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Evidence for a jacketed nematic polymer

F. Hardouin ⁽¹⁾, S. Mery ⁽¹⁾, M. F. Achard ⁽¹⁾, L. Noirez ⁽²⁾ and P. Keller ⁽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*(Received 5 November 1990, revised 21 January 1991, accepted 23 January 1991)*

Résumé. — Par des mesures de diffusion des neutrons aux petits angles nous montrons l'existence, pour un polysiloxane « en haltère », d'une structure « chemisée » à l'échelle de l'organisation globale d'une chaîne en phase nématique. On constate que cette anisotropie de forme du polymère a des conséquences sur l'évolution du coefficient de viscosité de torsion mesuré pour la première fois dans ce nouveau type de polymère à chaînes latérales.

Abstract. — The evidence for a « jacketed » structure at the scale of the chain dimensions in the nematic phase of a « side-on fixed » liquid crystal polysiloxane is reported by using small angle neutron scattering. We relate this anisotropy of chain conformation to the first measurements of the rotational viscosity coefficient in this new type of liquid crystal side-chain polymer.

1. Introduction.

« Side-on fixed » liquid crystal polymers form a new class of mesomorphic side chain polymers investigated in recent years. In these compounds the mesogenic groups are laterally attached to the backbone through a flexible spacer (Fig. 1a) instead of a longitudinal connection (« side-end fixed ») in the case of conventional liquid crystal side-chain polymers (Fig. 1b).

Fig. 1 — Schematic representation of a) side-on fixed side-chain polymer and b) side-end fixed side-chain polymer

Hessel and Finkelmann were the first to synthesize « side-on fixed » LCP composed of a polymethacrylate backbone and a p-phenylene dibenzoate type mesogenic moiety [1]. Using similar mesomorphic side-groups, polyacrylates [2, 3], polychloroacrylates [3] and polysiloxanes [4] have been reported subsequently. All these polymers were found to be purely nematic

We report here on small-angle neutron scattering (SANS) studies on a polysiloxane « P_{4,4,4} » (scheme 1), already studied by X-ray analysis [5], in order to establish the evolution with temperature of the global shape of the polymer from the isotropic to the nematic phase. We will also try to relate this evolution of the shape of the polymer as a function of temperature with some results obtained on a typical property of the nematic phase, namely the rotational viscosity coefficient γ_1 .

2. Study of the global conformation in the polysiloxane P_{4,4,4}.

Referring to experiments in the case of conventional L C. side chain polymers [6] small-angle neutron scattering is a convenient method to explore this problem.

In practice we use a pseudo-binary system of fully protonated polymer (P_{4,4,4}) with the same polymer selectively deuterated on the aliphatic tails. As usual, a mixture of 50/50 weight ratio is selected for a maximum scattered coherent intensity.

Both polymers exhibit the same isotropic-nematic transition temperature and in the 50/50 mixture we find that the biphasic region is rather sharp ($\sim 8^\circ\text{C}$).

The experiments were performed with the spectrometer « PAXY » on the Orphée reactor of the Laboratoire Léon Brillouin (CEA/CNRS) in Saclay.

The sample was placed in the oven at a temperature regulated to 0.2°C . A magnetic field of 1.4 T was applied to obtain a uniform orientation along the direction of the magnetic field in the nematic phase. The incident wavelength used was $\lambda = 10 \text{ \AA}$ and the distance between the detector and the sample was 2m. The range of scattering wave vector q studied was $8 \times 10^{-3} \text{ \AA}^{-1} < q < 0.1 \text{ \AA}^{-1}$. The scattering intensity $I(q)$ was obtained with a two-dimensional multidetector and the spectra were recorded in the XY-plane perpendicular to the beam.

In the limit of small scattering wave vectors (Guinier range) the scattering intensity $I(q)$ can be expressed as

$$I^{-1}(q_{\parallel}) = I^{-1}(0)(1 + q_{\parallel}^2 R_{\parallel}^2) \quad q_{\parallel} R_{\parallel} \leq 1$$

for a scattering wave vector $q_{\parallel}$ parallel to the magnetic field, where $R_{\parallel}$ is the quadratic size of the macromolecule in the direction parallel to the magnetic field. In the same way.

$$I^{-1}(q_{\perp}) = I^{-1}(0)(1 + q_{\perp}^2 R_{\perp}^2) \quad q_{\perp} R_{\perp} \leq 1$$

for a scattering wave vector $q_{\perp}$ perpendicular to the magnetic field, where $R_{\perp}$ is the quadratic size of the polymer in the direction perpendicular to the magnetic field.

Beside, in the isotropic phase we get

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

since
$$R_{\parallel} = R_{\perp} = \frac{R_g}{\sqrt{3}}$$

where R_g is the radius of gyration of the whole molecule averaged over all directions

For instance in figure 2 the experimental values of

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

in the nematic phase (70 °C) are shown.

From the linearity 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 %.

Fig. 2 — Inverse of the SANS intensity I plotted in arbitrary units as a function of q^2 in the nematic phase ($T = 70$ °C). For both direction (●) for $q_{\parallel}$, (×) for $q_{\perp}$, the straight lines are obtained from a least square method.

The general features of the polymer dimensions are reported in figure 3. We see that, cooling down from the isotropic state, an anisotropy of the polymer shape appears in the nematic phase which increases with further cooling. Far enough from the I-N transition, a large extension of the dimension parallel to the magnetic field gives rise to a high value for the anisotropy ($R_{\parallel}/R_{\perp} \approx 4$).

This behaviour is very different from that encountered in the nematic phases of conventional LC side chain polymers. In this case, whatever the nature of the backbone (polymethacrylate, polyacrylate, polysiloxane), the polymer exhibits small anisotropy which

Fig 3 — Quadratic sizes in directions respectively parallel ($R_{\parallel}$) and perpendicular ($R_{\perp}$) to the magnetic field as a function of temperature I isotropic liquid, N nematic

is generally of oblate shape ($R_{\parallel}/R_{\perp} < 1$) due to the strong tendency in comblike systems to give a smectic A phase at lower temperatures [6-9]

On the other hand, as in the present case, a qualitatively and quantitatively similar prolate extension has been observed by D'Allest *et al.* [10] in main chain nematic polymers

A tentative description of the structural arrangement in the nematic phase of $P_{4,4,4}$ at low temperatures needs the integration of SANS measurements as well as X-ray (or neutron) diffraction at large q -values. Although flexible, the polysiloxane backbone is strongly stretched in the average direction imposed by its mesogenic pendants (oriented on average along the magnetic field). Moreover the existence of S_c fluctuations revealed by X-ray analysis on single domain [5] suggests inter- and intra-chain correlations between the mesogens (Fig 4)

Thus in agreement with the molecular argument of Qi-Feng Zhou *et al.* [2] we give evidence for the first time for a «jacketed» structure at the scale of the chain dimensions in the nematic phase of a «side-on fixed» polymer.

Fig 4 — Schematic representation of a nematic jacketed side-on fixed polysiloxane with S_c local order

3. Rotational viscosity γ_1 in the nematic phase of the polysiloxane « P_{4,4,4} ».

Since the extension effect of the polymer is nearly saturated largely above the glassy state, one question can be raised. how is the viscosity for pure rotation of the director, γ_1 , affected by varying the ratio $R_{\parallel}/R_{\perp}$ in the nematic phase? In order to study this dissipative property of the system [11] we have followed in real time the evolution of the relaxation angle $\theta - \varphi$ of the nematic director with the magnetic field after sudden finite rotation angle θ of the applied magnetic field (Fig. 5). Indeed the rotational viscosity coefficient γ_1 is thought to be large enough in the nematic polymer to maintain the director at φ_0 in the sample at the initial time ($t = 0$) following the sudden change in the magnetic field direction.

A rotating field method has been used [12, 13] in which the sample is placed in a cylindrical cell suspended by a quartz wire. The magnetic field created by an electro-magnet is allowed to rotate about the axis of suspension of the cell.

The molecular reorientation process is described by a set of coupled equations

- i) the local hydrodynamic equation of the Ericksen-Leslie-Parodi theory [14-16]

$$\gamma_1 \frac{d(\varphi - \theta)}{dt} = \frac{1}{2} \Delta\chi B^2 \sin 2(\theta - \varphi) \quad (1)$$

where

B is the magnetic flux density and

$\Delta\chi$ is the anisotropy of the magnetic susceptibility per volume unit and

- ii) the sum of the torques undergone by the system in viscous regime

$$0 = -C\alpha + V\gamma_1 \left(\frac{d\varphi}{dt} - \frac{d\alpha}{dt} \right) \quad (2)$$

where

C is the twist constant of the quartz wire,

V is the volume of the sample and

α is the rotation angle of the sample with respect to its equilibrium position without field.

For small values of the angle α (i.e. $\alpha \ll \alpha_c$, α_c critical angle connected to the maximum

Fig 5 — Geometry corresponding to the determination of the rotational viscosity coefficient γ_1 : θ : constant angle of the applied magnetic field with the zero position φ : angle of the nematic director with the zero position α : rotation angle of the cell with the zero position

value $\theta - \varphi = \pi/4$), equation (1) may be simplified by taking the approximation .

$$\sin 2 (\theta - \varphi) \approx 2(\theta - \varphi) .$$

Solving equation (1) allows us to derive the characteristic time τ_1 .

$$\gamma_1 \frac{d(\varphi - \theta)}{dt} \approx \Delta\chi B^2(\theta - \varphi)$$

then .

$$(\theta - \varphi) = \text{Cte} \cdot e^{-\frac{t}{\tau_1}}$$

with :

$$\tau_1 = \frac{\gamma_1}{\Delta\chi \cdot B^2} \quad \text{and} \quad \text{Cte} = (\theta - \varphi_0)$$

From equation (2), one gets a sum of two exponential terms which gives rise to τ_1 and to a second characteristic time τ_2 with $\tau_2 = V\gamma_1/C$ which describes the evolution of the rotation angle α versus time.

However in the limit of the experimental long time region, the plots $\text{Ln } \alpha$ versus t are straight lines (Fig. 6), the relaxation of the cell to its initial position is governed by the following equation

$$\alpha \approx e^{-\frac{t}{\tau}}$$

if we take into account the linear evolution of τ versus $1/B^2$ (Fig 7) :

$$\tau \approx \tau_1 = \frac{\gamma_1}{\Delta\chi \cdot B^2}$$

Thus τ_1 is predominant in the limit of small values of B ($B < 1.1 \text{ T}$)

Fig 6 — Example of the evolution of the logarithm of the rotation angle α of the cell with the zero position

Fig 7. — Example of the evolution of the characteristic time τ as a function of $1/B^2$, where B is the magnetic flux density

A measure of the slope of the straight line $\tau = f(1/B^2)$ therefore gives the ratio $\gamma_1/\Delta\chi$. Using the magnetic susceptibility and density data previously reported for the «side-on fixed» polysiloxanes [5] it is possible to deduce the value of γ_1 for each temperature investigated.

In spite of the fact that each evaluation of τ requires large duration (as long as several hours), we have estimated the temperature dependence of γ_1 over the interval corresponding to a significant evolution of the polymer shape. In figure 8, experimental values of γ_1 as a function of the reduced temperature are presented. It appears that the rotational viscosity grows rapidly as the polymer becomes longer. The anisotropy dependence of the viscosity is illustrated in figure 9. This result is in qualitatively good agreement with recent measurements reported in solutions of a main-chain polymer nematic liquid crystal [18].

Fig 8 — Thermal dependence of the rotational viscosity coefficient γ_1 in the nematic phase

Fig 9 — Evolution in the nematic phase of the rotational viscosity coefficient γ_1 as a function of the ratio $R_{||}/R_{\perp}$ of the quadratic sizes in directions parallel ($R_{||}$) and perpendicular ($R_{\perp}$) to the magnetic field.

Relating the molecular aspect and the macroscopic properties the exaltation of the viscosity γ_1 appears essentially as a consequence of the thermal evolution of the chain extension in this « side-on fixed » polysiloxane nematic liquid crystals. This is in qualitative agreement with Brochard's calculation in the case of stick-like behaviour [19].

Here, the first step from the isotropic phase to the nematic phase leads to a shrink the dimension of the polymer in the direction perpendicular to the director ($R_{\perp}$) due to the localization of the labelling and to the spontaneous orientation of the mesogenic groups along the magnetic field. $R_{||}$ is hence weakly modified since the excluded volume is large enough. Thus, as shown in figure 8, γ_1 presents a regular evolution near T_{NI} . Then, with decreasing temperature, the mesogenic interactions are strengthened and they play an important role in the extension of the polymer. For $R_{||}$ a rapid increase to saturation is observed while $R_{\perp}$ remains rather constant. Thus in this final step, γ_1 becomes extremely large.

Comparing the orders of magnitudes, the values for γ_1 of this « side-on fixed » polysiloxane are two or three decades higher than the ones of comparable L.C. « side-end fixed » polymers [20-23]. Therefore (with equivalent molecular weight and mesogenic group at the same reduced temperature and with similar nematic order parameter) the apparent activation energy is expected to be larger for the « side-on fixed » polymers. Preliminary dynamic dielectric relaxation measurements [24] emphasized this difference between these two types of L.C. side chain polymers.

Finally, the increase in γ_1 in the « side-on » as compared to the « side-end » polysiloxanes is probably due to a larger anisotropy as well as larger friction coefficients.

4. Concluding remarks.

In the light of the results presented, we can look at the thermal evolution of the average radius of gyration R_g in the nematic range :

$$R_g = \sqrt{R_{||}^2 + 2 R_{\perp}^2}.$$

Fig 10 — Thermal evolution of the average radius of gyration R_g in the nematic range

Figure 10 shows a minimum of R_g located in an intermediate stage where the macroscopic magnetic anisotropy also exhibits an unusual minimum [5]. These striking results observed in $P_{4,4,4}$ raise the general question of the significant role played by the mechanisms of the chain extension in the establishment of the orientational order of polymer nematics. In addition, the existence of a non-regular dependence on temperature of the average radius of gyration should affect other static and dynamic physical properties in the nematic state

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