

50376
1986
185-2

50376
1986
185-2

RESULTATS EXPERIMENTAUX

de la Thèse présentée par

Romain NJEUMO

**CONTRIBUTION A L'ETUDE DE LA DYNAMIQUE
MOLECULAIRE DANS LES POLYMERES
CRISTAUX LIQUIDES PAR RELAXATION
DIELECTRIQUE A LARGE BANDE DE FREQUENCES**



FICHER DES
RESULTATS EXPERIMENTAUX

Nous présentons ici les résultats obtenus sur l'ensemble des échantillons étudiés. Afin de bien identifier les mécanismes moléculaires qui interviennent lors des mesures diélectriques, nous avons travaillé sur des échantillons orientés et sur des séries de polymères cristaux liquides obtenus par variation de la structure moléculaire. Les échantillons sont présentés individuellement sous forme de fiches où sont regroupées toutes les informations concernant l'étude statique et dynamique.

SOMMAIRE

**I - IDENTIFICATION DES MECANISMES DE RELAXATION DANS
UN POLYMERE AMORPHE, LE PMMA**

Fiche n°1, échantillon n°1 1

II - ETUDE DE POLYACRYLATES

Fiche n°2 : le PLBP12 (échantillon n°6) 5

Fiche n°3 : le PLBP10 (échantillon n°7) 17

Fiche n°4 : le PLBP28 (échantillon n°9 et
CL associé (M 28)..... 23

Fiche n°5 : le PLBP29 (échantillon n° 10) 32

Fiche n°6 : le PLBP30 (échantillon n°11)..... 38

III - ETUDE DE POLYSILOXANES

Fiche n°7 : le P4,1 (échantillon n°17) et le CL
associé (M4,1) 47

Fiche n°8 : le P4,Méthyl (échantillon n° 18)..... 59

Fiche n°9 : le P4,NO₂ (échantillon n° 22) 65

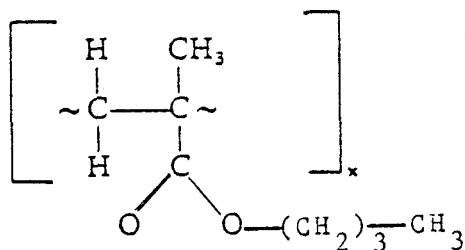
FICHE N° 1

Cette fiche concerne les principales caractéristiques diélectriques d'un polymère amorphe, le polyméthylméthacrylate (PMMA), qui est étudié depuis une trentaine d'années . Nous montrons ici pour la première fois, le comportement diélectrique du PMMA à large bande de fréquences. Ce comportement rappelle celui des polymères cristaux liquides (existence de la relaxation α liée à la transition vitreuse, et d'une relaxation supplémentaire de faible amplitude ($\epsilon''_{\text{max}} \sim 2 \cdot 10^{-1}$) liée à un mouvement de la chaîne pendante).

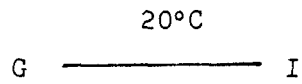
CODE DE LA SUBSTANCE : PMMA

PROVENANCE : échantillon disponible dans le commerce
(polysciences)

FORMULE STRUCTURALE :



SEQUENCE DE PHASES ET TEMPERATURES DE TRANSITION :



LISTE DES RESULTATS EXPERIMENTAUX PRESENTES :

Régime dynamique : Figure F-1 : Courbe ϵ' (F)
Figure F-2 : Courbe ϵ'' (F)

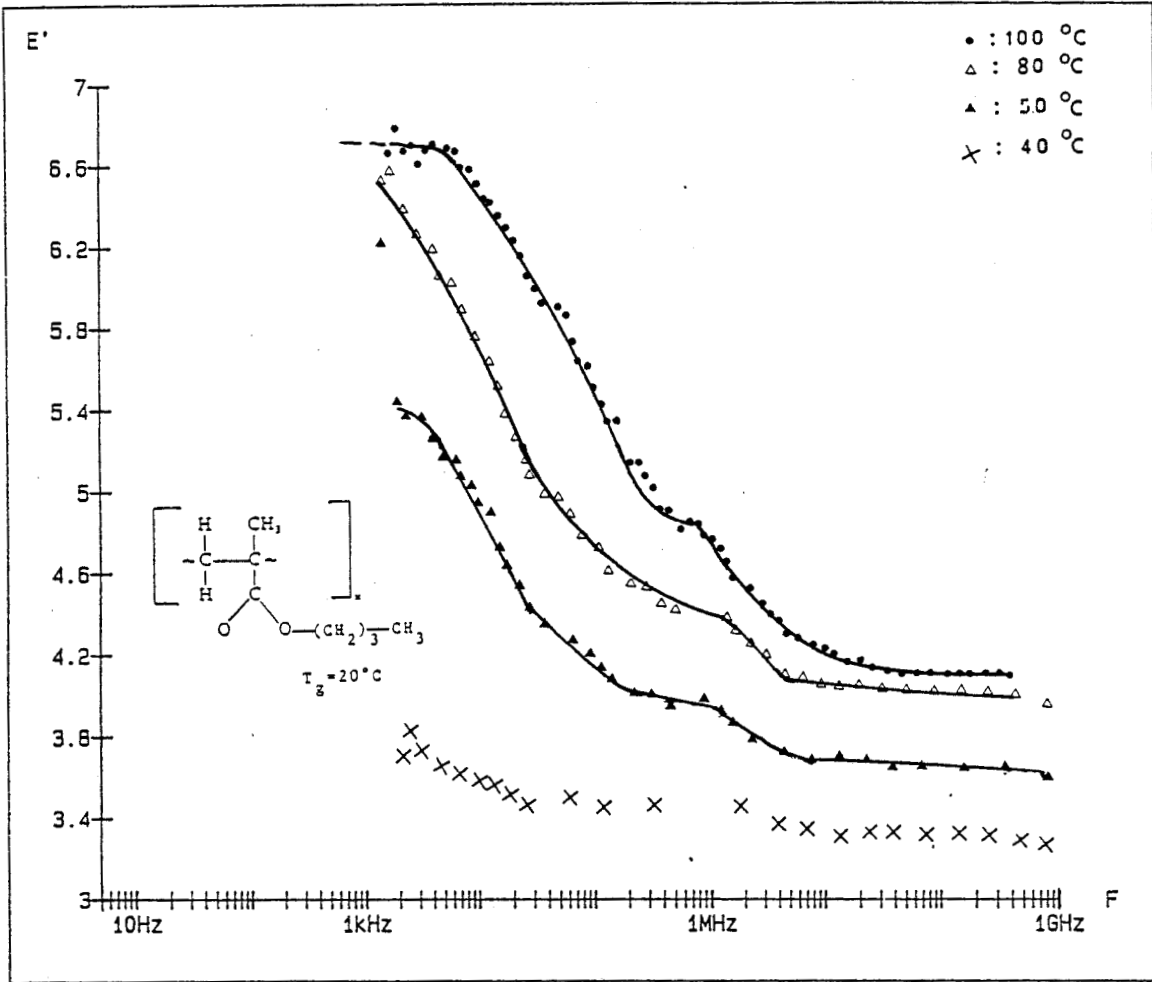


Figure F-1: PMMA Courbe ϵ' (F)



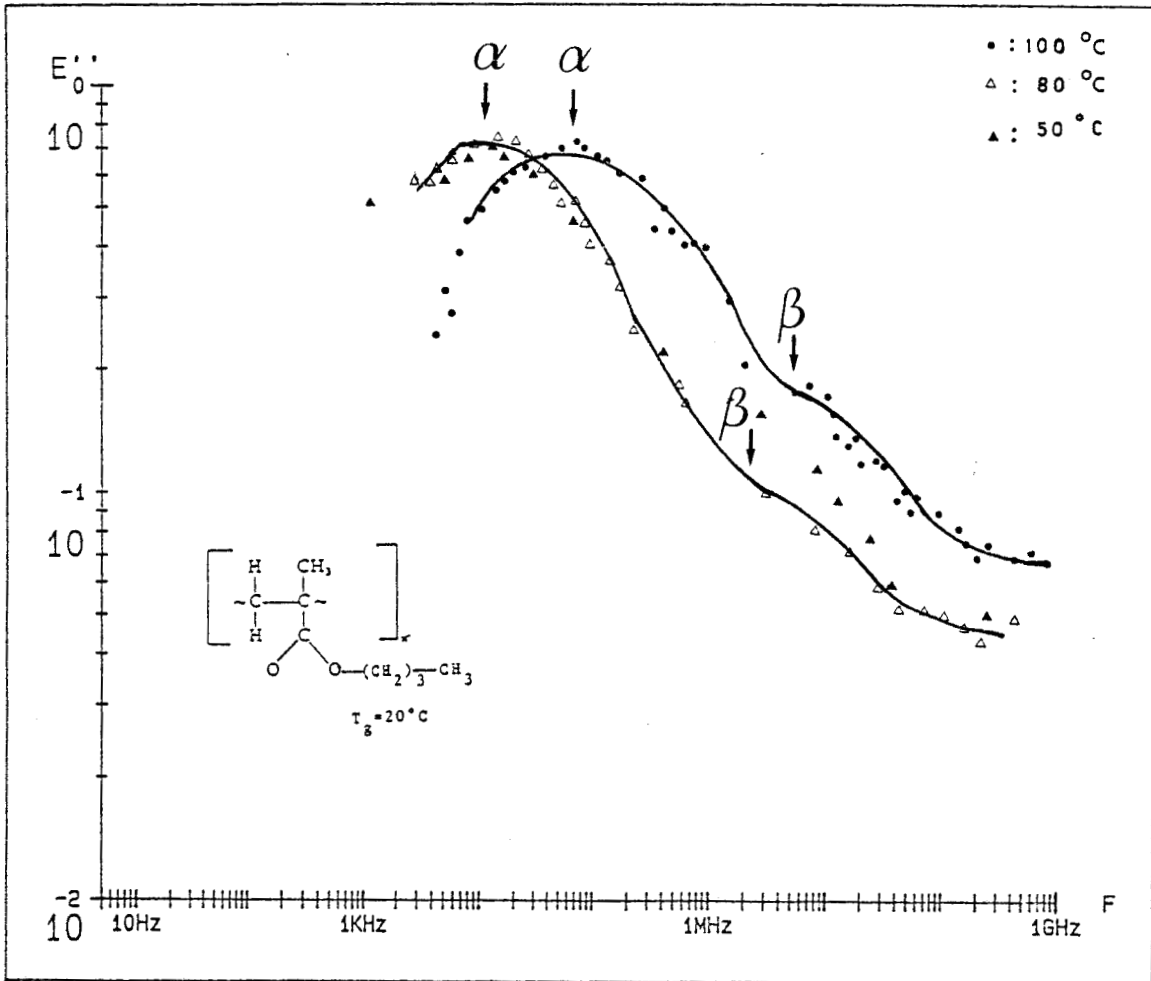


Figure F-2: PMMA Courbe ϵ'' (F)

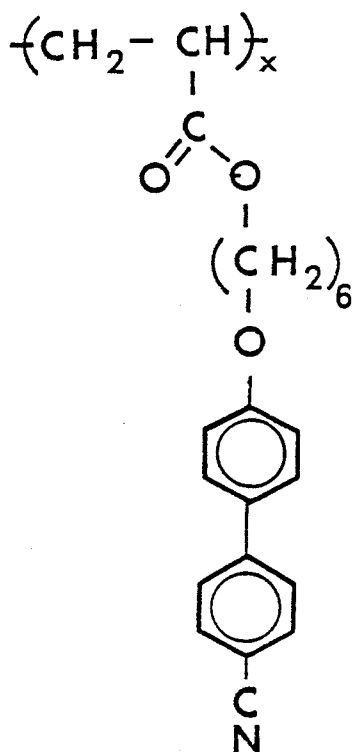


FICHE N° 2

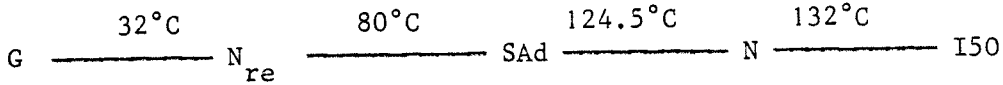
CODE DE LA SUBSTANCE : PLBP12

PROVENANCE : LCR THOMSON

FORMULE STRUCTURALE :



SEQUENCE DE PHASES ET TEMPERATURES DE TRANSITION :



LISTE DES RESULTATS EXPERIMENTAUX PRESENTES :

Régime statique

Figure F-3

Régime dynamique

- a) phase isotrope Figure F-4
- b) phase nématique, $E//n$ Figure F-5
- c) phase smectique Ad, $E//n$ Figure F-6
- " " " $E\perp n$ Figure F-7
- d) phase nématique rentrante, $E//n$ Figure F-8
- " " " $E\perp n$ Figure F-9
- e) en phase vitreuse Figure F-10

FREQUENCES CRITIQUES ET ENERGIES D'ACTIVATION :

Figure F-11 courbe $F_c = f(1/T)$

Figure F-12 courbe $W = f(n)$

Figure F-13 courbe $F_c = f(n)$

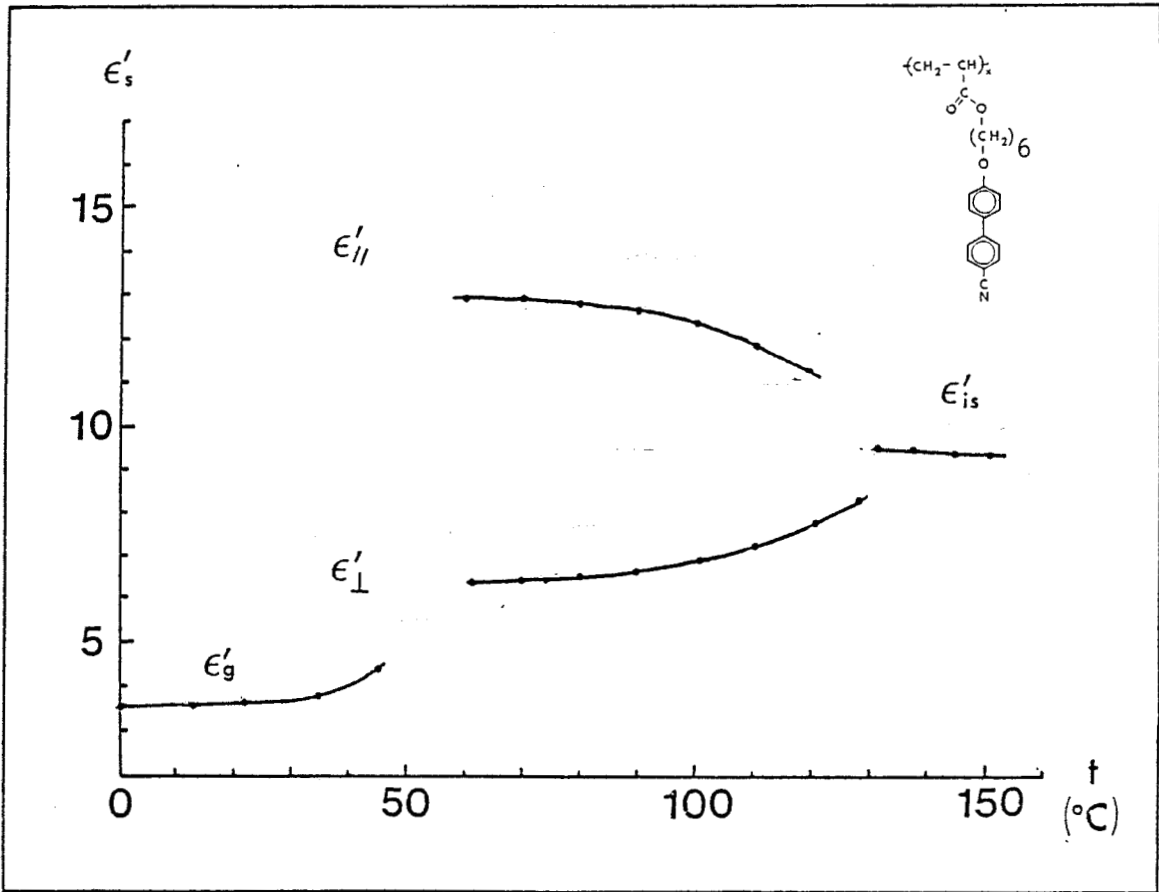
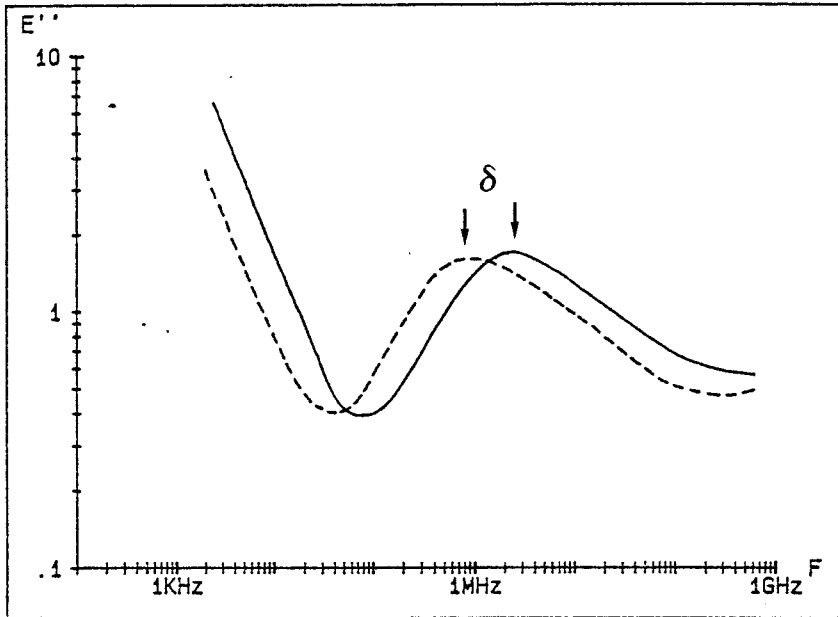
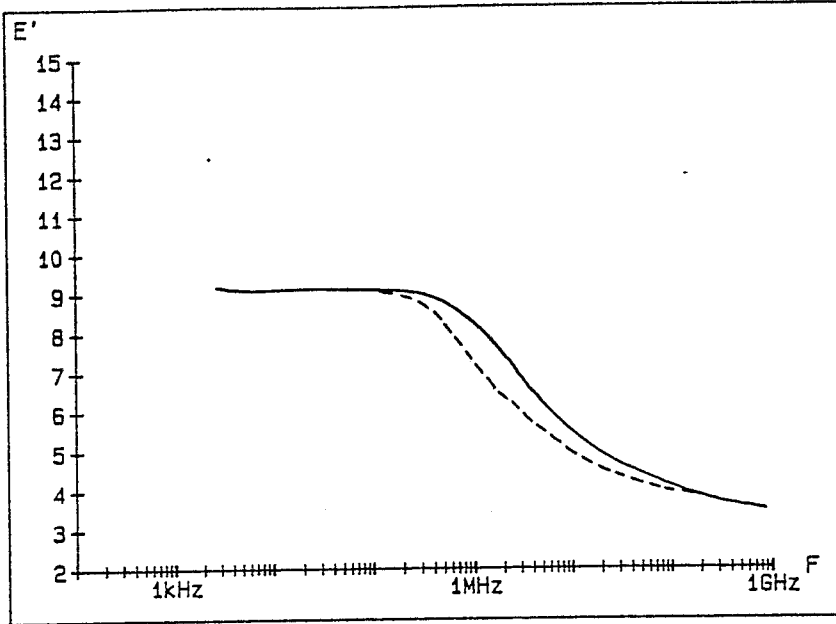


Figure F-3: Régime statique du PLBP12





— : 144°C
- - : 133°C

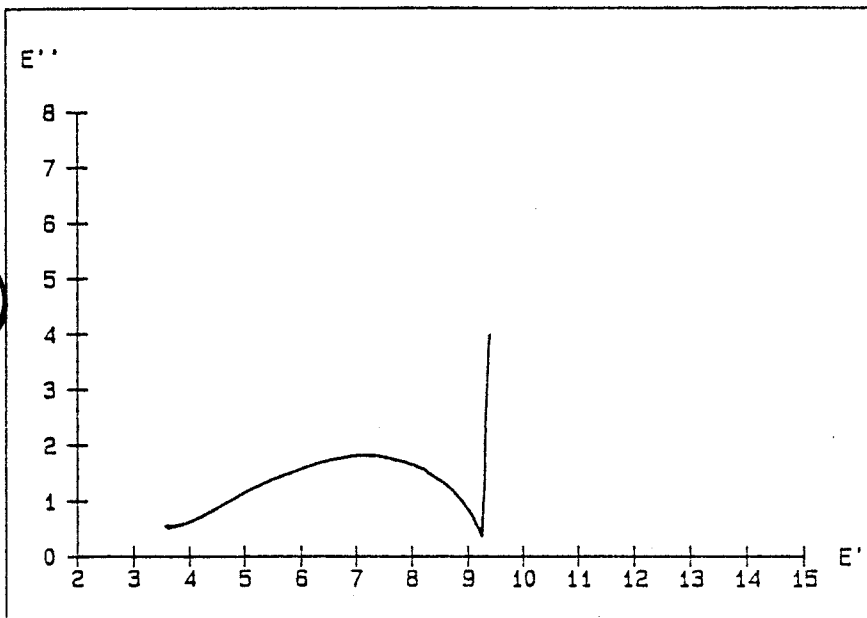
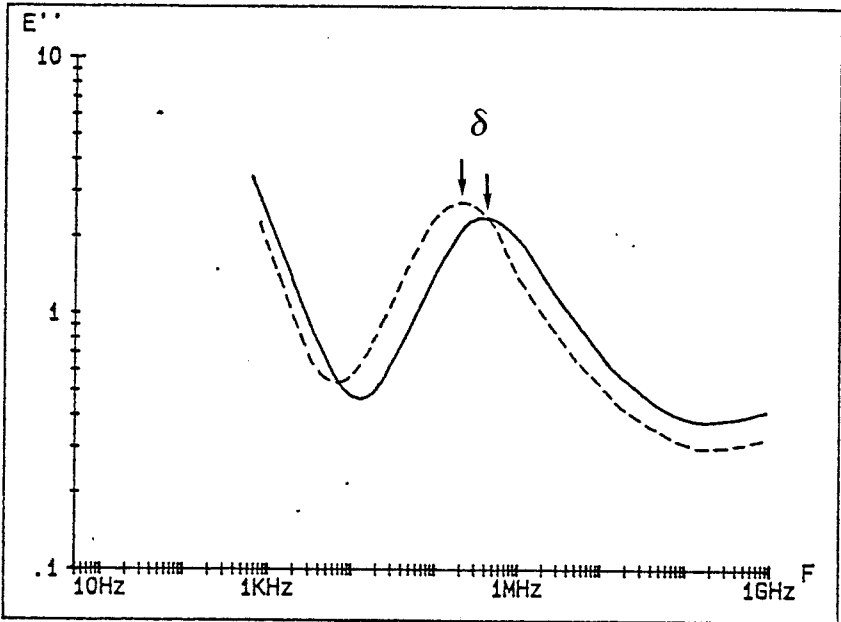
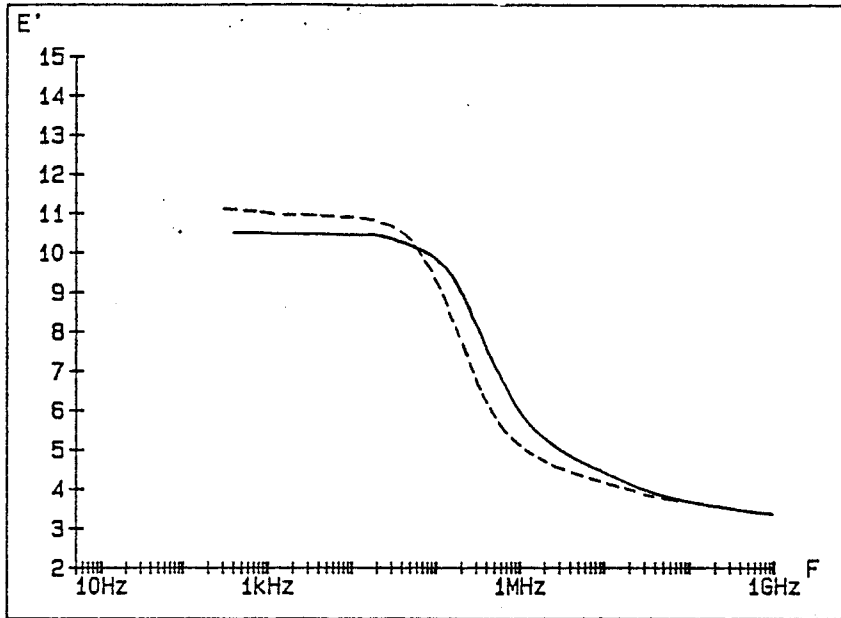


Figure F-4: PLBP12, phase I



—: 130 °C
- - : 125 °C

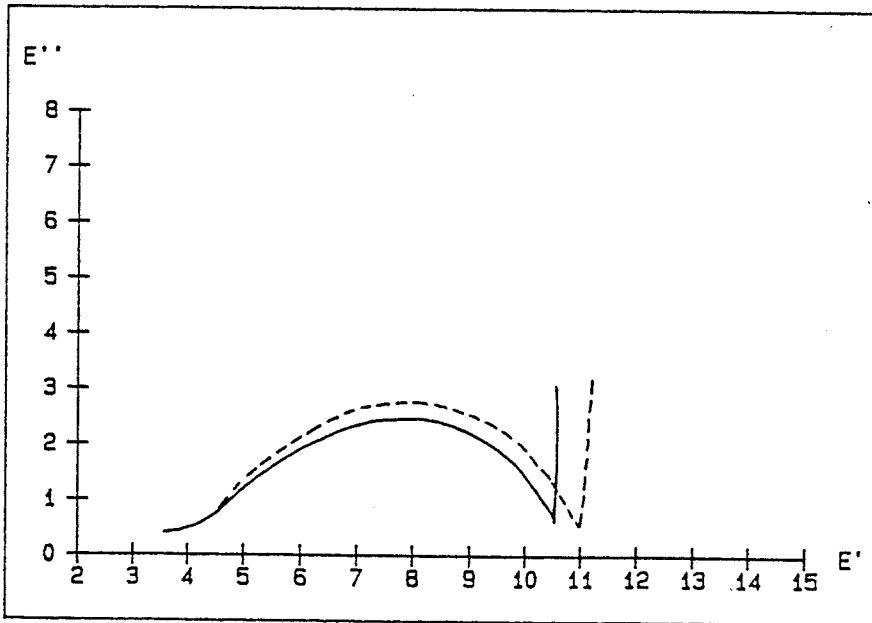
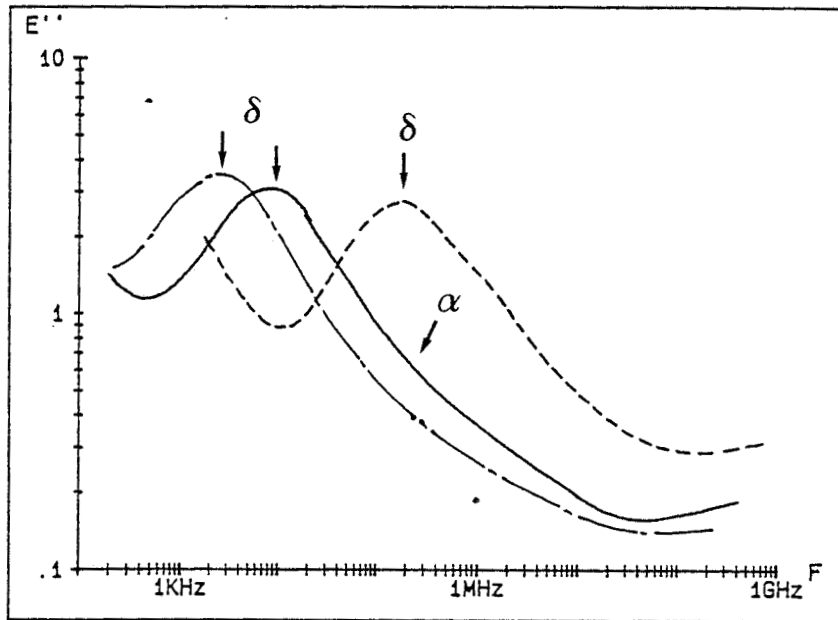
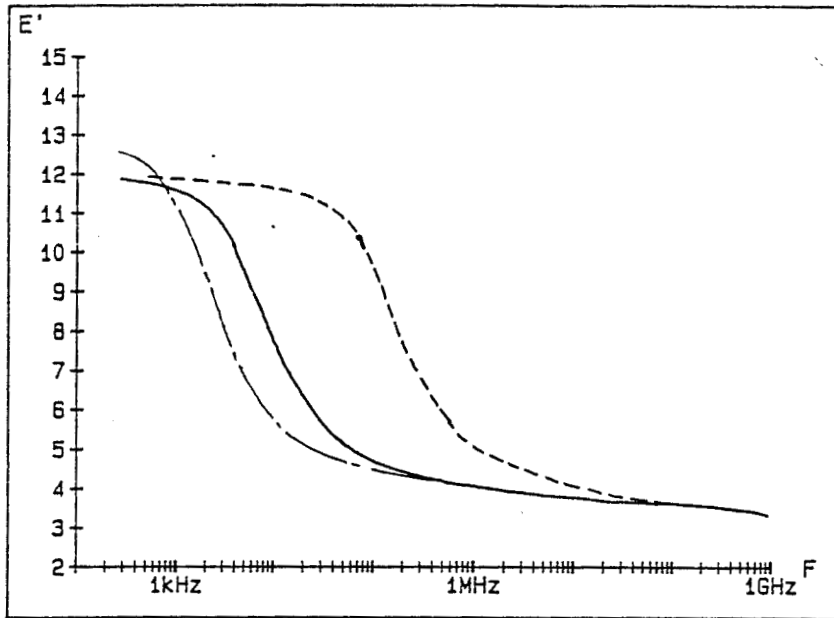
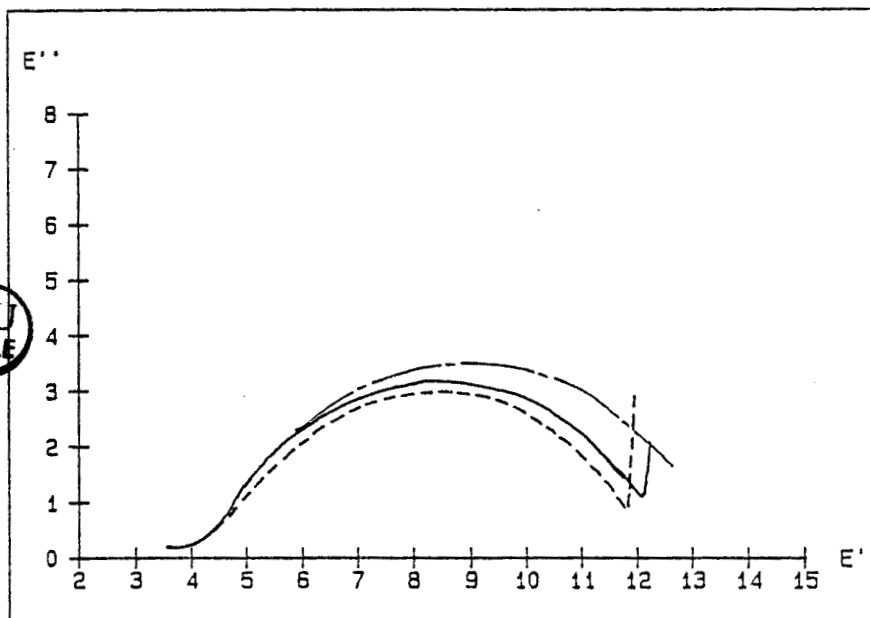


Figure F-5: PLBP12, phase N //



--:120 °C
—:91 °C
-·-:82 °C



BU
LILLE

Figure F-6: PLBP12, phase S_{Ad} //

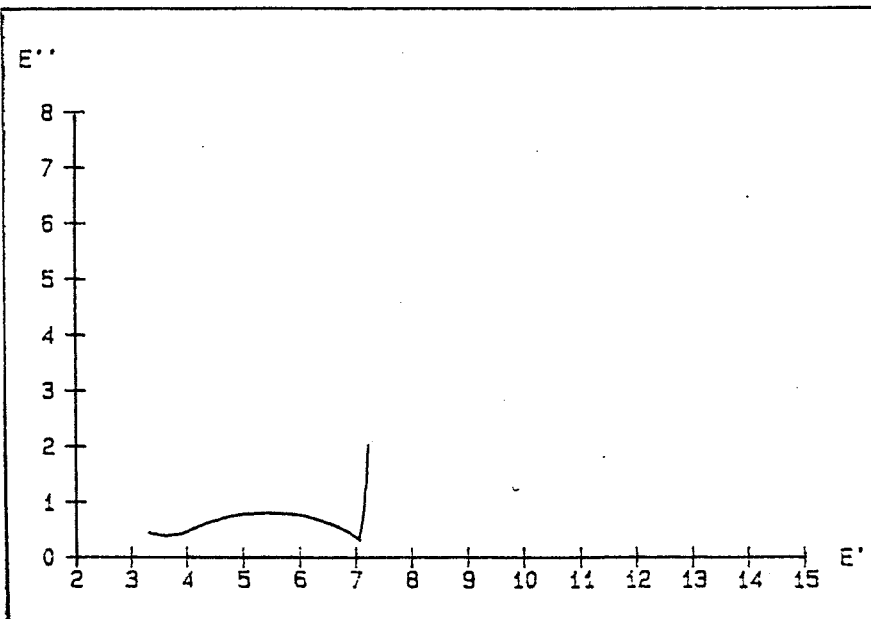
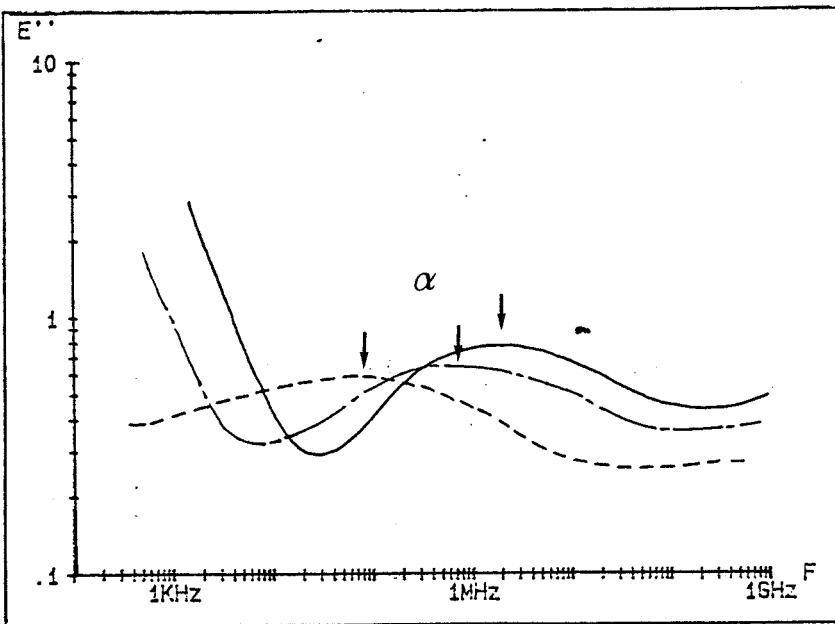
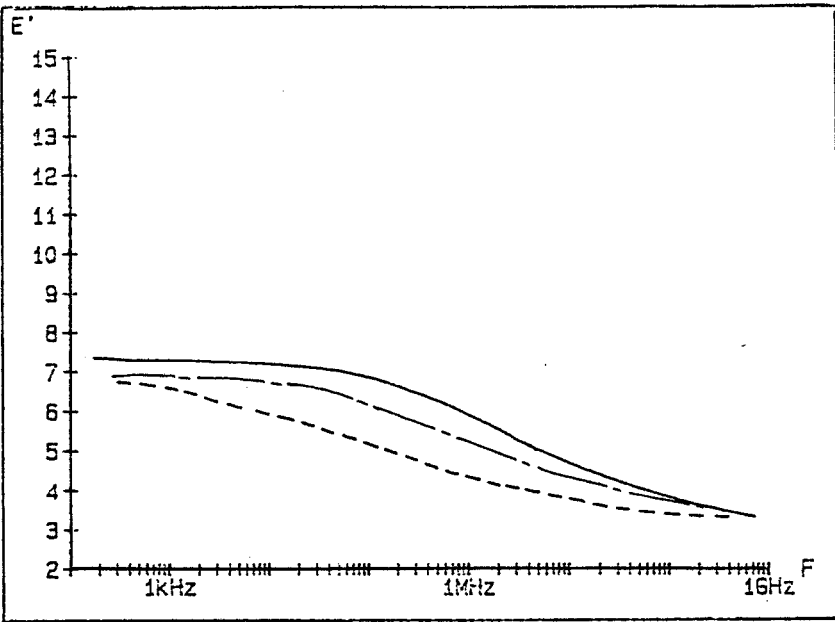
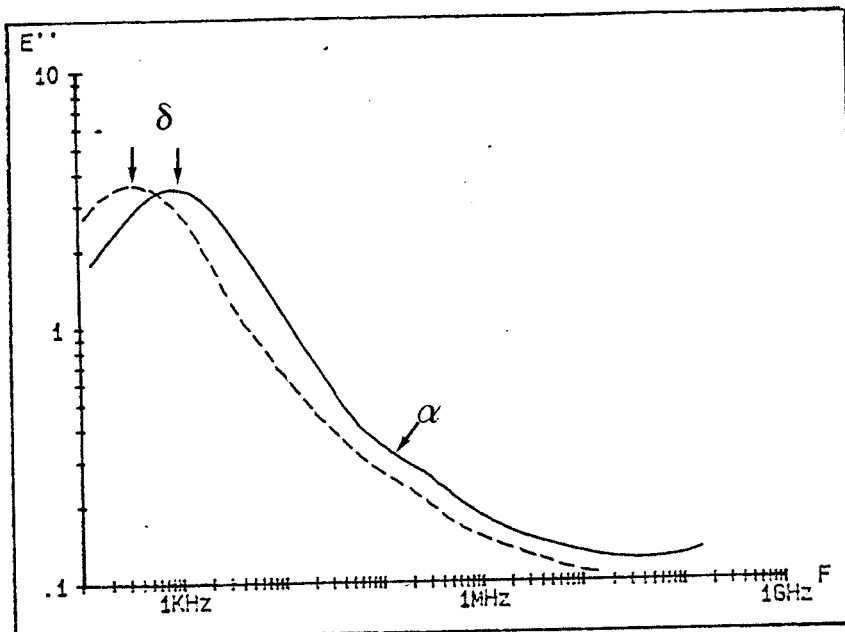
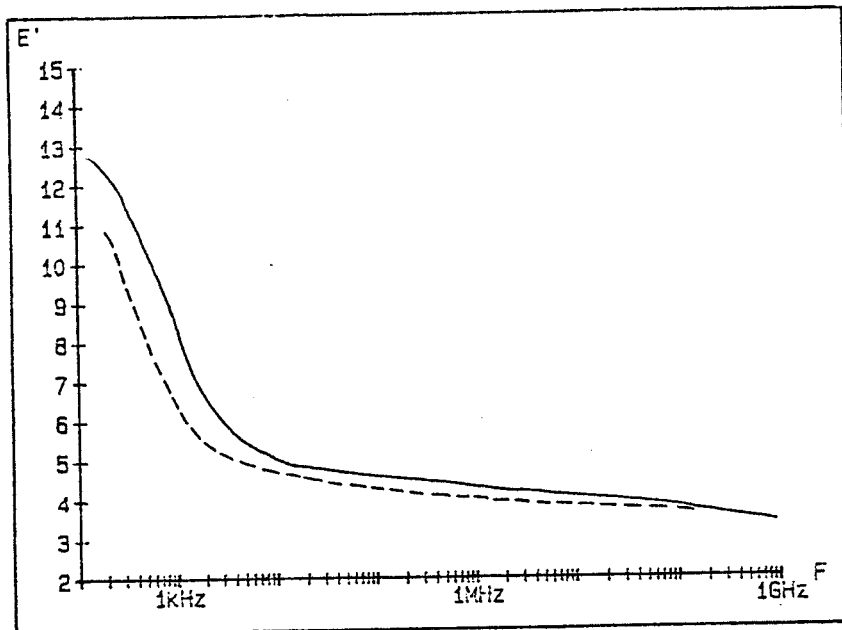


Figure F-7: PLBP12, phase S_{Ad} E_{In}



— : 76 °C
- - : 71 °C

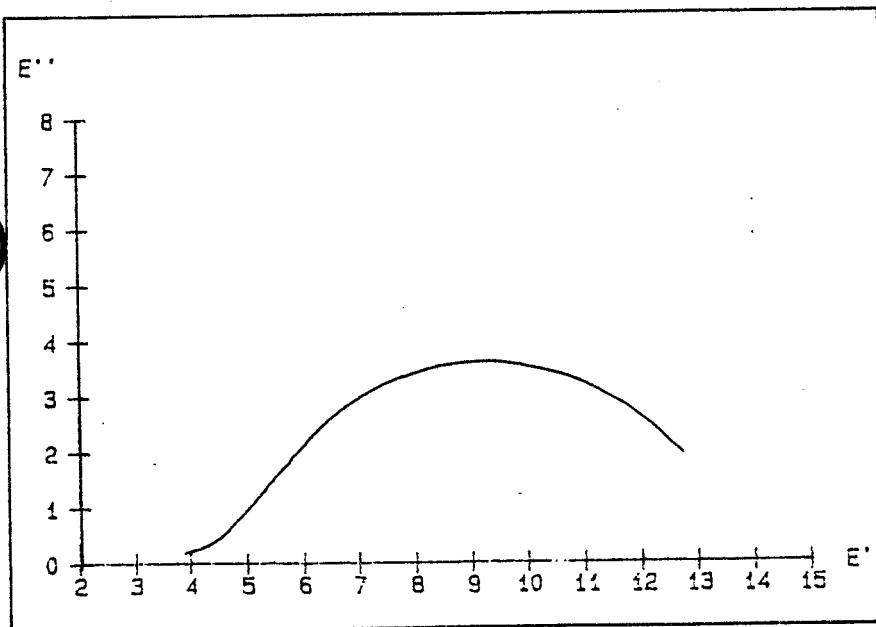
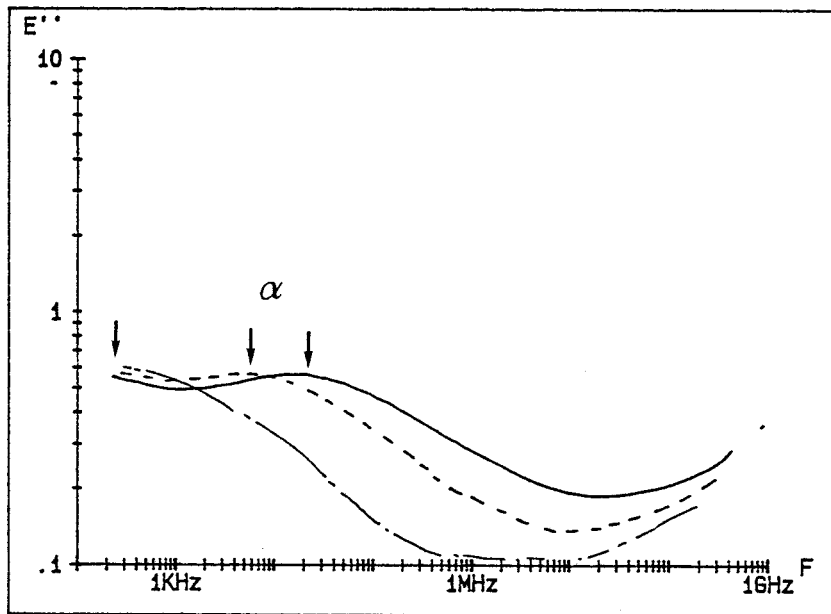
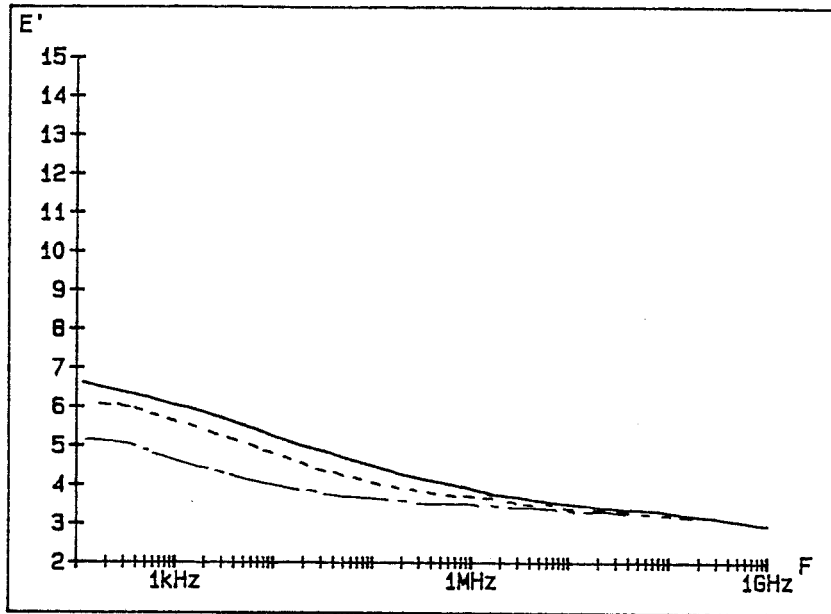


Figure F-3: PLBP12, phase $N_{re} E//n$



—: 72 °C
--: 63 °C
-·-: 53 °C

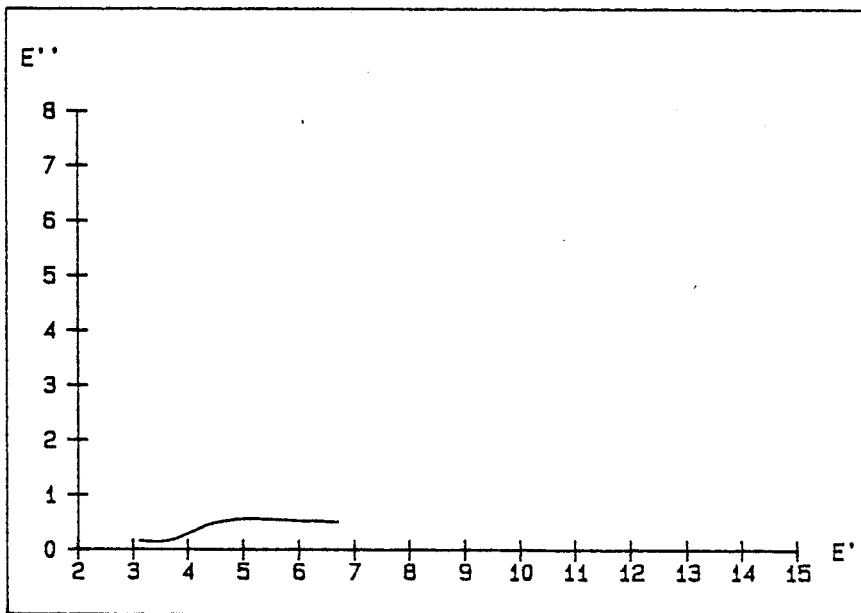


Figure F-9: PLBP12, phase N_{re} E_{in}

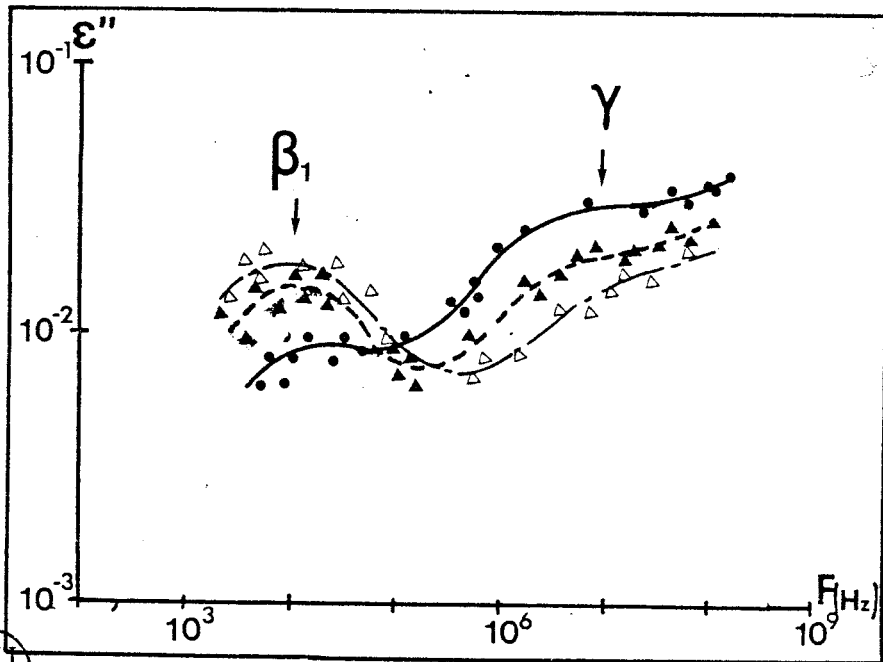
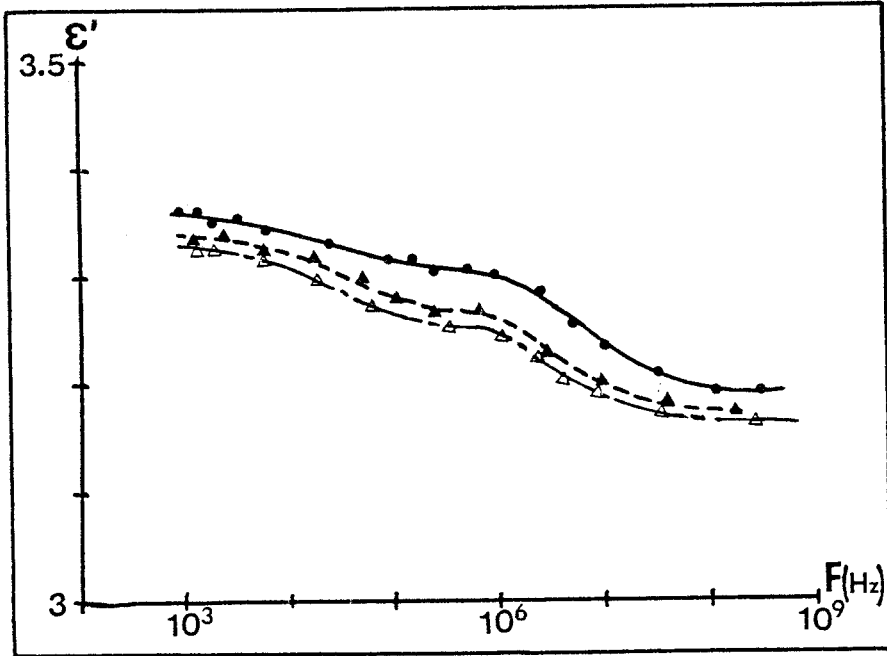


Figure F-10: Phase vitreuse du PLBP12

● : -30°C

▲ : -52°C

△ : -62°C

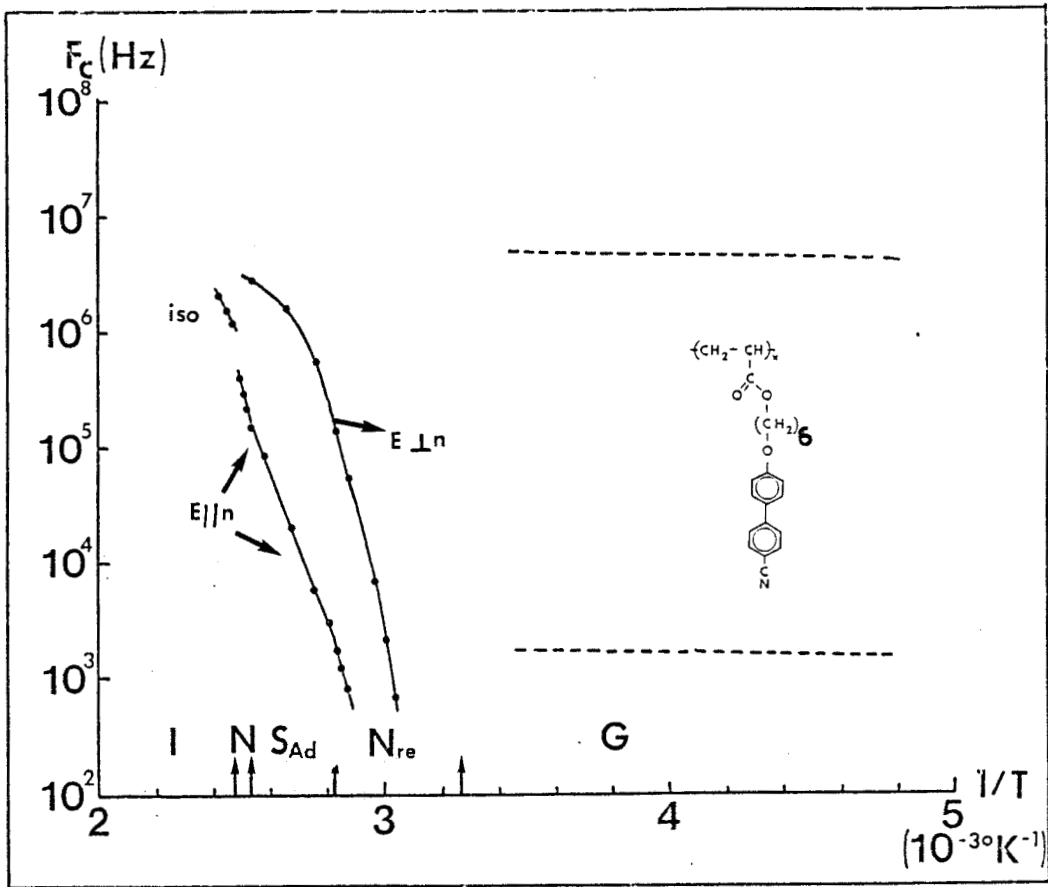


Figure F-11: Courbe $F_c = f(T^{-1})$ pour le PLBP12

(Les pointillés indiquent une allure qualitative, les pertes diélectriques étant très faibles en phase vitreuse) .



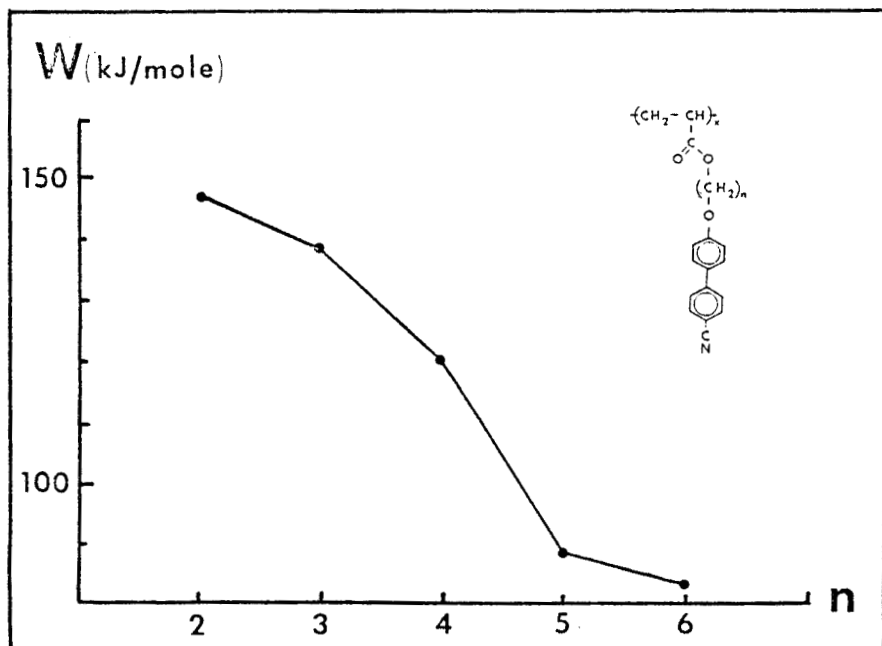
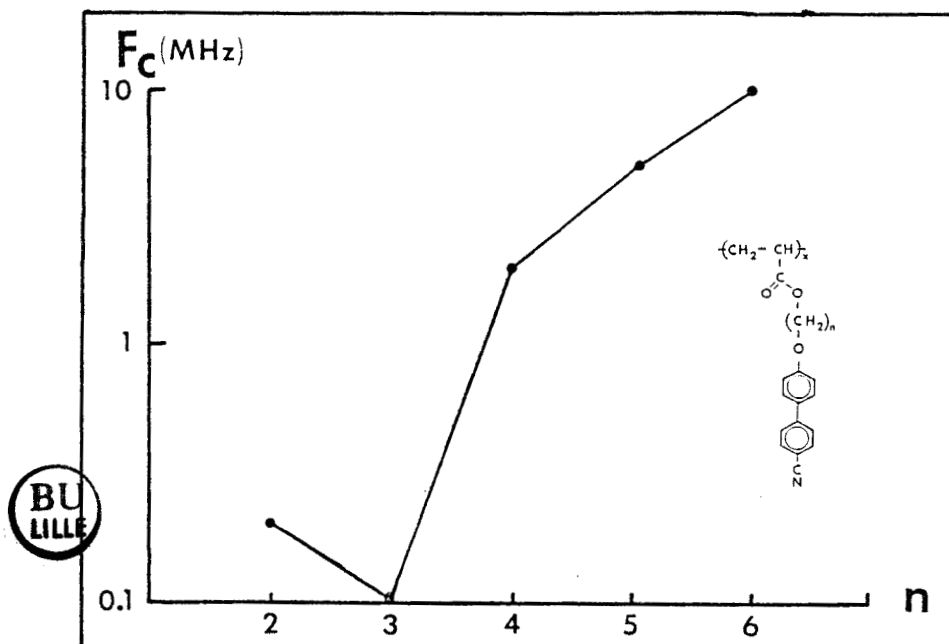


Figure F-12: Courbe $W=f(n)$ pour la série de polyacrylates (échantillons 2 à 6), phase isotrope



BU
LILLE

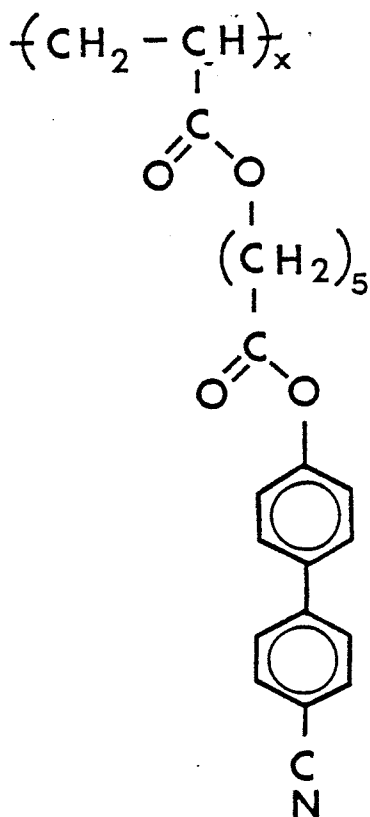
Figure F-13: Courbe $F_c=f(n)$ à $T/T_{NI} = 1.1$, pour la série de polyacrylates (échantillons 2 à 6), phase isotrope

FICHE N° 3

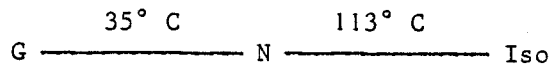
CODE DE LA SUBSTANCE : PLBP10

PROVENANCE : LCR THOMSON

FORMULE STRUCTURALE :



SEQUENCE DES PHASES ET TEMPERATURES DE TRANSITION :



LISTE DES RESULTATS EXPERIMENTAUX PRESENTES

Régime statique

Figure F-14

Régime dynamique

- a) en phase isotrope Figure F-15
- b) en phase nématique Figure F-16 (E//n)
Figure F-15 (E⊥n)

FREQUENCES CRITIQUES ET ENERGIES D'ACTIVATION

Figure F-17 Courbe $F_c = f(1/T)$

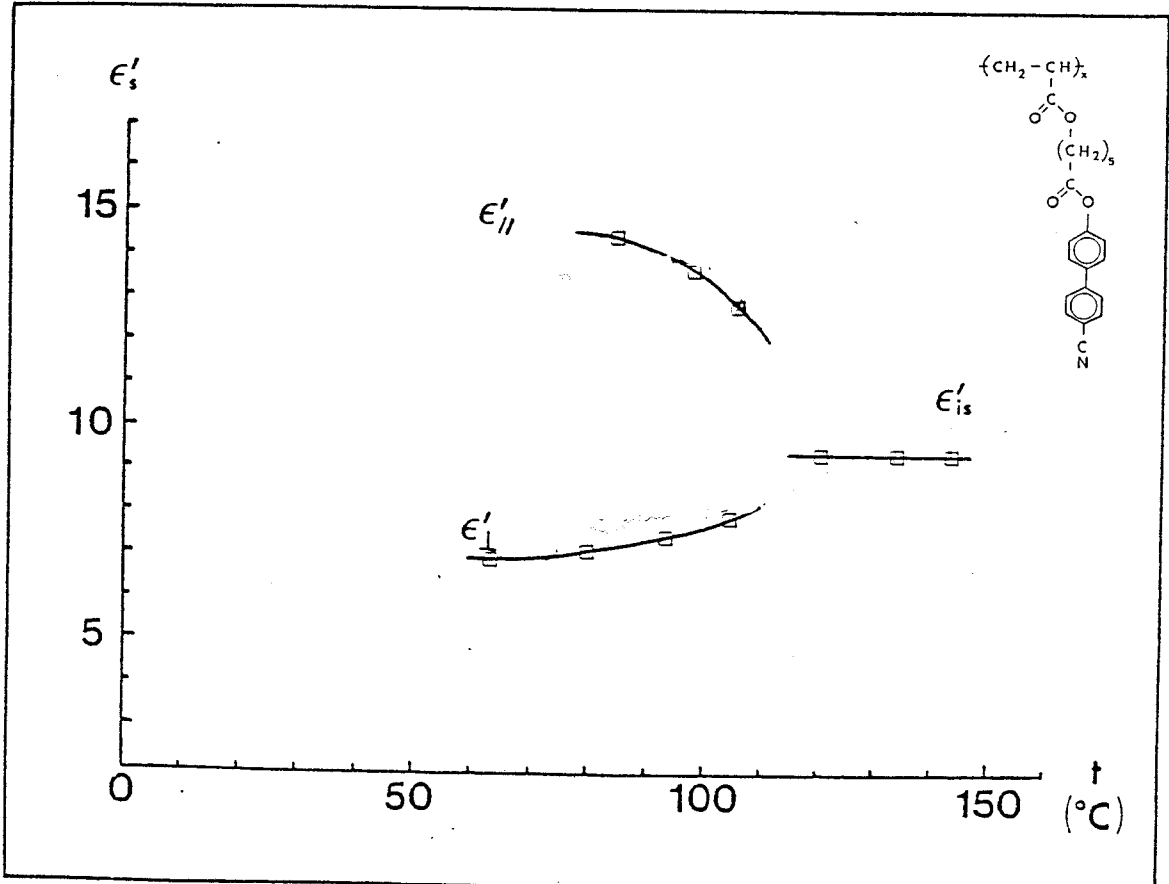
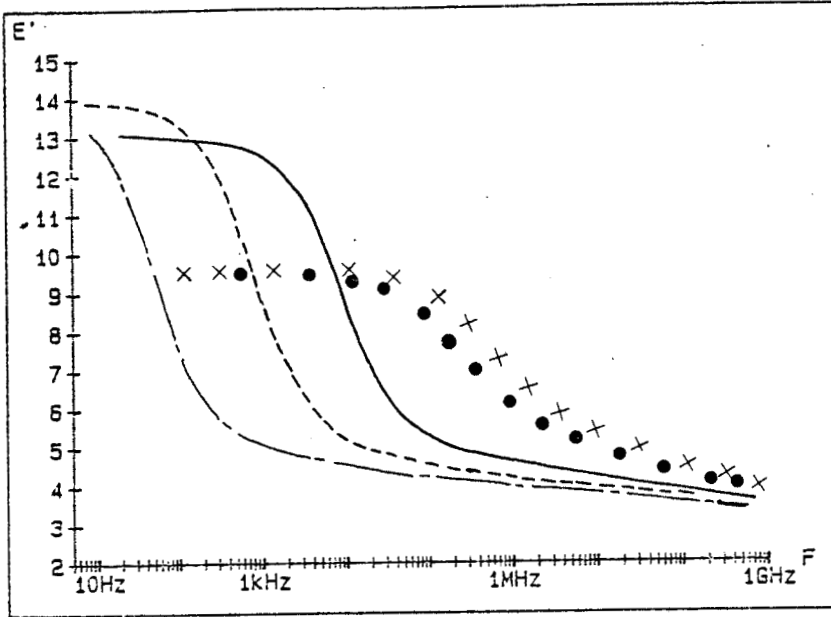
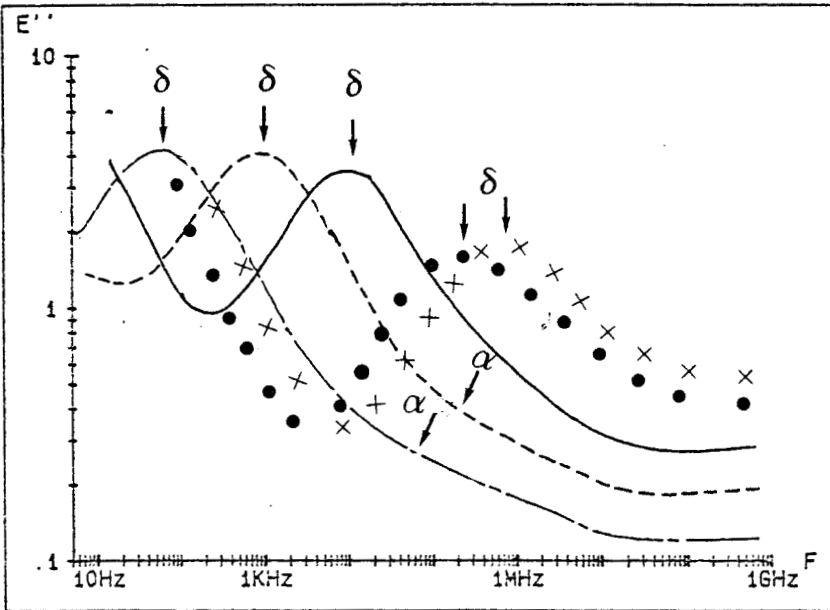


Figure F-14: Régime statique du PLBP10



x Iso 129°C
 • ISO 120°C



—:105°C
 ---:90°C N//
 -·-:75°C

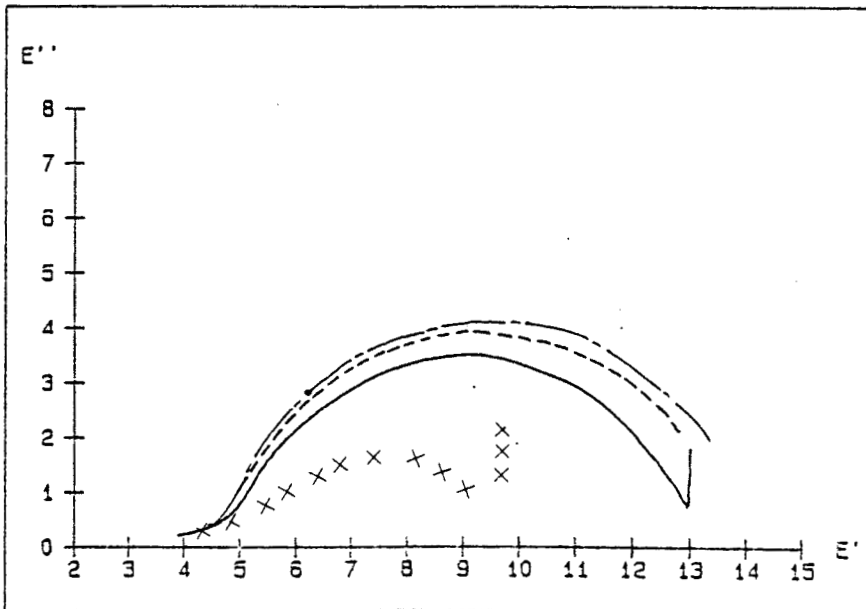
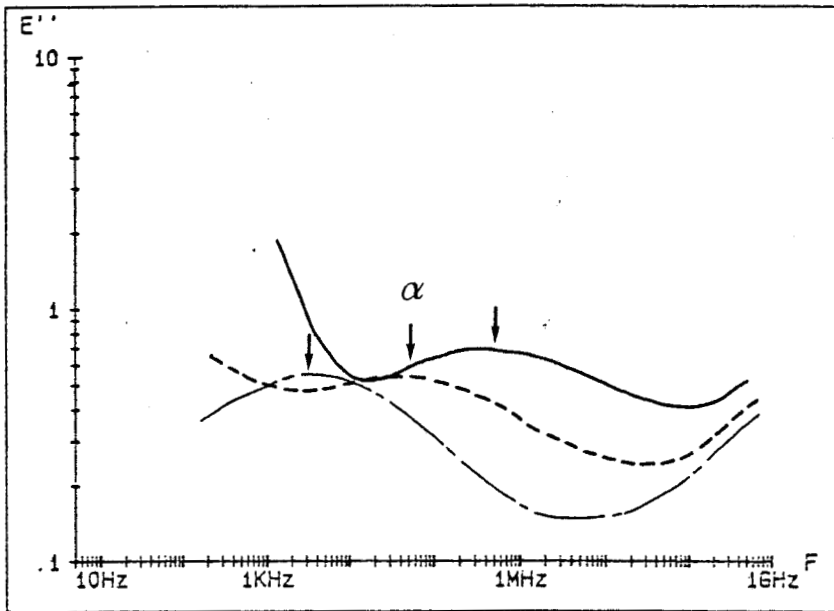
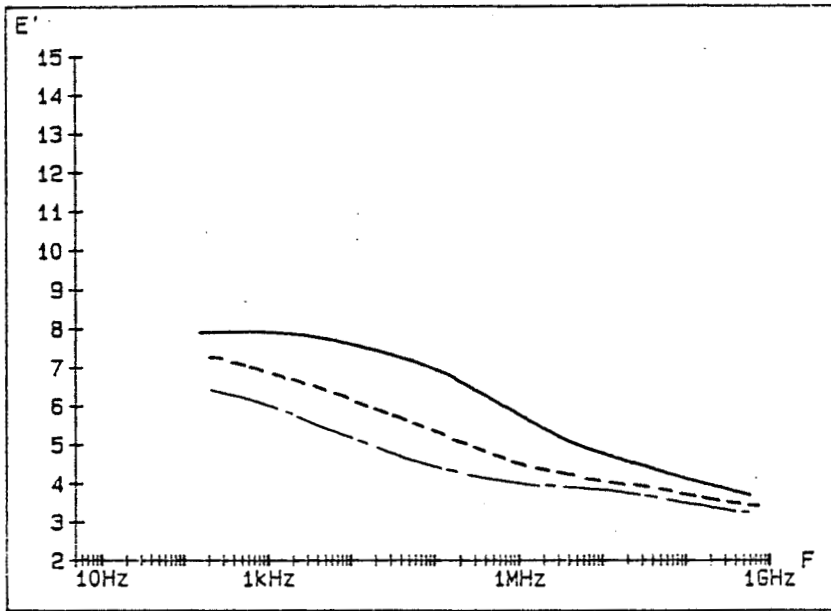


Figure F-15 :PLBP10, phase N, E//n ; et phase iso(x,•).



—:105°C
--:90°C
-·-:75°C

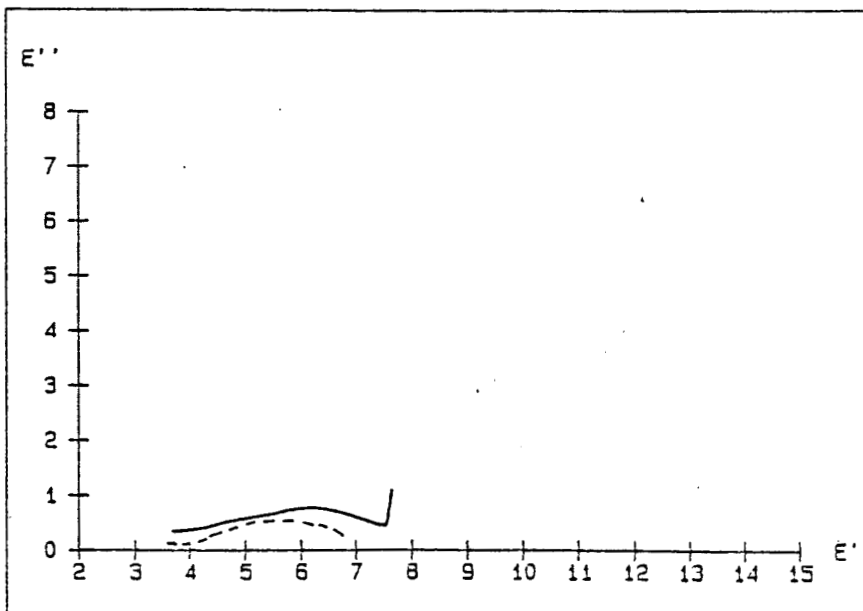


Figure F-16: PLBP10, phase N, E' in

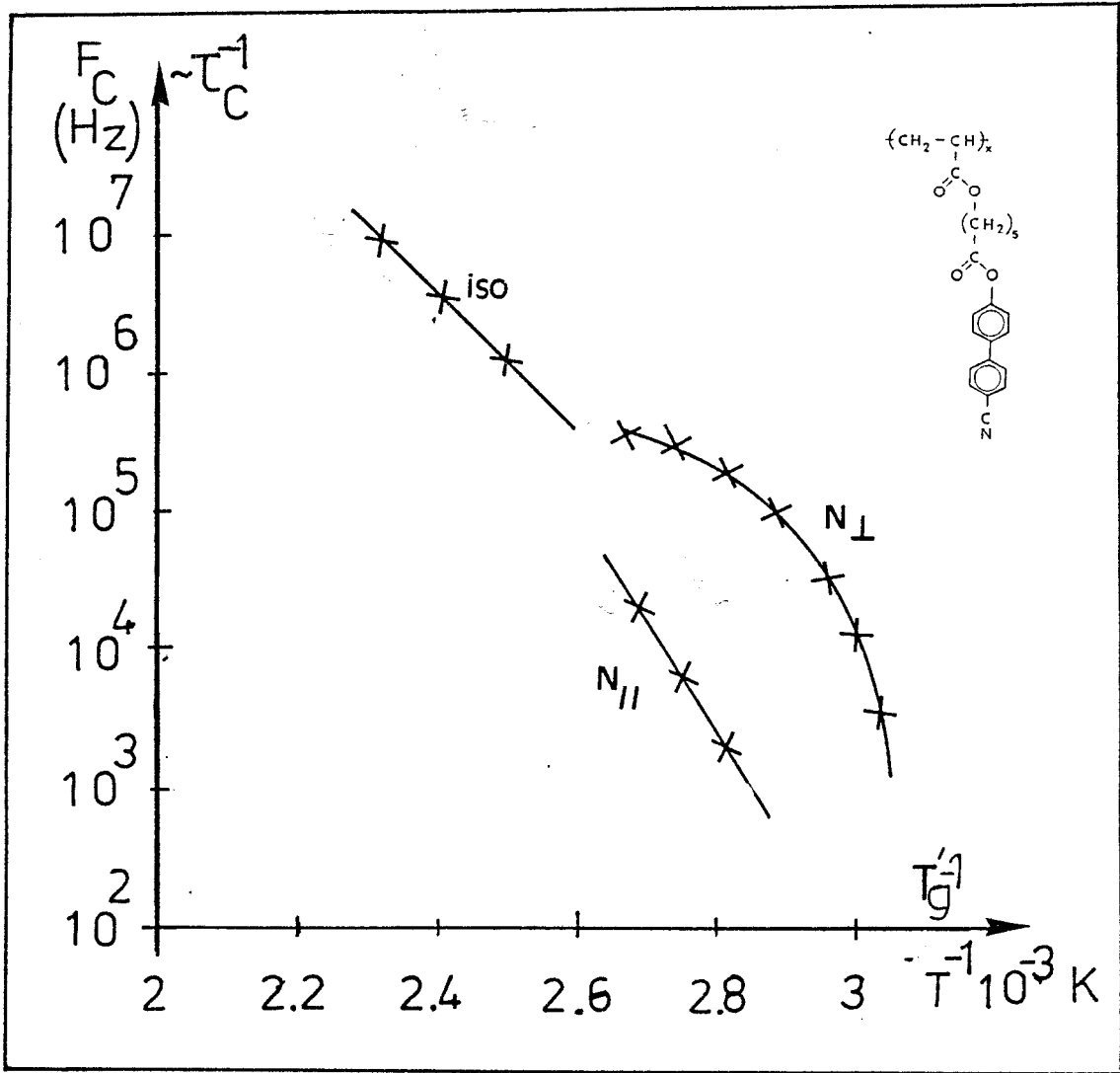


Figure F-17: Courbe $F_C = f(1/T)$ pour le PLBP10

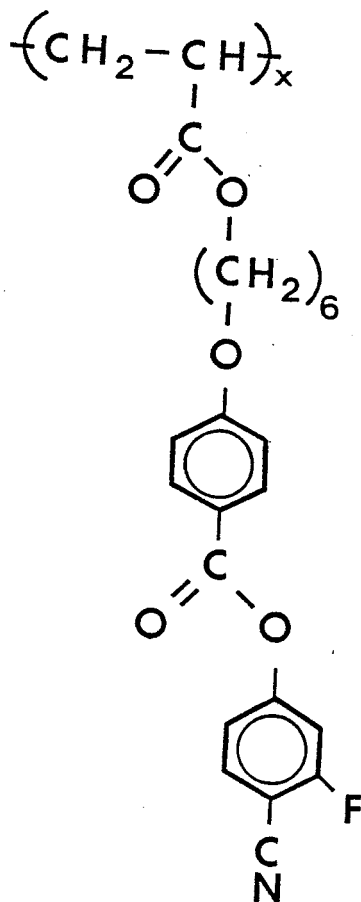


FICHE N° 4

CODE DE LA SUBSTANCE : PLBP28

PROVENANCE : LCR THOMSON

FORMULE STRUCTURALE



SEQUENCE DE PHASES ET TEMPERATURES DE TRANSITION :

G ———— 17° C ———— N ———— 69.5° C ———— Iso

LISTE DES RESULTATS PRESENTES :

Régime statique :

Figure F -18

Régime dynamique :

- a) phase isotrope Figure F-20
- b). phase nématique : E//n Figure F-21
- E⊥n Figure F-22

FREQUENCES CRITIQUES ET ENERGIES D'ACTIVATION

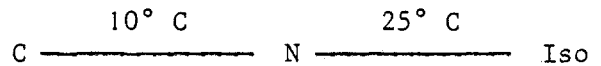
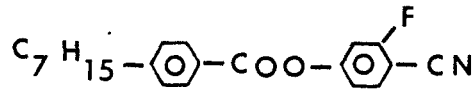
Figure F-23 : courbe $F_c = f(1/T)$

CRISTAL LIQUIDE DE FAIBLE POIDS MOLECULAIRE ASSOCIE AU PLBP28

CODE DE LA SUBSTANCE : M28

PROVENANCE : LCR THOMSON

FORMULE STRUCTURALE :



LISTE DES RESULTATS EXPERIMENTAUX PRESENTES :

Régime statiqueFigure F-19

Régime dynamiqueFigures F-20 à F-23

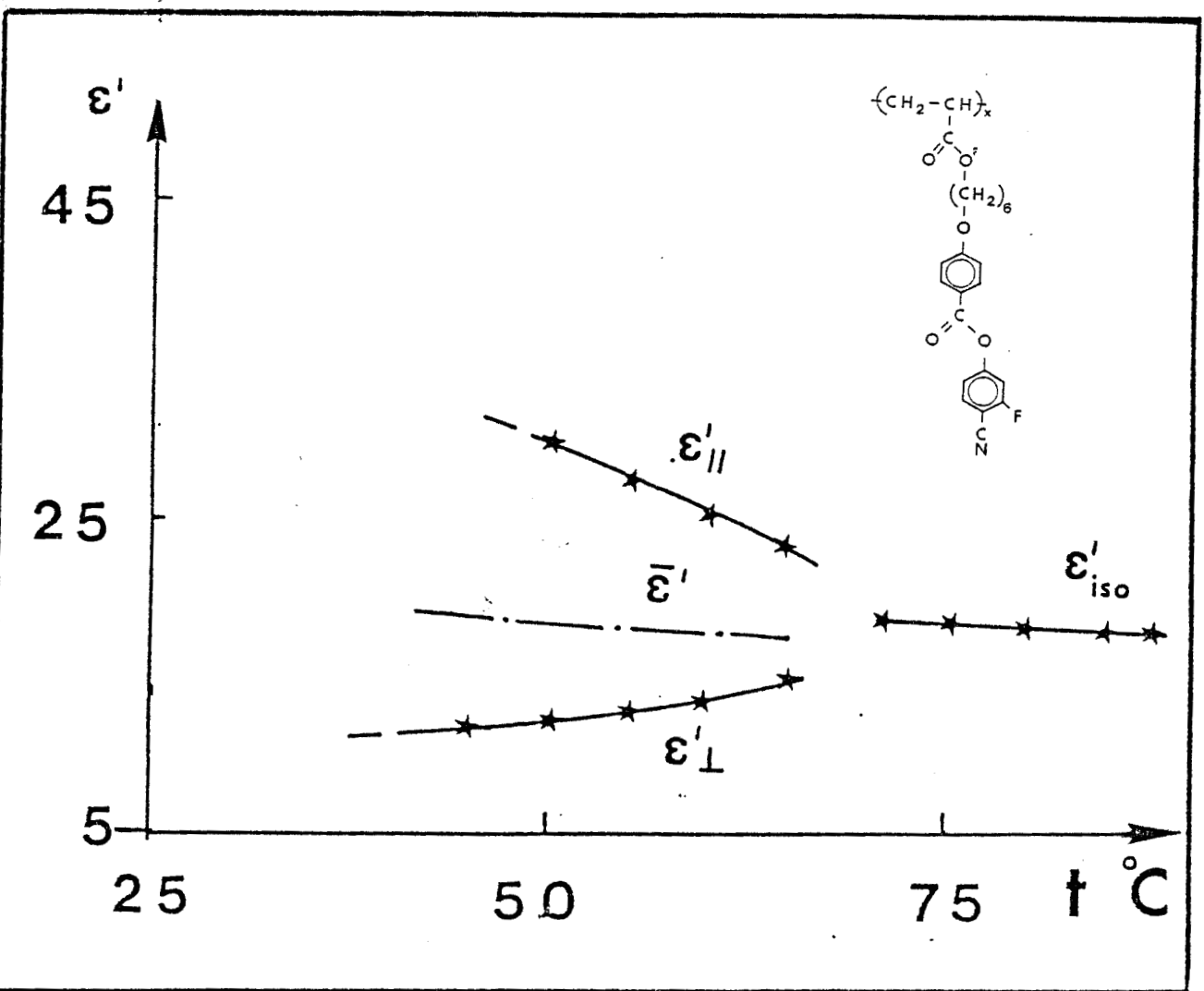


Figure F-18: Régime statique du PLBP28

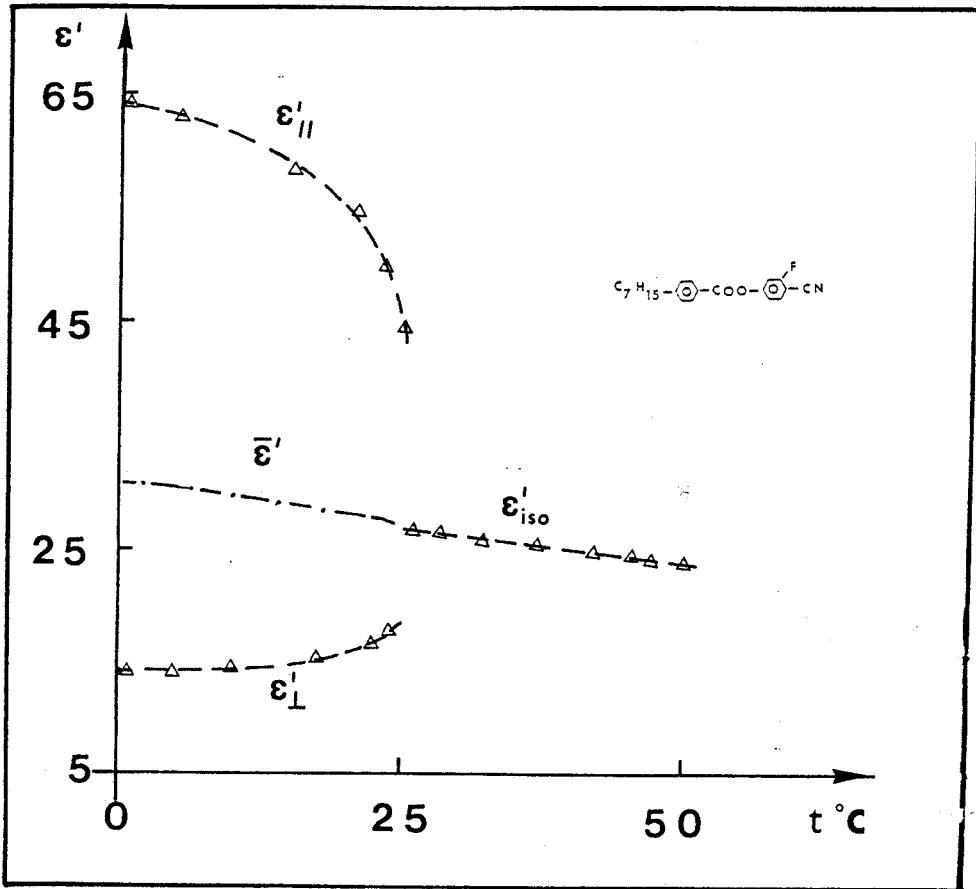


Figure F-23: Régime statique du M28



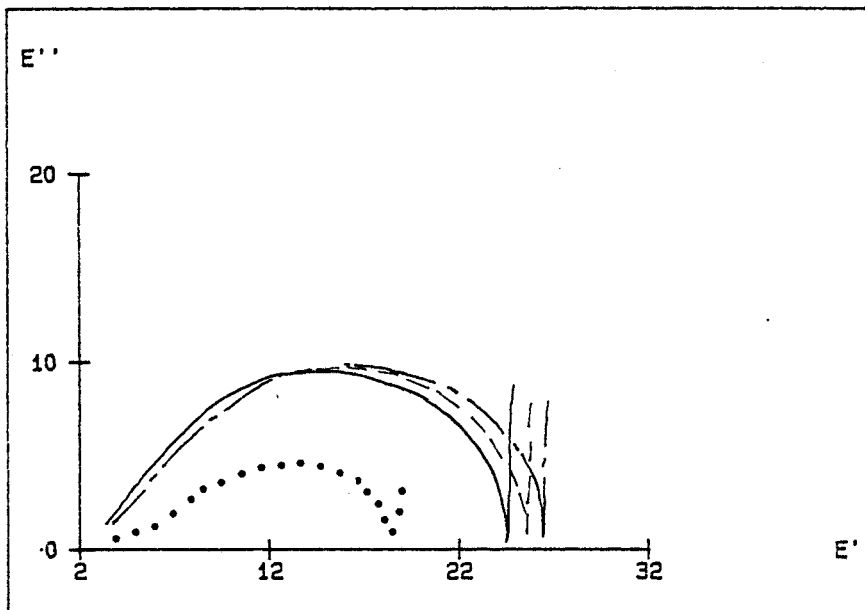
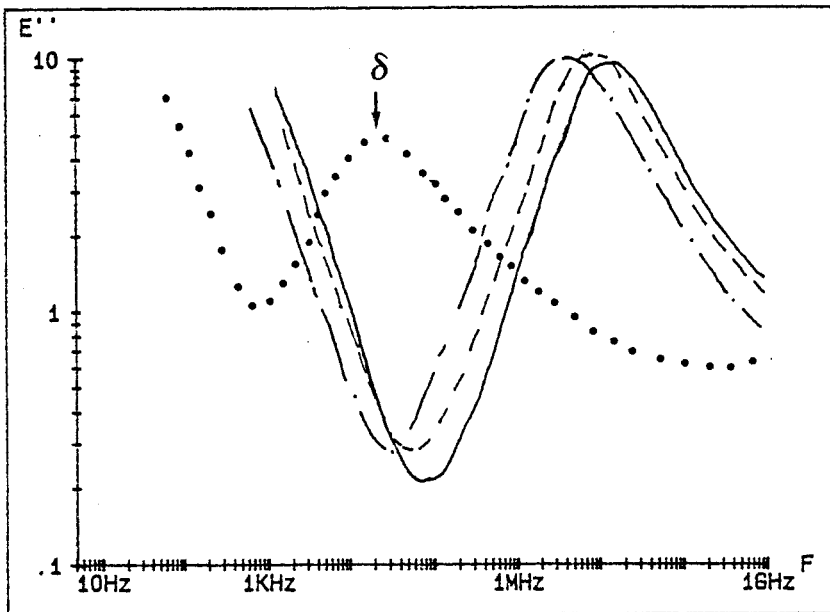
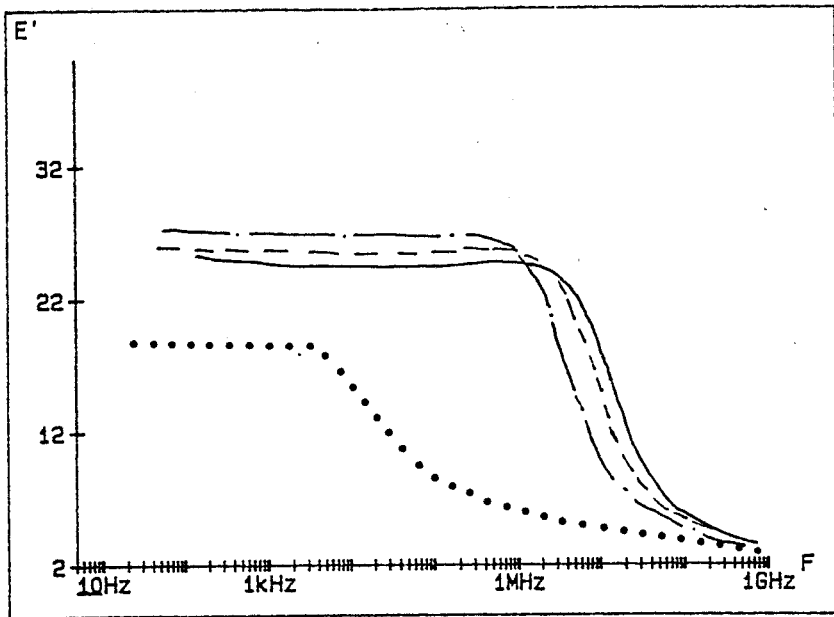


Figure F-19: PLBP28 et M28(LMWLC) , Iso

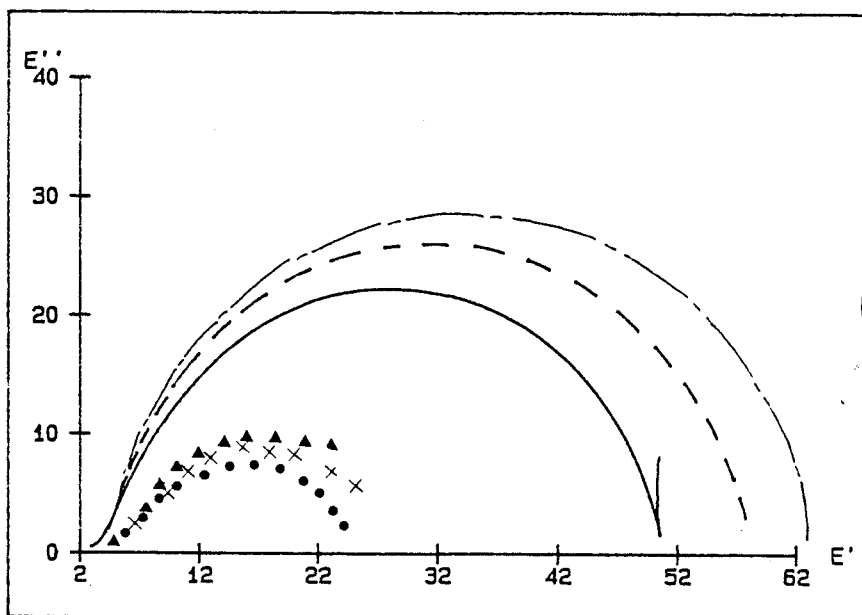
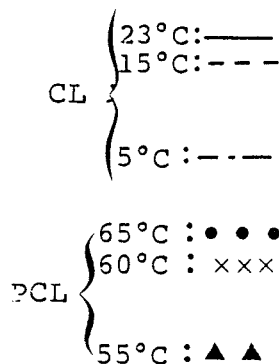
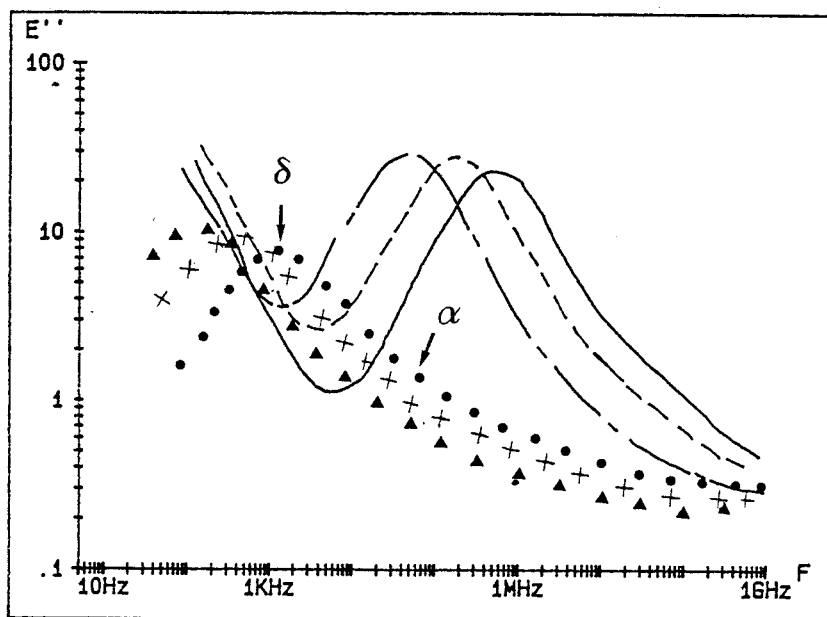
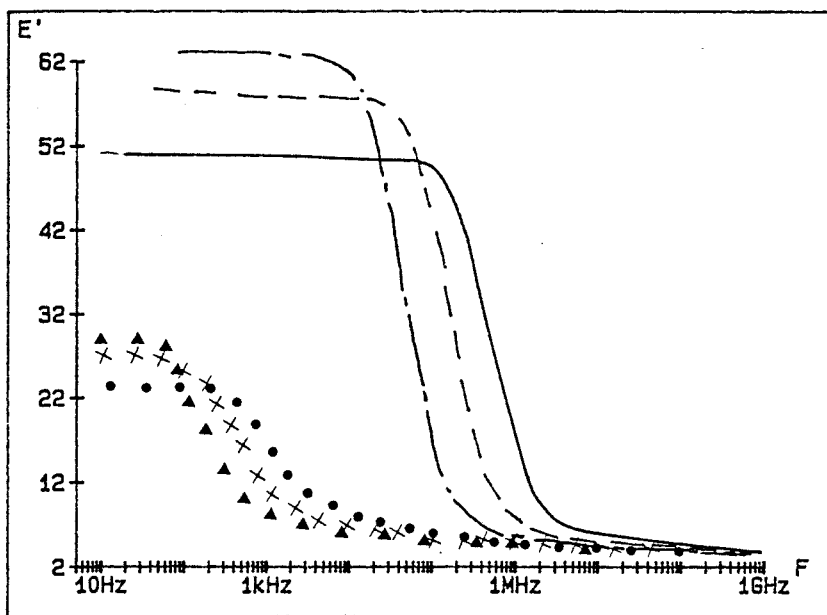
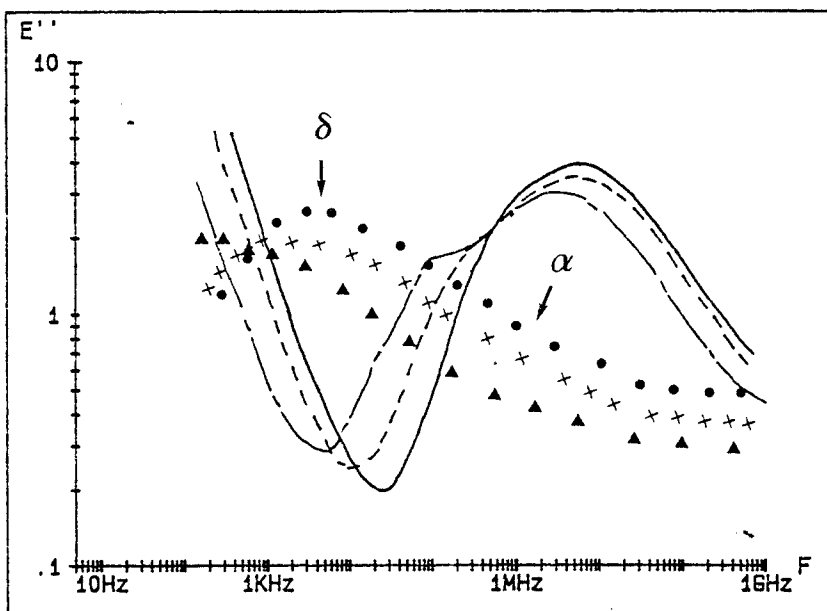
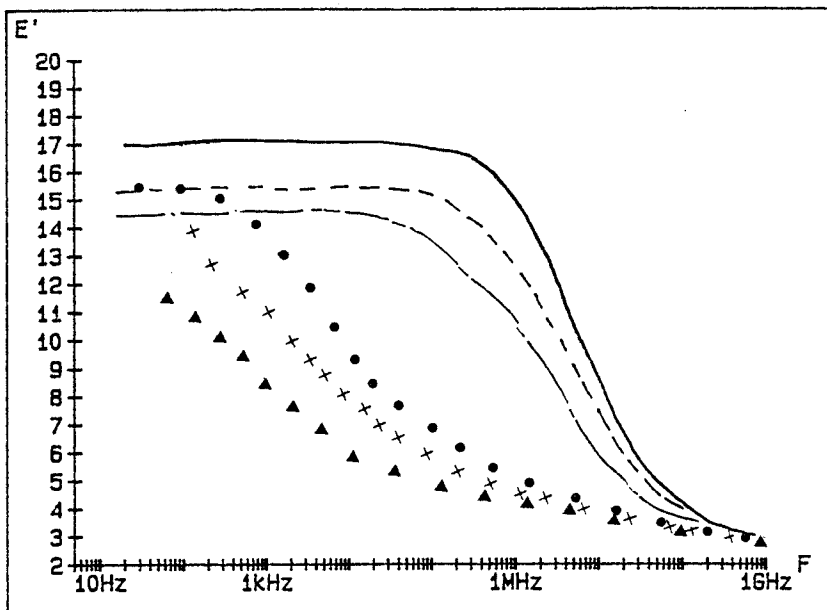


Figure F-20: PLBP28 et M28 (LMWLC) , Nem ($E//n$)



CL { 22°C : ———
 14°C : - - -
 5°C : - · - · -

PCL { 65°C : ● ● ●
 55°C : × × ×
 45°C : ▲ ▲ ▲

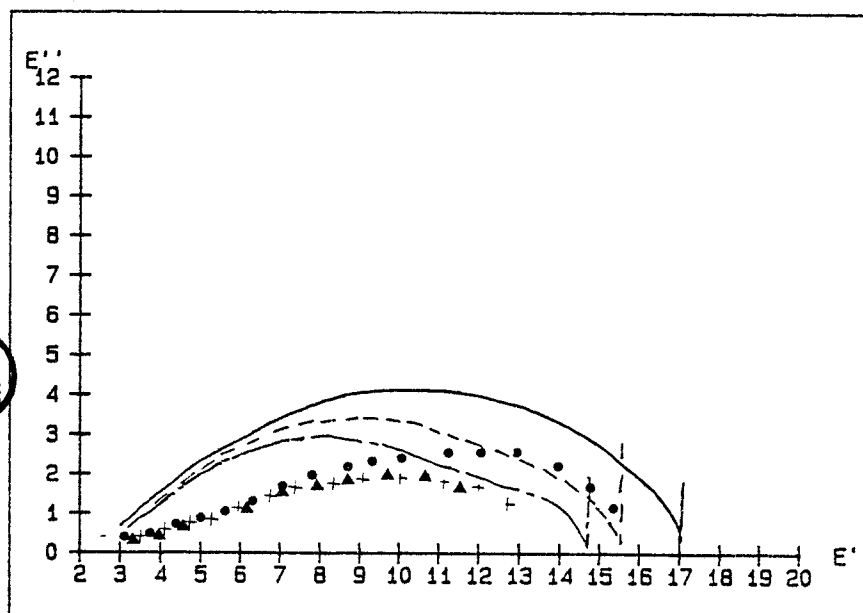


Figure F-21: PLBP28 et M28(CL) ,Nem (E1 n)

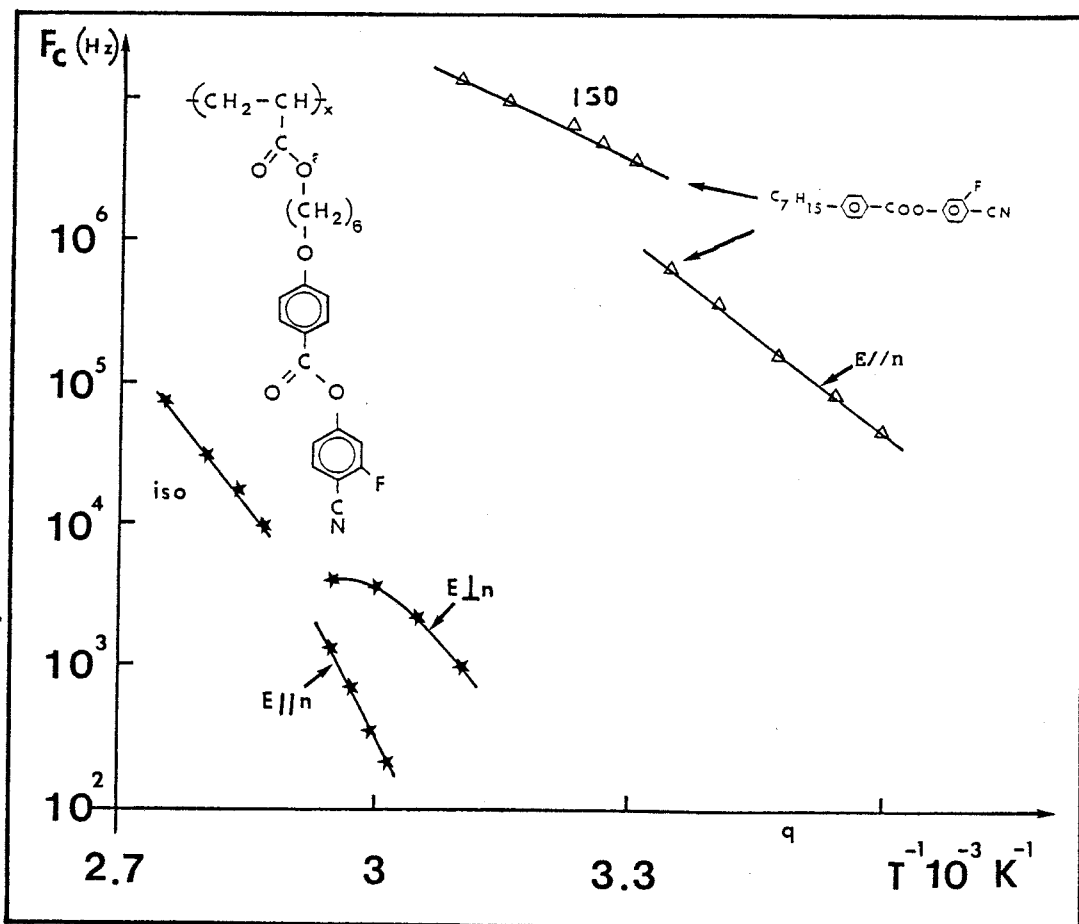


Figure F-22: Courbe $F_c = f(T^{-1})$ pour le PLBP28 (★) et le cristal liquide associé (Δ).

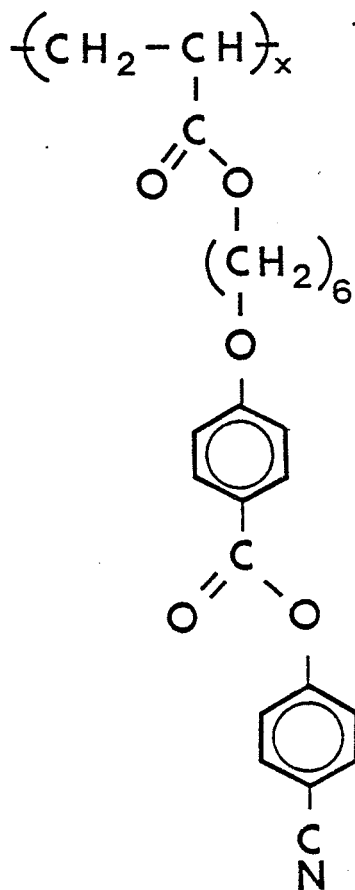


FICHE N° 5

CODE DE LA SUBSTANCE : PLBP29

PROVENANCE : LCR THOMSON

FORMULE STRUCTURALE :



SEQUENCE DE PHASES ET TEMPERATURES DE TRANSITION :

G $\xrightarrow{22.5^\circ \text{ C}}$ N $\xrightarrow{106^\circ \text{ C}}$ Iso

LISTE DES RESULTATS EXPERIMENTAUX PRESENTES :

Régime statique : Figure F-24

Régime dynamique

- a) phase isotrope et nématique $E//n$ Figure F-25
- b) phase isotrope et nématique $E \perp n$ Figure F-26

FREQUENCES CRITIQUES ET ENERGIES D'ACTIVATION

Figure F-27 : courbe $W = f(1/T)$

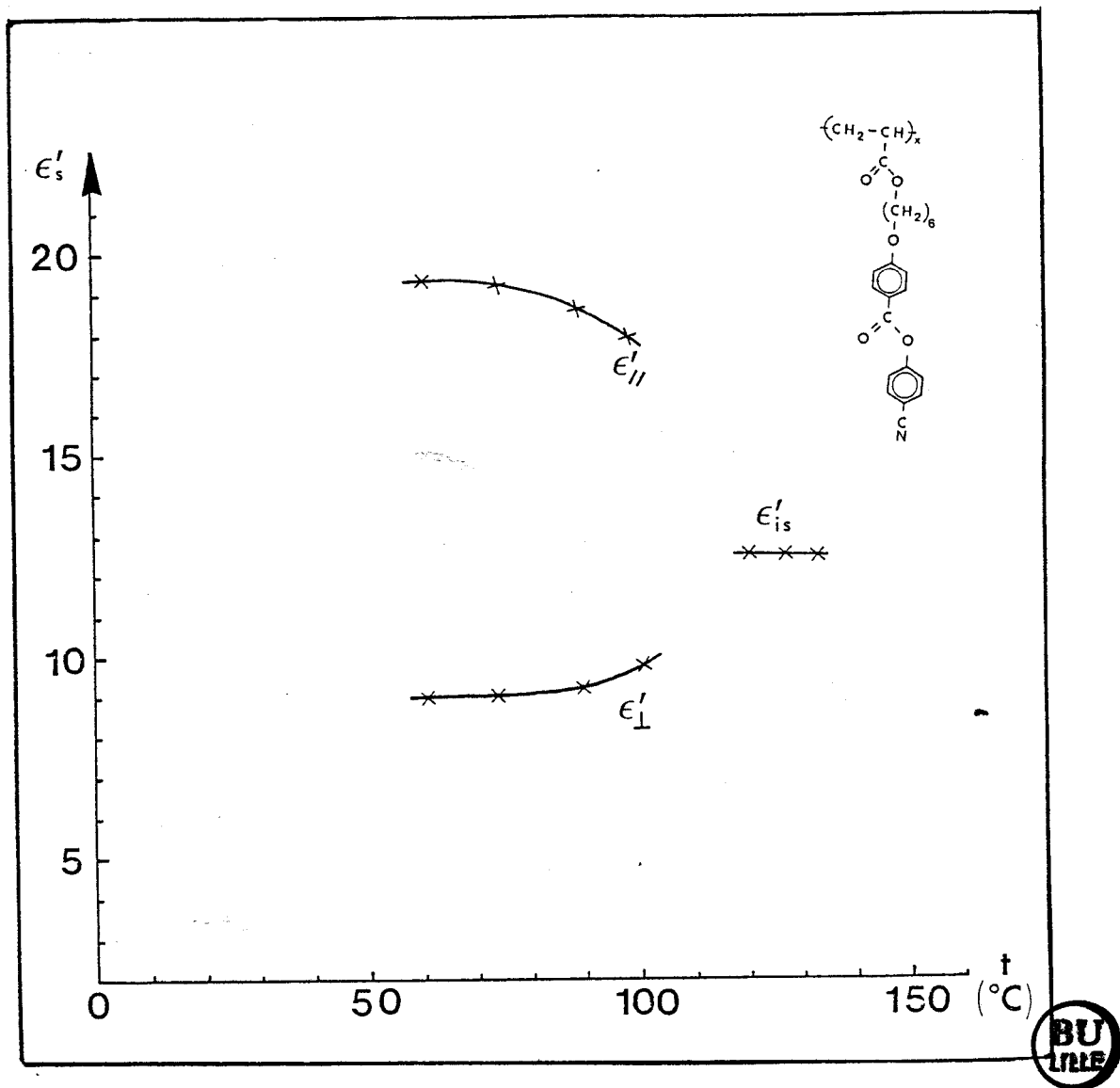
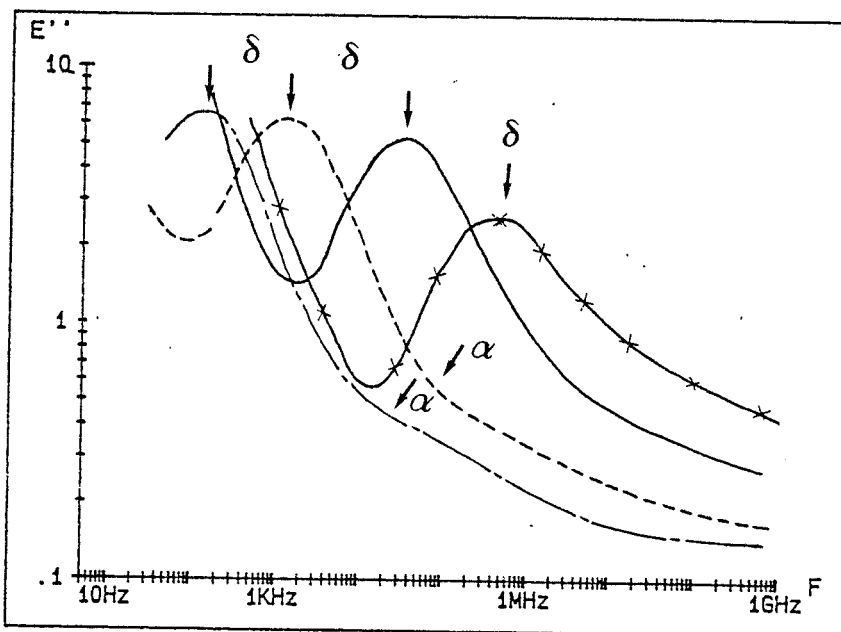
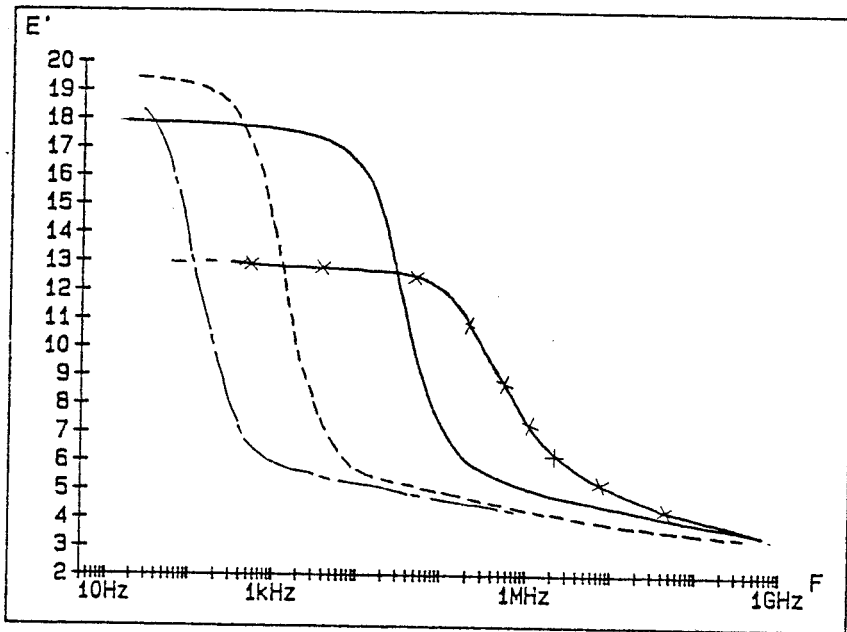


Figure F-24: Régime statique du PLBP29



x x x x 15°C (is
 ——— 100°C
 - - - 75°C
 - · - 60°C

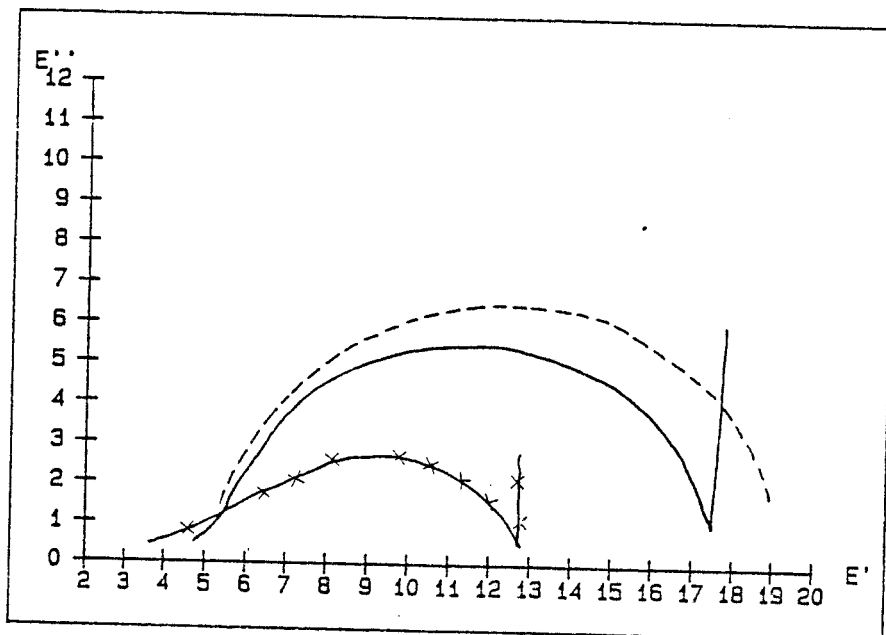
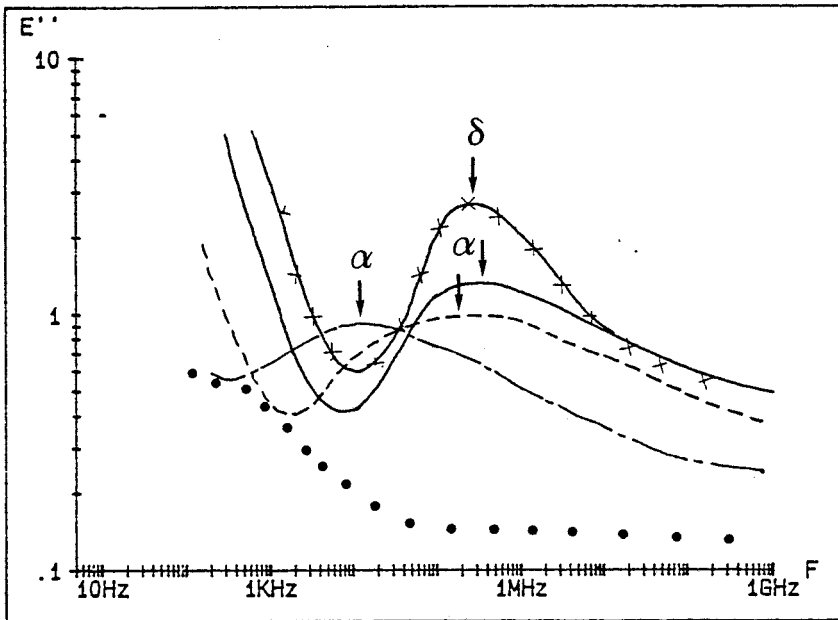
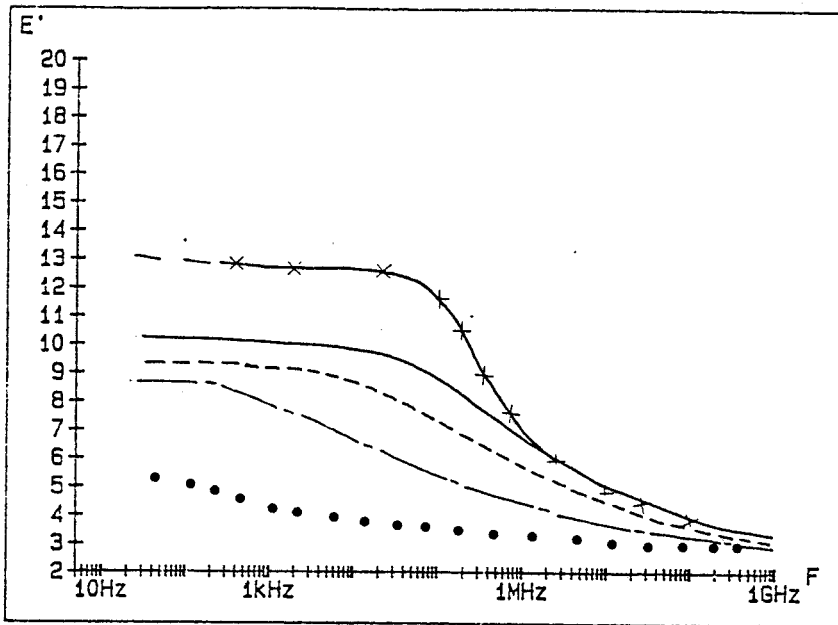


Figure F-25: :PLBP29 ,Nem (E''/n) et Iso



- ××××× 112°C (iso)
- 102°C
- - - - 85°C
- · - · 60°C
- • • 35°C

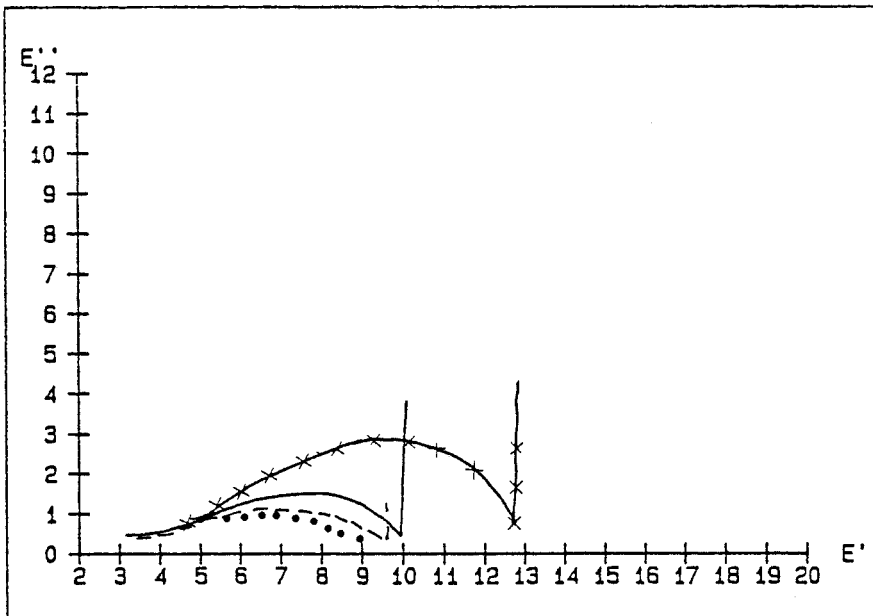


Figure F-26: PLBP29 ,Nem (E l n) et Iso

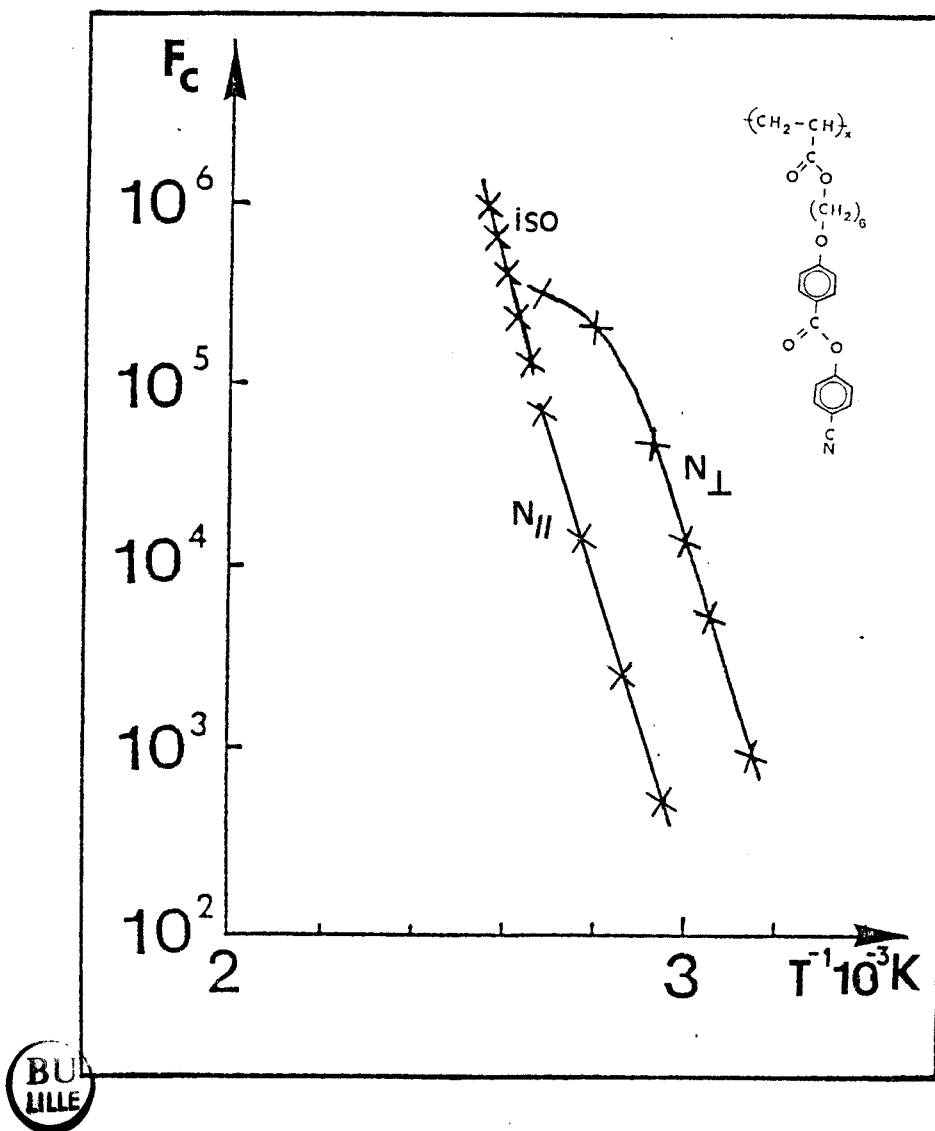


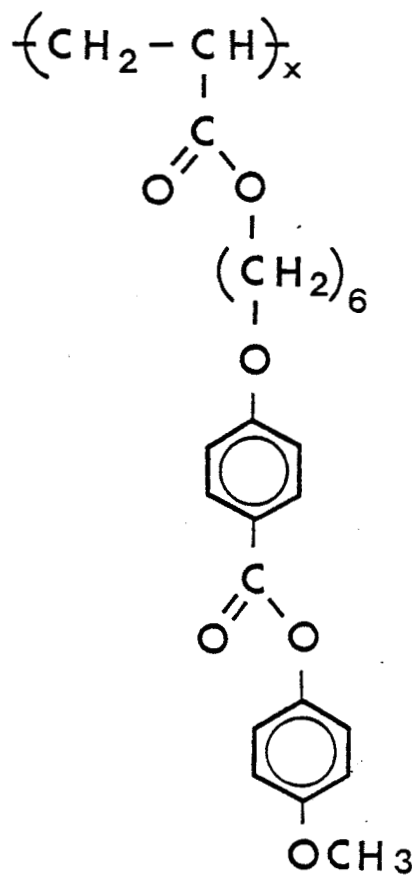
Figure F-27: Courbe $F_c = f(1/T)$ pour le PLBP29

FICHE N° 6

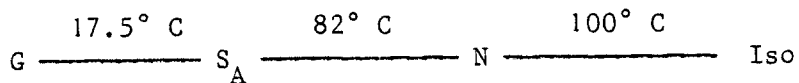
CODE DE LA SUBSTANCE : PLBP30

PROVENANCE : LCR THOMSON

FORMULE STRUCTURALE



SEQUENCE DE PHASES ET TEMPERATURES DE TRANSITION :



LISTE DES RESULTATS EXPERIMENTAUX PRESENTES :

Régime statique

Figure F-28

Régime dynamique

- a) phase isotrope Figure F-29
- b) phase nématique E//n Figure F-30
- E⊥n Figure F-31
- c) phase smectique A
- E//n Figure F-32
- E⊥n Figure F-33

Courbes donnant l'évolution : de la fréquence critique des domaines d'absorption dans les diverses phases en fonction de l'inverse de la température : Figure F-34

FREQUENCES CRITIQUES ET ENERGIES D'ACTIVATION :

Figure F-34 : courbe $W = f(1/T)$

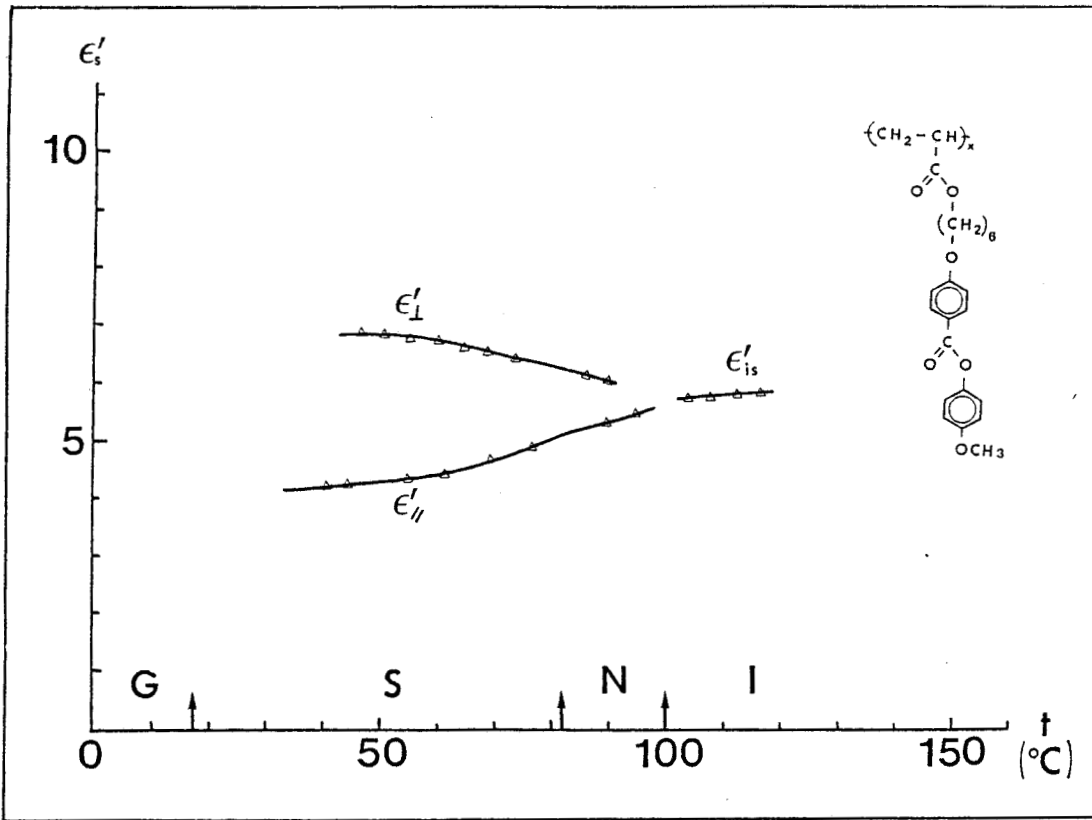
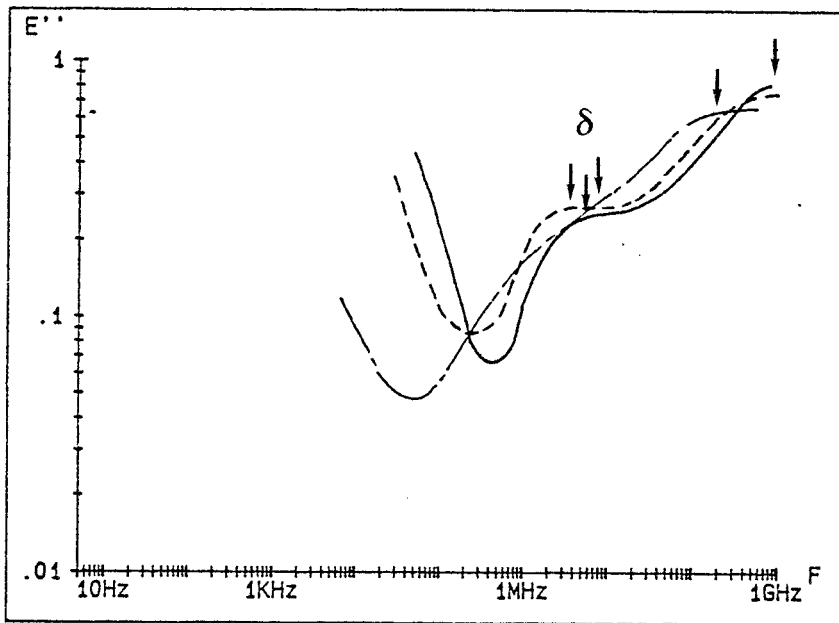
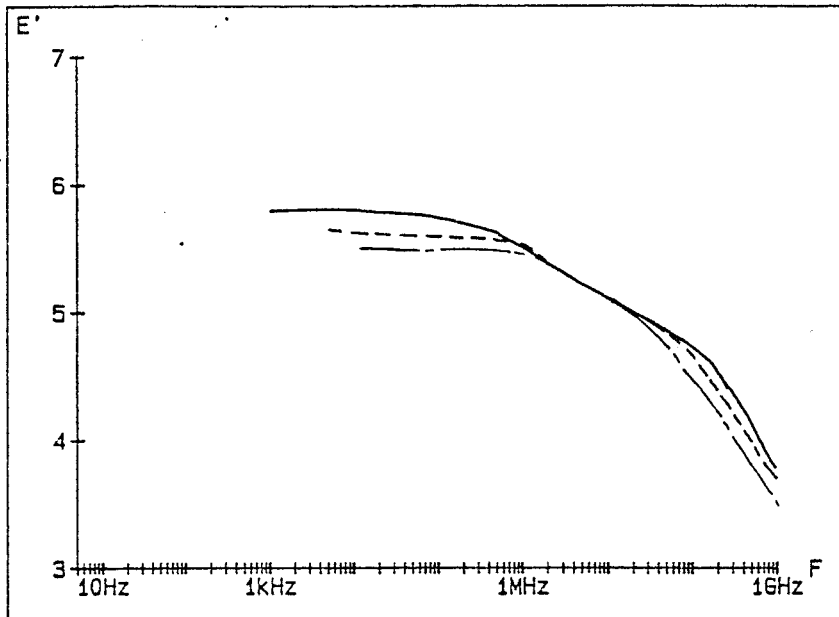


Figure F-28: Régime statique du PLBP30





— 159°C
- - - 135°C
- · - 116°C

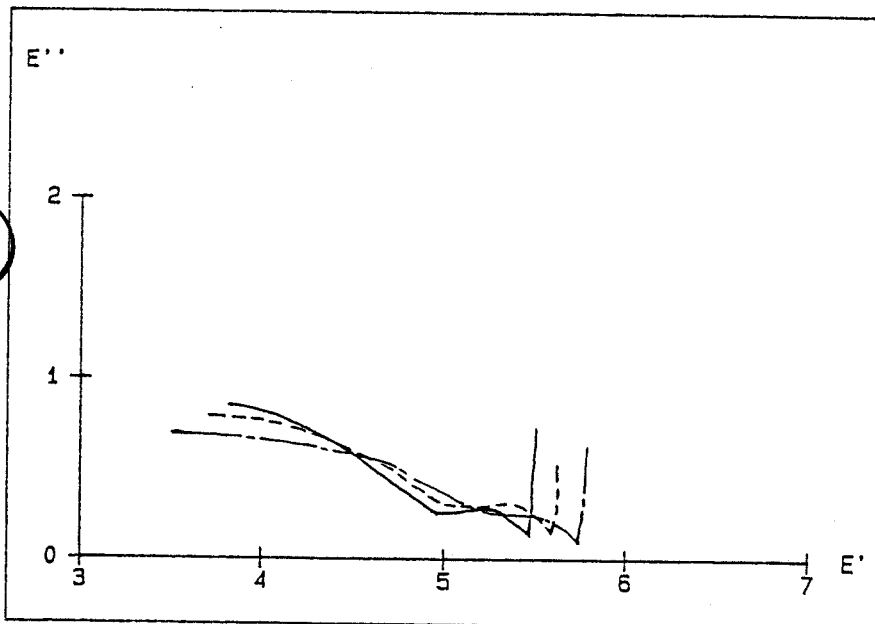


Figure F-29: PLBP30, Iso

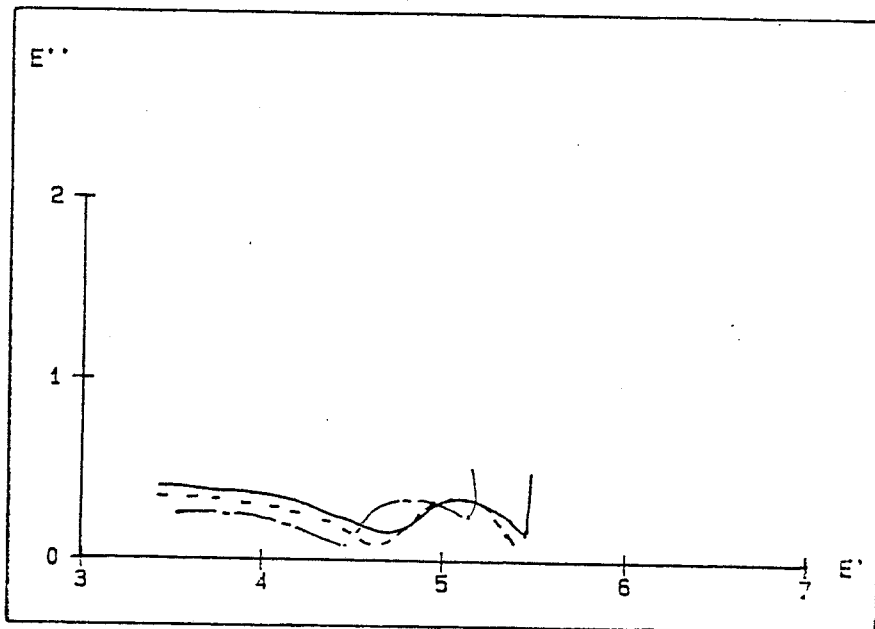
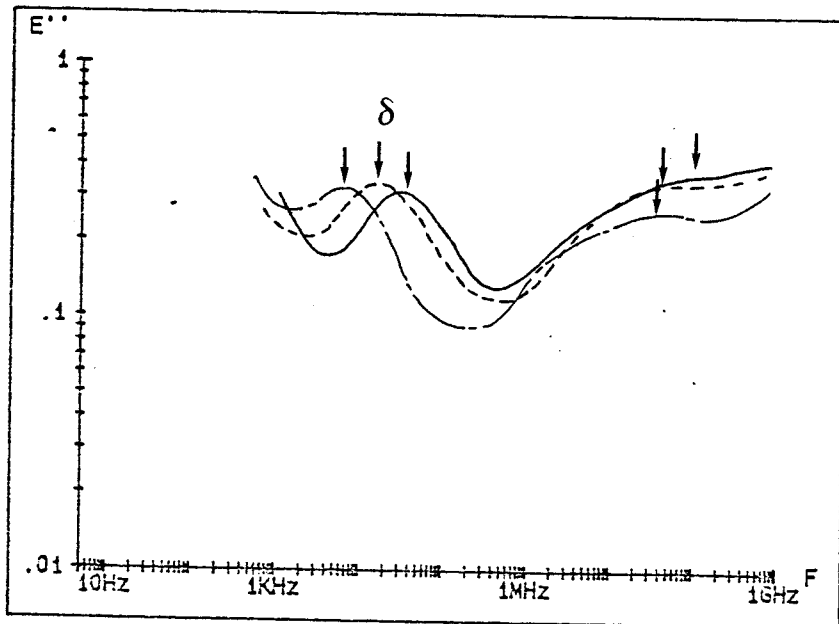
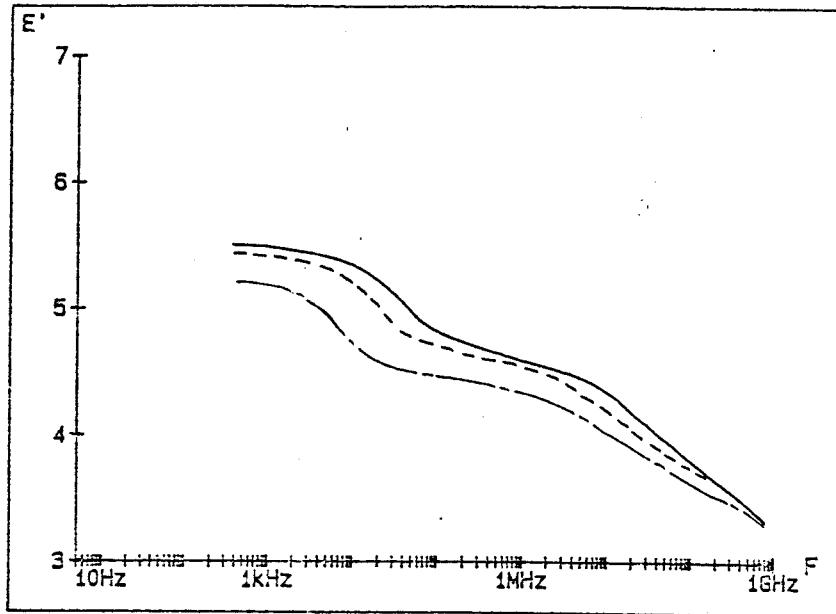
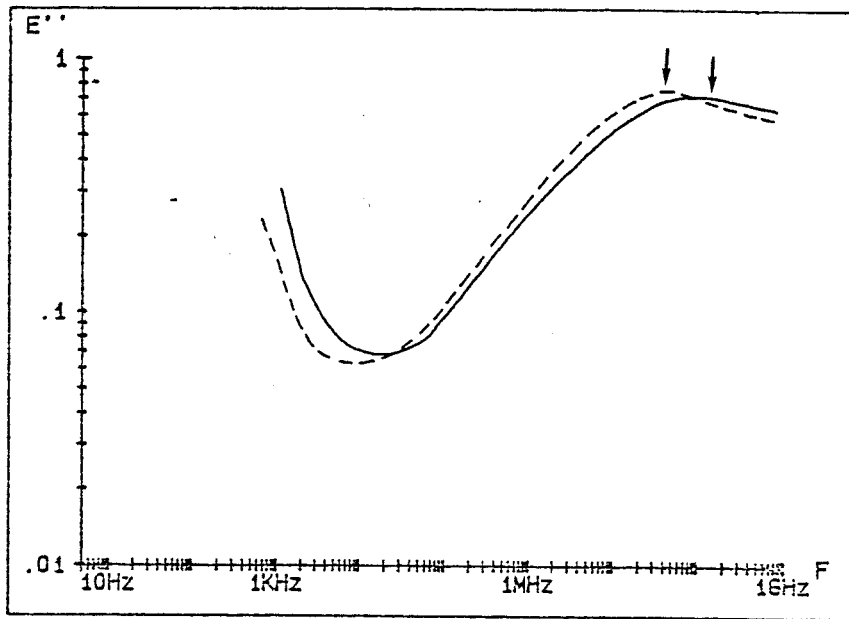
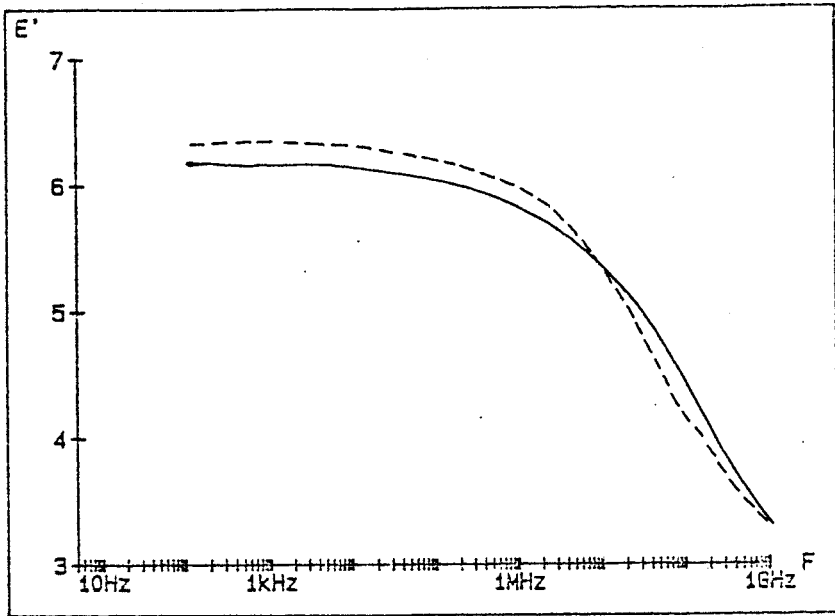


Figure F-30: PLBP30, Nem (E//n)



— 95°C
- - - 86°C

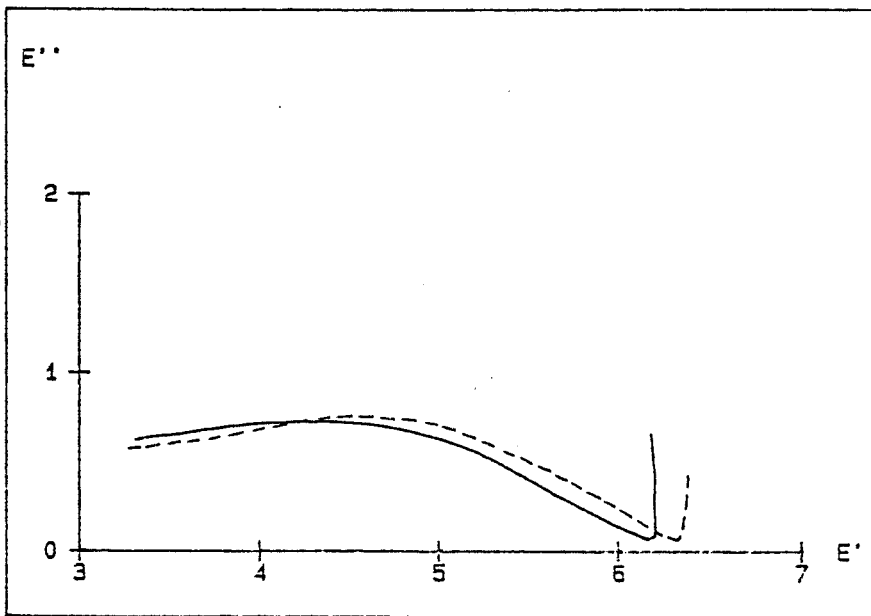


Figure F-31: PLBP30, Nem (E I n)

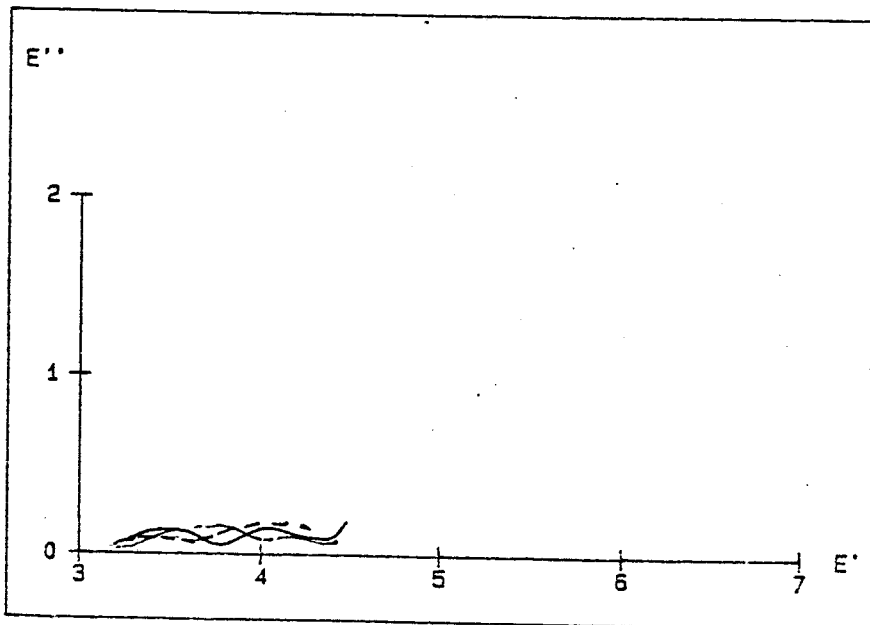
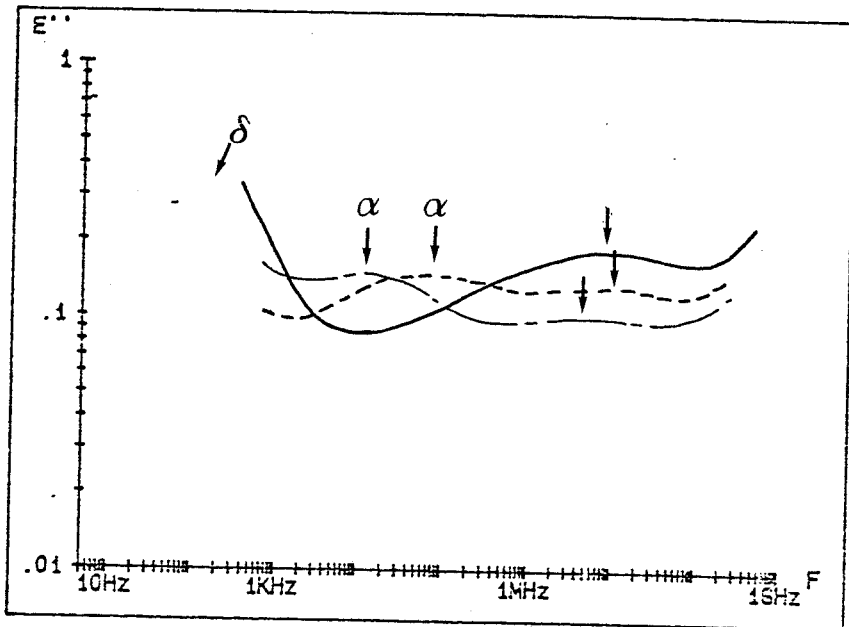
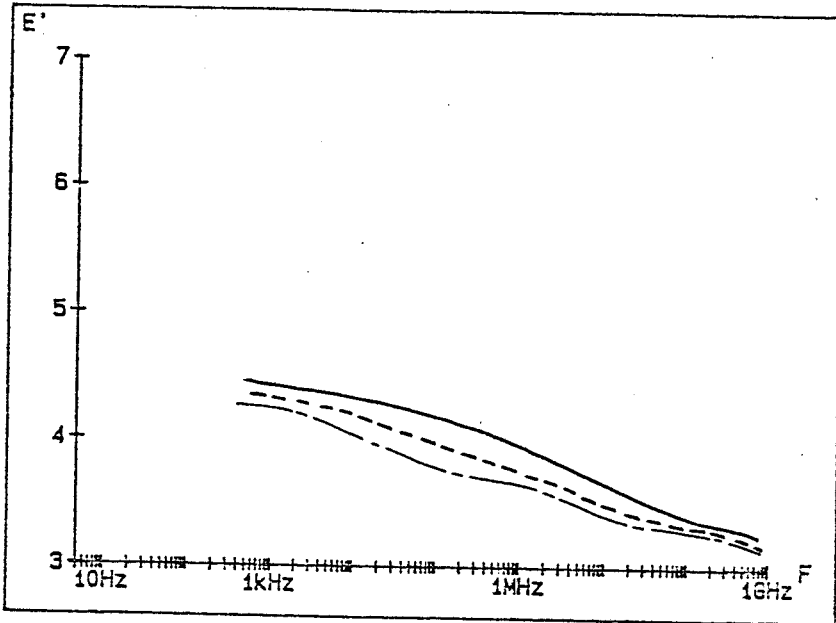


Figure F-32: PLBP30, S_A (E/n)

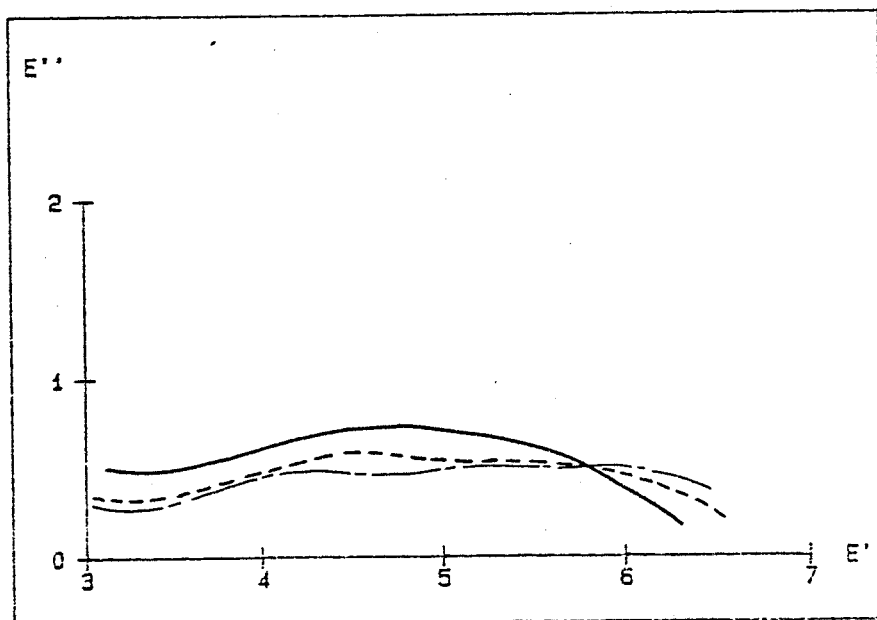
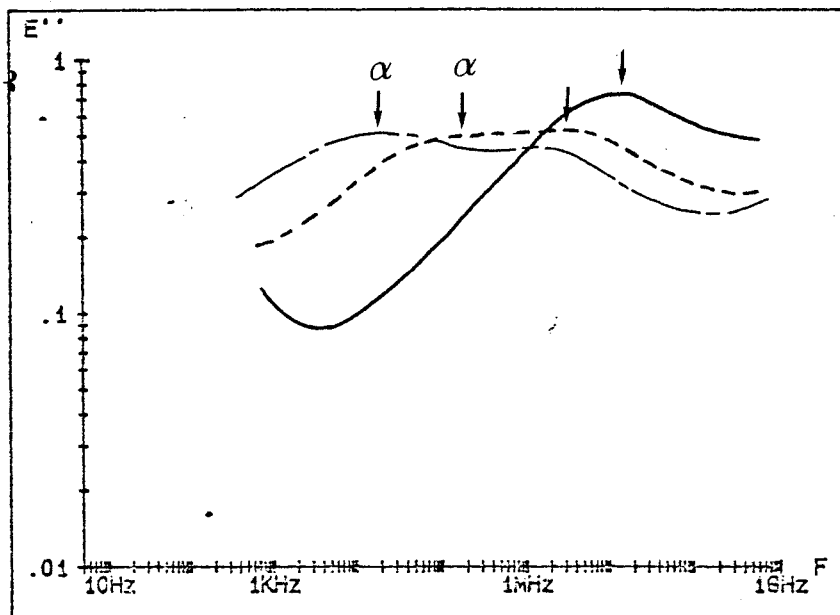
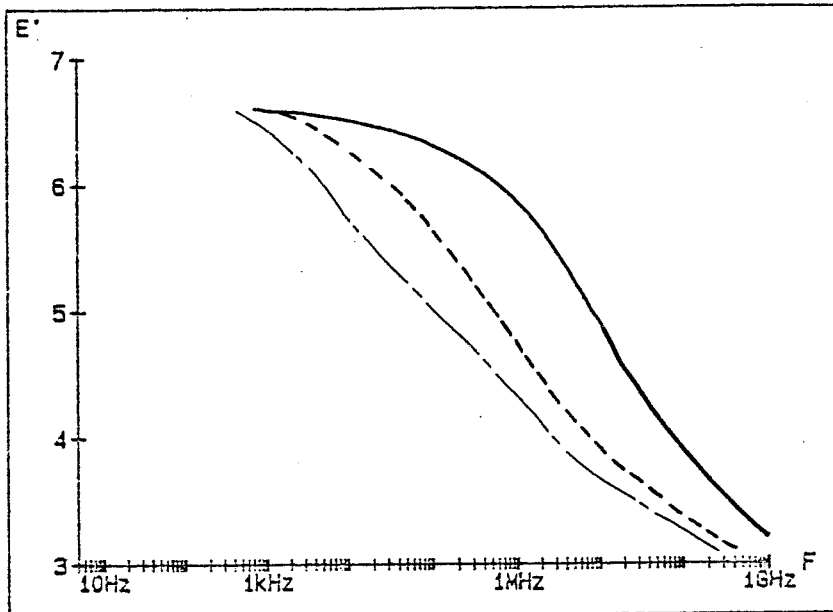


Figure F-33: PLBP30, S_A (E in)

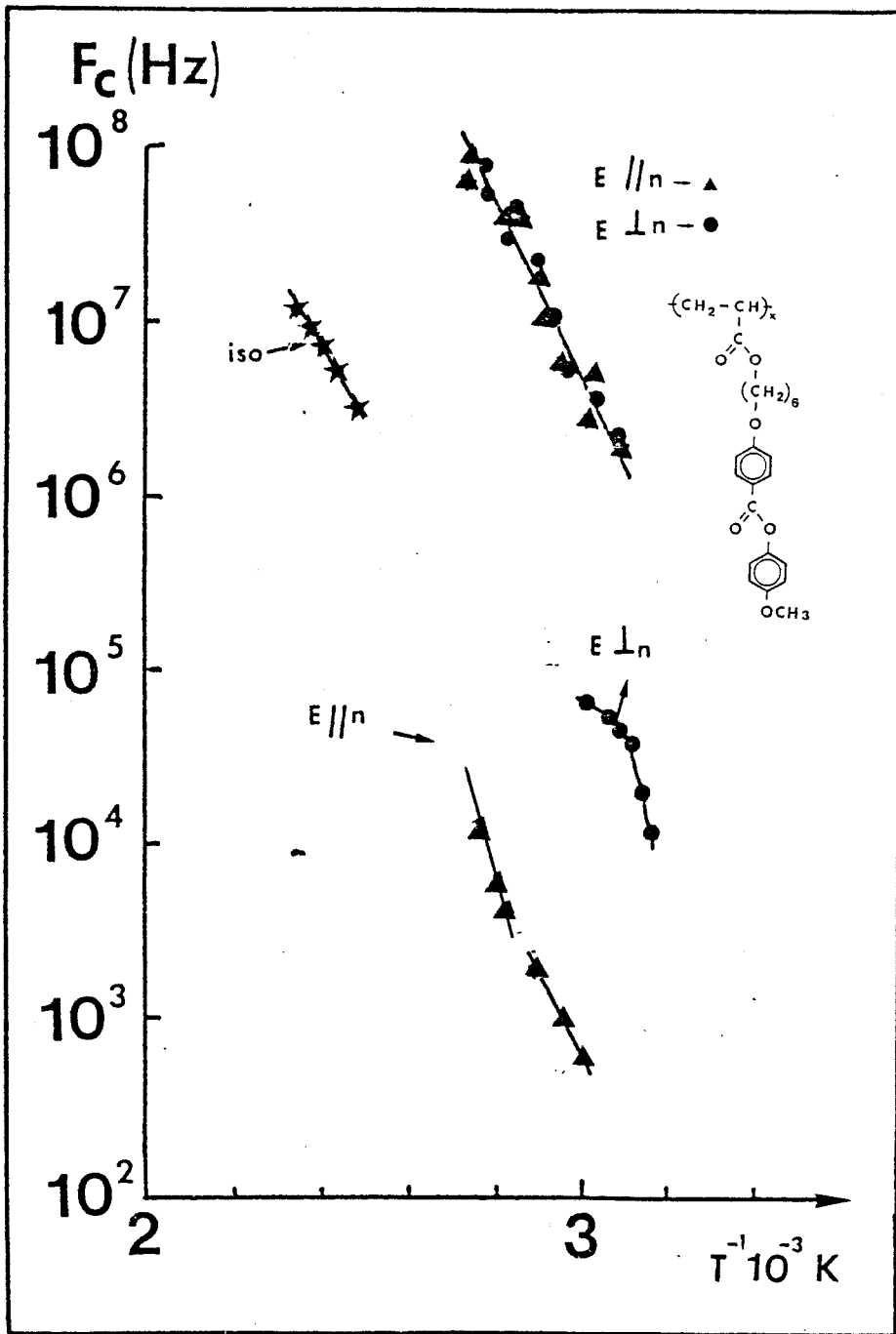


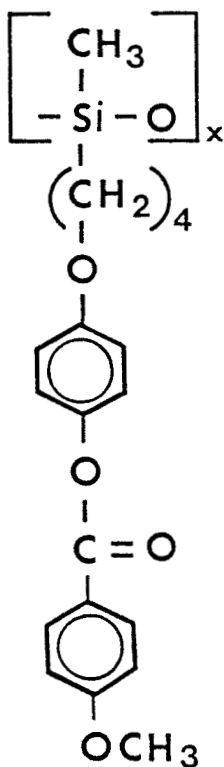
Figure F-34: Courbe $F_C = f(1/T)$ pour le PLBP30

FICHE N° 7

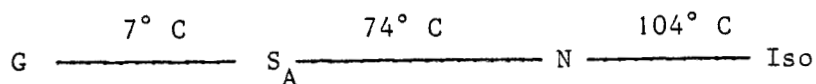
CODE DE LA SUBSTANCE : P4,1

PROVENANCE : CENTRE DE RECHERCHES PAUL PASCAL (BORDEAUX)

FORMULE STRUCTURALE :



SEQUENCE DE PHASES ET TEMPERATURES DE TRANSITION



LISTE DES RESULTATS EXPERIMENTAUX PRESENTES :

Régime statique

Figure F-35

Régime dynamique

- a) phase isotrope Figure F-36
- b) phase nématique et smectique A
 - pour E//n Figure F-37
 - pour E⊥n Figure F-38
- c) phase vitreuse Figures F-39 et F-40

FREQUENCES CRITIQUES ET ENERGIES D'ACTIVATION

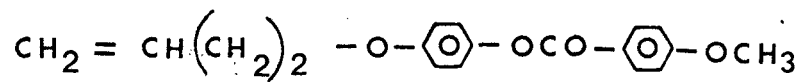
Figure F-41 : Courbe $W = f(1/T)$

CRISTAL LIQUIDE DE FAIBLE POIDS MOLECULAIRE ASSOCIE AU P4,1

CODE DE LA SUBSTANCE : M4,1

PROVENANCE : CENTRE DE RECHERCHES PAUL PASCAL (BORDEAUX)

FORMULE STRUCTURALE ET SEQUENCE DE PHASES :



K $\xrightarrow{[92^\circ]}$ N $\xrightarrow{51^\circ\text{C}}$ Iso

Liste des résultats expérimentaux présentes

Régime dynamique

a) phase isotropeFigure F-42

b) phase nématique

E//n et E⊥nFigure F-43

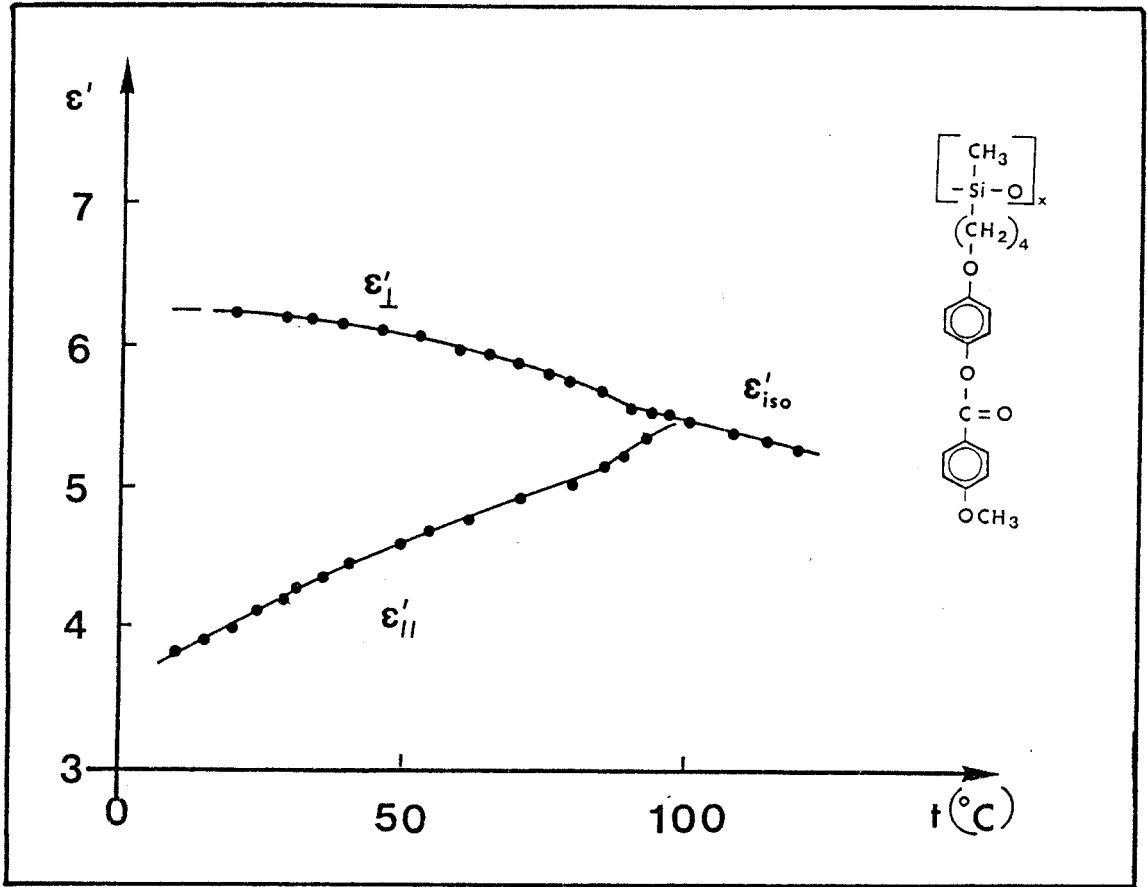


Figure F-35: Régime statique du P4,1



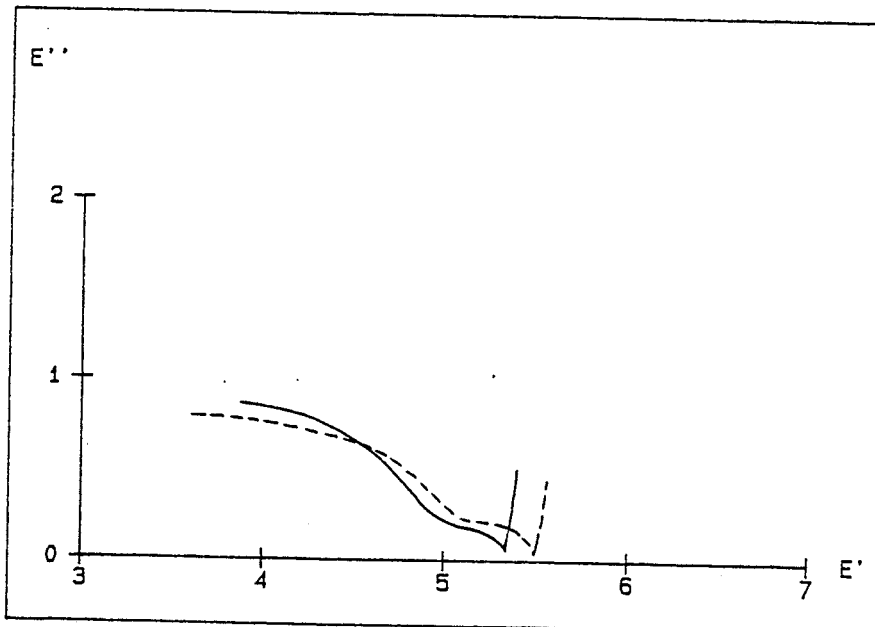
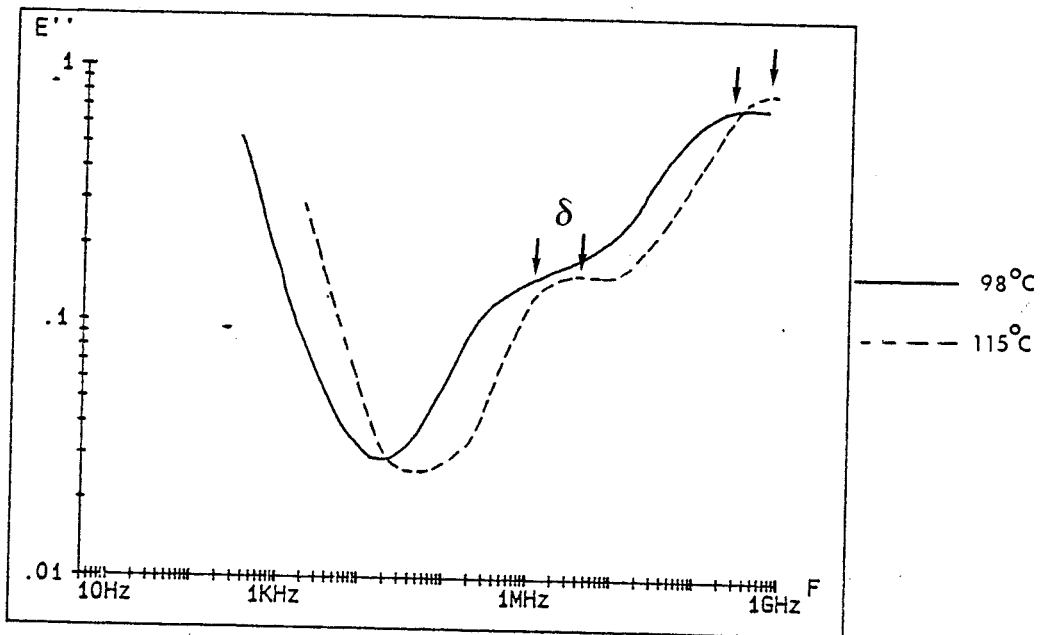
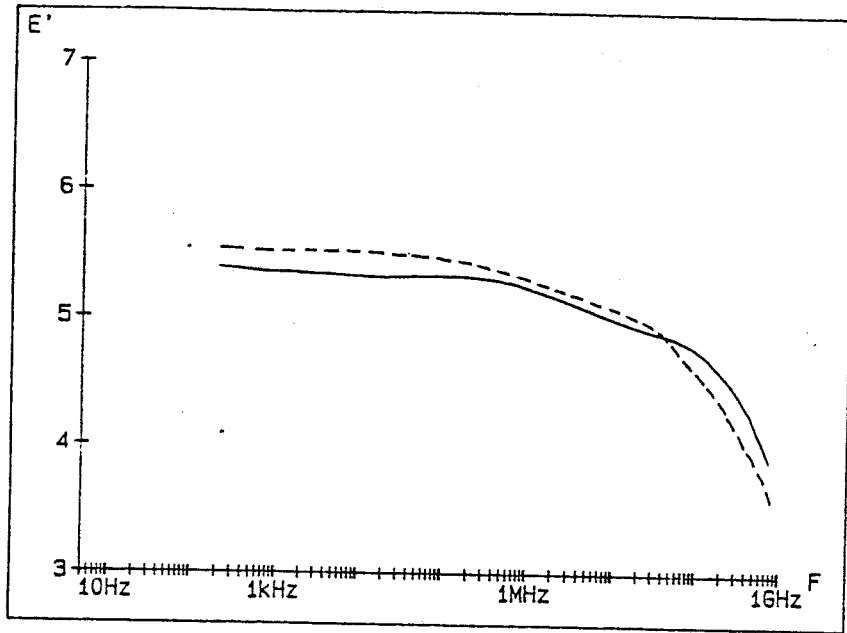
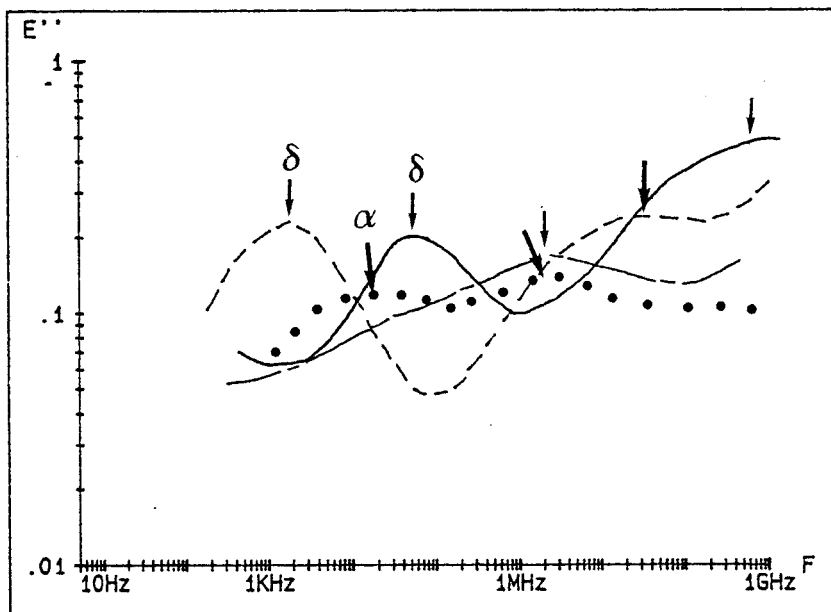
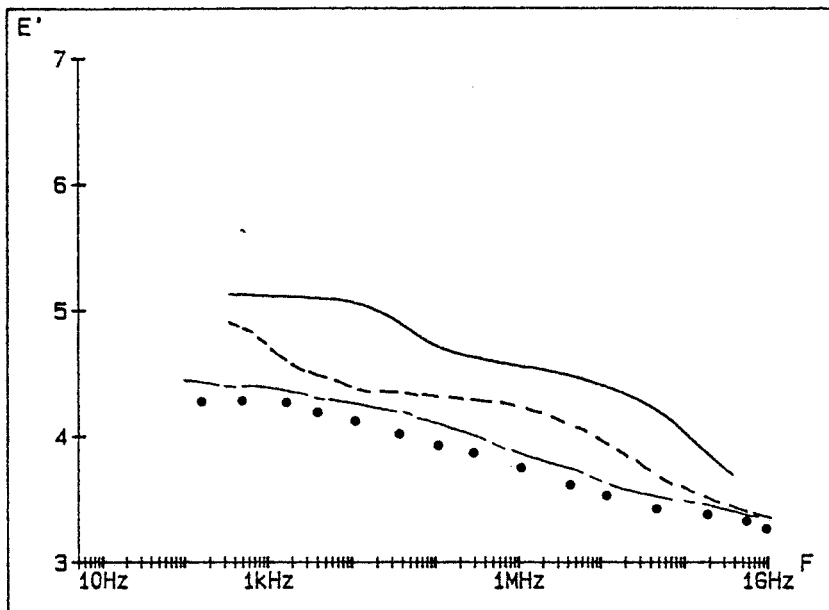


Figure F-36: P4,1 , Iso



BU
LILLE

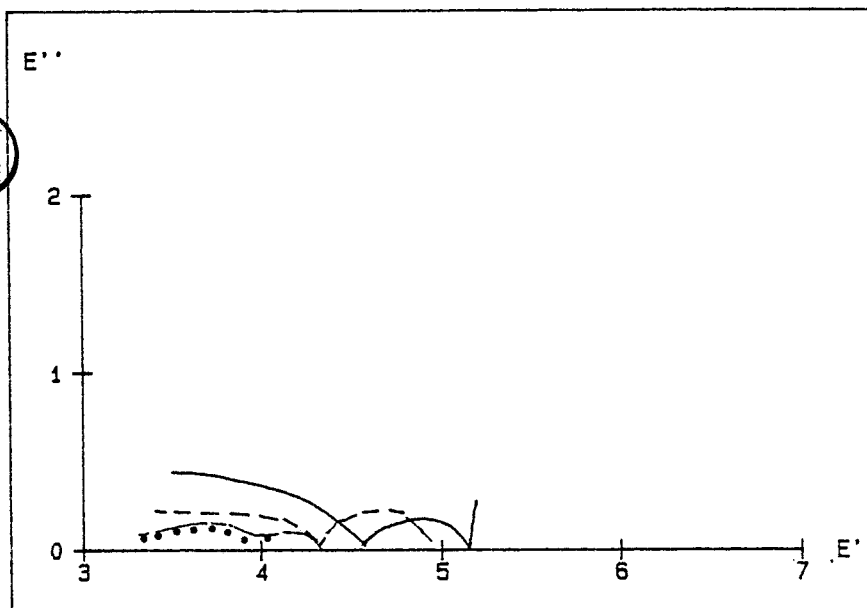
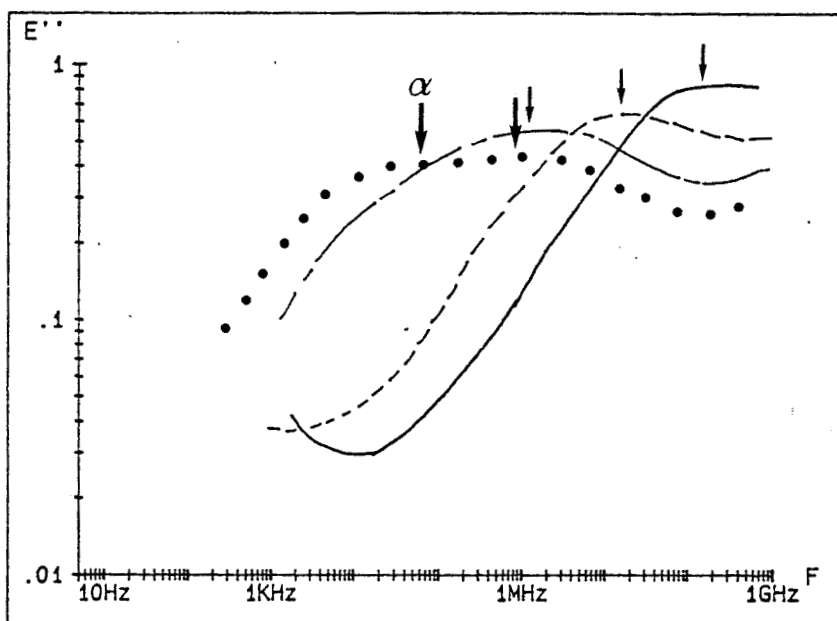
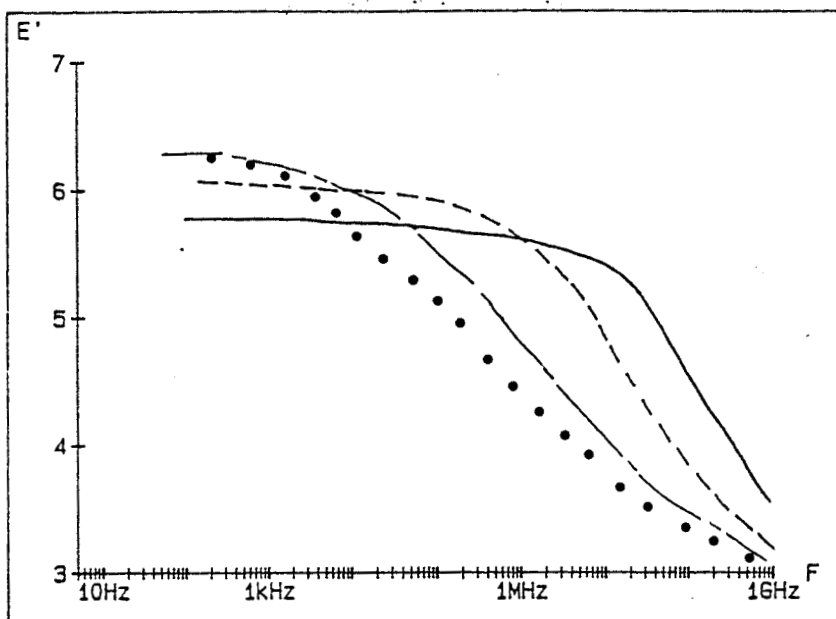


Figure F-37: P4,1 ; phase Nem et S_A (E/n)



- 85°C
- - - 58°C
- · - 37°C
- • • 30°C

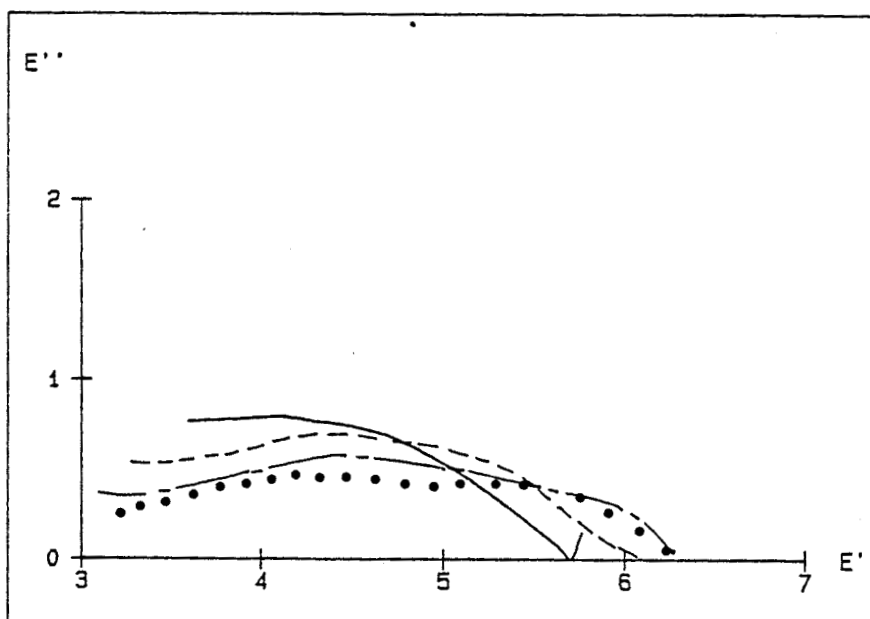
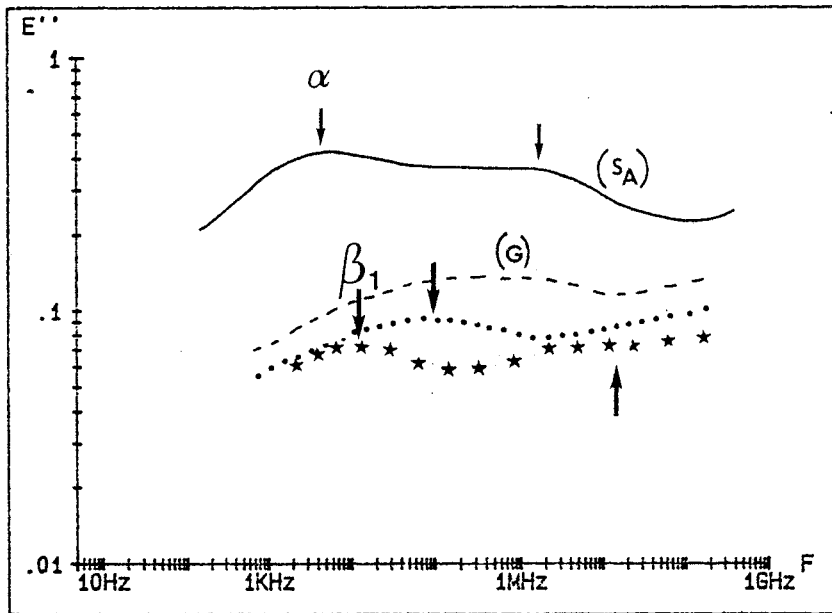
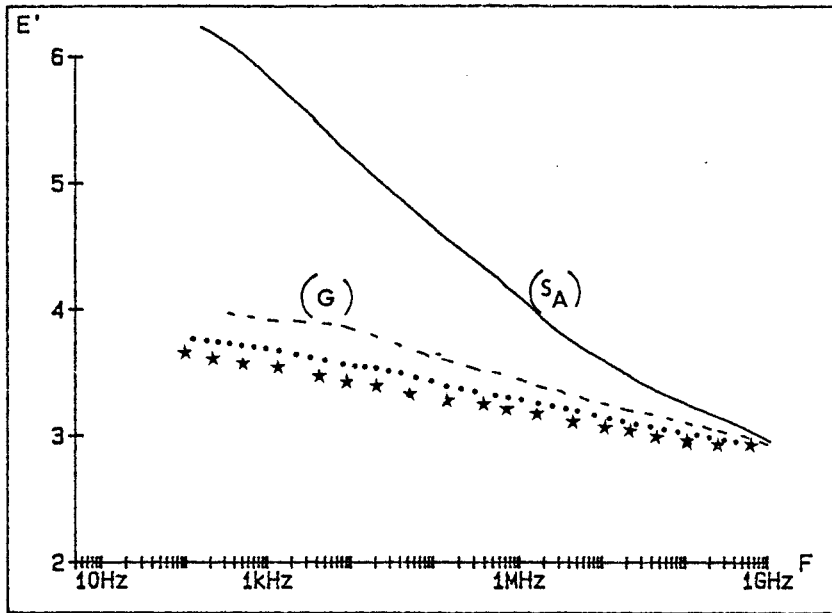


Figure F-38: P4,1; phase Nem et S_A (E In)



+23°C (—)
+5°C (---)
-8°C (....)
-20°C (***)

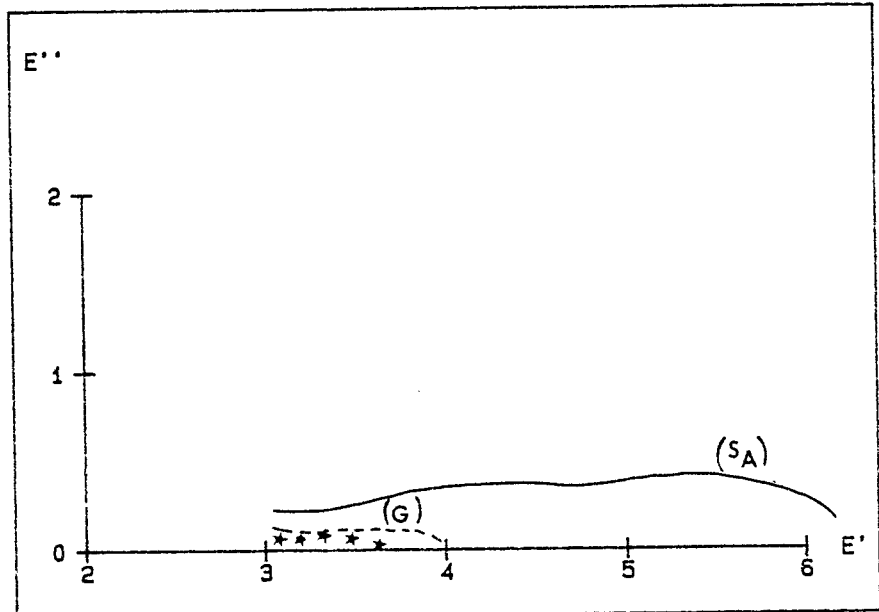


Figure F-39: Spectres diélectriques en phase vitreuse pour le P4,1.

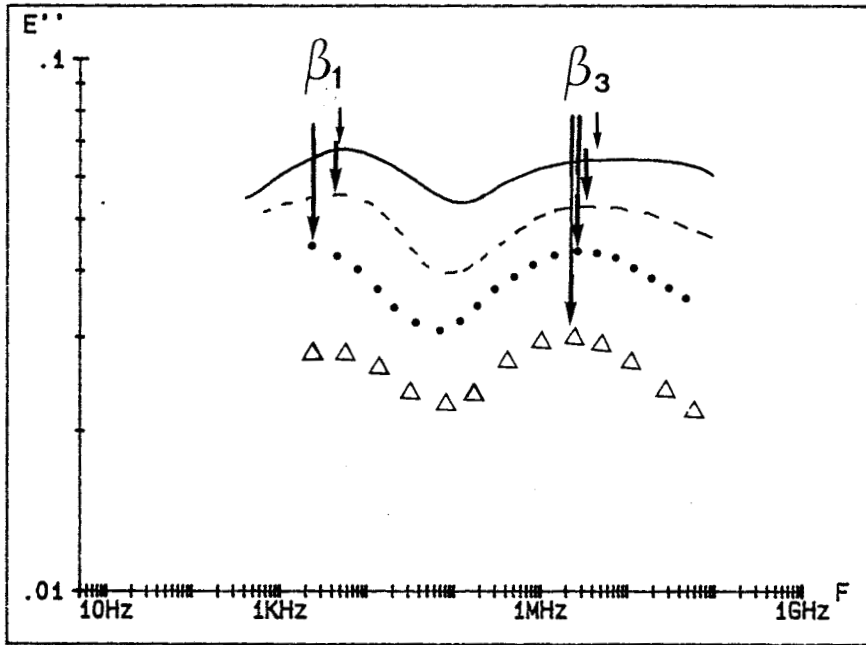
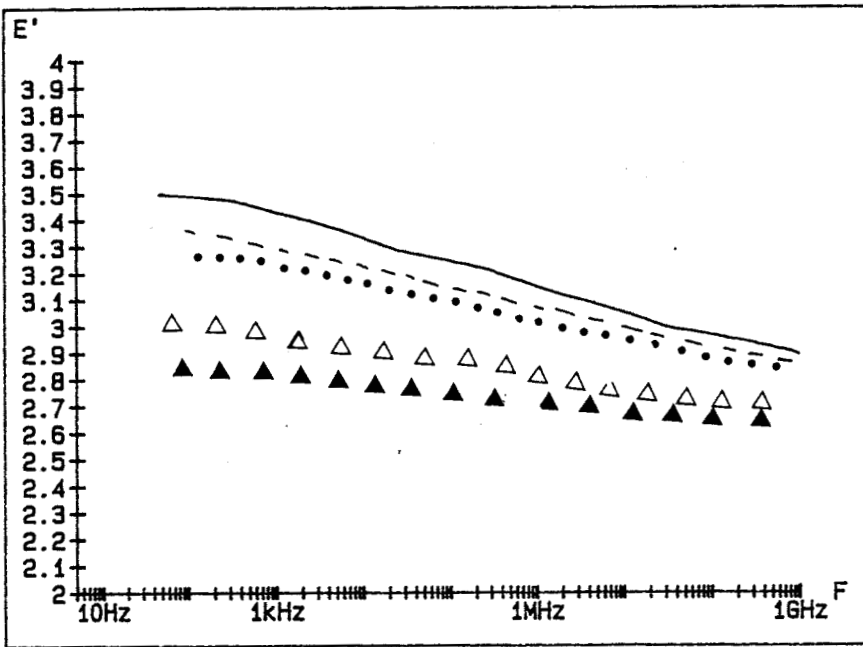


Figure F-40: Spectres diélectriques en phase vitreuse pour le P4,1.

- 35°C (————)
- 50°C (-----)
- 65°C (.....)
- 80°C (△ △ △)
- 100°C (▲ ▲ ▲)

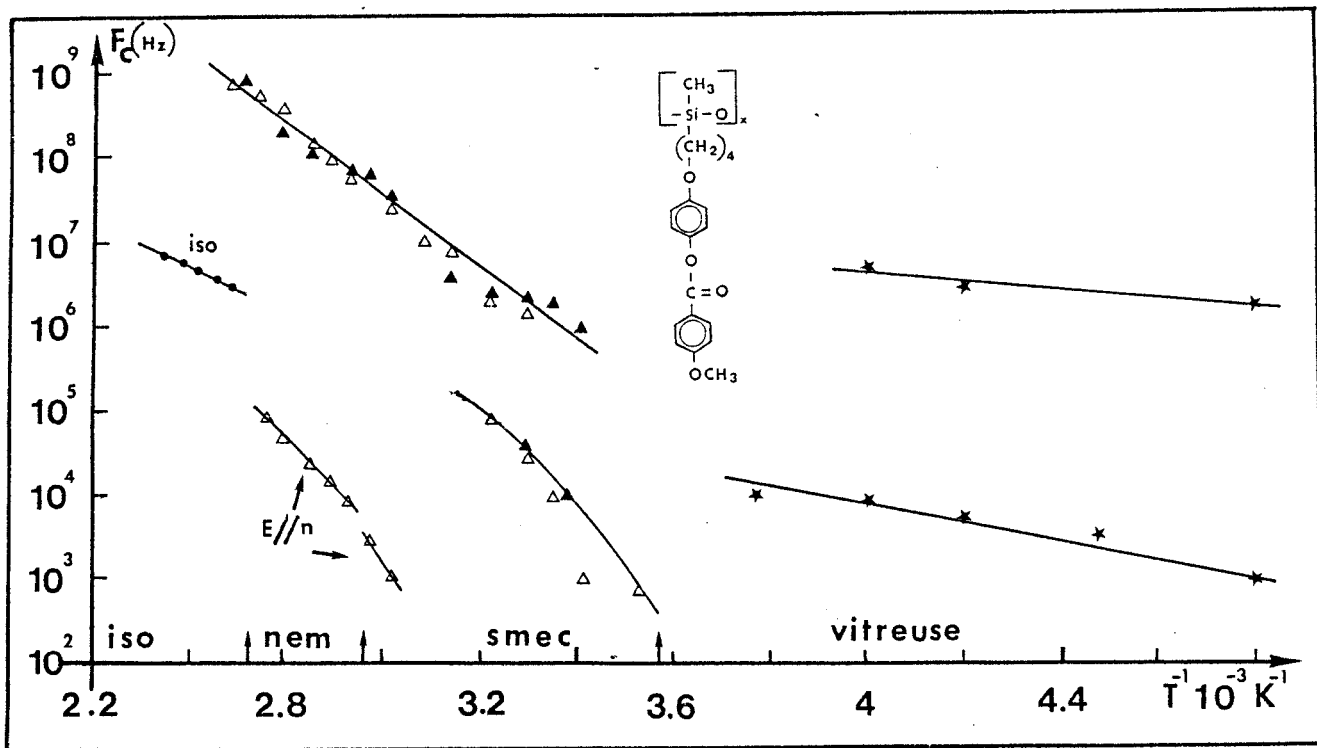


Figure F-41: Courbes $F_c = f(1/T)$ pour le P4,1

Δ : $E//n$

\blacktriangle : $E \perp n$



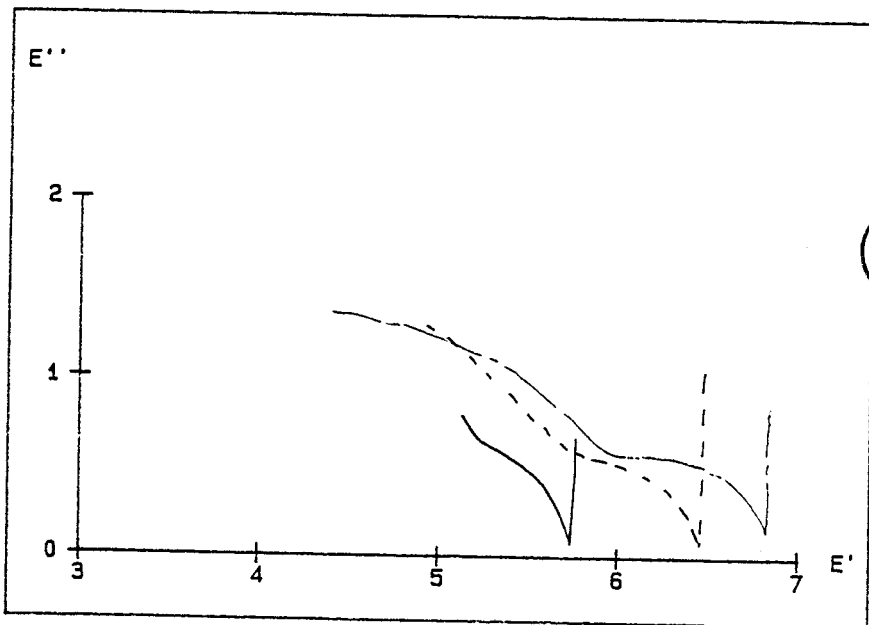
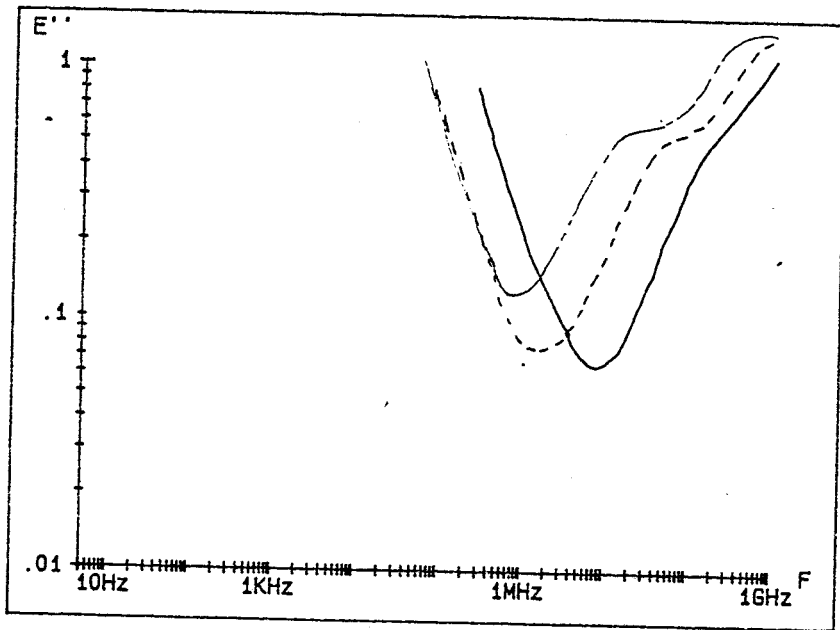
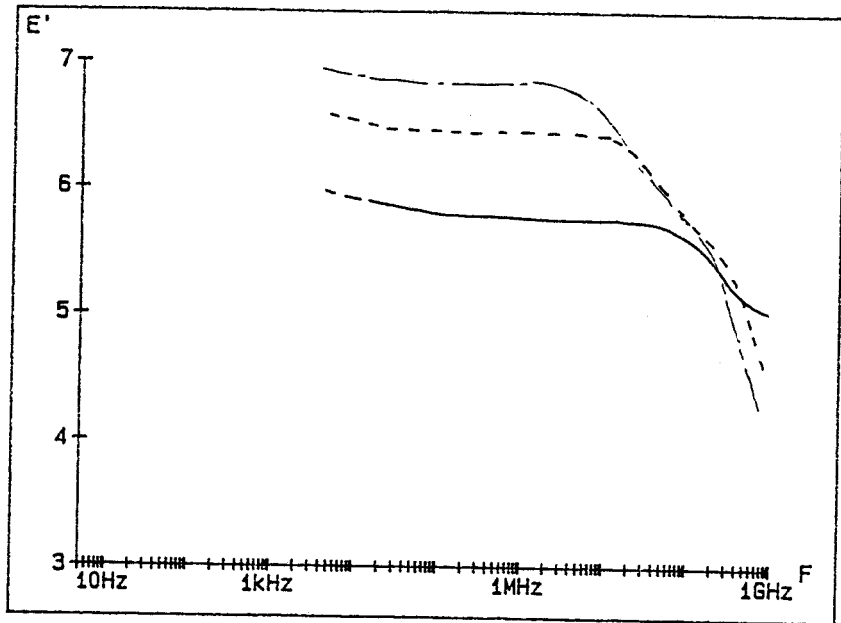
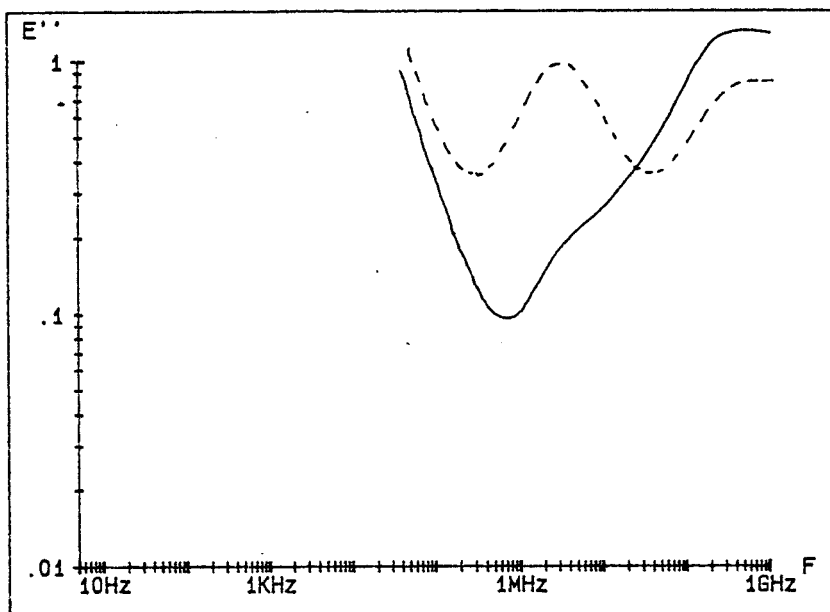
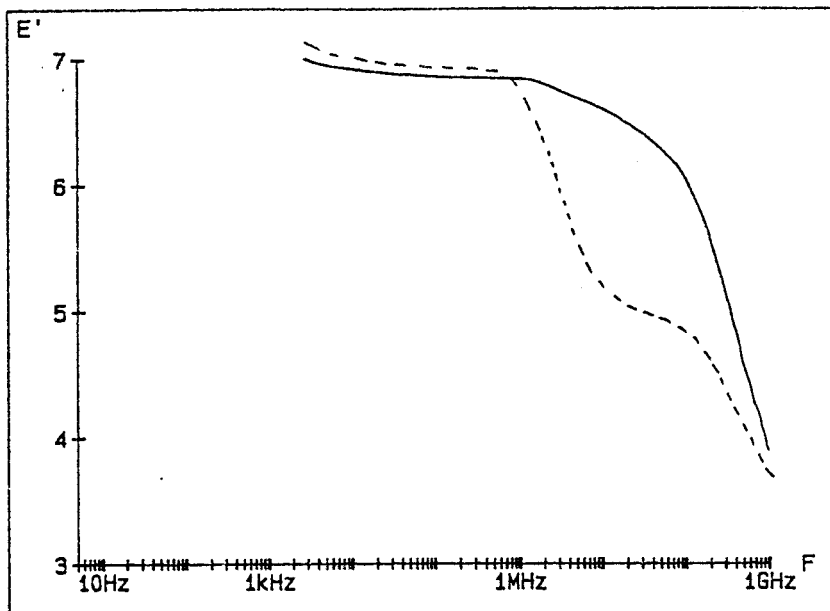


Figure F-42: M4,1; phase Iso



50°C

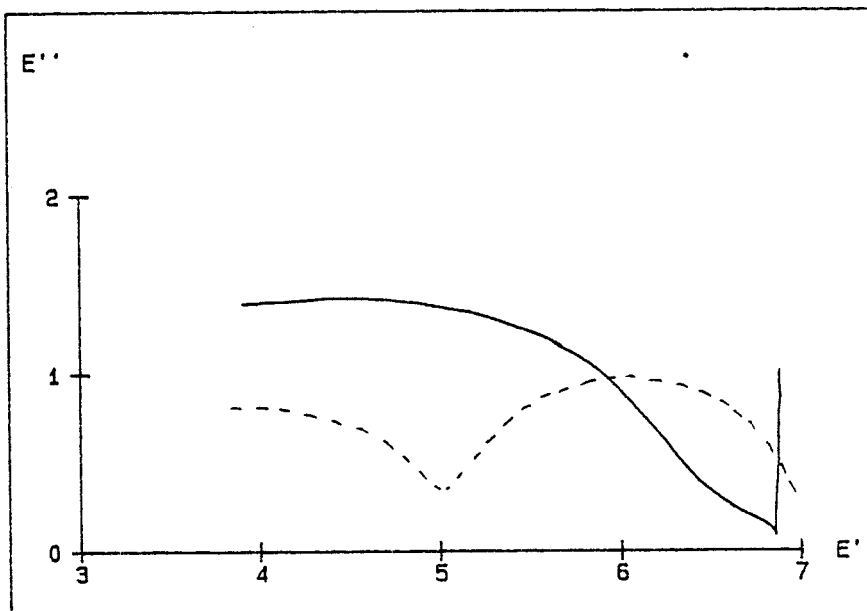


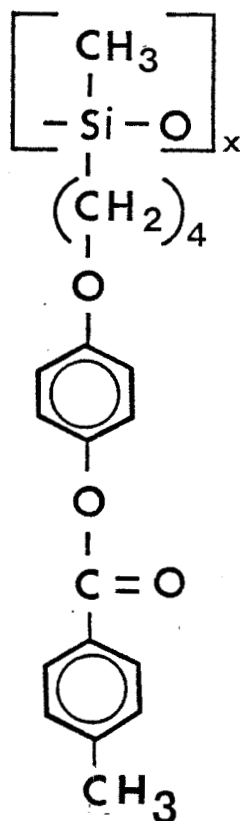
Figure F-43: M4,1; phase Nem (E'/n (---) et E'_{in} (—))

FICHE N° 8

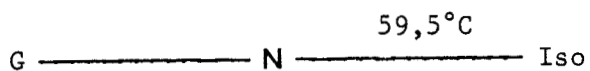
CODE DE LA SUBSTANCE : P4, METHYL

PROVENANCE : CENTRE DE RECHERCHES PAUL PASCAL (BORDEAUX)

FORMULE STRUCTURALE :



SEQUENCE DE PHASES ET TEMPERATURES DE TRANSITION :



LISTE DES RESULTATS EXPERIMENTAUX PRESENTES :

Régime statique

Figure F-44

Régime dynamique

- a) phase isotropeFigure F-45
- b) phase nématique
 - pour E//nFigure F-46
 - pour E⊥n.....Figure F-47

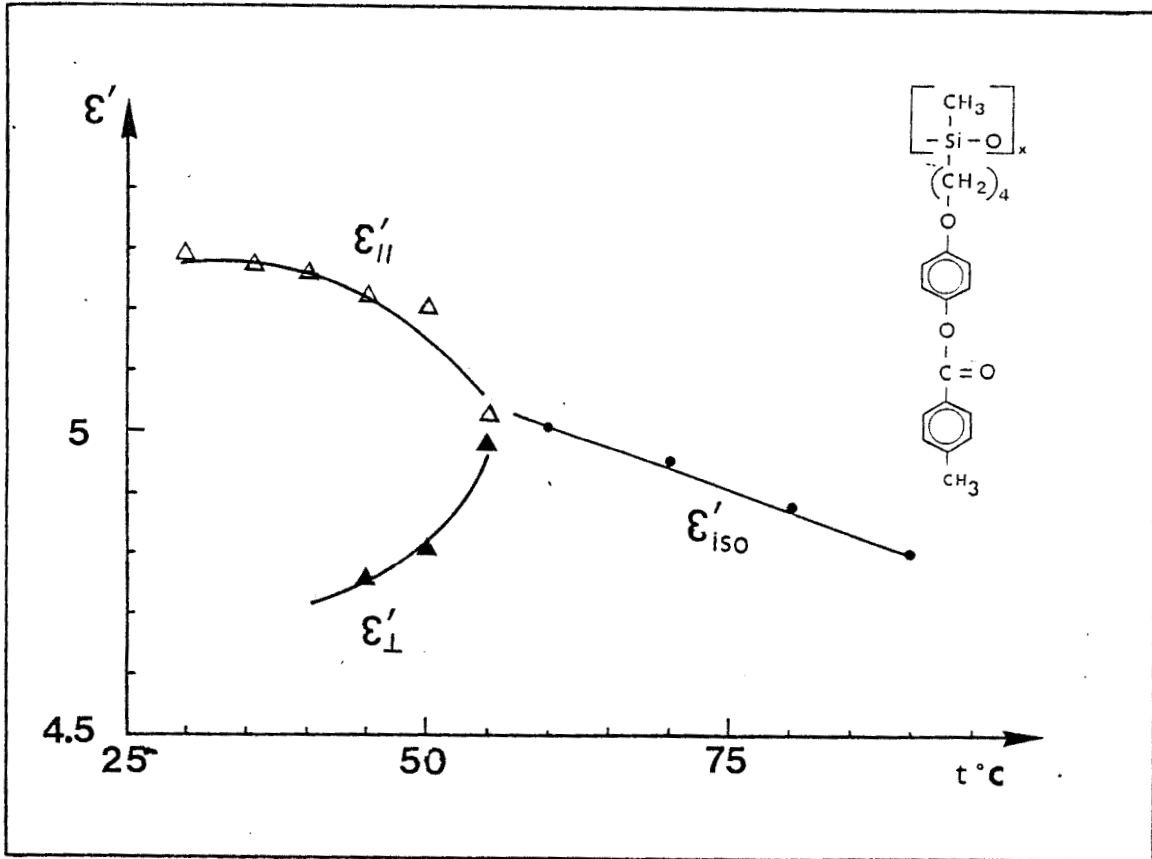


Figure F-44: Régime statique du P4, Methyl



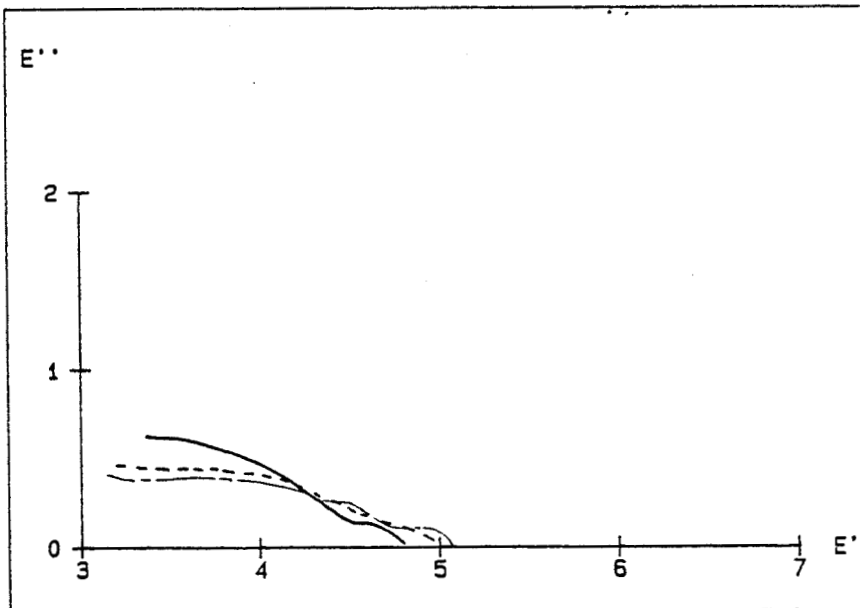
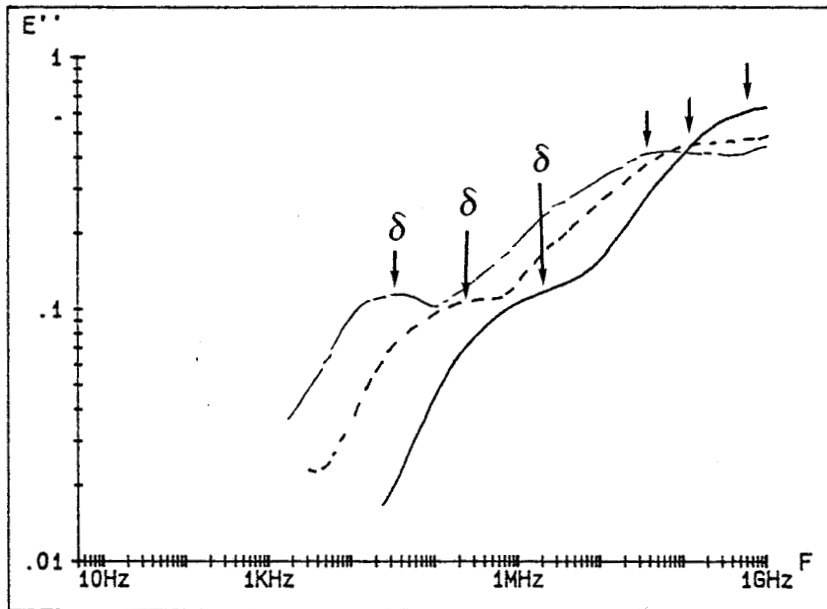
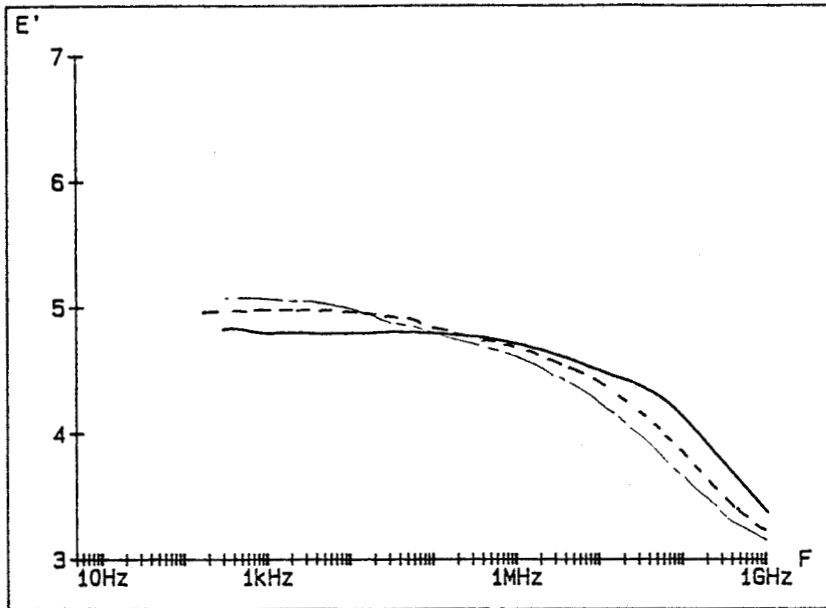


Figure F-45: p4, Methyl; phase Iso

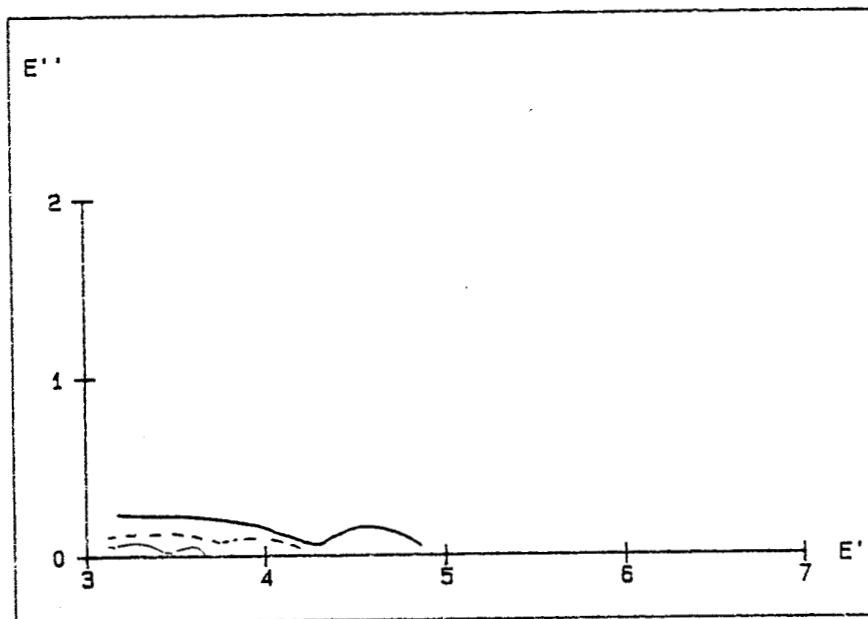
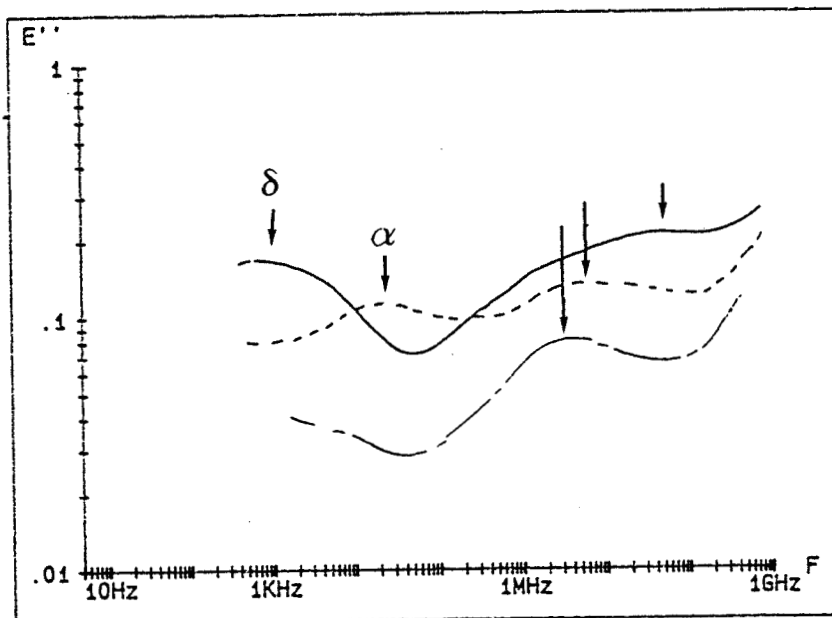
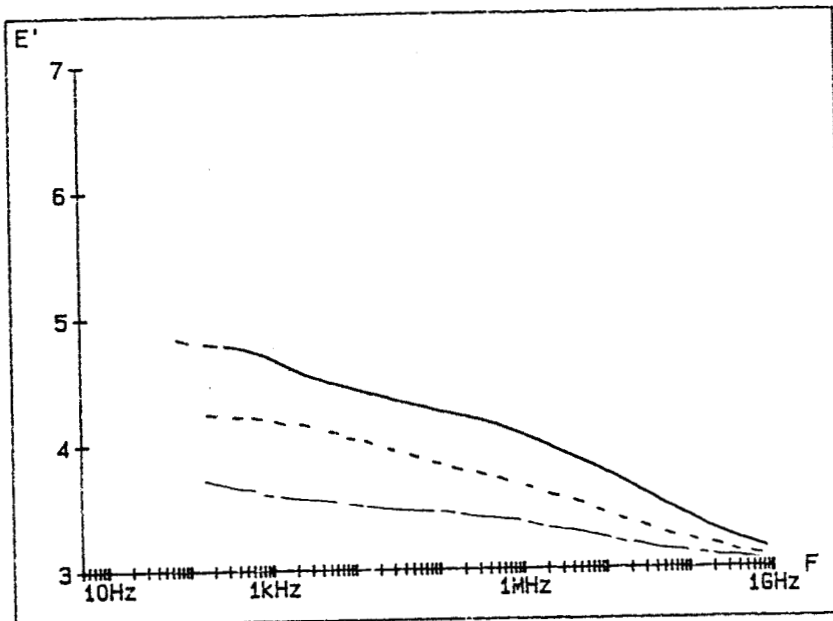
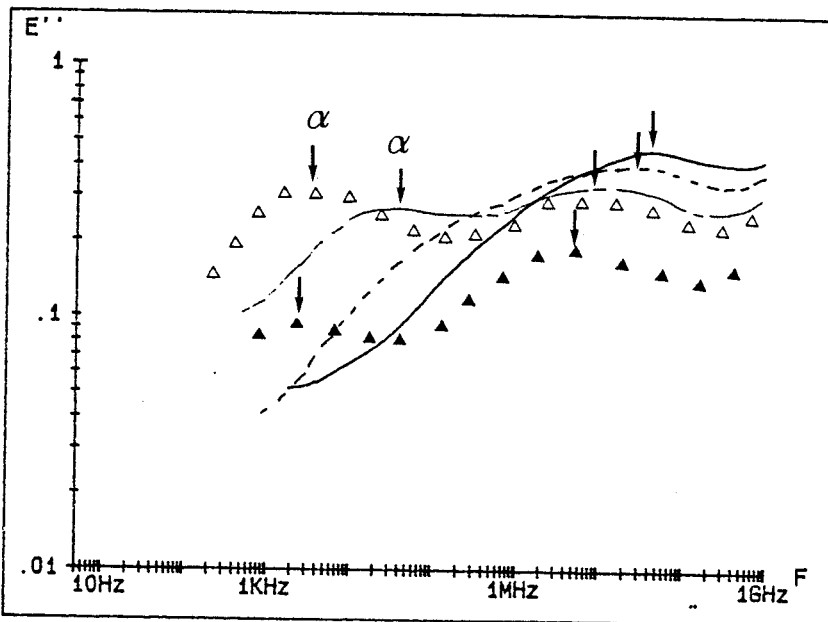
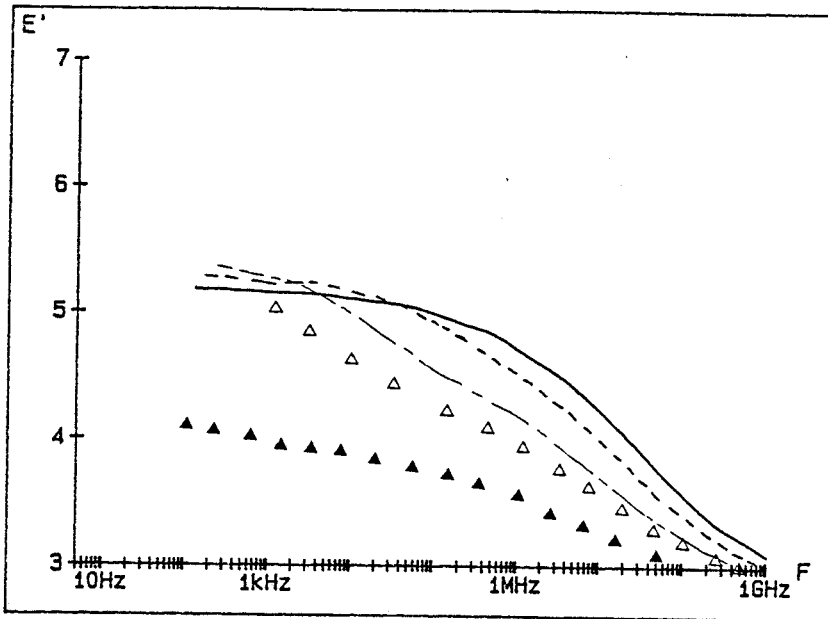


Figure F-46: P4, Methyl; phase Nem ($E//n$).



- 50°C
- - - 40°C
- · - 30°C
- △ △ 22°C
- ▲ ▲ 10°C

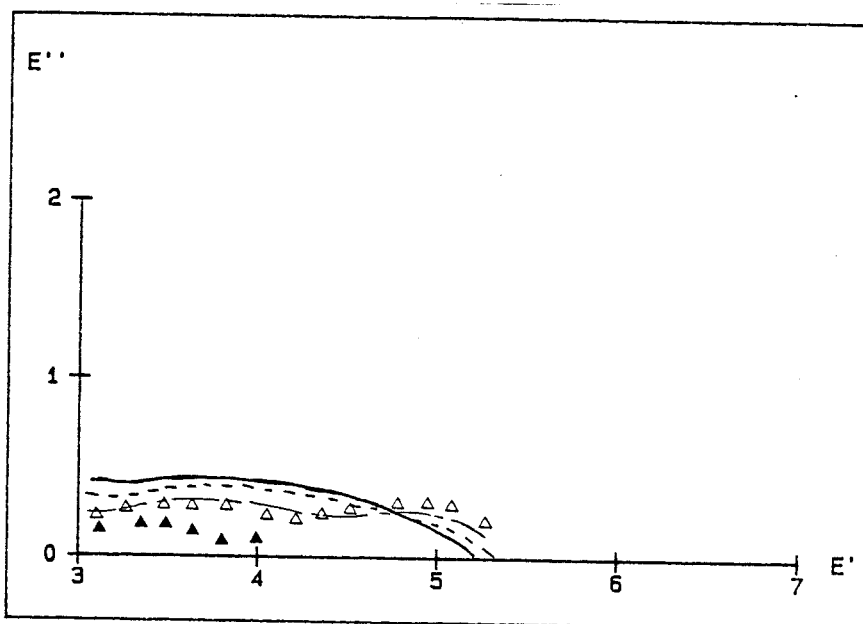


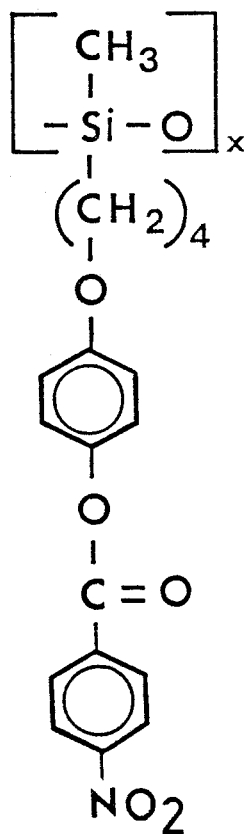
Figure F-47: P4, Methyl ; phase Nem (E'_{1n})

FICHE N° 9

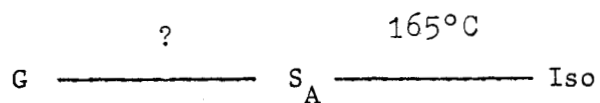
CODE DE LA SUBSTANCE : P4, NO₂

PROVENANCE : CENTRE DE RECHERCHES PAUL PASCAL (BORDEAUX)

FORMULE STRUCTURALE :



SEQUENCE DE PHASES ET TEMPERATURES DE TRANSITION

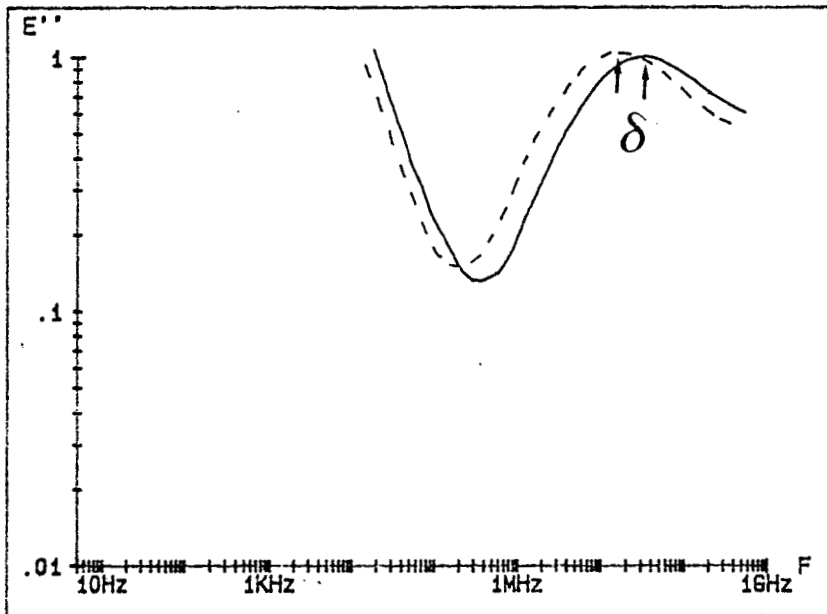
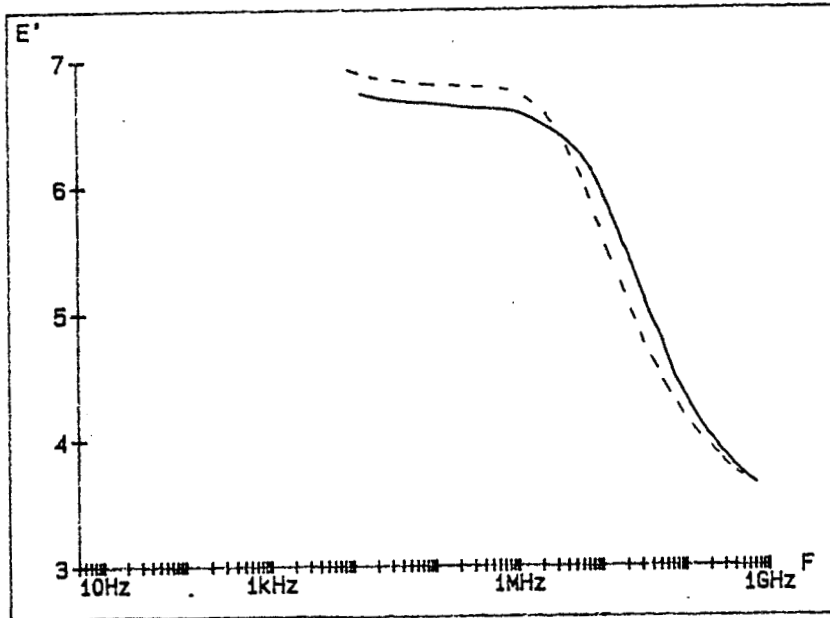


LISTE DES RESULTATS EXPERIMENTAUX PRESENTES

Nous ne présentons pas le régime statique car l'échantillon ne présente qu'une mésophase smectique qui ne s'est pas orientée sous champ magnétique.

Régime dynamique

- a) phase isotrope Figure F-48
- b) phase S_A Figure F-49



— 200 °C
- - - 180 °C

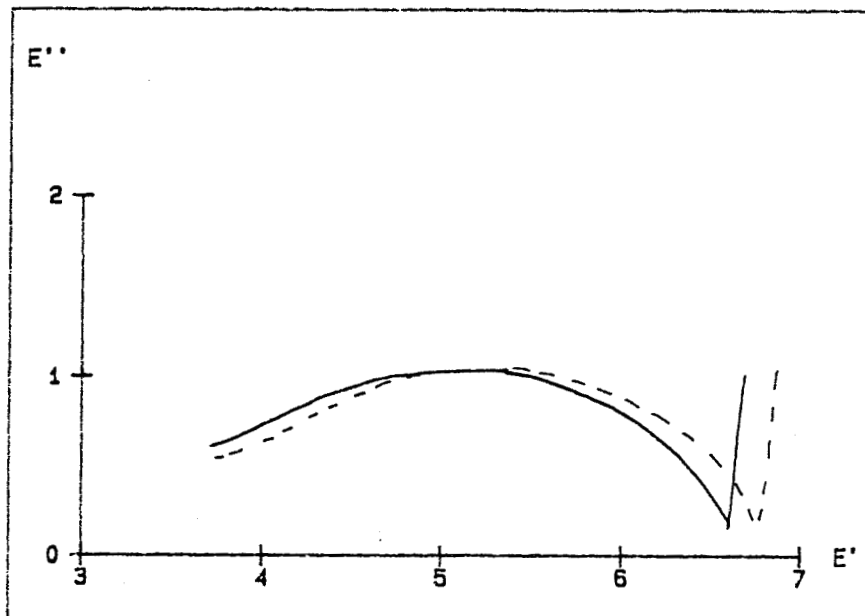


Figure F-48: P4,NO ; phase iso

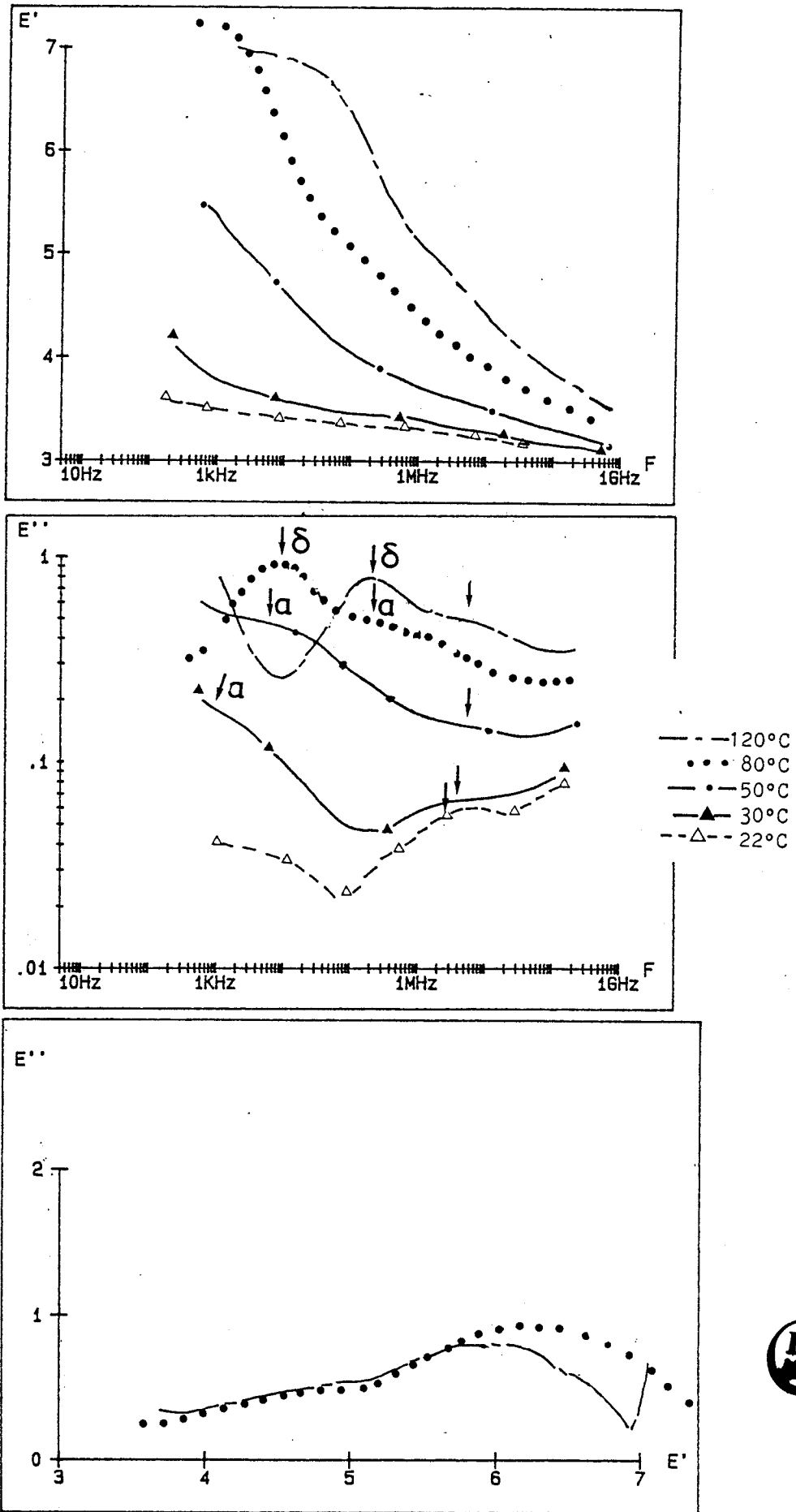


Figure F-49: P4,NO₂ ; phase S_A



SEQUENCE DE PHASE		Nre	SAd	N	I
CODE DE LA SUBSTANCE	ESPACEUR n	ENERGIES (KJ/mol)			
SSP2F1	2	-	-	-	147
PLBP24	3	-	-	-	137
PLBP25	4	-	-	177	120
PLBP14	5	-	-	131	88
PLBP12	6	241	126	192	82
CL	-	-	48	73	-
PLBP 10	5 + COO	-	-	143	60
CL	-	-	46	70	-
PLBP29	6	-	-	149	110
CL	-	-	-	84	46
PLBP30	6	-	82	163	88



TABLEAU F1 : Tableau récapitulatif des énergies d'activation des différents mécanismes de relaxation observés dans les diverses mésophases de l'ensemble des substances étudiées.

Séquence de phases		vitreuse (G)	S _B	S _A	N	I
Code échantillon	espaceur n	ENERGIES D'ACTIVATION (KJ/mol)				
RGP4	6				138 121	146
PLBP16	5,2					143
PLBP26	6				145 24	92
PLBP20	2					187
PLBP23	4					82
P4,1	4	18 8		169	110 86	47
P4, Methyl	4				50	161
P4, 8	4	61	85	116		48
P4,CN	4			1,27		89
M4,1					174 7	56
PLBP27	6					164
PLBP28	6				222	145
M 28					81	59
Remarques		β γ	HF	BF	BF HF	



TABLEAU F1 (suite)