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Small Angle Neutron Scattering experiments on « side-on fixed » liquid crystal polyacrylates

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Résumé. — Par diffusion des neutrons aux petits angles nous observons que la chaîne de polyacrylates « en haltère » adopte une conformation de type prolata en phase nématique. Son anisotropie est d'autant plus grande que l'espaceur est plus court. Dans tous les cas, nous retrouvons à basse température la forte extension de la chaîne polymère qui fut d'abord révélée dans les polysiloxanes.

Abstract. — Small Angle Neutron Scattering experiments were carried out on liquid crystalline « side-on fixed » polyacrylates: we observe that the polymer backbone adopts a prolata conformation in the nematic phase. Such anisotropy of the global backbone is larger for smaller spacer length. In every case we measure at low temperatures a large chain extension as previously described in polysiloxanes.

1. Introduction.

Small Angle Neutron Scattering (SANS) is the basis technique to determine polymer conformations [1]. Following a well described procedure [2-4] we use in practice a mixture of fully protonated and partially deuterated liquid-crystalline polymers in equal parts for a maximum scattered coherent intensity.

« Side-on-fixed » liquid crystalline polyacrylates are part of a peculiar class of side-chain mesomorphic polymers for which the mesogenic groups are laterally fixed to the polymer backbone in the direction perpendicular to their long molecular axis *via* a flexible spacer (Fig. 1). They exhibit only the nematic mesophase [5-10] except « side-on fixed » polymers

Fig. 1. — Schematic representation of « side-on fixed » polymer.

with laterally incorporated naphthalene groups in the mesogenic moieties which also exhibit a smectic phase [11].

Previous SANS experiments [12] have been performed on « side-on fixed » polysiloxanes $P_{4,4}(\overline{DP}_n)$, which correspond to the following formula :

It has been demonstrated that these polysiloxanes exhibit a global prolate conformational anisotropy in the nematic phase : the polymer stretches on average in the direction of the mesogenic groups. We also observed that this nematic « jacketed » structure tends to be reinforced as the degree of polymerization decreases : indeed the prolate anisotropy of the global polymer conformation is weaker for the polysiloxane with $\overline{DP}_n = 70$ ($R_{\parallel}/R_{\perp} = 4$) than for that with $\overline{DP}_n = 35$ ($R_{\parallel}/R_{\perp} = 6$) [12].

These previous results were based on SANS studies for polysiloxanes labelled on the mesogenic groups and concerned mostly the conformation of the whole polymer.

In this paper we describe SANS studies on « side-on fixed » polyacrylates which can be deuterated within the main chain. By this way our aim is to specify the conformational anisotropy of the polymer backbone in the nematic state in new systems by changing here the type of flexible main chain. Thus we use polyacrylates as main chains and we compare the behaviour of this new backbone with the polysiloxane one. In addition, we study the effect of the variation of the spacer length on the nematic « jacketed » structure for « side-on fixed » polyacrylates [13].

2. Materials.

The investigated polymers have the following general formula :

with $X = \text{H}$ for the hydrogenated polymers, and $X = \text{D}$ for the partially deuterated polymers.

These polymers are labelled $PA_{n,4,4}$, where n is the spacer length ($n = 4, 6$).

The molecular weights ($\overline{M}_w$) and the polydispersity (I) have been determined by light scattering and gel permeation chromatography on line for each polyacrylate [14] (see Tab. I).

Table I. — Molecular weight ($\overline{M}_w$), polydispersity (I) and degree of polymerization ($\overline{DP}_n$) for the hydrogenated (H) and deuterated (D) polyacrylates.

Polymer	$\overline{M}_w$	I	$\overline{DP}_n$
$PA_{4,4,4}$ H	$96\,000 \pm 3\,000$	1.79	84 ± 3
$PA_{4,4,4}$ D	$87\,000 \pm 5\,000$	1.75	78 ± 5
$PA_{6,4,4}$ H	$34\,000 \pm 2\,500$	1.87	27 ± 3
$PA_{6,4,4}$ D	$92\,800 \pm 5\,000$	1.75	80 ± 5

For each polyacrylate, the transition temperatures of the hydrogenated and the partially deuterated polymers are the same. Following this observation, we can claim that, although the molecular weight of the hydrogenated and the partially deuterated polymers are different in the case of $PA_{6,4,4}$, the degree of polymerization is large enough for the transition temperatures to reach the plateau of the macromolecular systems, for each spacer length ($n = 4$ or 6). The results of the DSC and optical measurements of the polyacrylates are summarized in table II.

Table II. — Phase transition temperatures for $PA_{4,4,4}$ and $PA_{6,4,4}$. g : glassy state, N : nematic phase, I : isotropic liquid phase. * from DSC (Perkin Elmer DSC7), (heating rate of 10 K/mn).

Polymer	Transition Temperature (°C)
$PA_{4,4,4}$ (H or D)	g . 40* . N . 116 . I
$PA_{6,4,4}$ (H or D)	g . 28* . N . 105 . I

3. Experimental.

The experiments have been performed on the SANS spectrometer « PAXY » of the Laboratoire Léon Brillouin (CEA : CNRS, CE Saclay, Orphée reactor) using a procedure reported elsewhere [1-4, 15, 16].

The bulk samples have been set in an oven which is placed in the directory of the neutron beam. An aligned nematic phase could be obtained by cooling from the isotropic state under an external magnetic field of 1.4 T ; the orientation is produced perpendicularly to the neutron beam and the neutrons scattered by the sample are collected on the XY position sensitive multidetector « PAXY ».

The incident wavelength used was $\lambda = 6.29 \text{ \AA}$ and the sample-multidetector distance was 3 m ; we have explored the scattering vector range ($q = 4 \pi \sin \theta / \lambda \# 4 \pi \theta / \lambda$, 2θ is the

scattering angle) :

$$0,01 \text{ \AA}^{-1} \leq q \leq 0,1 \text{ \AA}^{-1}$$

In this range, we used the following equations which relate the small angle scattering intensity $I(q)$ to the backbone conformation of the « side-on fixed » polyacrylates :

$$\begin{aligned} I^{-1}(q_{\parallel}) &= I^{-1}(0)(1 + q_{\parallel}^2 R_{\parallel}^2) & q_{\parallel} R_{\parallel} &\leq 1 \\ I^{-1}(q_{\perp}) &= I^{-1}(0)(1 + q_{\perp}^2 R_{\perp}^2) & q_{\perp} R_{\perp} &\leq 1 \end{aligned}$$

suitable in the Guinier domain, where $R_{\parallel}$ and $R_{\perp}$ are the apparent quadratic size of the polymer backbone parallel and perpendicular to the magnetic field.

We have also to take into account the difference in molecular weight of the labelled and unlabelled polymer (particularly for the $\text{PA}_{6,4,4}$) and then we have applied an extension of the Guinier approximation [17]. R_{iA} ($i = \parallel$ or $\perp$), used above, is an apparent quadratic size in the direction q_i which is induced by the molecular weight difference between the two polymers. It is related to the real size R_i of the labelled chains by [4, 17] :

$$R_{iA}^2 = R_i^2 [1 + \Omega_D / (\Omega_H + M_D / (M_H - M_D))]$$

where Ω_H and Ω_D are the volume fractions, M_H , M_D the molecular weights of the hydrogenated chains and the deuteriated chains respectively.

This relation, primarily established for isotropic systems [17], is valid for our experiments. In fact this scattering law assumes that no specific interaction occurs between labelled and unlabelled polymers ; this is experimentally checked by following the extrapolated intensity value at the origin for each temperature [18]. Since this value does not change, we conclude that there is no isotopic segregation in our polymer melts.

In our case, we have :

$$\Omega_D = \Omega_H = 1/2 .$$

Then we get :

$$R_i^2 = 1/2 R_{iA}^2 [1 + M_D / M_H] .$$

Therefore we obtain :

$$R_i = R_{iA} \cdot 0.976 \quad \text{for } \text{PA}_{4,4,4}$$

and

$$R_i = R_{iA} \cdot 1.366 \quad \text{for } \text{PA}_{6,4,4} .$$

These corrections are important especially for $\text{PA}_{6,4,4}$, but they change neither the scattering shape nor the type of the backbone anisotropy.

4. Results.

From the scattered intensity distribution in the XY plane of the multidetector, we have drawn the experimental values of $I^{-1}(q_i)$ versus q_i^2 for different temperatures.

Since we have checked the linearity of this relation in the range of q_i , $R_i \leq 1$, R_{iA} can be deduced and then R_i . The error is estimated to be 5 %-10 %.

Figures 2 and 3 display the scattered iso-intensity distribution in the XY plane of the spectrometer : figures 2 for $\text{PA}_{4,4,4}$ and 3 for $\text{PA}_{6,4,4}$ correspond to the nematic phase and the scatterings in the reciprocal space present oblate shapes which mean that in both cases the backbone adopts a prolate conformation in direct space.

Fig. 2. — Scattered iso-intensity in the XY plane of the multidetector « PAXY » for the $PA_{4,4,4}$ in the nematic phase ($T = 97^\circ\text{C}$). The magnetic field is horizontal.

Fig. 3. — Scattered iso-intensity in the XY plane of the multidetector « PAXY » for the $PA_{6,4,4}$ in the nematic phase ($T = 68^\circ\text{C}$). The magnetic field is horizontal.

Figures 4 and 5 show the temperature dependence of the backbone dimensions $R_{\parallel}$ and $R_{\perp}$ for $\text{PA}_{4,4,4}$ and $\text{PA}_{6,4,4}$ respectively; we notice that the conformations of the two polyacrylates exhibit quite the same behaviour *versus* temperature: in the isotropic phase, $R_{\parallel}$ and $R_{\perp}$ are both equal for the two polymers ($R_{\text{isotropic}} = 25 \text{ \AA}$) and by decreasing the temperature in the nematic state, $R_{\parallel}$ jumps to about $76 \text{ \AA}$ for $\text{PA}_{4,4,4}$ and $73 \text{ \AA}$ for $\text{PA}_{6,4,4}$, while $R_{\perp}$ decreases slightly to about $13 \text{ \AA}$ for $\text{PA}_{4,4,4}$ and $16 \text{ \AA}$ for $\text{PA}_{6,4,4}$.

Fig. 4. — Temperature dependence of the backbone dimensions $R_{\parallel}$ and $R_{\perp}$ for $\text{PA}_{4,4,4}$.

Fig. 5. — Temperature dependence of the backbone dimensions $R_{\parallel}$ and $R_{\perp}$ for $\text{PA}_{6,4,4}$.

In the nematic phase, at low temperatures, there is a large extension of the polymer backbone dimension parallel to the magnetic field. The shapes of the two polyacrylate backbones are highly anisotropic prolate shapes:

$$R_{\parallel}/R_{\perp} = 6.0 \quad \text{for } \text{PA}_{4,4,4}$$

and

$$R_{\parallel}/R_{\perp} = 4.5 \quad \text{for } \text{PA}_{6,4,4}.$$

In addition, we observe that the increase of the spacer length reduces the anisotropy of the backbone conformation.

5. Discussion.

Firstly we notice that in the same manner as polysiloxanes [12], « side-on fixed » polyacrylates exhibit a large prolate anisotropy of conformation in their nematic phase : the nematic « jacketed » structure is observed whatever the kind of the flexible backbone and whatever the location of the deuteriums.

Besides, we remark that this nematic « jacketed » effect really creates a backbone stretching on average in the direction parallel to the magnetic field and therefore along the nematic orientation of the mesogenic cores. It is clearly demonstrated by the high prolate anisotropy values at low temperatures for the polyacrylate backbones. Thus we claim that for « side-on fixed » polymers, there is a supra nematic ordering formed by the highly anisotropic polymers. The nematic phase primarily imposed by the mesogenic moities laterally attached is hence reinforced by the « jacketed » structure of the backbone.

In fact, the strong coupling which forces the backbone and the mesogenic groups to be parallel is allowed by the flexible spacer. This nematic orientation of « side-on fixed » liquid crystal polymers is quite similar to the behaviour observed for the thermotropic main chain polymers [19-22] where a nematic structure of the backbone was obtained ; in the latter case, the mesogenic cores naturally impose their anisotropic order on the main chain since they are part of it. In our experiments, we can speak of a nematic phase of N_{III} type described in the Wang and Warner theory [23] referring to liquid crystal side chain polymers.

The polymer backbone in the isotropic liquid phase has, as expected, the same size for the two spacer lengths ($n = 4, 6$) and is smaller than the size of the « side-on fixed » polysiloxane $P_{4,4,4}(70)$ labelled on the mesogenic moities : this difference is probably due to the different labelling positions since the degree of polymerization is nearly the same.

Moreover, when we compare the polyacrylate $PA_{4,4,4}$ and the polysiloxane $P_{4,4,4}(70)$ we notice that for a quite similar degree of polymerization, the nematic anisotropy values ($R_{\parallel}/R_{\perp}$) are smaller for the conformation of the global polysiloxane system than for that of the polyacrylate backbone ; this is a coherent result when we take into account those the different labelling positions of these two polymer systems as well as the difference in persistence lengths.

In addition, we observe for the first time that, in the nematic phase, the anisotropy of the backbone conformation decreases with an increase of the spacer length. For « side-on fixed » polymers, the backbone adopts a prolate conformation in the nematic phase reinforced by the cross-coupling *via* the spacer so that the larger the spacer length, the smaller the backbone-mesogenic core orientationnal interactions and thus the smaller the nematic « jacketed » effect.

Finally considering the previous results on « side-on fixed » polysiloxanes with different backbone lengths and those on « side-on fixed » polyacrylates with different spacer lengths, we suggest that the persistence length of « side-on fixed » liquid crystal polymers is a function of both the main chain and the spacer lengths.

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