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CONFORMATION OF COMB LIQUID CRYSTAL POLYMERS BY NEUTRON SMALL ANGLE SCATTERING

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Abstract

A review is made of the direct information obtained by small angle neutron scattering about the anisotropy of the components parallel and perpendicular to the orienting magnetic field of the radius of gyration of comb like liquid crystal polymers. The behaviour of the conformation versus temperature is reported for several samples. Until now all samples show an oblate conformation in the smectic phase and probably the whole range of the nematic phase. The results are compared with the available theoretical predictions.

1. Introduction

Among the new materials, liquid crystal polymers belong to one of the most fascinating domain, from both the engineering as the fundamental research point of view, because of their surprising physical and mechanical properties. The Kevlar fibre (Dupont de Nemours registred trade mark), remains one of the most famous and used in spite of its difficult preparation and thence its price. This success has forwarded an intense research for more easily processable materials, and still better mechanical properties. These liquid crystal polymers are of the main chain type, which means that the mesogenic moïties are incorporated into the backbones [1]and linked by flexible units called spacers, which provide flexibility to the system [2]. It is also possible to graft the mesogenic units transversally to the backbone creating therefore an other type of polymer called comb like liquid crystal polymer : this is an other way to conjugate polymer and liquid crystal properties [3,4]. While the main chain route research keeps very important, this latest route could be also promising for domains like conducting liquid crystal polymers [5] or optically active liquid crystal polymers [6].

These particular properties are bound to the antagonistic character of the two components : polymer and liquid crystal [1]. The polymer is entropy-driven, which is in competition with the ordering character of the mesophases. The resulting compound comes from an equilibrium between these two opposite tendencies. The mesophases succeed to limit the chain perturbation, thence the chain conformation may be deeply affected. Therefore the study of the chain conformation appears crucial for a better understanding of these systems. Few experimental methods are available. NMR is one of the most commonly used, nevertheless it gives local information about the orientation of some atomic links, which are not necessarily representative of the whole molecule orientation [7]. A more global and direct method is small angle X-ray scattering. While some beautiful experiments on liquid crystal polymers solutions have been performed [8], this method is handicaped by the usually small contrast, and the small wave-length generally at hand. The neutron small angle scattering technique, allows to use large wave-lengths, and specific labelling of the backbone or part of the mesogen by deuteration. This was first applied to comb like liquid polymethacrylates by Kirste and Ohm in 1984 [9]. After that one, many experiments have followed, in the field of side chain thermotropic liquid crystal polymers, to which we restrict now.

2. Theories

Lastly several publications have appeared which make predictions about the liquid crystal phase diagrams and the polymer backbone conformation ; measurable quantities, like the anisotropy of the components of the radius of gyration, or the order parameter are considered. The points of view vary from classical liquid crystal theory incorporating movement hindrance due to the backbone, to polymer behaviour modified by a nematic or smectic field.

For the nematic phase, an early athermal calculation by Vasilenko et al. [10] was based on Flory's steric repulsion model for polymers [11] : this drives to consider a partition function as a product of two terms : "molecule orientation" and "steric hindrance". It predicted various nematic phases acccording to the type of anisotropic ordering. Indeed a different thermal approach appeared with a paper by Warner et al., who after having considered the main chain polymers transitions and conformation [12] paid special attention to the comb like polymer case [13,14,15]. Their model is a mean-field Maïer Saupe approach including mesogenic order and worm like chain order. The modelisation is built on five interactions between the different parts of the macromolecule (backbone, spacer, mesogenic core, outside the flexible tail of the mesogen), and the partial volume of the mesogenic moïeties χ. They identify three main uniaxial nematic phases according to the sign of the backbone and the mesogen order parameters (fig.1). They also distinguish phases where one of the order parameters is small. They deduce phase diagrams for chosen sets of interactions temperature and mesogen ratio χ. This latter parameter seems to play an important role : in most case N_{II} and N_{III} phases convert into N_I while χ increases (see Fig.1).

How the smectic ordering may appear from a nematic N_I, was discussed by Renz and Warner [16]. The central idea is the following : the smectic field born by the smectic layers conflicts with the drive to maximize the backbone entropy by exploring all three space dimensions ; thence the backbone merely tunnels through the layers, which leads to an activation law for the temperature dependence of $R_{/\!/}$ (the component of the radius of gyration parallel to the mesogenic axis)

$$R^2_{/\!/} \propto \exp\left(-\frac{E}{k_B T}\right) \qquad (1)$$

Recently Renz [17] and Renz and Warner [18] discussed again the phase diagrams in relation with changes in the backbone flexibility and proposed variants of the backbone conformation in the smectic A phase.

In the meantime Kunchenko et al.[19] published for the nematic phase partly phenomenological calculations of the pair distribution functions of distances taking into account an anisotropic persistence (Kuhn) length, together with Boltzmann statistics. This leads the authors to predict the following variation versus temperature of the anisotropy of the radius of gyration

$$\left(\frac{R_{\perp}}{R_{/\!/}}\right)^2 = 1 + \frac{2u}{3k_B T}$$

where u is the differential energy of the Kuhn segment according to its relative orientation versus the director.

Basing another theoretical calculation about the smectic phase on the first experimental results, which showed that the backbone tends to be confined between two adjacent smectic layers, the same authors propose a formula for the ratio of chain segments crossing the layers [20]

$$k = \frac{6\ R^2_{/\!/}}{D \times L}$$

where D is the layer period and L the overall backbone length. For $R_{/\!/}$ they assume the same temperature variation (1) as Renz and Warner [16].

The papers of F. Dowell [21] start instead from the liquid crystal side, using basic experimentally known interactions between all the building blocks : backbone monomers, mesogenic cores, spacers and tails.

She then constructs a detailed partition function which hopefully will describe real systems in nematic and smectic phases as well. A computerized treatment of it allows to predict phase diagrams, including reentrance. This is here clearly linked to the tail flexibility, a feature scarcely considered in other models. This method aims to design compounds with predetermined properties. Results about the backbone conformation will appear latter [22].

At the Bordeaux Conference on Polymer Liquid Crystals, Rieger [23] paid special attention to the excluded volume effect (in smectics), a polymer feature somewhat neglected till now, in the comb like liquid crystal polymer case. He examined three models differing by the type of 2 dimensional walk of the backbone, restricted between smectic layers : random, self avoiding or straight walk. No difference in the large scale properties could be exhibited. However this does not preclude the possibility of random backbone arrangement : the study of the intermediate range of the scattering vector $\vec{q}$ might give some information about it [24].

3. Experimental method

The deuteration labelling method and experimental set-up for small angle neutron scattering have now been described many times (for instance [25]). One more appended with an interesting comparison with NMR can be found in a paper by Dubault et al. [7]. We shall here merely remind a few points. The samples are mixtures of two compounds ; in each of them some protons have been replaced by deuterium on the backbone or as close to it as possible, as the conformation of the backbone is to be studied. Thanks to the incompressibility of liquids,to first order approximation the neutron forward scattering is proportional to the scattering function of a single chain ; one prefactor is proportional to the contrast, i.e. the squared difference of the relative scattering lengths a_D ,a_H of the H/D macromolecules $(a_D - a_H)^2$. The other prefactor is proportional to c(1-c) where c is the concentration of one of the two compounds. It is then maximized when c=1/2.

In all the experiments described below, the sample was aligned by a powerful magnetic field perpendicular to the neutron beam, and the forward neutron scattering measured by a 2 dimensional position sensitive detector. After substraction of the incoherent background, evaluated from a fully protonated sample, the forward intensity was analysed in the frame of an anisotropic Guinier approximation :

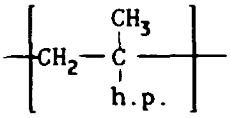
$$I(\vec{q})^{-1} = I(0)^{-1} \left(1 + q_{/\!/}^2 R_{/\!/}^2 + q_\perp^2 R_\perp^2\right)$$

where $q_{/\!/}$, $q_\perp$ are the components of the scattering vector $\vec{q}$ parallel and transverse to the magnetic field , and $R_{/\!/}$, $R_\perp$ are the longitudinal and transverse components of the radius of gyration.

4. Samples

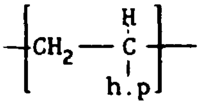
In order to understand the influence of the backbone flexibility three classes of polymers have been examined, according to an increasing flexibility :

Polymethacrylate (PMA)



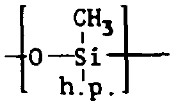
$$-\!\!\left[CH_2-\overset{CH_3}{\underset{h.p.}{C}}- \right]\!\!-$$

Polyacrylate (PA)



$$-\!\!\left[CH_2-\overset{H}{\underset{h.p}{C}}- \right]\!\!-$$

Polymethylsiloxane (PMS)



$$-\!\!\left[O-\overset{CH_3}{\underset{h.p.}{Si}}- \right]\!\!-$$

where h.p. holds for the hanging part. While the length and flexibility of the spacer crucially acts on the decoupling of the mesogenic core from the backbone, and thence on the liquid crystal structure, only one type was used for the PMA and PA and two for the PMS.

The hanging parts which were incorporated in the comb like liquid crystal polymers studied by SANS are gathered on Table 1.

5. Discussion of the experimental results

In the first experiment performed on a comb-like liquid crystal polymer (samples 1 and 2 : PMA-OCH_3) Kirste and Ohm [9] observed a backbone anisotropy for the nematic phase : shape oblate relatively to the orienting magnetic field (sample 3 being only smectic could not be aligned by the field). Indeed this feature is now proved to be general for all the samples in the smectic phase reviewed here. The backbone conformation looks similar in the nematic phase. Nevertheless the anisotropy of the radius of gyration being usually small, some uncertainties must still be cleared out. Moreover studies versus temperature exhibit a variety of behaviours.

We invite the reader to compare the evolution of the radius of gyration versus temperature for two polymethacrylates (samples 4,5, Fig.2). For these, which exhibit a large smectic temperature range, the parallel component of the radius of gyration $R_{/\!/}$ seems to follow the activation law (1), with indeed the same activation energy in both cases : $E = 0.8$ eV. The two compounds differ only by the tails of the mesogenic moïety, which, of course, may induce different interactions. No theory takes this into account, except possibly that of F.D. ; anyway no specific calculation is available up tc now. For PMA-CN Rieger [23] interprets the decrease of $R_{\perp}$ with the temperature, by the backbone being still out of equilibrium, while the liquid crystal part is already smectic. The sample 4 (PMA-OC_4H_9) low angle scattering shows some variations of the diffuse spots according to the deuteration and the mixture observed (Fig.3). The cases of the macromolecule being deuterated on the backbone [26,27] or the tails [28,30] was discussed This lead the authors to propose a model exhibiting some small regions with local bilayer ordering, with restriction of the backbone at the border of these, together with long range monolayer smectic ordering. A third polymethacrylate PMA-OCH_3 is nematic over a much broader range than the two others. It gave some experimental problems. In the early Kirste and Ohm experiment [9] no temperature change of the backbone conformation was found contrarily to another publication [29]. Recent measurements [24] show that below 75°C this material exhibits a smectic phase. Indeed its behaviour is similar to that of PMA-OC_4H_9 in both the nematic and the smectic phases.

The case of comb like polysiloxanes is delicate. In a first experiment [27] (sample 7) the radii of gyration did not change versus temperature and its anisotropy was reversed, corresponding to a prolate shape The authors had yet doubts about the actual backbone conformation, because the deuteration had been performed on the nematogen tails, and the small degree of polymerisation might induce an artefact in the interpretation. Indeed a second experiment with the same kind of deuteration, but a much larger degree of polymerisation (sample 8) showed that the global polymer becomes oblate in the smectic phase and in most of the nematic phase, where an anisotropy reversal seems to occur. The discussion about the artefact origin was published [29]. Recently a third experiment [24] with a deuteration on the spacer confirmed that the backbone is oblate in most of the nematic range. In the meantime results about an other polysiloxane (sample 9) was published at the Bordeaux Conference, which showed also an oblate conformation [31].

Remained a very controversed case : a polyacrylate (sample 6), for which NMR measurements [32] hinted to a prolate conformation. Recent SANS experiments undertaken at Saclay, show without any doubt that the backbone adopts an oblate shape, already in the nematic domain [33] (Fig.4). The anisotropy reversal at the higher border of the nematic phase, stays inside the error bars. This experiment shows the limits of the NMR spectroscopy which gives only local measures, which are not directly related to the relative position of the backbone as a whole, versus the liquid crystal director.

6. Conclusion

The small angle scattering method gives a direct knowledge about the conformation of the polymer backbone (provided the labelling is on the backbone or close to it). Applied to a set of comb-like liquid crystal polymers in melt, SANS shows an oblate anisotropy in all the observed smectic phases and most of the nematic temperature range, if not all.

The studied polymethacrylates and polyacrylate possess the same hard core and spacer, they have therefore similar interactions (in the sense of Wang and Warner theory) and mesogenic ratio χ. Thence, it is not surprising that they exhibit the same nematic phase (i.e. N_I). It would be of interest to look for new systems with other interactions and possibly χ.

In the smectic phases, the backbone conformations is strongly confined between two adjacent layers. The study of the components of the radius of gyration versus temperature reveals some behaviour changes, when the mesogenic tail is modified. An activation law seems to be a good model for $R_{/\!/}$.

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Figure Captions

Fig.1. The three uniaxial nematic phases possible for comb polymers (drawing from reference [13]. Courtesy of the authors).

Fig.2. Radius of gyration of polymethacrylates versus temperature. (samples 4 and 2).

▲ $R_\perp$
● $R_{/\!/}$.

Fig.3. PMA-OC_4H_9 in the smectic phase. Fig. 2a : model. Fig. 2b,c,d low angle neutron scattering for samples deuteration at various position and mixtures. The anisotropic forward scattering is specially visible on Fig.2d.

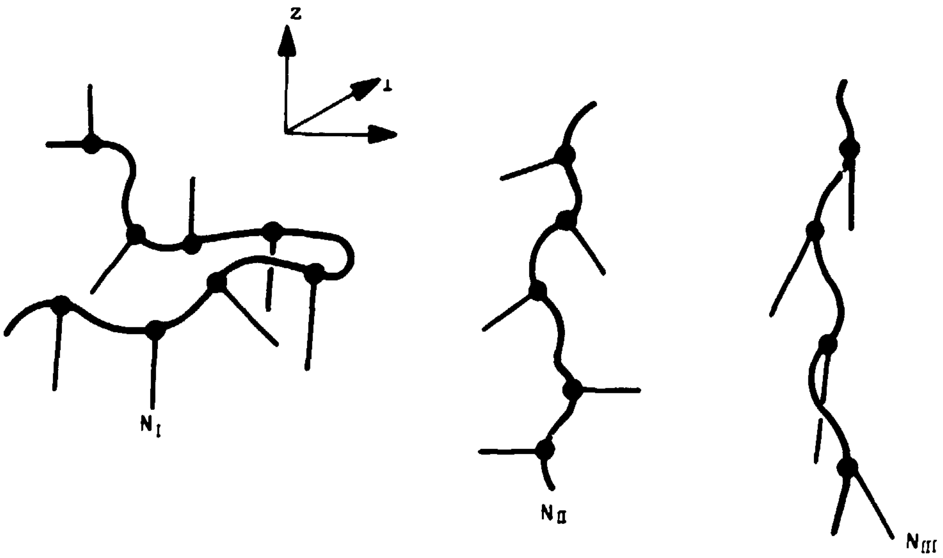
Fig.4. Radius of gyration of a polyacrylate versus temperature (sample 6).

+ $R_\perp$
● $R_{/\!/}$

Sample N°	Backbone type	Hanging part formula	Weight average polymerisation degree	Poly-dispersity	References	Neutron site
1	PMA	$-COO(CH_2)_6-O-\phi-COO-\phi-OCH_3$	900	1.5	9	ILL.Grenoble
2			770	2.6	9,29	ILL/Saclay
3		$-COO(CH_2)_6-O-\phi-COO-\phi-(CH_2)_5CH_3$	1000	1.5	9,29	ILL
4		$-COO(CH_2)_6-O-\phi-COO-\phi-OC_4H_9$	700	2.4	26,27 28,29 30	Saclay
5		$-COO(CH_2)_6-O-\phi-COO-\phi-CN$	300	2.2	27 29 30	"
6	PA	$-COO(CH_2)_6-O-\phi-COO-\phi-OCH_3$	80	2.3		"
7	PMS	$-(CH_2)_4-O-\phi-OCO-\phi-O-OCH_3$	35	1	27,29	Saclay
8			80	1	29,30	"
9		$-(CH_2)_3-O-\phi-\phi-CN$	63		31	Dubna

TABLE 1

(Note : Weight average polymerisation degree are mean values for several samples)



L. Noirez G. Pépy Fig 1

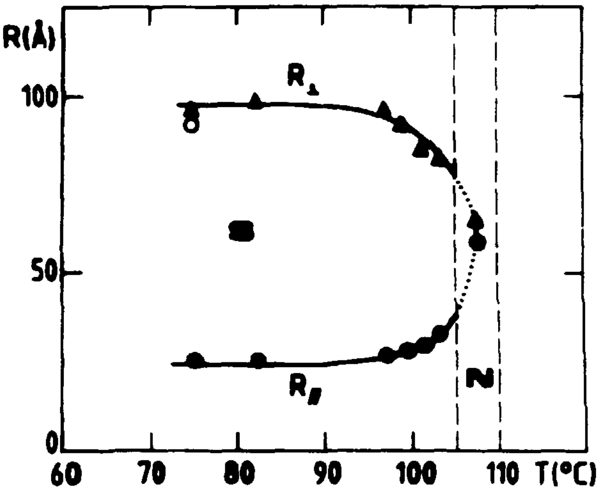


Fig.3a. PMA-OC_4H_9

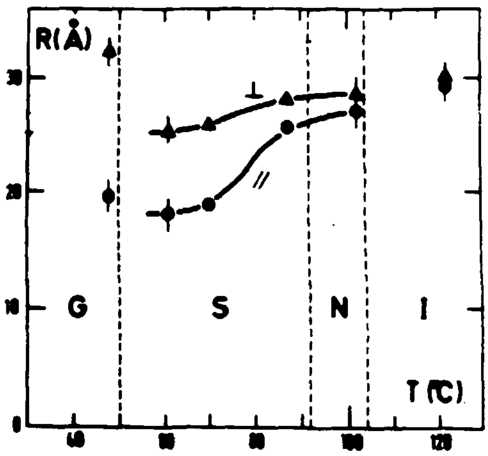
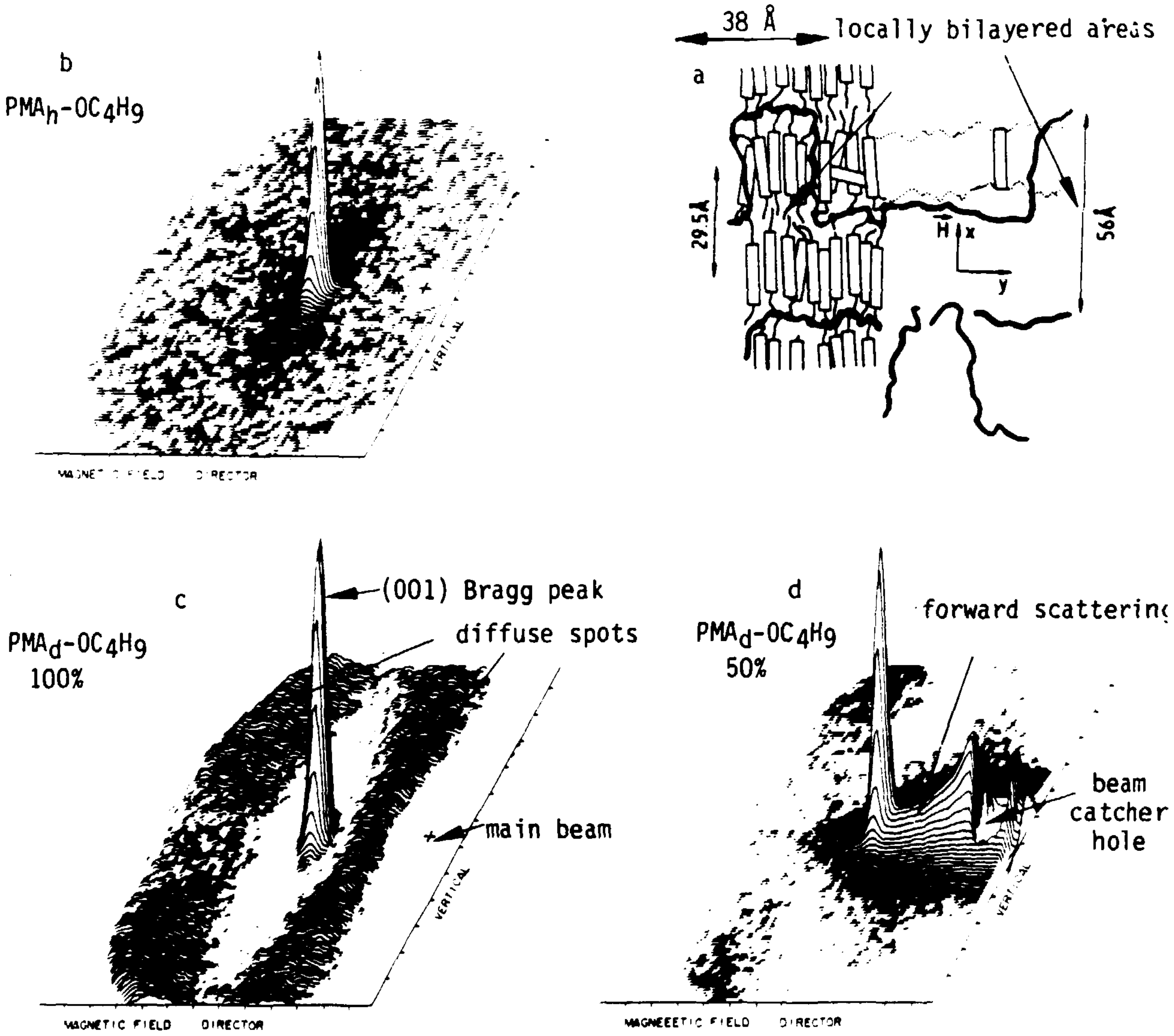
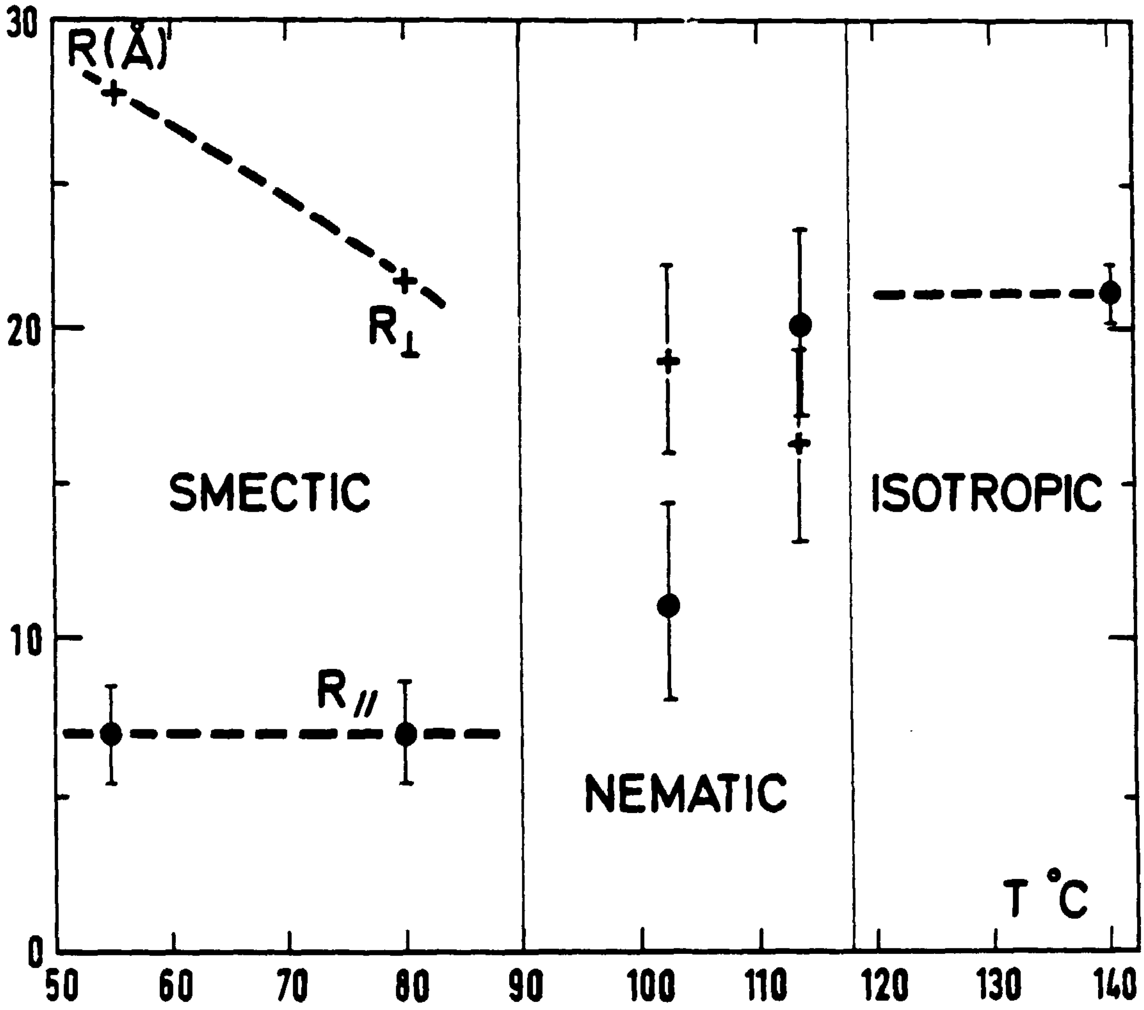


Fig.3b. PMA-CN

L. Noirez G. Pépy Fig 2



L. Noirez G. Pépy Fig 3



L. Noirez G. Pépy Fig 4