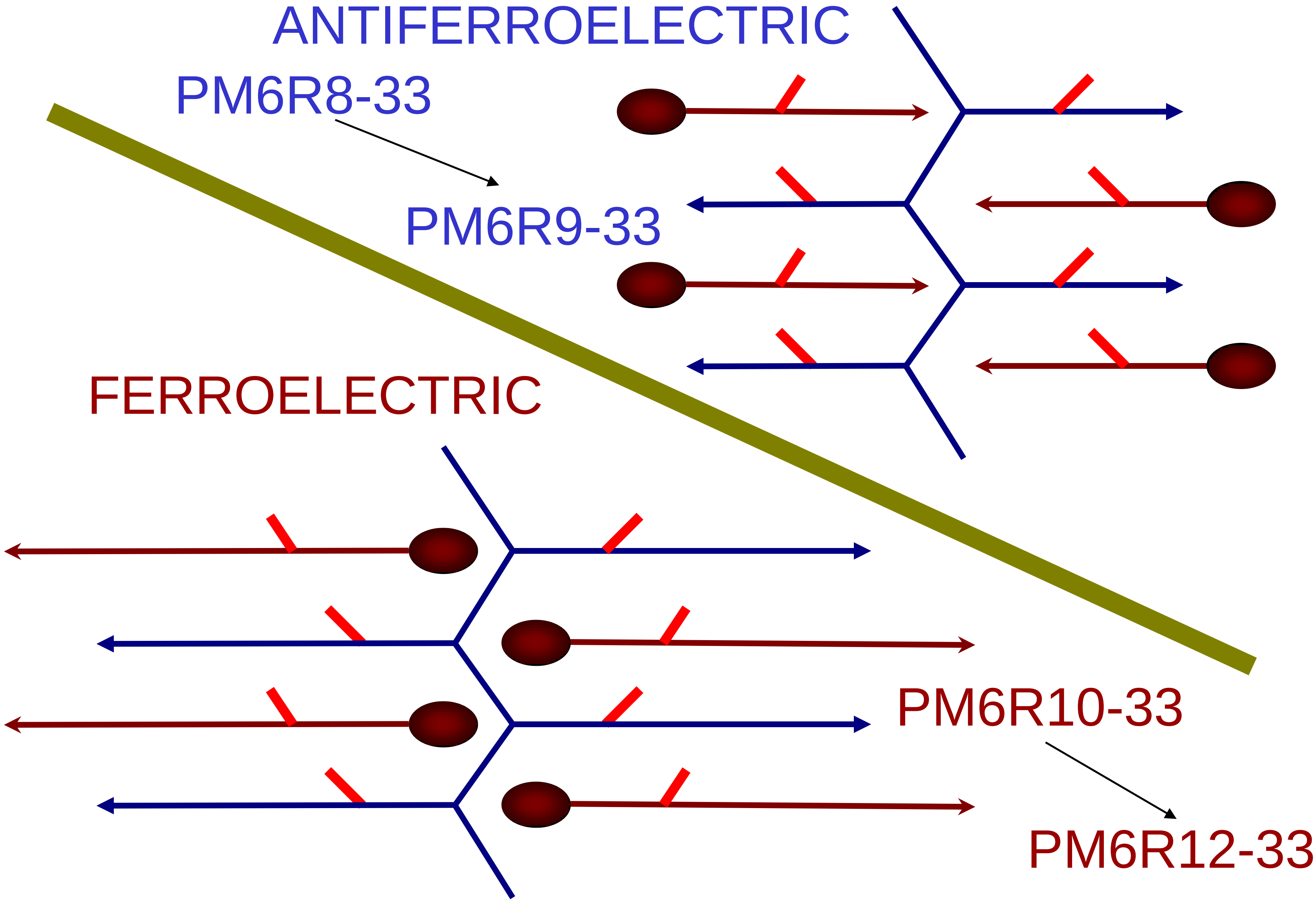


PM6R12-M4R8





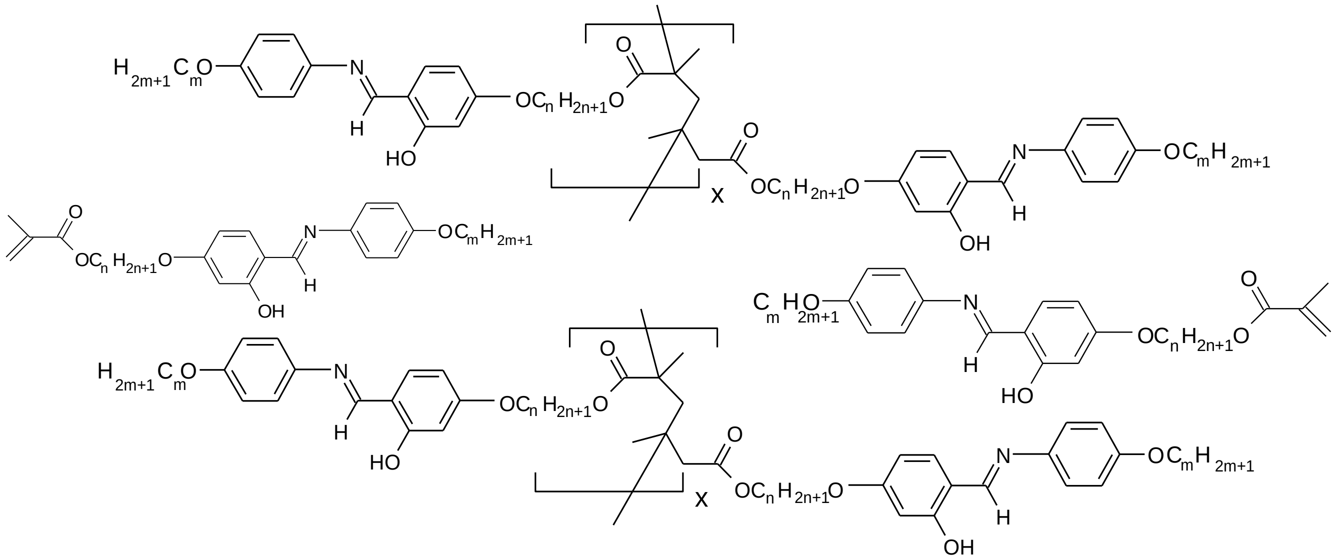
PM6R7-33
γ [nC/cm²K]
Voltaje Aplicado[V]
-100
-50
0
50
100
PM6R8-33
γ [nC/cm²K]
Voltaje Aplicado[V]
-100
-50
0
50
100
PM6R9-33
Magnitud
γ / nC/cm²K
Campo Externo / V
-150
-100
-50
0
50
100
150
PM6R10-33
Voltaje aplicado [V]
-100
-50
0
50
100
PM6R11-33
γ [nc/cm²K]
Voltaje Aplicado [V]
-100
-50
0
50
100
PM6R12-33
γ [nC/cm²K]
Voltaje aplicado[V]
-100
-50
0
50
100


ANTIFERROELECTRIC
PM6R8-33
PM6R9-33
FERROELECTRIC
PM6R10-33
PM6R12-33

ANTIFERROELECTRIC

PM6R6-33

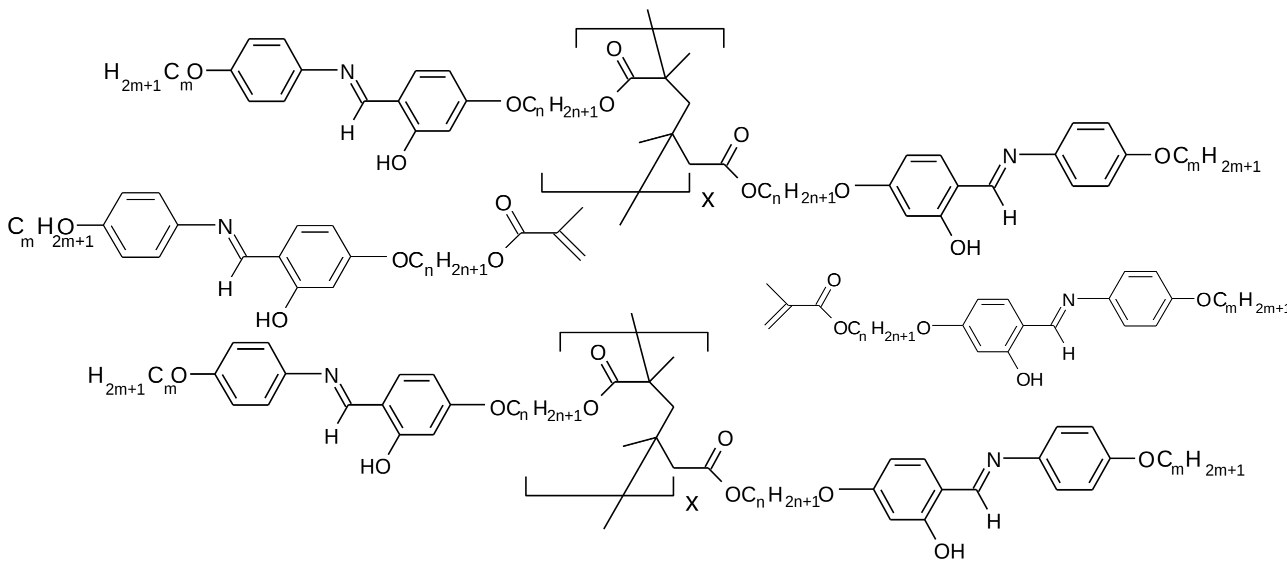
PM6R9-33



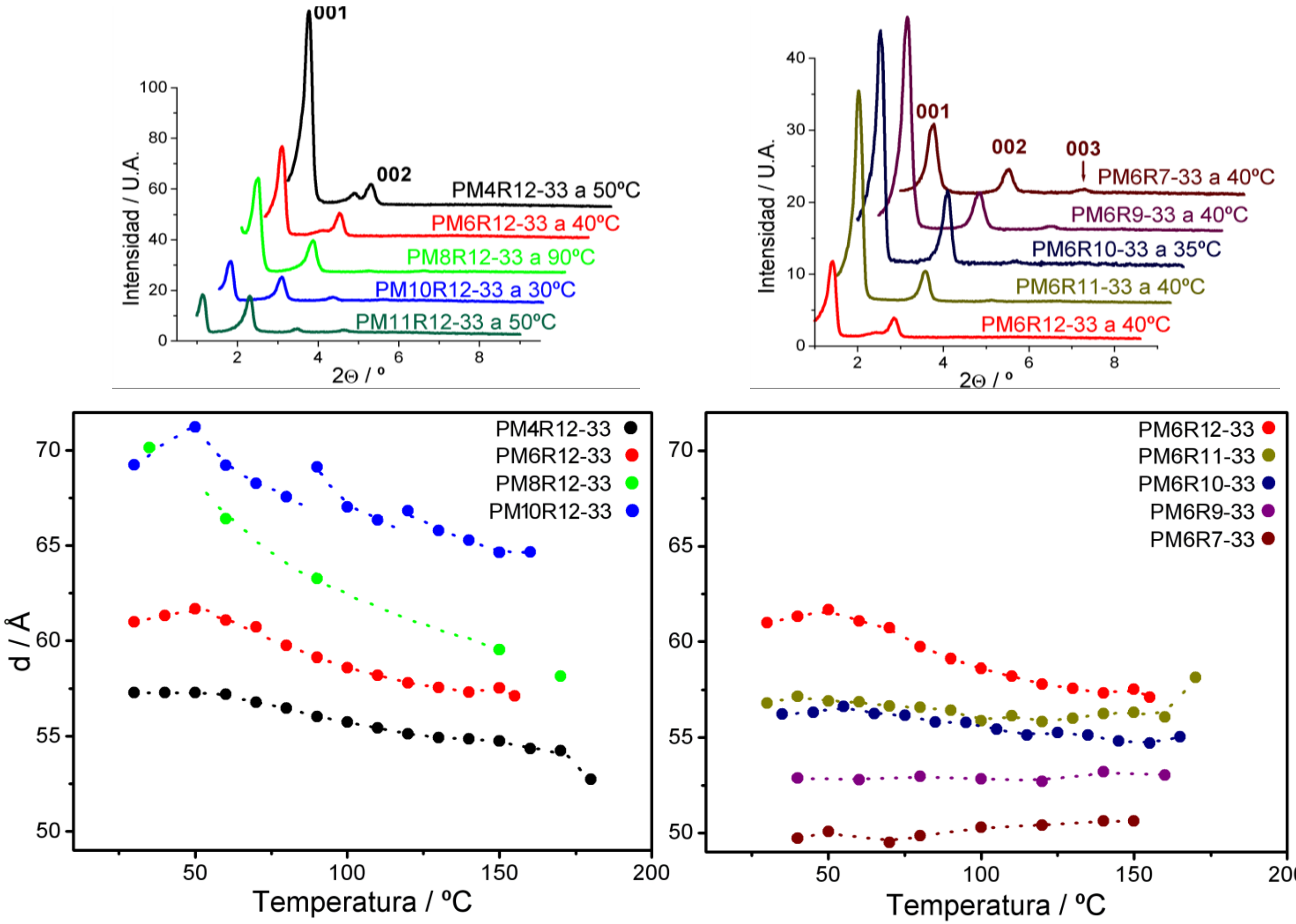
PM6R10-33

FERROELECTRIC

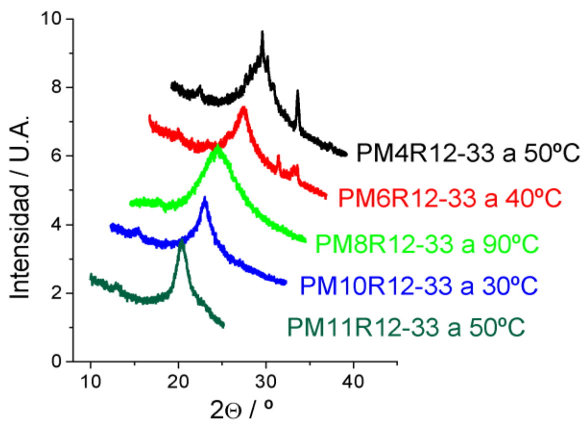
PM6R12-33

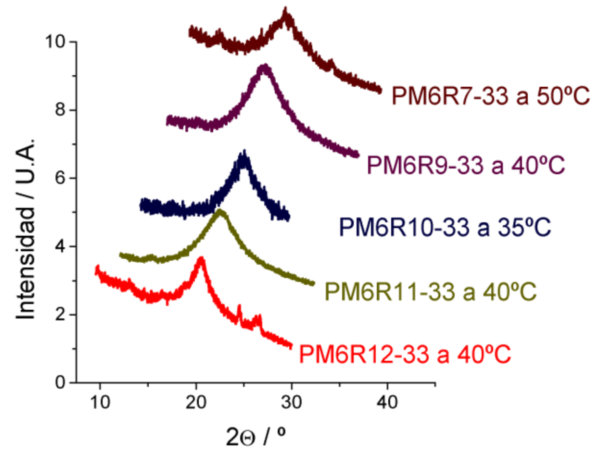


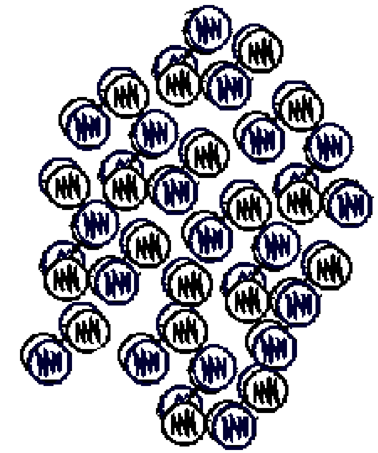
X-Ray studies in composites
Interlayer distance: small angles reflexes

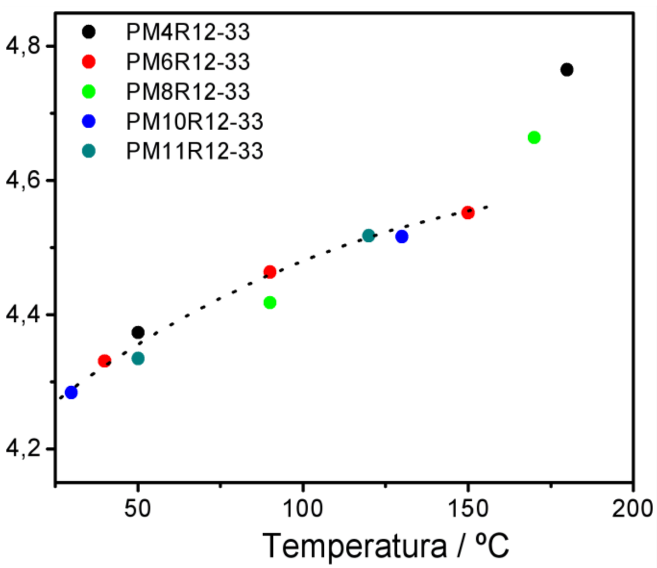


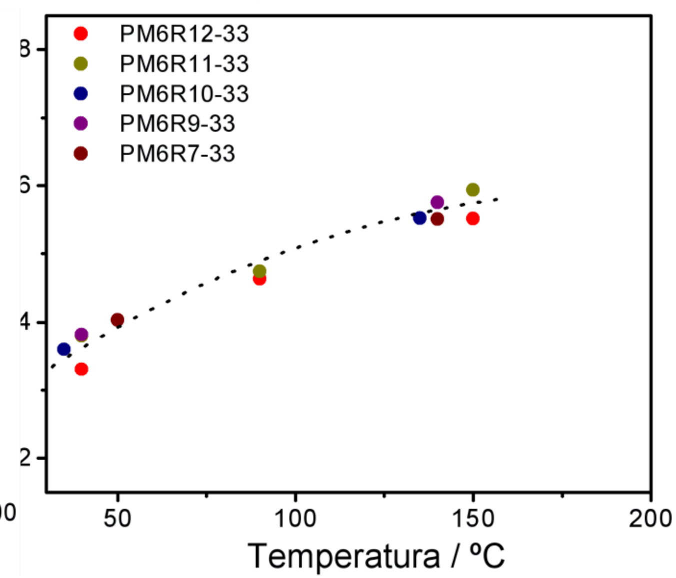
Fluidty: Wide angle reflexes

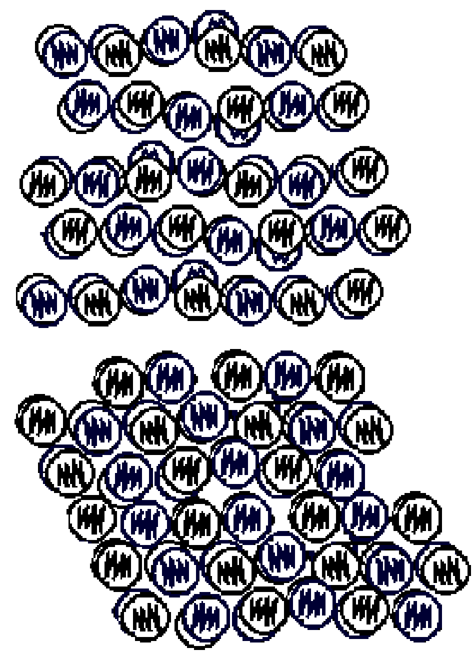




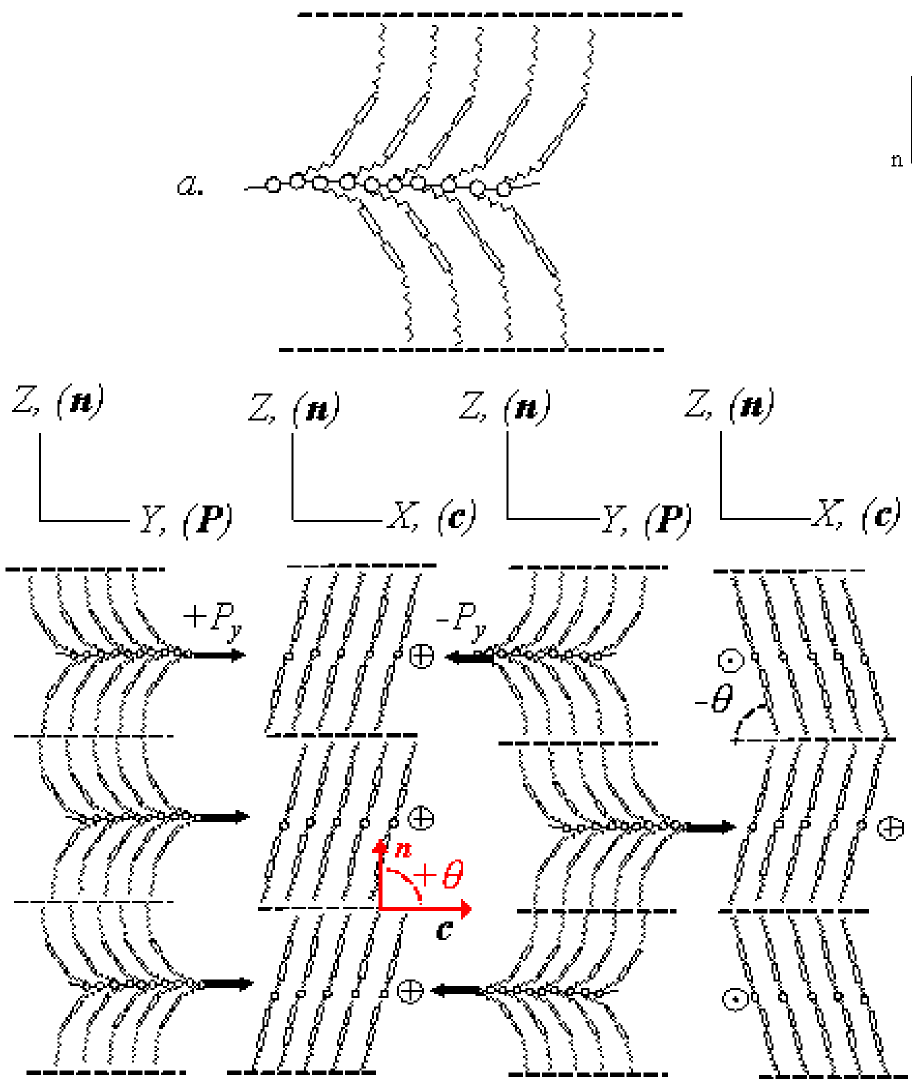


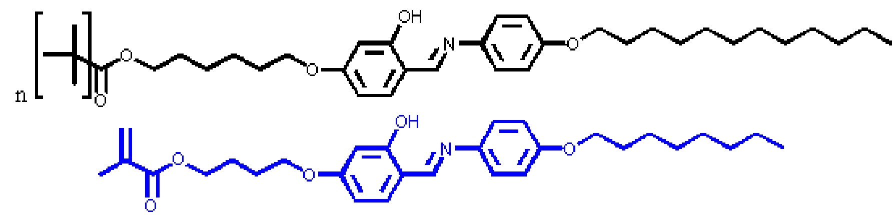


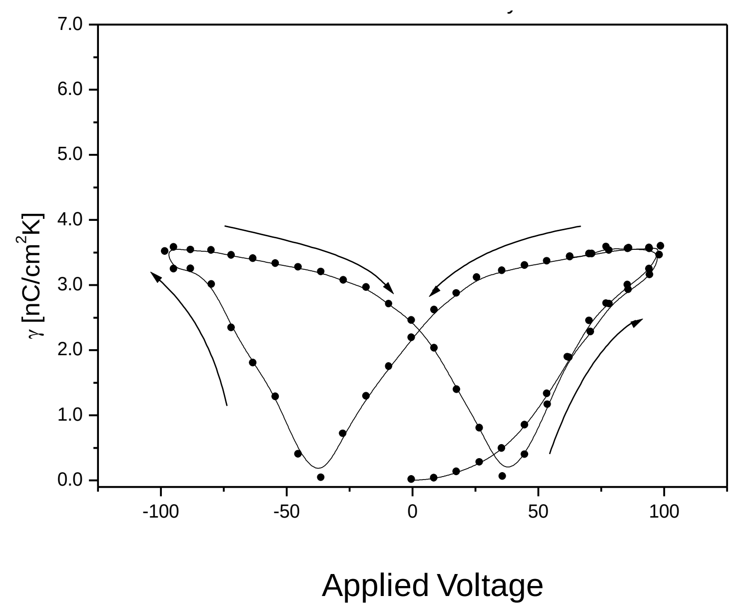




Described model for PM6R12-M4R8[1]

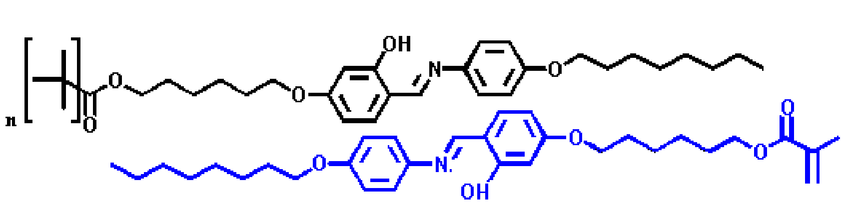




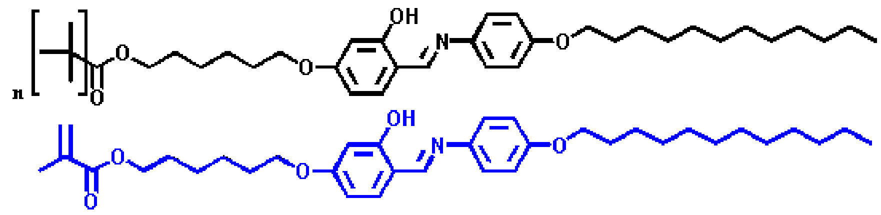


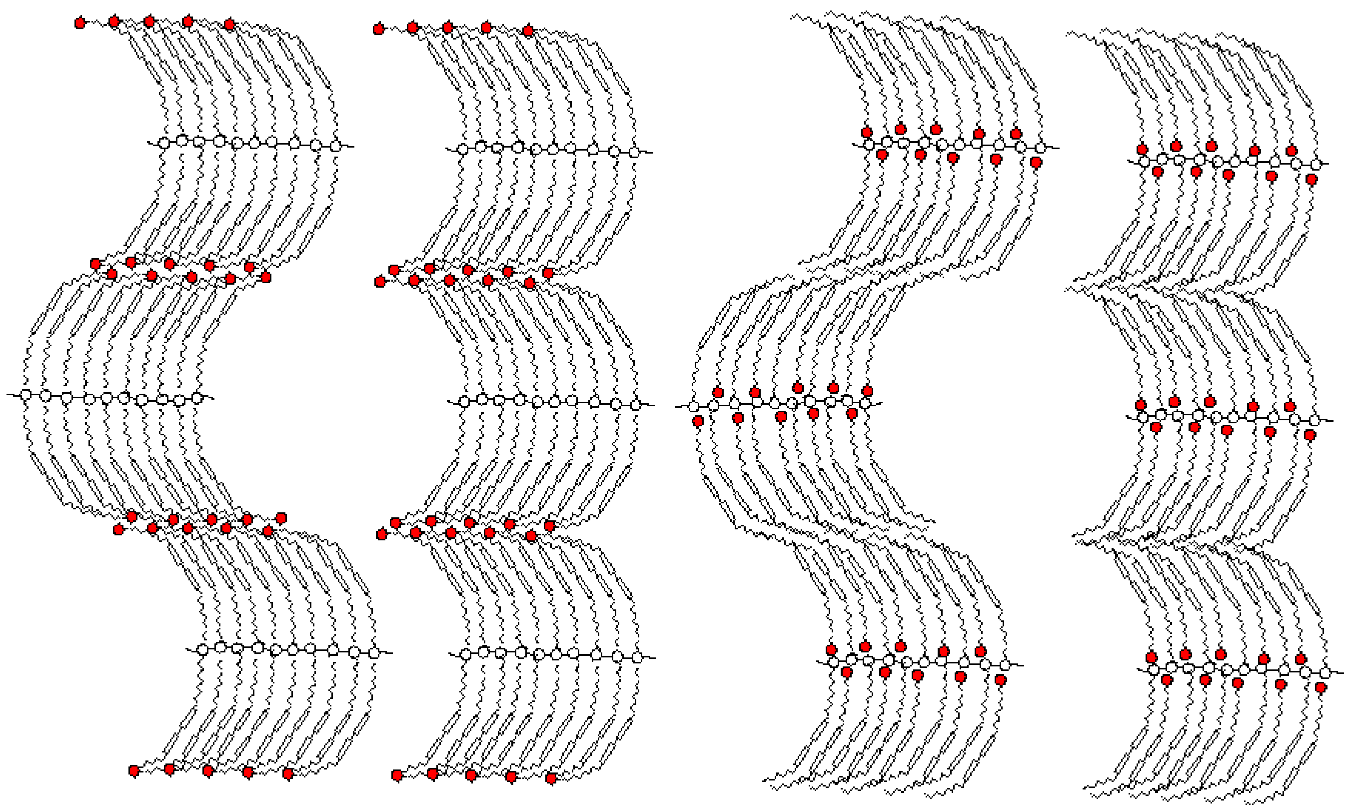
[1] S. V. Yablonskii, E. A. Soto-Bustamante*, R. O. Vergara-Toloza, W. Haase.
Ferroelectricity in Achiral Liquid Crystal Systems. ***Adv. Mat.*, 16, 1936-1940, 2004.**

PM6R8-33%

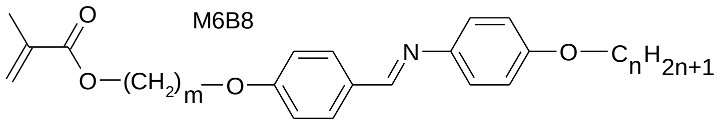


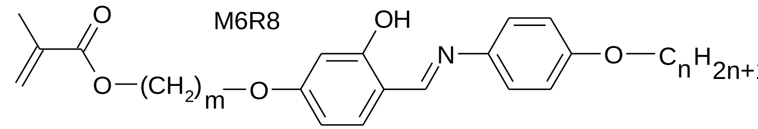
PM6R12-33%

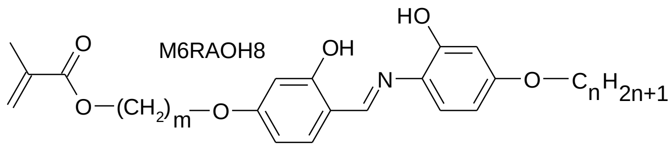


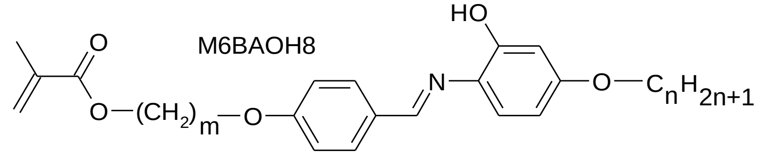


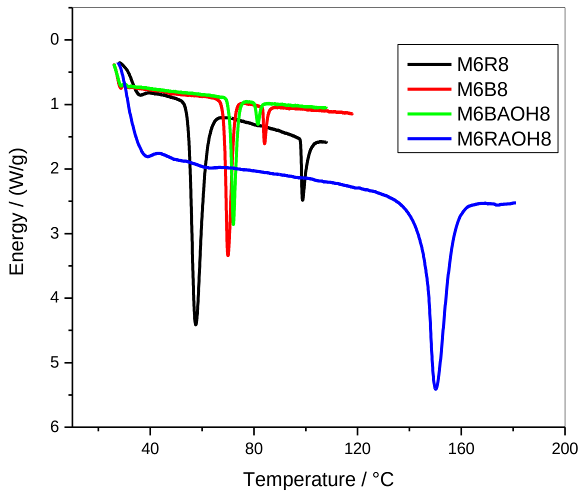
Other systems

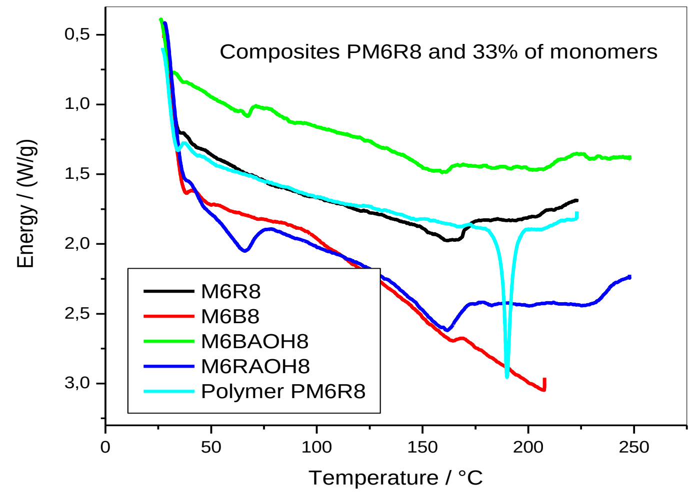




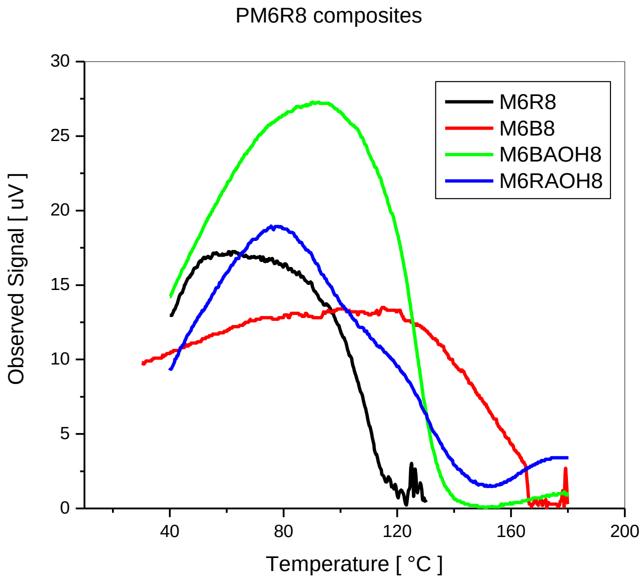


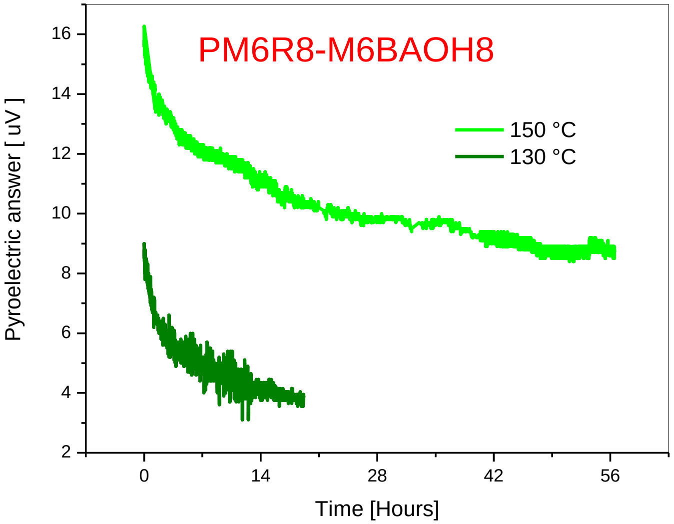






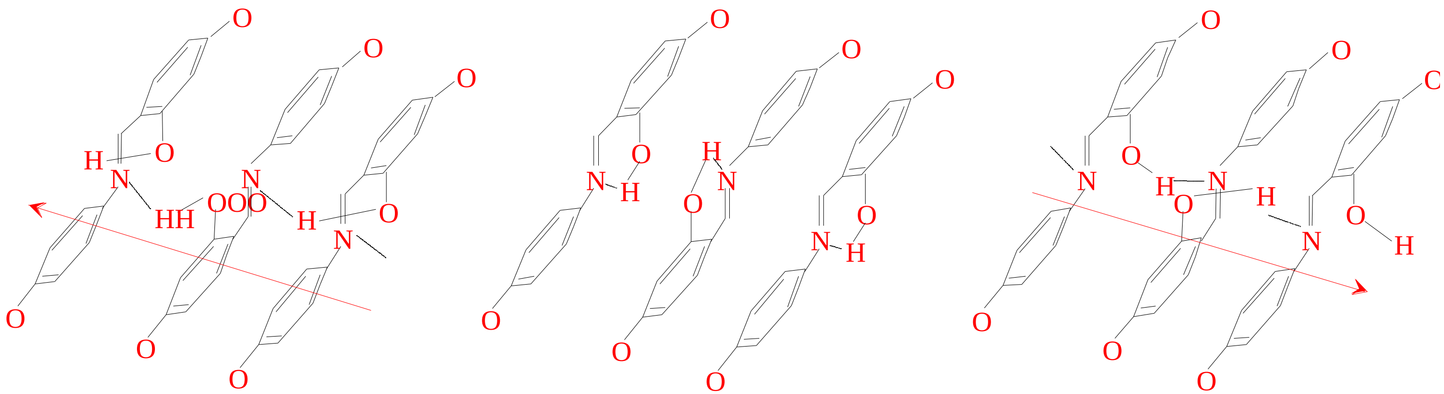
Pyroelectric behaviour and signal stability

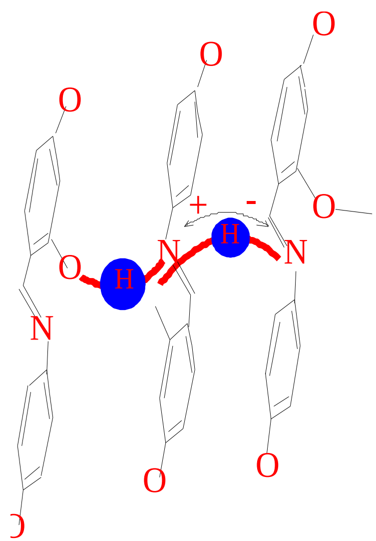




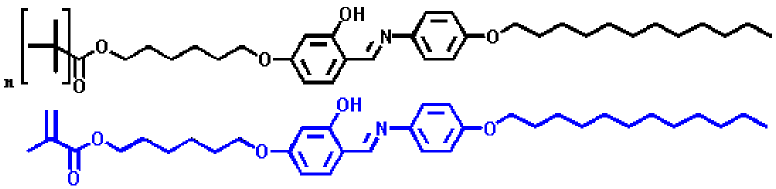
Hydrogen bonding

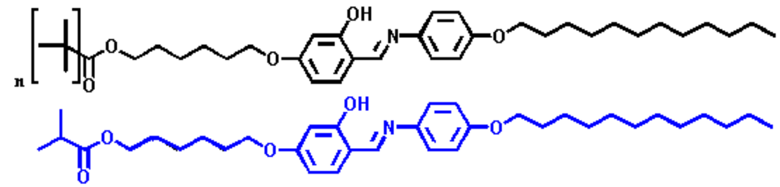
-E | E=0 | +E

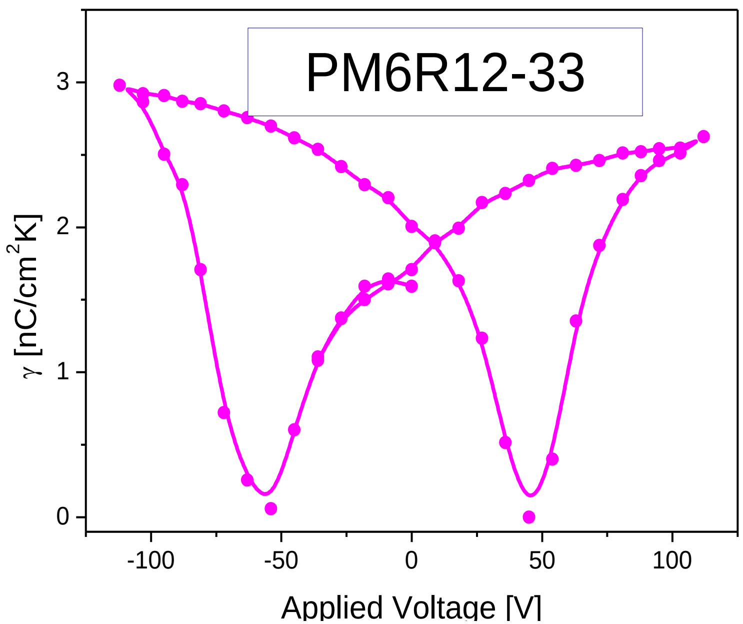


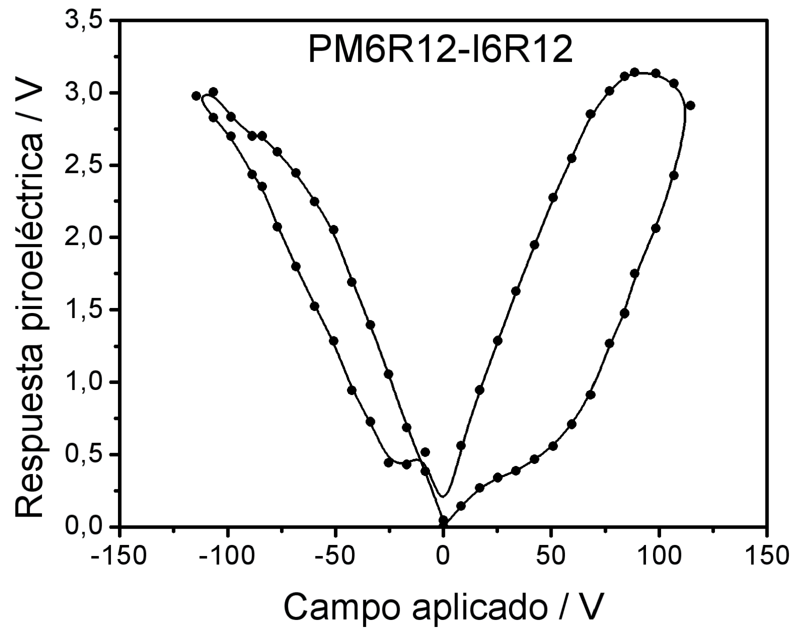


PM6R12-I6R12: no methacrylic group

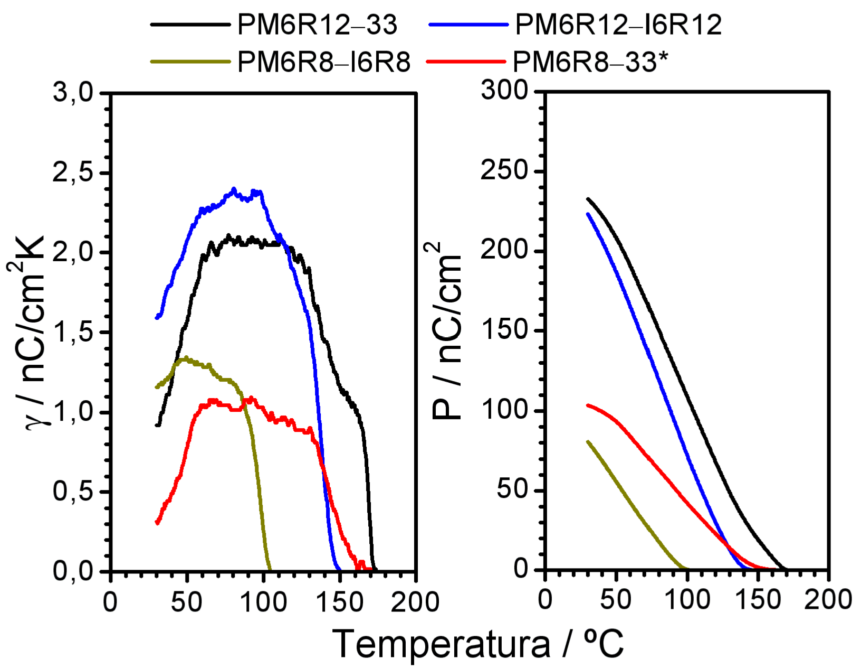


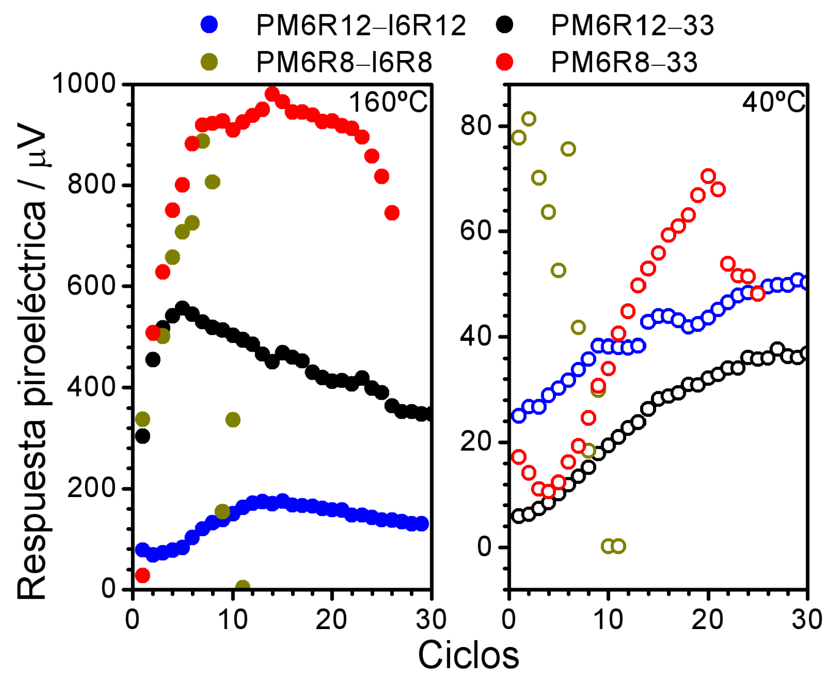


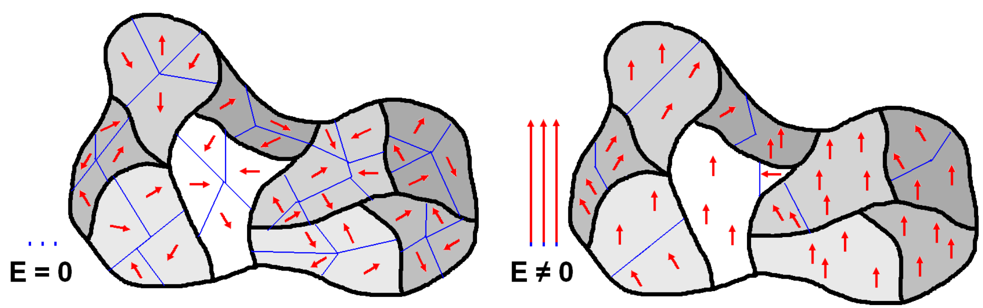


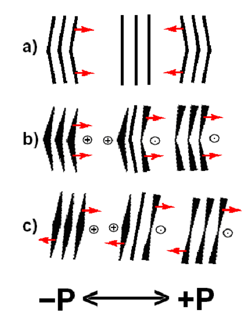


Signal stability









Acknowledgments

Telekom
Fundación Andes
Universidad de Chile
FONDECYT
VW-Stiftung

Pyroelectric detectors

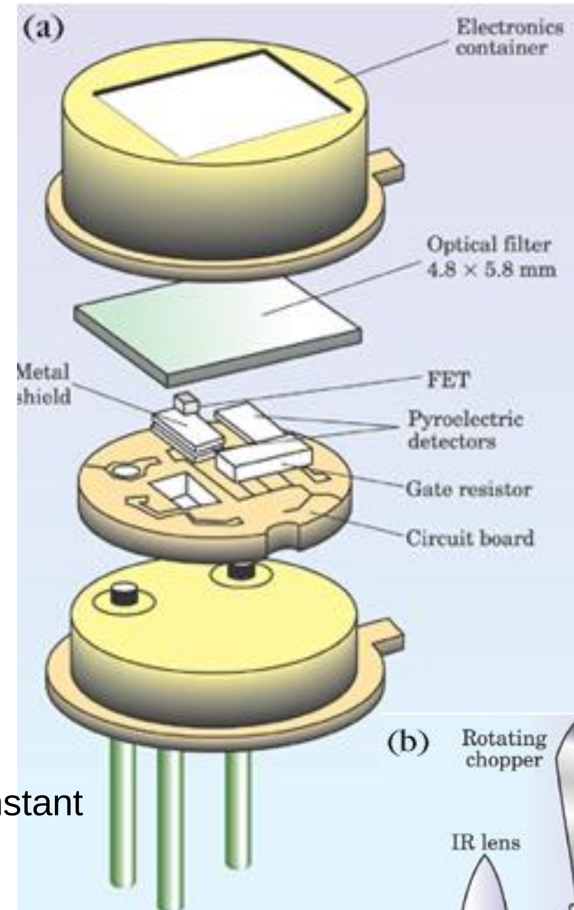
Detector materials:

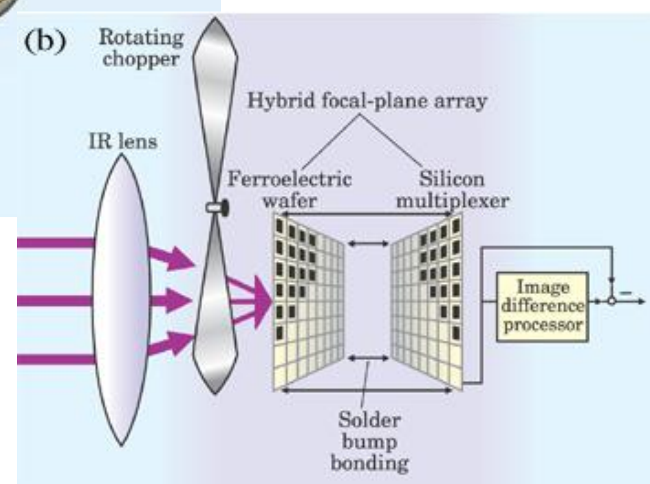
Triglycine sulfate (TGS) :
High pyroelectric coefficients
Relatively low permittivity.
Favorite for high-sensitivity applications.

Lithium tantalate:
High Stability
Insensitivity to humidity and vacuum
Used for space applications.

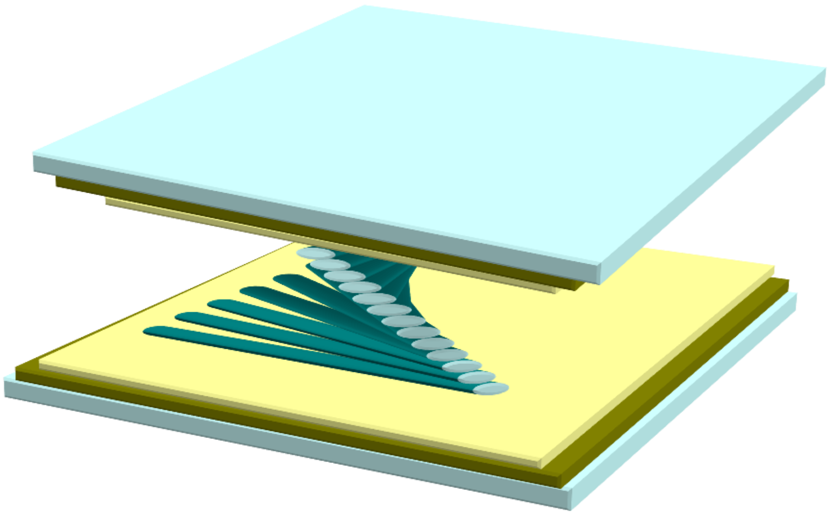
Polyvinylidene fluoride polymer (PVDF)
Low pyroelectric coefficients
Low thermal conductivity and dielectric constant
Useful for large-area detectors and arrays.

Ceramics based on the lead zirconate titanate
The most widely used materials
Relatively cheap to manufacture
Mechanically and chemically robust.





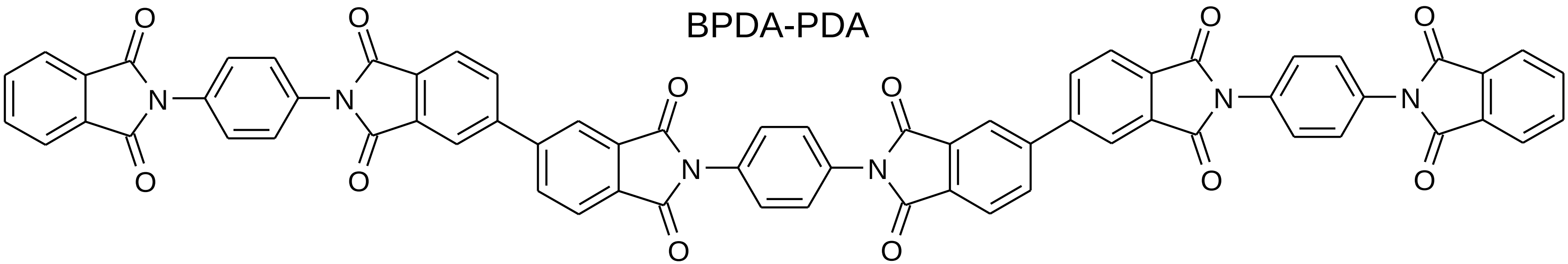
Development of FLC's is a well explored field in the last decade, due to their strong technological applications in liquid crystal displays.



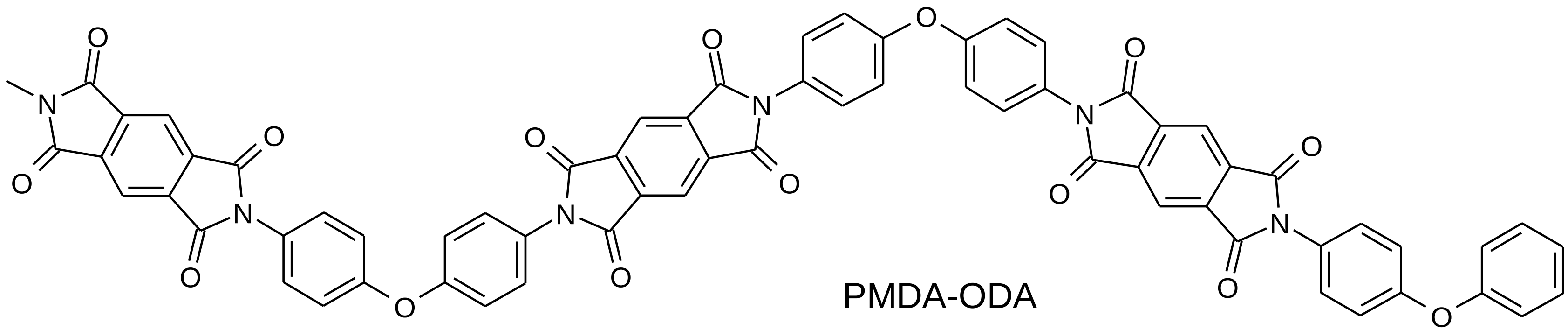
One of the mayor task is to find a system able to align preferentially molecules with a good order degree and strong enough anchoring forces.

Nowadays, coated surfaces with mechanically oriented polyamide are one of the most used approach.
Other improvements are carried out by using fotolaignement of azodyes.
This last approach avoid generation of induced charges that later on can produce screen defects.

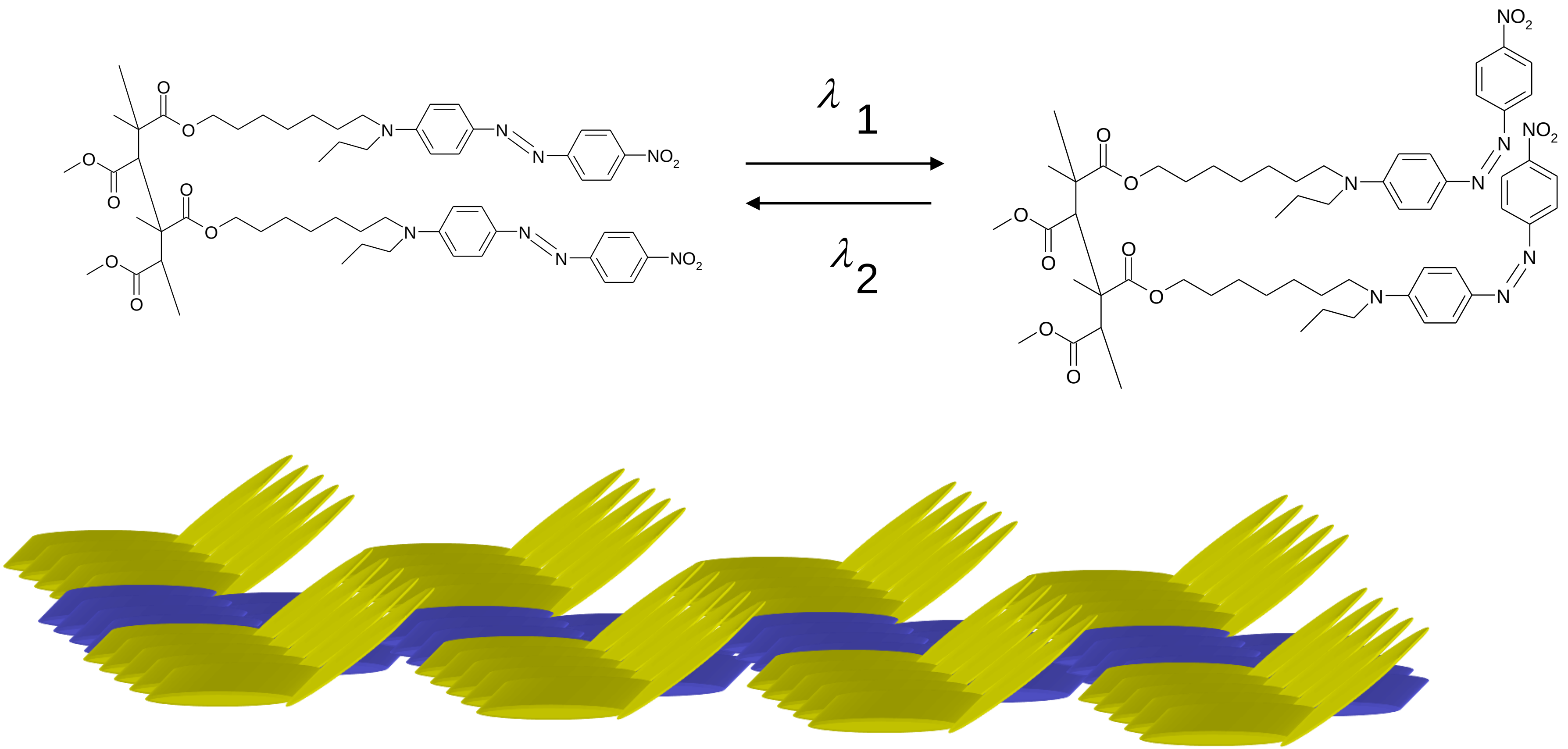
Polyamide



Macromolecules, **31**, 1930 (1998).



Macromolecules, **29**, (1996), 8335.


λ 1
λ 2

PM6R8-33%

PM6R12-33%