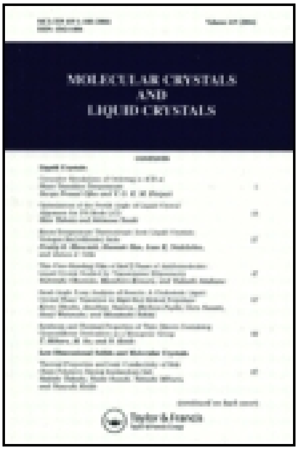

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LIQUID CRYSTAL POLYMERS : A SMALL ANGLE NEUTRON SCATTERING STUDY

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Abstract : One reports Small Angle Neutron Scattering (SANS) studies on mesogenic comb-like polymers. One has drawn attention on different polymethacrylates specially in nematic phase. A way to determine the conformation of these polymers, consists to measure their quadratic sizes by the labelling method. One has also tested this method in function of the molecular length of a LC-polysiloxane. It appears that wathever the chemical species, the backbone of polymers prefer to be perpendicular to their mesogenic groups in the smectic phase. The situation is less simple in the nematic phase.

INTRODUCTION

During the last years, liquid crystal polymers have given rise to a growing interest in theoretical, experimental and applied physics (Ref.1). A liquid crystal comb-like polymer is characterized by : i) a backbone, ii) a hanging mesogenic unit, iii) a spacer joining the backbone to the mesogenic moieties.

backbone
spacer
mesogenic unit

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Each of these three elements plays a peculiar role, the backbone, if alone, would be a random coil, but it undergoes the liquid crystal order imposed by the mesogenic cores, the strength of this compulsion depends on the spacer which assumes more or less the decoupling between these two parts of the polymer.

Is there a general response from the backbone to this liquid crystal order ? How is the conformation of the backbone in the different liquid crystal phases ? These are the main questions one tries to answer .

First, one recalls the previous measurements and results on polymethacrylates and polysiloxanes with small angle neutron scattering, specially in their smectic phases. Then, one reports new studies on polysiloxanes and on another polymethacrylate which exhibits a large domain in temperature of the nematic phase. Finally, one compares rapidly these results to available theories.

I. EXPERIMENTAL :

Small Angle Neutron Scattering (SANS) associated to a labelling method is a good way to measure the polymer conformation (Ref.2). The bulk samples are mixtures of fully protonated and partially deuterated polymers in equal parts. The deuterium can be on the backbone, in the case of polymethacrylates, or on the terminal groups of mesogenic cores, this is the case for the polysiloxanes. In the last case, this is mostly the conformation of the whole polymer which is measured and no more only that of the backbone (case of polymethacrylates).

The neutron experiments have been performed on the SANS spectrometer PAXY at Orphée Reactor (CEN Saclay). An XY position sensitive multidetector (15 500 cells of size 5X5 mm2) allowed to measure the anisotropic intensity.

One has used the following relations which join the anisotropic intensity to the anisotropy of the polymer conformation :

$$I^{-1}(Q_{//})=I^{-1}(0).(\ 1 + Q_{//}^2.R_{//}^2) \quad \text{parallel to the magnetic}$$
$$I^{-1}(Q_{\perp})=I^{-1}(0).(\ 1 + Q_{\perp}^2.R_{\perp}^2) \quad \text{perpend.} \qquad \text{field}$$

available when $Q.R < 1$; where $Q=2\pi\theta\ /\lambda$ is the scattering vector, θ is the scattering angle and λ the wavelength. So, $R_{//}$ and $R_{\perp}$ are the quadratic characteristic sizes of the backbone or of the polymer according to the location of the labelling.

Two scattering vector ranges have been explored :

i) $8.10^{-3} < Q < 3.10^{-2}$ Å^{-1} for SANS experiments at λ =15 Å and D=2m (sample-multidetector distance)

ii) $0.05 < Q < 0.2$ Å^{-1} for Neutron Diffraction (ND) experiments at λ =3.7 Å and D=1.2 m

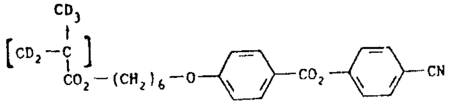
The different samples (15mm of diameter, 1mm of thickness and 7mm for neutron beam diameter) have been set in an oven (temperature regulation better than 0.2°C) which is placed on the trajectory of neutrons. Cooling from the isotropic state, one has applied a magnetic field of 1.4 T in order to obtain aligned nematic and smectic phases (For more details see Ref.3).

The suitable alignment of a sample at a given temperature is controlled by ND, then the SANS study is achieved with the same conditions for the sample.

II. PREVIOUS RESULTS :

We have shown for two polymethacrylates (Ref.3 and 4), noted PMA-CN and PMA-OC_4H_9, that the backbone was rather confined into the plane perpendicular to the magnetic field.

More precisely, this PMA-CN has the formula:



$$\left[CD_2-\overset{CD_3}{\underset{CO_2-(CH_2)_6-O-C_6H_4-CO_2-C_6H_4-CN}{C}}\right]$$

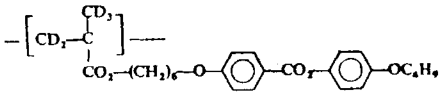
Its molecular weight Mw and its polydispersity (I) have been determined: Mw = 110 000, I = 2.3 (There are nearly the same for the deuterated backbone polymer and the hydrogenated one - Ref.5).

Only one SANS measurement has been made in nematic phase, at 102°C : $R_{\perp}$ = 28.2 Å

$R_{//}$ = 26.5 Å

showing that the backbone begins to have a slightly anisotropic conformation. In the smectic phase, the anisotropy strongly increases and is thermally activated (Ref.4).

In the case of the PMA-OC_4H_9, with formula :



$$-\left[CD_2-\overset{CD_3}{\underset{CO_2-(CH_2)_6-O-C_6H_4-CO_2-C_6H_4-OC_4H_9}{C}}\right]-$$

and molecular weight Mw=300 000 (I=3.3)(Ref.5), the narrow temperature range of the nematic phase has allowed only one measurement at 112°C; $R_{\perp}$ = 65 Å

$R_{//}$ = 59 Å

This anisotropy is much more emphasized in smectic phase, where the backbone is confined into one or two smectic layers (Ref.3).

We have then completed these studies in nematic phase, choosing a polymer with a large nematic temperature range. *(see results section IV).*

We had also begun the study of Polysiloxanes PMS (Ref.6). A first result (Ref.3) was that this PMS exhibited an opposite anisotropy (i.e. $R_{//} > R_{\perp}$). But, this polymer had a small degree of polymerisation n=35, and moreover it was labelled on the terminal groups OCD_3. So, was the deuterium location responsible of an "apparent" anisotropy of PMS? *(aggravated by the small length of the molecule),* or was the behaviour of PMS completely different of that of PMA ?

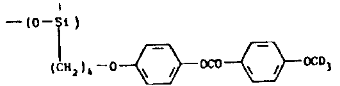
$R_{\perp} > R_{//}$ $R_{//} > R_{\perp}$

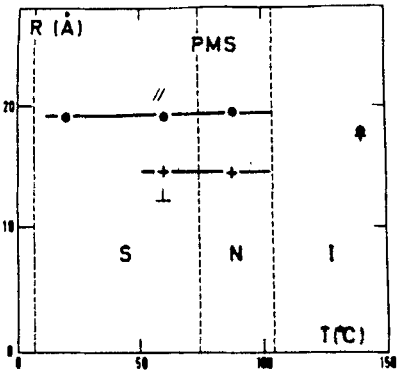
figure 1: the backbone can be perpendicular to the magnetic field, whereas the global polymer is parallel.

One way to answer this question consists to study an identical deuterated PMS, but with a greater degree of polymerisation. This experiment has performed and has given the results shown in the following section.

III. EFFECT OF VARIATION OF MOLECULAR LENGTH IN PMS:

We compare the behaviour of two PMS of different degrees of polymerisation (n = 35 and n = 80) in function of the temperature (fig. 2 and 3).





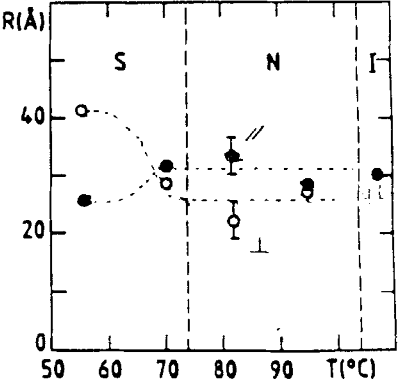


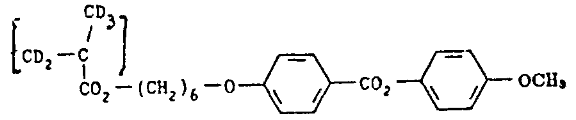
figure 2
quadratic sizes of PMS(35)
in function of temperature

figure 3
quadratic sizes of PMS(80)
in function of temperature

We are now sure that the PMS(80) presents the same configuration as the polymethacrylates in smectic phase. Indeed, $R_\perp$ becomes larger than $R_{//}$ as soon as the LC-polymer is in the smectic phase. In nematic phase, it is possible that the backbone of PMS is also perpendicular to the magnetic field although $R_\perp$ is smaller than $R_{//}$, for the same reasons called up above (Section II). One must again outline the problem of the labelling of the terminal groups which appears when the anisotropy is too weak or the molecular length too small. Let us notice that the mesogenic unit length is about 20 Å, which contributes to increase the value of $R_{//}$ in nematic phase. So, no definitive conclusion can be drawn in the nematic phase. Anyway, one can ascertain that, in the smectic phase, changing the chemical species of the backbone of a comblike polymer keeps unchanged the direction of the anisotropy of the conformation and the backbone remains confined into one or two smectic layers.

IV. NEMATIC PHASE STUDY IN FUNCTION OF THE TEMPERATURE

The experiments (Ref.7) were made with a PMA-OCH_3 of formula :



which has a large temperature range of the nematic phase:65°C

Its average molecular weight is about Mw=320 000 (I= 2.7) (Ref. 7). One observes the thermal dependence of characteristic sizes of the backbone in the nematic phase :

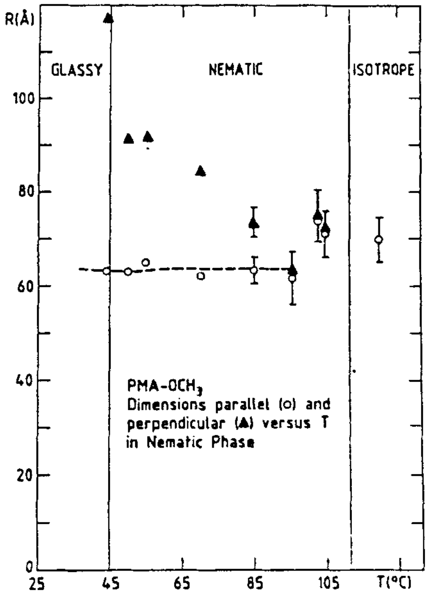


Figure 4

In the limits of the experimental accuracy, the size parallel to the magnetic field is constant, it seems to be frozen whereas the size in the perpendicular direction increases significantly with decreasing temperature.

The point at the lowest temperature (in figure 4) is very high. It was measured in glassy state. The PMA-CN presents also a higher point at low temperature (Ref. 3), is it a same behaviour, or perhaps the beginning of a weak crystallization ?

V. ATTEMPT TO COMPARE WITH MODELS :

As it was predicted, we have in several cases verified that the backbone, in the nematic phase, was rather directed perpendicular to the magnetic field. For these cases, $R_\perp$ was larger than $R_{//}$ with sometimes an important difference between these two parameters. This agrees with the scheme of the nematic oblate phase called NI in the Wang-Warner's diffusion model (Ref.8) where the main chain explores the plane perpendicular to the director.

No unique power law between $R_\perp$ and the temperature can be deduced from our measurements. This is due perhaps to the lack of accuracy in the determination of the $R_\perp$ values and also to the weak number of measurements which satisfy the low temperature conditions of the model. In the same way, there is no better quantitative agreement with the model described in Ref.9 and 10 .

CONCLUSION :

We have shown for different polymethacrylates that their backbone prefers always to be mostly perpendicular to the magnetic field even in nematic phase. It appears in the special case of PMA-OCH_3, that the size of the backbone in the direction parallel to the magnetic field is not temperature dependent within the experimental precision. On the other hand, the polymer expands widely perpendicularly to the director as the temperature decreases. As to the polysiloxane (n=80), its backbone is also confined into layers in smectic phase. In the nematic phase, the situation is less clear.

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