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INTEREST OF NEUTRON SCATTERING FOR THE INVESTIGATION OF LIQUID-CRYSTALLINE POLYMERS

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Small-Angle Neutron Scattering is the unique method wich allows the determination of the polymer conformation in the bulk. This method has been applied to several kinds of liquid crystalline polymers. We report here general results obtained on side-chain liquid-crystal polymer, main-chain liquid-crystal polymer and finally combined liquid-crystal polymers. It is shown that the polymer conformation is largely dependent of the insertion site of the liquid crystal molecule and of the structure of the mesophase.

The conformation of a polymer in the bulk is an isotropic coil for which characteristic size is proportional to the root mean square of its length. The liquid crystal molecules have rod-like shapes and are able to align their long axis parallel to each other in the nematic phase (N), while in the smectic phase (SA), they are in addition stacked in layers of well defined thickness. When the liquid-crystalline molecules are inserted in a polymer chain via a small chain (usually an alkyl chain) called "spacer", the mesomorphic properties of the liquid crystal molecules are not lost. The introduction of "flexible spacer concept"[1] has enabled the synthesis of broad variety of liquid crystal polymers using all the possible combinations to include the liquid crystal in a polymer chain. These new polymers have obviously generated much interest the last years, not only because of the understanding challenge, but also because of the technological interest for optical data storage, high molecules fibers easely processable with extrusion, moulding methods ...

Neutron Scattering is a particularly well-adapted method to investigate these systems. The dimensions and the anisotropy of the polymer chain in the bulk are provided by Small-Angle Neutron Scattering (SANS), whereas several informations concerning the mesophase structure are obtained by Neutron Diffraction. In addition, the layers in the smectic A phase are thick enough to allow the observation of the first Bragg reflections (and usually liquid crystal polymers don't possess high reflection orders) with the same SANS device. The simultaneous study of the polymer conformation and of the mesophase structure is then possible.

We propose to compare the main-chain conformation of different liquid crystal polymers in the following situations:

- when the liquid crystal molecule is grafted on the side of a polymer chain, obtaining the side-chain liquid crystal polymers.
- when the liquid crystal molecule is inserted along the polymer chain giving the main-chain liquid-crystal polymer.
- when the polymer possesses at the same time, a liquid crystal molecule on the side part and along the polymer chain, one obtains the combined liquid-crystal polymer.

These polymers have various degrees of polymerization included between 10 and 300, measured by using Gel Permeation Chromatography-Light Scattering on line[2].

Neutron scattering experiments:

The scattering cross section S(q) at small q values (where $q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$ with θ the scattering angle and λ the wavelength) gives information on the macroscopic aspect of the sample. An artificial mean to create heterogeneities in polymers in bulk, is to prepare samples of hydrogenated polymers mixed with selectively deuterated polymers. It has been demonstrated[3,4] that the scattering function of a mixture containing X_H hydrogenated polymers and X_D deuterated polymers ($X_H + X_D = 1$) is given by:

$$S(q) = N.X_H.X_D\,(a_D-a_H)^2\,P(q)$$

where N is the total number of polymer chains, a_H, a_D are the coherent scattering lengths of the protonated and deuterated monomers respectively (at small q values, each monomer can be considered as a scatterer of coherent scattering length a) and P(q) is the Form Factor of a single chain. P(q) is directly related to the square of the radius of gyration R_g^2 or to its components R_x^2, R_y^2, R_z^2 following the Ox, Oy, Oz axis. At small q values, the Guinier domain defined by $q \leq 1/R_g$, is reached and the Zimm approximation can be applied; P(q) becomes:

$$P(q_x,q_y,q_z) \propto n^2(1 - q_x^2.R_x^2 - q_y^2.R_y^2 - q_z^2.R_z^2)$$

q_x, q_y, q_z are the projections of the scattering vector along Ox, Oy, Oz axis. In the case of liquid crystal polymers, the direction of the magnetic field which aligns the liquid crystal molecules is a symmetry axis of the polymer. If Ox is parallel to the direction of the magnetic field, R_x^2 is called $R_{//}^2$. The two other components are then perpendicular to the magnetic field:

$$R_y^2 = R_z^2 = R_\perp^2$$

The radius of gyration is then given by:

$$R_g^2 = 2R_\perp^2 + R_{//}^2$$

So, when the magnetic field and the scattering plane are placed perpendicular to the incident beam, we measure the scattering intensity in the planes containing the parallel and the perpendicular directions to the magnetic field:

$$\frac{1}{I} = \frac{1}{I(0)}.(1+.q_{//}^2.R_{//}^2 + q_\perp^2.R_\perp^2)$$

The polymer anisotropy is then calculated in terms of components of radius of gyration ($R_{//}$) and perpendicular ($R_\perp$) to the magnetic field.
In most cases, the liquid-crystal polymers are only partially deuterated. It is indeed difficult from a chemical point of view to substitute all the protons. But moreover, the partial labeling presents the advantage that we can choose the part of the macromolecule to be observed.
Indeed, the intensity scattered by a mixture of hydrogenated polymers with partially deuterated polymers, is associated to the form factor of the labelled part of the macromolecule. This can be experimentally demonstrated using the expression of the scattering function of a polymer chain with several scatterers (a_H or a_D for the labelled part, a_2, ..., a_n):

$$S(q,(a_H,a_D),a_2,\ldots a_n) = NX_HX_D(a_H,a_D)^2P(\bar{q}) + S_o(q,(a_H,a_D),a_2,\ldots a_n)$$

where $P(\bar{q})$ is the partial form factor of the labelled part of the polymer. Experimentally, we show by tacking either hydrogenated sample ($X_H=1$) or a fully partially deuterated sample ($X_D=1$), that there is no coherent scattering contribution from S_o in the small q-range (fig.1). S_o is then negligible compared to the first term.

fig.1: Intensity scattered by a sample containing X_H of hydrogenated polymers and X_D of polymer deuterated on the main-chain only.
1. obtained with $X_D=1$.
2. obtained with $X_H=1$.
3. obtained with $X_D=X_H=0.5$.

In the case of side-chain liquid-crystal polymers and combined liquid crystal polymers, we were interested in the main-chain conformation, so only the main-chain has been deuterated, whereas only the spacer of the main-chain are deuterated in the case of main-chain liquid-crystal polymers[5].

Experimental results:

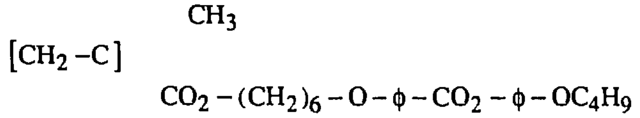
The neutron experiments presented here have been carried out on the SANS spectrometer PAXY of the Lab. Léon Brillouin. The experimental conditions are described in details in two PhD thesis which subjects were respectively the study of side-chain liquid-crystal polymer[6] and the study of main-chain liquid-crystal polymer[7]. Let just recall that the q-range used for these studies is typically $0.01Å^{-1} < q < 0.3Å^{-1}$ and that the samples are monodomains oriented by a magnetic field of 1.4 T by decreasing the temperature from the isotropic phase down to the glassy state.

Side-chain liquid crystal polymers (fig.2):

Side-chain liquid crystal polymers are deuterated on the main-chain only, in order to study the main-chain conformation of the polymer in the different mesophases. The main-chain is usually a polyacryiate or polymethacrylate chain with a spacer of six methyl, a biphenyl or a phenyl benzoate group as a hard core ended by a small alkyl chain of variable length.
The series of liquid-crystal polymer studied presents, following the nature of the hard core or the length of the terminal chain, two types of succession of phases by decreasing the temperature.:

I(isotropic phase) - N - S_A - T_g(glassy state)
or I(isotropic phase) - N - Tg

For example, the polymethacrylate PMA-OC_4H_9:



$$[CH_2-\overset{CH_3}{\underset{CO_2-(CH_2)_6-O-\phi-CO_2-\phi-OC_4H_9}{C}}]$$

corresponds to these transition temperatures:

I - N(108°C) - - S_A(98°C) - T_g(35°C)

Excepted in the isotropic phase, the conformation of the polymer backbone is no more an isotropic coil in the different phases.

- when the liquid-crystal polymer presents only a nematic phase, the polymer backbone adopts a prolate conformation in which the average direction of the backbone is that of the liquid crystal axis. This situation is sterically convenient since the packing is fulfilled simultaneously for the side-chain part and the backbone.

- when the liquid-crystal polymer presents the S_A-N-I phase succession, the anisotropy of the polymer backbone is always such that the backbone is mostly oriented perpendicular to the direction of the liquid-crystal molecules ($R_{//}<R_{\perp}$). This anisotropy corresponding to an oblate backbone shape, is small in the nematic phase. It increases in the S_A phase reaching anisotropy ratios of $R_{\perp}/R_{//}=4$. It has been experimentally ascertained by neutron diffraction[8] that the polymer backbone is mostly localized between the liquid crystal layers in the S_A phase. The stronger the smectic order is, the more the polymer backbone is excluded from the liquid crystal zones. Even in the nematic phase, it remains some smectic fluctuations (corresponding to a smectic order of short range but still comparable to the polymer dimension (100Å)). These fluctuations could be suffucient to induce the oblate anisotropy observed in the nematic phase.

Main-chain liquid-crystal polymers :

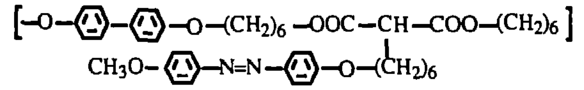
The only experimental observations of the conformation of a main-chain liquid-crystal polymers concern a nematic polyester synthesized by A. BLUMSTEIN[9], and successively studied by SANS by J.F. d'ALLEST et al [10] and M.H. LI et al [5].
This polymer presents the advantages of a broad nematic phase with a relatively low temperature for the isotropic-nematic transition. The SANS results indicate in the nematic phase that the chain is extremely stretched in the direction of the applied magnetic field. The anisotropy is so large that the Zimm approximation can no more be used to obtain the component $R_{//}$. Using the cylinder model for the scattering function, they show that the ratio (cylinder radius/cylinder length) can reach a value greater than thirty ! On the other hand, this polymer has the behaviour of a random coil in the isotropic phase with a size proportional to the root mean square of its length (gaussien coil). The flexibility of the chain is then totally recovered in this phase[7].

Combined liquid-crystal polymers :

Combined liquid-crystal polymers is a combination of a main-chain and a side-chain polymer. What will be the resulting polymer conformation? Is there a competition between the liquid crystal molecules or a reinforcement of the liquid crystal effect (coooperative effect)?

The only combined liquid crystal polymer studied by SANS until now, presents a main-chain liquid crystal molecule of length 32Å and a shorter side-chain liquid crystal molecule of 23Å (10).

It corresponds to the following formula:



$$\left[-O-C_6H_4-C_6H_4-O-(CH_2)_6-OOC-\underset{\displaystyle CH_3O-C_6H_4-N{=}N-C_6H_4-O-(CH_2)_6}{CH}-COO-(CH_2)_6\right]$$

and shows the following phase succession by decreasing the temperature:

I(153°C) - N(136°C) - S_A(130°C)- S_C(109°C)(tilted smectic phase).

By labelling the biphenyl group of the main-chain, one obtains by SANS, the conformation of the main-chain alone. This study shows that the main-chain is only sligthly oriented in the direction of the magnetic field in the nematic and the S_C phases (30% of deformation $R_{//}/R_{\perp}$). This prolate anisotropy increases in the S_A phase without reaching the extreme stretching found for the linear polymer[5]. The smectic layer thickness corresponds moreover to the length of the side-chain molecule. All these results seem to indicate that the main-chain does'nt contribute to the mesomorphic character of the phase which is then dominated by the side-chain contribution.
In this sense, there is neither competition, nor cooperative effect between these two liquid crystal molecules. This polymer can be considered as a very "diluted" side-chain

polymer. Indeed, the distance between two side-chain neighbours is large (30Å) compared to the case of the preceding side-chain polymers which possess lateral liquid crystal molecule every (meth)acrylate bonds. In this case, the interactions occur no more between side-chains of a same polymer (which provides $R_{//}<<R_{\perp}$) but also and perhaps mainly between side-chains belonging to other polymers. The slight stretching ($R_{//}\geq R_{\perp}$) can even be understood as the result of the packing effect similar to what was found for nematic side-chain polymers. However, it can be hazardous to generalize these results since several other combined liquid-crystal polymers present the smectic phases for which the layer thickness is very different from the length of both liquid crystal parts.

Concluding remarks:

General features of three large families representative of the liquid crystalline polymers have been drawn here. In all the cases, we have shown, using the SANS technique associated to the labelling method, that the polymer chain is always affected by the liquid crystal order. Althrough the spacer plays a decoupling role between the rigid part of the liquid crystal and the polymer itself, the main-chain can be extremely deformed in the mesophases. It is the case of the main-chain liquid-crystal polymer, in which even the spacer is itself stretched in the nematic phase, or the case of side-chain polymer confined between liquid crsytal layers in the smectic phase. On the other hand, adding supplementary liquid crystal molecules on the side of a main-chain liquid crystal polymer does'nt necessary procure a supplementary ordering. Obviously, the behaviour of combined liquid crystal polymer is more complicated and needs other studies in order to generalize these results. A selective deuteration of either the main-chain or the side-chain, could be a good solution to identify by neutron diffraction as it has been done in ref.8, the role of each liquid crystal molecule. This method can be particularly interesting when the layer thickness is not commensurable with the length of the liquid-crystal molecules.

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