Are nematic side-on polymers totally extended? A SANS study

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Are nematic side-on polymers totally extended? A SANS study

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The strong prolate anisotropy of the backbone conformation observed in the nematic phase of 'side-on fixed' LCP is found to be as great as for main chain LCP. From this remark originated this SANS study of a 'jacketed' polymer $PA_{4,4,4}$. A form factor of cylinders is used to model the experimental scattering data as in the case of main chain LCPs. The data are well fitted by this model and the backbone appears as a long and very thin rigid rod.

1. Introduction

Side chain Liquid Crystal Polymers (LCPs) are a large class of thermotropic LCP in which the mesogenic side groups are linked to a polymer backbone via a flexible spacer. The mesophases of this kind of LCP have been extensively studied during recent years. Some general tendencies can be stated: 'side-end' fixed LCPs generally present a nematic and smectic A polymorphism [1], while 'side-on' fixed LCPs are generally purely nematic [2–5]. Nevertheless, some examples of smectic phases in this kind of LCP have been shown recently [6–9].

More than the polymorphism, the conformation of the polymer backbone in the mesophase is of interest, since there is a competition between long range orientational order and the tendency of the polymer to maximize its entropy by having a Gaussian conformation. In this sense, during these last ten years, the determination of the global backbone conformation in the nematic and smectic phases of side chain LCPs has raised considerable interest and has been the subject of extensive experimental and theoretical studies [10, 11]. Small Angle Neutron Scattering (SANS) is a major tool to determine the conformation of a single chain in its bulk state. The general result is that the side-end LCP exhibits an oblate shape of the backbone in the smectic A phase, resulting from a confinement of the chains between the mesogenic layers [12, 13]. On the contrary, the side-on LCP presents a huge prolate anisotropy of the polymer in the nematic phase [14–17]: the backbone is strongly aligned in the average direction imposed by the mesogenic groups. A similarly strong anisotropy was observed for main chain polymers [18–21]. In the nematic phase, the main chain conformation is stretched and presents hairpin defects [19, 21, 22].

Our purpose was to study whether the analogy between main chain polymers and side-on fixed LCPs, first based on their similar strong anisotropy in the nematic phase, could be extended to the occurrence of hairpin defects. Alternatively, would the presence of numerous rigid mesogenic units along the backbone be an obstacle to such abrupt changes in the conformation?

side-end fixed LCP

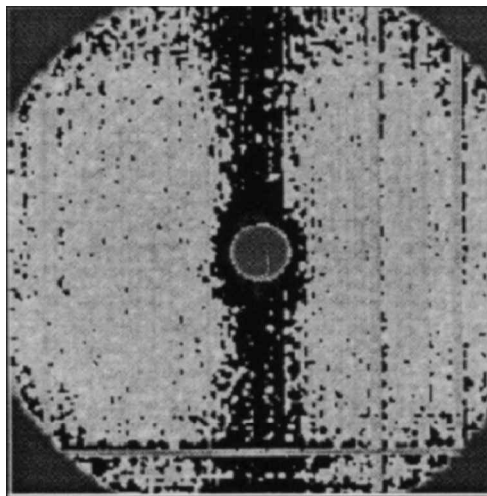side-on fixed LCP

main chain LCP
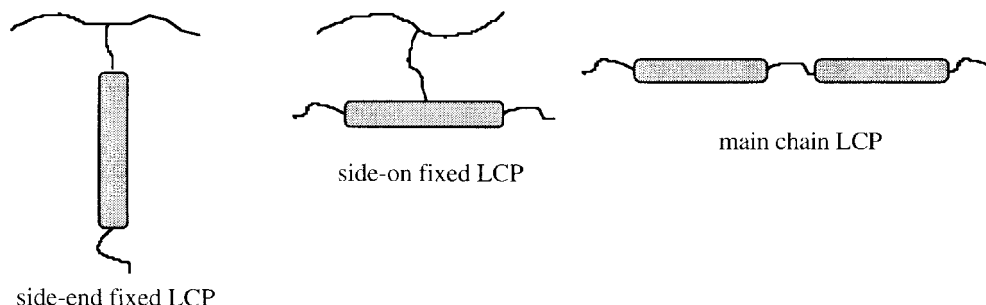
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Figure 1.   Scattering pattern on the multidetector PAXY for the 50/50 PA$_{4,4,4}$ sample in the oriented nematic phase at 70°C ($\lambda = 10$ Å, $D = 3.055$ m). The direction of the magnetic field is horizontal.

This is the question experimentally studied in this paper using a side-on fixed polyacrylate PA$_{4,4,4}$ [16]. As we can see in figure 1, its SANS pattern is very anisotropic. It is not possible to reach the Guinier range and to determine the quadratic size of the polymer chain in the nematic direction. Since figure 1 shows a pattern very similar to those observed with main chain LCPs, the same procedure [19, 21] will be tested in these experiments: the SANS data will be fitted to a model of a cylinder in which the polymer backbone could be confined. In this model, three relevant parameters have to be determined: the length of the cylinder $2H$, its radius R and the order parameter P_2 of the cylinders.

The paper in fact reports the first study of the whole chain conformation of a side-on LCP by the SANS technique through a model of a cylinder. The characterization of the sample and the experimental details are described in §2. The determination of the radius of the cylinder R in the isotropic and unoriented nematic phase is reported in §3 and §4. In §5, the results obtained for the oriented nematic phase are described. Finally, the

results are discussed and compared with those obtained with main chain LCPs.

2.   Sample characterization and experimental details
2.1.   *Sample characterization*

Let us recall that SANS studies require a mixture consisting of ϕ parts of partially deuteriated polymer (D) and $(1 - \phi)$ parts of hydrogenous polymer (H) in order to obtain the form factor of the deuteriated part of a single chain [12]. The chemical formula of the polyacrylate used in this study (PA$_{4,4,4}$) is the following:

$$C_4H_9O \!-\!\!\bigcirc\!\!-COO\!-\!\!\bigcirc\!\!-OOC\!-\!\!\bigcirc\!\!-OC_4H_9$$
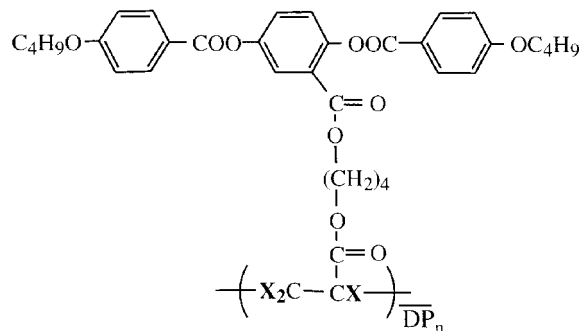
where $X = $ H or D and DP_n is the degree of polymerization. The synthesis of the polymer is described elsewhere [16]. The transition temperatures have been determined by differential scanning calorimetry (DSC). The number and weight average molecular weights were measured by size exclusion chromatography with light scattering on line (SEC-LS with dn/d$c = 0.14$ in THF). These results are summarized in table 1.

Table 1 shows that the thermodynamic and molecular characteristics of both polymers (H and D) are very similar. The mixture of H and D PA$_{4,4,4}$ in equal parts ($\phi = 0.5$) was prepared in concentrated solution in tetrahydrofuran and then coprecipitated in cold methanol. The sample was vacuum dried in an oven at 80°C during one day.

In order to investigate the nematic order on the scale of the mesogenic units, the polymer PA$_{4,4,4}$ was studied by X-ray diffraction in a q range between 0.1 and 1.5 Å^{-1}.

Table 1.   Transition temperatures (°C), enthalpies (ΔH) and entropies (ΔS) of transition determined by DSC. I: isotropic phase. N: nematic phase. g: glassy state. T_g measured at 10°C min^{-1} and T_{IN} measured at 2°C min^{-1}. M_n and M_w are the number and weight average molecular weights; $I = M_w / M_n$ characterizes the polymolecularity.

Polymer	Transition temperatures/ °C			ΔH_{IN} /J mol^{-1}	ΔS_{IN} /J mol^{-1} K^{-1}	M_n	M_w	I
	g	N	I					
PA$_{4,4,4}$ H	40	127		1580	4.0	59300	162000	2.73
PA$_{4,4,4}$ D	39	126		1651	4.1	55100	141000	2.54
50/50 PA$_{4,4,4}$	39	126		1620	4.0	—	—	—

This experiment was performed at room temperature on an oriented sample. A classical nematic pattern without smectic fluctuations was observed.

2.2. *SANS experiments*

The polymer melt was placed in a quartz cell of 1 mm thickness and 15 mm diameter. Aligned samples were obtained by cooling them slowly from the isotropic to the nematic phase under an external magnetic field of 4·2 T in an NMR spectrometer and then quenching. The cell was then put in an oven placed in a magnetic field of 1·4 T perpendicular to the incident neutron beam. The field *in situ* just kept the sample aligned. The scattered neutrons were collected on the SANS-XY position multidetector PAXY consisting of 128×128 cells of 5×5 mm^2 at the Orphée reactor (LLB, Saclay). Two ranges of the scattering vector q were used: the sample to detector distance D was 3·055 m and the incident wavelength λ was 10 Å ($7 \times 10^{-3} < q < 7 \times 10^{-2}$ Å^{-1}) or 5 Å ($2 \times 10^{-2} < q < 0.15$ Å^{-1}). The data treatment was carried out using the usual procedure [23]. The background was determined from the half sum of the incoherent intensity delivered by the pure samples containing either hydrogenous chains or partially deuteriated chains. An absolute calibration was obtained from the direct determination of the number of neutrons in the incident beam. This allowed us to obtain the absolute intensity $I(q)$ in cm^{-1} and to determine the M_w value of the polymers. The intensity scattered by the samples is [23]:

$$I(q) = 3^2 (b_H - b_D)^2 \phi (1 - \phi) \left(\frac{\rho_H \, M_{wH}}{m_H^2} \right) N_A P(q)$$

$$= k \, M_w P(q) \qquad (1)$$

where b_H and b_D are the coherent scattering lengths (cm) of the atoms H and D, respectively, ϕ is the volume fraction of the D polymer in the mixture ($\phi = 0.5$), N_A is the Avogadro number, ρ is the density of the H sample ($\rho = 1.16$ g cm^{-3}), m_H is the molecular weight of the hydrogenous monomer ($m_H = 632$) and $P(q)$ is the form factor of one chain ($P(0) = 1$). For this polymer, the k value is found to be $k = 4.24 \, 10^{-6}$ cm^{-1}.

For the isotropic scattering, the data were regrouped inside rings of 1 cell width. In the oriented nematic phase, where the scattering is anisotropic, the data were regrouped in rectangles of 14×128 cells for the direction parallel and 8×128 cells for the direction perpendicular to the nematic director (i.e. to the magnetic field direction). This allowed us to measure the scattering intensities $I(q_\parallel)$ and $I(q_\perp)$.

3. Chain conformation in the isotropic phase

The 50/50 PA$_{4,4,4}$ was characterized by SANS in the isotropic phase at 140°C using the smallest q range. In

this range, the data are fitted to the Zimm relation [24] valid in the Guinier range [25], $qR_g < 1$, where R_g is the radius of gyration of one chain:

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

In this way we obtained $R_g = 52 \pm 3$ Å. The value of $I^{-1}(0)$ is found to be 2.1 ± 0.2 by extrapolating the data to zero q square value. Equation (1) gives a value of $M_w = 115\,000 \pm 10\,000$. This is rather low compared with the values of the molecular weight of the H and D polymers given in table 1. This measure will be a reference for the interpretation of data obtained with the oriented nematic phase. Moreover, it is known that for flexible amorphous polymers (like polystyrene) in the bulk, the radius of gyration of the chain is found to be proportional to the square root of its molecular weight, $M^{1/2}$ in the Guinier range. This proved the Gaussian character of the chain in the melt [23]. In the intermediate q range, the linear dependence of $q^2 I(q)$ versus q demonstrates this Gaussian character. Such a behaviour has been found in main chain LCP when there is a large fraction of rigid mesogenic moieties in the backbone [19]. We wondered whether the side-on PA$_{4,4,4}$ also has a Gaussian conformation. In the q range explored ($10^{-2} < q < 10^{-1}$ Å^{-1}), the representation of $q^2 I(q)$ versus q seems to tend to the plateau characteristic of a random conformation of the polymer (figure 2). In this sense, it appears that the polymer backbone of the PA$_{4,4,4}$ has a Gaussian character in the isotropic phase. This result is confirmed by a rather low value of R_g
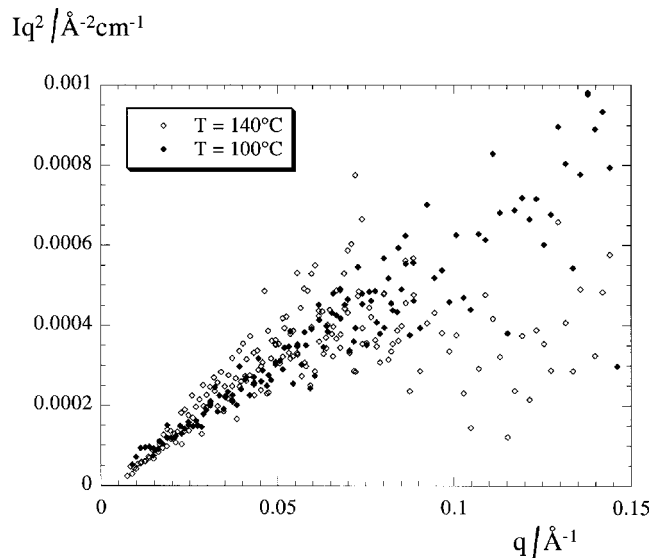
Iq^2 /Å^{-2}cm^{-1}

Figure 2. Kratky plot $q^2 I$ of the intensity I versus the scattering vector q for 50/50 PA$_{4,4,4}$ in the isotropic phase ($T = 140$°C) and in the nematic phase ($T = 100$°C).

($R_g = 52$ Å). The R_g value of a polystyrene (standard for flexible polymers) with the same number of monomer units is 38 Å.

4. Chain conformation in the unoriented nematic phase

The chain was studied for the unoriented nematic phase in order to see whether the scattering data could be interpreted with a form factor of a cylinder and it its radius could be determined. In this approach, the intensity scattered by randomly oriented cylinders is used [25]:

$$I(q) = k \left(\frac{\pi M}{2Hq} \right) \exp \left(-\frac{q^2 R^2}{4} \right) \text{ with } (2H)^{-1} \ll q < R^{-1} \tag{3}$$

where ($M/2H$) is the linear density of the cylinders.

The scattering of the 50/50 PA$_{4,4,4}$ in the unoriented nematic phase was obtained in the intermediate q range ($2 \times 10^{-2} < q < 0.15$ Å^{-1}) at three temperatures (30, 70, 100°C). Figure 2 represents the evolution of $q^2 I(q)$ versus q in this range. Unlike the isotropic phase, a linear dependence of this function is observed in the nematic phase. This is the result of a certain rigidity of the polymer backbone.

Figure 3 shows $\ln(qI)$ versus q^2. In this figure, a striking result appears: the slope is quite horizontal. Thus the radius of the cylinder is very small ($R = 3 \pm 2$ Å), too low to be determined with precision in this very small q range. As a matter of fact, the conformation is that of a rigid rod. This result is confirmed from the fit
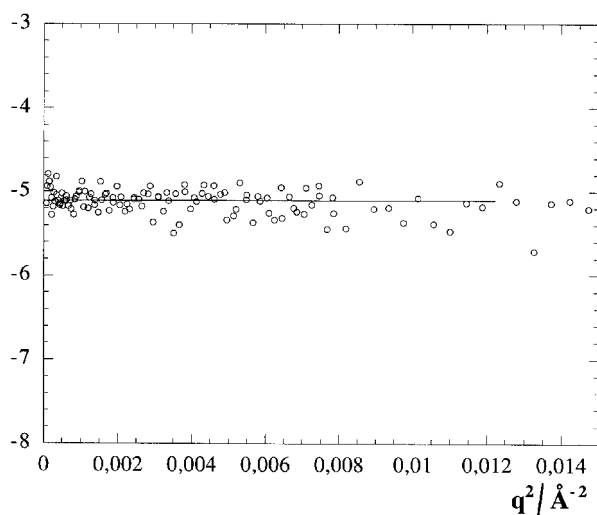
ln(qI) Å^{-1}cm^{-1}

Figure 3. Representation of $\ln(qI)$ versus q^2 in the intermediate q range for 50/50 PA$_{4,4,4}$ in the unoriented nematic phase at 100°C. The full line is a linear fit; the slope corresponds to a radius $R = 3 \pm 2$ Å.

of the whole curve to equation (3). The value of ($M/2H$) found is about 434 Da Å^{-1}. Let us compare this value with the linear density of the monomer (m/d). This is calculated from the molecular weight of the hydrogenous monomer repeat unit ($m = 632$ Da) and from the estimated repeating unit length of the backbone ($d = 2.54$ Å, that of a –C–C– bond). We find (m/d) = 250 Da Å^{-1}. Thus, the value of the linear density ($M/2H$) is about twice that of the monomer. This result actually implies about 2 strands of a chain in the cylinder, which is incompatible with a radius below 5 Å. This result is in contradiction to all the others and is not understood.

5. Chain conformation in the oriented nematic phase

The unknown parameters which must be determined are the length $2H$ of the cylinders and their distribution of orientation P_2. The scattering study of the oriented 50/50 PA$_{4,4,4}$ was performed in the small q range ($7 \times 10^{-3} < q < 7 \times 10^{-2}$ Å^{-1}) at three temperatures (30, 70, 100°C). In this range, only the data obtained in the direction perpendicular to the nematic field can be fitted to the Zimm approximation since, in the parallel direction, such an equation is valid only for $5qR_\parallel < 1$ [26]:

$$I^{-1}(q_\perp) = I^{-1}(0)(1 + q_\perp^2 R_\perp^2) \qquad q_\perp R_\perp \lesssim 1 \tag{4}$$

The dimensions $R_\perp$ obtained in the Guinier range for the three temperatures are reported in table 2.

Table 2 shows that the values of $R_\perp$ are constant in the low temperature range of the nematic phase (between 30 and 70°C). This value of $R_\perp$ is far greater than the values of R found for the unoriented nematic phase. This is due to the fluctuation of orientation of the cylinders. Thus the projection of the length $2H$ of the cylinder in the direction perpendicular to the field has to be taken into account. In this sense, the experimental data are adjusted with a model of the cylinder in the parallel and perpendicular directions simultaneously. The form factor of the cylinder is [25]:

$$F(R, 2H, \beta, q) = \left[\frac{\sin(qH \cos\beta)}{qH \cos\beta} \frac{2J_1(qR \sin\beta)}{qR \sin\beta} \right]^2 \tag{5}$$

Table 2. Parameters of the chain conformation and results of the fits to a cylinder model for the polyacrylate PA$_{4,4,4}$ in the oriented nematic phase. $R_{\perp calc}$ is the value of $R_\perp$ calculated with the model of the cylinder.

Temperature /°C	Guinier range $R_\perp$/Å	Parameters of the cylinder model				
		R/Å	a	P_2	$2H$/Å	$R_{\perp calc}$/Å
30	29 ± 2	1–5	8	0·793	250 ± 10	32
70	29 ± 2	1–5	8	0·793	250 ± 10	32
100	37 ± 2	1–5	6	0·711	250 ± 10	36

where $J_1(x)$ is the Bessel function of the first order and β the angle between the scattering vector q and the axis of the cylinder. The angular distribution of the cylinders around the nematic director is that of Maier–Saupe [27]:

$$P(a, \beta) = A \exp\left(a \cos^2 \beta\right)$$

$$A^{-1} = 4\pi \int \exp\left(a \cos^2 \beta\right) \sin \beta \, d\beta \qquad (6)$$

The fluctuation of orientation of the cylinder is thus described by the order parameter P_2 corresponding to:

$$P_2 = \int \frac{3 \cos^2 \beta - 1}{2} P(a, \beta) \sin \beta \, d\beta \qquad (7)$$

Since here $q_\parallel$ is colinear with the nematic director, the angle $\beta_\parallel$ is also β.

As a result, the parallel and perpendicular scattering intensities are fitted with the following functions [28]:

$$I(q_\parallel) = I(0) \int P(a, \beta) F(R, 2H, \beta, q_\parallel) \sin \beta \, d\beta \quad (8)$$

$$I(q_\perp) = I(0) \frac{2}{\pi} \int_0^{\pi/2} \int_0^{\pi/2}$$

$$\times P(a, \beta) F(R, 2H, \beta_\perp(\alpha), q_\perp) \sin \beta \, d\beta \, d\alpha \quad (9)$$

where α is the azimuthal angle of the cylinder axis in the plane $(q_z, q_\perp)$ of the set of coordinates $(q_z, q_\perp, q_\parallel)$ with $(\cos \beta_\perp = \sin \beta \cos \alpha)$. $I(0)$ is the value obtained for $I(q_\perp) = 0$. Both fits give the values of $2H$ and P_2 as a function of temperature (table 2). A typical example of the fit is shown in figure 4.

The fits are rather good in both parallel and perpendicular directions. In the parallel direction, the fit is sensitive to the value of $2H$ (250 Å) which is large, and not to those of either R or a. Thus $2H$ is determined only with $I(q_\parallel)$. Now the only undefined parameter a (or P_2, equation (7)) is deduced from the fit of $I(q_\perp)$ to equation (9) where $2H$ and R values are introduced. The value of R is small and imprecise. It is not possible to improve it from $I(q_\perp)$ since the calculated functions $I(q_\perp)$ with $2H = 250$ Å and $a = 8$ are exactly the same for $R = 1$ or 5 Å. *Thus the cylinder is reduced to a rod.* The only parameter P_2 of this rod consequently does not change with temperature: it remains relatively high, lying between 0·711 and 0·793. All these results show that the cylinders are very long, very thin and have fluctuations of orientation around the nematic director. Let us notice that the fit in the parallel direction has no oscillation; this is due to a distribution of the cylinder length induced by the large polymolecularity of the chains [19].

Let us return to the values of $R_\perp$ measured using equation (4). They are at least six times greater than
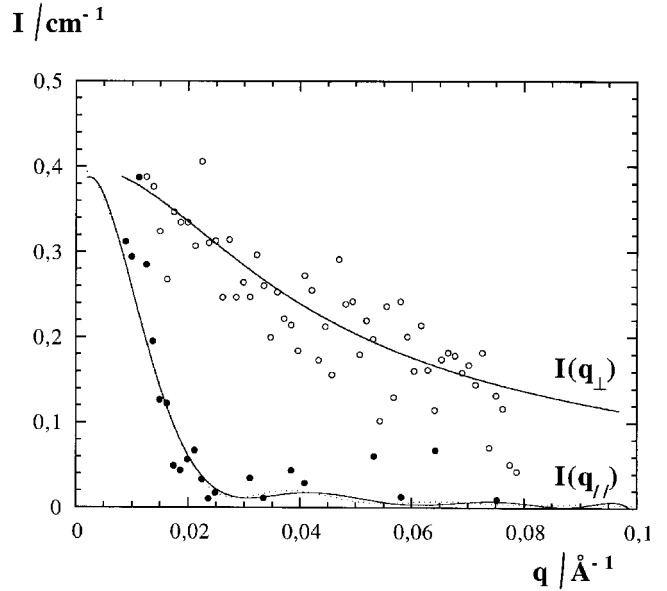

Figure 4. Absolute intensity $I(q)$ in the direction parallel ($\parallel$) and perpendicular ($\perp$) to the magnetic field as a function of the scattering vector q. The 50/50 $PA_{4,4,4}$ is in the oriented nematic phase at 100°C. Full lines represent fits to the cylinder model, equations (8) and (9); $2H = 250$ Å, $R = 5$ Å, $P_2 = 0·711$.

those of R (radius of the cylinder). This is due to the fluctuations of orientation of the cylinder which give a contribution of $2H$ in the determination of the $R_\perp$ value (see equation (9)). In this sense, using the small q expansion of equation (9), we can estimate this correction:

$$I^{-1}(q_\perp) = I^{-1}(0)$$

$$\times \left\{ 1 + q_\perp^2 \left[\frac{4H^2 \langle \cos^2 \beta_\perp(\alpha) \rangle}{12} + \frac{R^2 \langle \sin^2 \beta_\perp(\alpha) \rangle}{4} \right] \right\}$$

$$= I^{-1}(0)(1 + q^2 R_{\perp \text{calc}}^2) \qquad (10)$$

with $q_\perp R_\perp < 1$, $q_\perp H \cos \beta_\perp(\alpha) < 1$, and where the brackets indicate an average with the Maier–Saupe distribution. For $P_2 = 0·793$, $2H = 250$ Å and $R = 4$ Å, we find a calculated value of $R_{\perp \text{calc}} = 32$ Å. These values are thus in good agreement with those measured in the Guinier range (table 2).

In order to simplify the procedure, we have tried to measure directly the parameters of the cylinder model for the unoriented nematic phase. This method should be of great interest, allowing us to determine $2H$ from the value of $R_g = 2H/12^{1/2}$, and so in a larger q range ($qR_g < 1$). The experiment made in the small range ($7 \times 10^{-3} < q < 7 \times 10^{-2}$ Å^{-1}) gives data which are fitted

with the cylinder form factor:

$$P(q) = \int F(R, 2H, \beta, q) \sin \beta \, d\beta \qquad (11)$$

The fit shown in figure 5 is good with $R = 2\,Å$ and $2H = 190\,Å$. This value of $2H$ is thus smaller than the value obtained for the oriented nematic phase $(250\,Å)$. This simplified method for determination of $2H$ is not however good, since defects in the unoriented nematic phase are too numerous and create folding in the conformation.

6. Discussion and conclusion

The measurement of the form factor of a polymer $PA_{4,4,4}$ has been made by SANS. The experimental data are well fitted by a model of a cylinder for the oriented nematic phase as for main chain LCPs [18–21]. Now we have to calculate the number of hairpins from a comparison of $2H = 250\,Å$ with the total length L of the fully extended chain. The latter is obtained from the repeating unit length of the backbone $(d = 2 \cdot 54\,Å)$ and the number average degree of polymerization $(DP_n = 87)$: $L = 87 \times 2 \cdot 54 = 221\,Å$. This comparison shows that the polymer backbone is totally extended, without hairpins, and agrees with the very low value of the radius of the cylinder. Moreover, while the monomer length is very small $(d = 2 \cdot 54\,Å)$ and the mesogenic unit length is very large $(33\,Å)$, it is difficult for the backbone abruptly to execute contour reversal (see figure 6). These results are
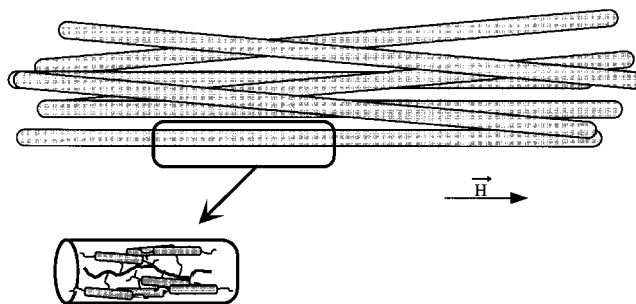

Figure 6. Schematic representation of the model of the side-on LCP $PA_{4,4,4}$. The 'jacketed' structure is consistent with the cylinder model.

consistent with previous ones (16), since the calculated anisotropic ratio taking into account the value of 2H (corresponding to $R_\parallel$) and $R_\perp = 7 \cdot 5$.

As a matter of fact, the side-on fixed LCP $PA_{4,4,4}$ is completely elongated like a rod. Moreover, the parameters found for the cylinder perfectly agree with the model of the 'jacketed' side-on LCP [3, 14, 15]. In fact, the 'jacketed' structure for the nematic phase of side-on LCPs creates a stretching of the backbone in the direction parallel to the magnetic field. This stress is a maximum since the polymer backbone is a rod.

I /cm^{-1}
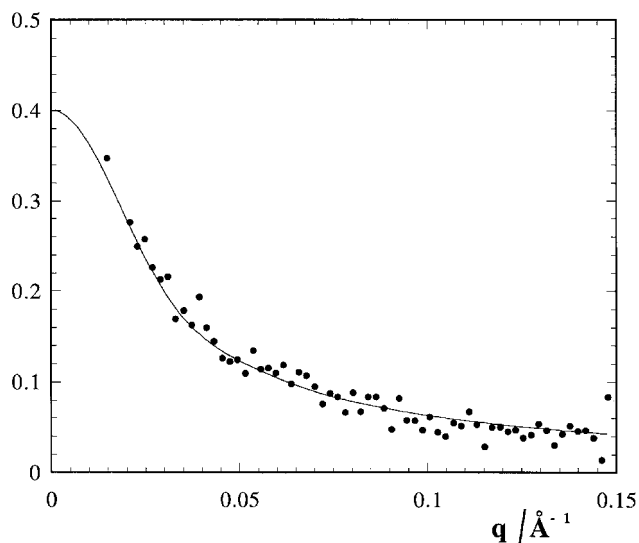

Figure 5. Absolute intensity scattered $I(q)$ in the unoriented nematic phase $(T = 100°C)$ as a function of the scattering vector q. Full line represents the fit to the cylinder model, equation (11); $2H = 190\,Å$, $R = 2\,Å$.

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