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Short Communication

Small angle neutron scattering experiments on “side-on fixed” liquid crystal polysiloxanes

F. Hardouin⁽¹⁾, N. Leroux⁽¹⁾, S. Mery⁽¹⁾ and L. Noirez⁽²⁾

⁽¹⁾ Centre de Recherche Paul Pascal, Université de Bordeaux I, Av. A. Schweitzer, F-33600 Pessac, France

⁽²⁾ Laboratoire Léon Brillouin, CEA - CNRS/CEN Saclay, F-91191 Gif sur Yvette, France

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Résumé. — Par diffusion des neutrons aux petits angles nous révélons un renforcement de la structure “chemisée” des polysiloxanes “en haltère” en phase nématique lorsque le degré de polymérisation décroît. Nous constatons par ailleurs que dans un copolymère homologue contenant une plus faible proportion de mésogènes, l’anisotropie de conformation globale est fortement réduite.

Abstract. — Small-angle neutron scattering (SANS) studies clearly demonstrate a reinforcement of the nematic “jacketed” structure as the degree of polymerization decreases for a “side-on fixed” liquid crystal polysiloxane. In addition, we show that the dilution of the mesogenic content in a copolymeric homologous strongly reduces the anisotropy of the global polymer conformation.

1. Introduction.

The “side-on fixed” liquid crystal polymers form a new class of liquid crystal side-chain polymers. With special features: first, they are built with the mesogenic groups appended laterally to the backbone via a flexible spacer (Fig. 1), and second, these systems generally exhibit, only the nematic state [1-5]. A previous small-angle neutron scattering (SANS) study [6] on a

“side-on fixed” polysiloxane “P_{4,4,4}” of the following formula:

showed that this polymer adopts a prolate extension of the chain in the nematic phase (Fig. 2). Such a “jacketed nematic polymer” structure is highly anisotropic ($R_{\parallel}/R_{\perp} \approx 4$) far enough from the isotropic-nematic (I-N) transition with a large extension of the dimension parallel to the external field.

Our aim is now to modify the chemical constitution of the known “side-on fixed” polysiloxane P_{4,4,4} with a degree of polymerization $\overline{DP}_n = 70$ in a way to test the influence of $\overline{DP}_n$ as well as the proportion of mesogenic groups substituted on the backbone [7].

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

Fig. 2. — Quadratic sizes in directions respectively parallel ($R_{\parallel}$) and perpendicular ($R_{\perp}$) to the magnetic field as a function of temperature for P_{4,4,4}, 100% ($\overline{DP}_n = 70$). I: isotropic liquid phase, N: nematic phase.

2. Materials.

The polymers investigated have the following formula:

These polymers are labelled $\text{P}_{4,4,4}$, $X \left(\overline{\text{DP}}_n \right)$ where X is the proportion of mesogenic groups defined as:

$$X = \frac{b}{a + b} \quad (\text{in percent})$$

The following three polymers are selected:

$$\begin{array}{ll}
 \underline{1} - \text{P}_{4,4,4}, 100\% & \left(\overline{\text{DP}}_n = 70 \right) \text{ previously reported;} \\
 \underline{2} - \text{P}_{4,4,4}, 100\% & \left(\overline{\text{DP}}_n = 35 \right); \\
 \underline{3} - \text{P}_{4,4,4}, 30\% & \left(\overline{\text{DP}}_n = 30 \right).
 \end{array}$$

The mesogenic groups were obtained via a classical scheme described in [8]. These mesogenic moieties were then attached to the backbone following a hydrosilylation reaction [9]. Thus, three kinds of backbone from Petrach Systems Inc were used:

- i) a homopolymethylhydrogenosiloxane, $\overline{\text{DP}}_n = 70$ for 1;
- ii) a homopolymethylhydrogenosiloxane, $\overline{\text{DP}}_n = 35$ for 2;
- iii) a copolymer, $\overline{\text{DP}}_n = 30$, with $X = 30\%$ of methylhydrogenosiloxane and 70% of dimethylhydrogenosiloxane for 3.

The ratio weight to number average molecular weight $\overline{M}_w / \overline{M}_n$ of the liquid crystalline polymers have been found to be comparable, as those for the prepolymers used (1.2 – 1.5). The results of the DSC and optical analysis of the polysiloxanes 1, 2, 3 are summarized in the table I.

For each polymer, the transition temperatures of the partially deuterated and the fully protonated polymers are quite the same.

Table I. — *g*: glassy state, *N*: nematic phase, *I*: isotropic liquid phase. * measured with a Perkin Elmer DSC7 (heating rate of 10 K mn⁻¹).

Sample	Transition temperatures		
	g	N	I
P _{4,4,4} , 100% ($\overline{DP}_n = 70$)	• 36*	• 130	•
P _{4,4,4} , 100% ($\overline{DP}_n = 35$)	• 39*	• 129	•
P _{4,4,4} , 30% ($\overline{DP}_n = 30$)	• 13*	• 77	•

3. Experimental determination of the global conformation of the polymers P_{4,4,4}.

Small angle neutron scattering (SANS) is a convenient method to explore this problem [10]. In practice we use a pseudo-binary system of fully protonated polymer with the same polymer selectively deuterated on the aliphatic tails. As usual, in each case a mixture of 50/50 weight ratio is selected (for maximum scattered coherent intensity) and we find that the I-N biphasic region is rather sharp (< 10°C).

The SANS experiments were performed by following the usual procedure [10-15]. Aligned samples in the nematic phase could be obtained by cooling them through the isotropic-nematic phase transition under a strong external magnetic field (1.4 T) oriented perpendicularly to the neutron beam. The neutrons scattered by the sample are collected on the SANS-XY position multidetector "PAXY" of the laboratoire Léon Brillouin (CEA/CNRS, CEN Saclay, Orphée reactor).

The incident wavelength used was $\lambda = 10 \text{ \AA}$ and the distance between the detector and the sample was 2 m. Consequently the range of the scattering vector q

$$q = \frac{4\pi}{\lambda} \theta \quad (2\theta \text{ is the scattering angle})$$

was between $8 \times 10^{-3} \text{ \AA}^{-1} < q < 0.1 \text{ \AA}^{-1}$.

From the measurement of the scattering intensity $I(q)$ the apparent quadratic size $R_{\parallel}$ and $R_{\perp}$ (parallel and perpendicular to the magnetic field) of one polymer are deduced.

We stress that the distribution of this small angle scattering intensity informs here on the global conformation instead of the backbone conformation alone since the deuteration has been made on the flexible parts of the mesogenic side-groups.

Then we have in the Guinier domain:

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

Beside, since in the isotropic phase

$$R_{\parallel}^2 = R_{\perp}^2 \quad \text{and} \quad R_{\parallel}^2 + 2R_{\perp}^2 = R_g^2$$

(where R_g is the apparent radius of gyration of the whole macromolecule averaged over all directions),
we get:

$$I^{-1}(q) = I^{-1}(0) \left(1 + q^2 \frac{R_g^2}{3} \right)$$

4. Results.

From the anisotropic distribution of the scattered intensity collected on the multidetector, we have drawn the experimental values of:

$$I^{-1}(q_i) = f(q_i^2) \quad q_i = q_{\parallel} \text{ or } q_{\perp}$$

for different temperatures. Since we have checked the linearity of $I^{-1}(q)$ versus q^2 in the range of $q_i R_i \leq 1$, $R_{\parallel}$ and $R_{\perp}$ can be deduced. The error is estimated to be 5% – 10%.

For instance, figure 3a corresponds to the experimental values for $P_{4,4,4}$, 100% ($\overline{DP}_n = 35$) in the nematic phase at $T = 81^\circ\text{C}$. Figure 3b displays in the same way $I^{-1}(q)$ versus q^2 for $P_{4,4,4}$, 30% ($\overline{DP}_n = 30$) at $T = 61^\circ\text{C}$.

The general features of the temperature dependence of the polymer dimensions $R_{\parallel}$ and $R_{\perp}$ are reported in figure 4a for the homopolymer and in figure 4b for the copolymer.

In the former case, we see that decreasing temperature in the nematic phase leads to a large extension of the dimension parallel to the magnetic field whereas $R_{\perp}$ decreases only slightly (Fig. 4a). Far enough from the I-N transition, the saturated values correspond to a large chain extension with a highly anisotropic prolate shape ($R_{\parallel}/R_{\perp} \approx 6$).

In the latter case (Fig. 4b), the striking feature is that the prolate shape tendency of the polymer conformation is dramatically reduced. Indeed, we find in the nematic phase at low temperatures a very weak anisotropic ratio $R_{\parallel}/R_{\perp} \approx 1.2$ connected with the lack of significant extension of the size $R_{\parallel}$ in the direction parallel to the magnetic field.

5. Discussion.

The "jacketed" nematic structure initially revealed in $P_{4,4,4}$, 100% ($\overline{DP}_n = 70$) is qualitatively confirmed with $P_{4,4,4}$, 100% ($\overline{DP}_n = 35$). Nevertheless, the effect of molecular weight is strong.

Reducing the chain dimension, a decrease of $R_{\parallel}$ and $R_{\perp}$ in the nematic phase is found as well as a decrease of the apparent radius of gyration R_g in the isotropic phase. For highly

parallel molecules in the rigid-rod regime, the ratio $\frac{R_{\parallel}(\overline{DP}_n = 70)}{R_{\parallel}(\overline{DP}_n = 35)}$ is expected theoretically

to be larger than what we observe at saturation (1.20 ± 0.07). In fact, with these flexible polysiloxanes, we see that, as the backbone becomes longer (twice here), the chain extension

Fig. 3. — Inverse of the SANS intensity I plotted in arbitrary units as a function of q^2 in the nematic phase ($T = 70^\circ\text{C}$). For both direction: ($\diamond$) for $q_{\parallel}$, ($\square$) for $q_{\perp}$, the straight lines are obtained from a least square method. a) $P_{4,4,4}$, 100% ($\overline{DP}_n = 35$); b) $P_{4,4,4}$, 30% ($\overline{DP}_n = 30$).

effect is found to be less efficient. Indeed $R_{\perp}$ grows ($10 \text{ \AA} \rightarrow 20 \text{ \AA}$) and the anisotropy decreases ($\frac{R_{\parallel}}{R_{\perp}} \cdot 6 \Rightarrow 4$). Considering the coupling between the mesogens and the flexible backbone, we claim that the “jacketed effect” is weaker for long chains, possibly as a result of the persistence length and/or of hairpins. Consequently, it must be recognized that the fall in $\overline{DP}_n$ which tends generally to decrease the isotropic-nematic transition and the glass transition [16] can be balanced here by the opposing influence of the increase in the anisotropy of the polymer by the “jacketed effect” (see Tab. I).

On the other hand, the dilution of the mesogenic content in the copolymer $P_{4,4,4}$, 30% ($\overline{DP}_n = 30$) gives rise to a large reduction in the nematic order and in the isotropization temperature. Moreover, we have observed that in $P_{4,4,4}$, 30% ($\overline{DP}_n = 30$) the chain ex-

Fig. 4. — Quadratic sizes in directions respectively parallel, $R_{//}$ ($\square$) and perpendicular, $R_{\perp}$ ($\diamond$) to the magnetic field as a function of temperature. I: isotropic liquid phase, N: nematic phase.

a) $P_{4,4,4}$, 100% ($\overline{DP}_n = 35$); b) $P_{4,4,4}$, 30% ($\overline{DP}_n = 30$).

tension is also considerably reduced compared with those of homopolymers. The weakening of the mesogenic interactions in the "diluted" system dominates the reduction of the thermal stability of the nematic phase but the increase of the intrinsic flexibility achieved by incorporating non-mesogenic units in the backbone amplifies the loss of anisotropy of the polymer conformation. In other words, the "jacketed" effect is hence smaller and also less efficient.

Finally, earlier SANS studies [14, 17, 18] have also shown that, for "side-end fixed" (or comblike) liquid crystal polyacrylates, the backbones adopt a prolate shape in a nematic phase devoid of smectic A fluctuations. However the extension effect is hence much weaker than that observed in the present "side-on fixed" homopolysiloxanes.

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