SANS Study of a Semiflexible Main Chain Liquid Crystalline Polyether

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ABSTRACT: A main-chain semiflexible polyether (TPB-10) has been studied in the nematic phase by small angle neutron scattering (SANS) and by neutron and X-ray diffraction. Principally, we have determined the polymer chain conformation by SANS for mixtures of deuterated and hydrogenous polymers, aligned using a strong magnetic field (4.2 T). In good agreement with previously reported results on nematic polyesters, our data are well fitted to a model of a cylinder in which the main chain forms one hairpin defect including two very confined and extended wires. Moreover, the X-ray diffraction patterns show that smectic C fluctuations occur in the low-temperature nematic range. Referring to the layer normal of the local S_C arrangement, the mesogens are tilted with respect to the field. Strikingly, the whole chains are also tilted with the same angle as the mesogenic units.

1. Introduction

Thermotropic main-chain liquid crystalline polymers are generally obtained by combining rigid mesogenic segments and flexible spacers (like for example alkyl groups) in alternating succession. Such polymer melts exhibit mesomorphic phases of nematic or smectic order. In the nematic phase, the competition between the long range orientational order and the tendency of the polymer to maximize its entropy by having a Gaussian conformation is expected to give a chain conformation presenting hairpin defects where the chain abruptly executes contour reversals.[1] The number of hairpins is predicted to increase exponentially with temperature, and the theoretical temperature dependence of the chain size for different chain lengths is discussed elsewhere.[2–4] The most effective way to check this hairpin conformation consists of measuring the chain dimensions in an aligned sample in the direction parallel (||) and perpendicular (⊥) to the nematic director. Small angle neutron scattering (SANS) is the main tool available to determine the conformation of a single chain in its bulk state from a mixture of 50% deuterium labeled (D) and 50% nonlabeled (H) polymers.[5] The first attempt to confirm the existence of hairpins by measuring the chain dimension was reported on main-chain polyesters[6] synthesized by Blumstein et al.[7] For these polymers, the major drawback encountered in the determination of the chain conformation is the occurrence of the transesterification reaction. This phenomenon is frequently observed and studied in a great number of polymers.[8–13] Despite these difficulties the observation of the hairpins and the determination of their number per chain as a function of temperature and of molecular weight has been reported recently[14–16] on novel polyesters with different spacer lengths. Using appropriate experimentation conditions of temperature, it was possible to minimize the effects of transesterification. However, these results needed confirmation in systems avoiding the problem of transesterification.

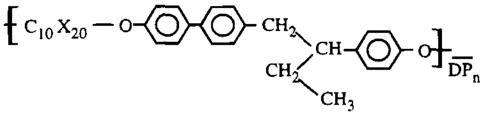
In this paper, we study a linear polyether synthesized recently by Percec and co-workers[17,18] by the polyetherification reaction of 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane with 1,10-dibromodecane (TPB-10). This polymer exhibits a nematic phase below 110 °C, and in contrast with the polyesters previously reported, it does not crystallize and therefore allows the study of the glassy state.

This paper reports preliminary SANS results on the chain conformation of this polyether. In the following section (section 2), we describe the characterization of the sample, by SANS setup and X-ray analysis. The determination of the chain conformation in the nematic phase is reported in section 3. Specific SANS results obtained near the glass transition temperature (T_g) are reported in section 4.

At last we expect a valuable comparison of these results with a ^{2}H-NMR analysis conducted separately for the same polymer describing the evolution of the conformational and orientational order of the spacer.[19]

2. Experimental Details and Sample Characterizations of TPB-10 Samples

2.1. The SANS studies need a mixture of partially deuterated (D) polyether and undeuterated one (H). The chemical formula of the polyether used (TPB-10) is the following:



where X is either H or D and $\overline{DP}_n$ is the degree of polymeri-

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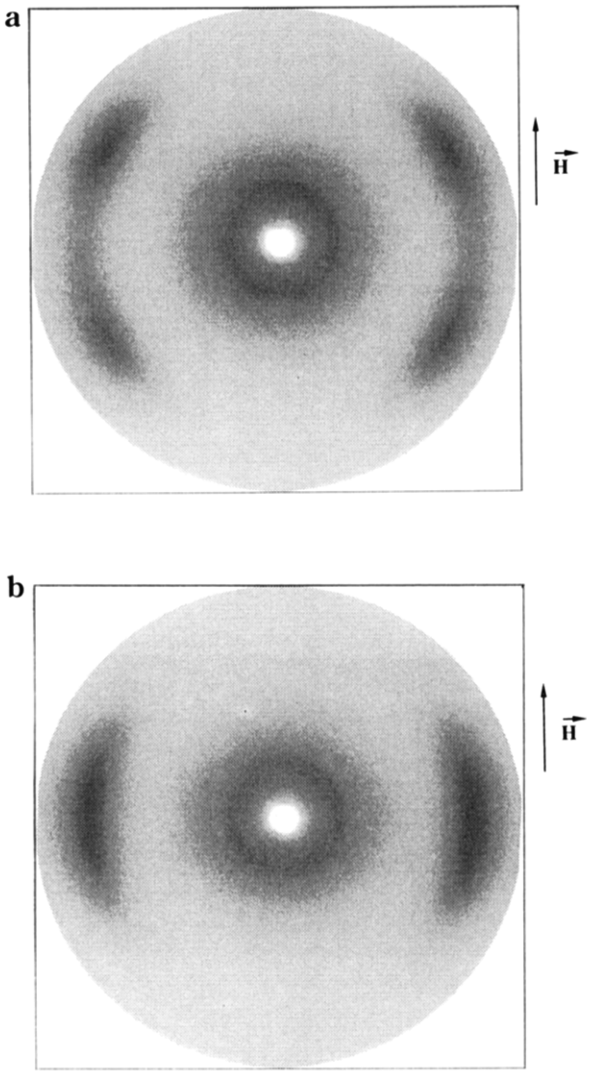

Figure 1. X-ray diffraction pattern in the wide-angle region of the polyether TPB-10 sample in the oriented nematic phase: (a) at 30 °C in the glassy nematic state; (b) at 70 °C. Note that the diffuse ring at small angle is due to the kapton windows.

zation. The synthesis and the determination of the number and weight absolute average molecular weights are described elsewhere.[17,18] For the H polymer the weight average molecular weight $\bar{M}_w$ is 24 800 with $\bar{M}_w/\bar{M}_n = 2.3$. The molecular weight of the D polymer is very similar, $\bar{M}_w = 22\,400$ and $\bar{M}_w/\bar{M}_n = 2.0$. Since the difference between the molecular weights of the H and D chains is weak, the corrections (around 6%) of the SANS data, following the RPA equation, are negligible. The nematic–isotropic transition temperature (T_{IN}) is around 105–110 °C, and the glass transition temperature is 40 °C.

Three samples have been prepared, one with the deuterated polymer ("100D"), one with the hydrogen one ("100H"), and the third containing a mixture of half of each species ("50/50"). This was obtained by coprecipitating in cold methanol a concentrated solution of the right amount of both polymers in chloroform. Subsequently, the mixture was thoroughly vacuum dried in an oven.

2.2. SANS Experiments. To prepare a SANS cell, the isotropic melt is allowed to fill the 15 mm space in the middle of a circular strut 1 mm thick, fitting exactly on a quartz window, 22 mm diameter. In the open cell the melt is annealed in the isotropic phase during 24 h in order to avoid the bubbles which could give a predominant spurious central scattering. Then the second quartz window is put on the top to seal the cell. One of the samples ("50/50") was aligned in the nematic phase by a strong magnetic field of 4.2 T in a NMR spectrometer. This procedure allows us to keep the alignment by quenching the sample at room temperature. We note that the order parameter measured earlier by ^{2}H-NMR has the value $S = 0.88 \pm 0.02$ at 90 °C.[19]

The scattering data were obtained on the PAXY SANS spectrometer at the Orphée reactor (LLB, Saclay) using its XY multidetector of 128 × 128 cells of 5 × 5 mm^2 and a wavelength λ definition of 10%. Three ranges of the scattering vector q ($q \cong 2\pi\theta/\lambda$ where θ is the scattering angle) were used: one with $\lambda = 10$ Å and a sample–detector distance $D = 3.08$ m ($8 \times 10^{-3} < q < 8 \times 10^{-2}$ Å^{-1}), another with the same D value and $\lambda = 5$ Å and one with $\lambda = 3.5$ Å and $D = 1.40$ m ($0.05 < q < 0.5$ Å^{-1}). The last allows us to observe diffuse lines corresponding to the longitudinal distance (20–30 Å) between two consecutive monomers of the main chain in the aligned sample (see refs 15, 16, and 20).

The quartz cell was put in an oven placed in a magnetic field of 1.4 T perpendicular to the incident neutron beam (see ref 21). This field was not sufficient to align the sample in situ but helps in keeping the alignment of the sample already oriented. We stress that this magnetic field direction coincides with the alignment direction of the sample.

The treatment of the data was carried out using the usual procedure.[5c] The background was determined from the weighted sum of the incoherent intensity delivered by the pure samples 100H and 100D. An absolute calibration was obtained from the direct determination of the number of neutrons in the incident beam. It allows us to report $I(q)$ in cm^{-1} and to determine the $\bar{M}_w$ value of the polymer.

For the isotropic scattering, the data of the *XY* detector are regrouped inside rings of 1 cell width whereas in the anisotropic nematic phase, the data are regrouped in a rectangle of 4 × (128) cells for the direction perpendicular to the nematic director (where the shape of the isointensity curves is very sharp) and in a rectangle of 11 × (128) cells for the parallel direction (where the shape of the isointensity curves is quite smooth).

The 50/50 sample has been characterized by SANS in the isotropic phase at 111 °C using the smallest q range. The data are fitted to the Zimm relation[22]

$$I^{-1}(q) = I^{-1}(0)(1 + q^2 R_G^{\,2}/3) \qquad (1)$$

valid[23] in the Guinier range $qR_G \leq 1$, where R_G is the radius of gyration of one chain.

The value obtained for this polymer is $R_G = 71 \pm 4$ Å. The value $I(0)$ is related to the molecular weight $\bar{M}_w$ of the polymer following the relation:[21]

$$I(0) = (a_H - a_D)^2 \Phi(1 - \Phi)\varrho N_A \bar{M}_w/\bar{m}^2 = k\bar{M}_w \qquad (2)$$

where a_H is the coherent length (cm) of the H monomer, a_D is that of the D one, Φ is the volume ratio of the D polymers in the melt, ϱ is the melt density (here the value of 1 g·cm^{-3} has been adopted), N_A is the Avogadro number, and $\bar{m}$ is the mean molecular weight of the monomer ($m_H = 466$, $m_D = 476$). The value of 6.5 cm^{-1} found for $I(0)$ by extrapolating the data to zero q value using eq 1 gives a $\bar{M}_w$ value of 21 500. This is in rather good agreement with those obtained[18] by size exclusion chromatography using a calibration constructed with TPB-10 monodisperse oligomers (see section 2–1 and refs 17 and 18).

2.3. X-ray Analysis. The polymer TPB-10 was separately studied by X-ray diffraction in order to scan larger q-range values (0.1–1.5 Å^{-1}) and thus to investigate the nematic order at the scale of the mesogenic units. The sample was previously aligned by a magnetic field of 4.2 T using the same thermal procedure as for the neutron cells.

X-ray scattering experiments were performed using Cu Kα radiation of a 18 kW rotating anode X-ray generator. A flat pyrolytic monochromator delivered a 0.5 × 0.5 mm^2 beam onto the sample. The scattered radiation was collected on a two-dimensional detector imaging plate system. The sample–detector distance was 200 mm.

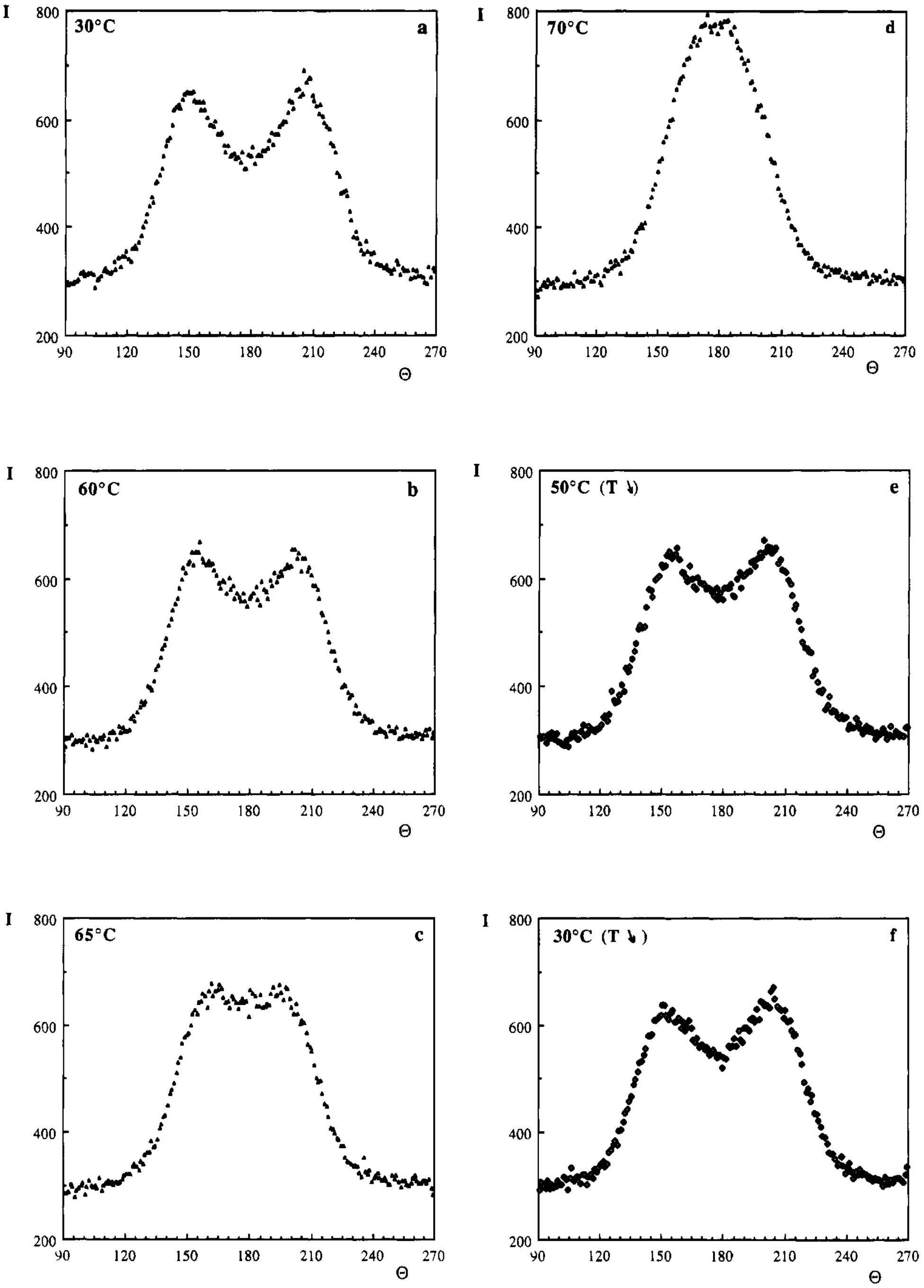

Figure 2. X-ray intensity profiles with scattering vectors parallel to the magnetic field ($\theta = 180^\circ$ corresponds to the diffraction along the equator direction).

The X-ray diffraction patterns observed at 30 and 70 °C are presented in Figure 1a,b in which the alignment direction is vertical. The characteristic wide-angle diffuse scattering at $q = 2\pi/4.7\ \text{Å}^{-1}$, indicating the liquid-like association of the aligned mesogenic groups, is clearly seen on both but shows a striking difference. The wide-angle diffuse scattering centered on the equator at a high temperature (70 °C), as expected for a conventional uniaxial nematic phase, becomes more complex at a low temperature (30 °C) with a dip in intensity on the equator and intensity symmetrically placed just above and below this.

The thermal variation of the corresponding angular intensity profiles at several intermediate temperatures is shown in Figure 2. This evolution underlines the remarkable difference of the X-ray patterns observed above and below 70 °C. Hence, up to 70 °C, the repeat units are tilted with respect to the direction of alignment produced by the magnetic field and the tilt angle decreases from 30 to 0° upon heating. Finally, at $T \geq 70$ °C, the long axes of the repeat units are, on average, parallel to the magnetic field. Figure 2 shows also the reversibility of the tilt of the mesogens as a function of temperature.

Taking into account that off-equatorial diffuse spots are expected for a nematic structure with "skewed cybotactic groups", we suggest that a tilt angle of the mesogens relative to the layer normal of smectic C fluctuations is observed below 70 °C with the layers orientationally ordered (i.e., the layer normal is parallel to the magnetic field). Thus the thermal evolution of the splitting can be interpreted from a tilt angle evolution, as reported in Figure 3. It must be noted that this tilting cannot be connected to the T_g which occurs some 30 deg below. Once the system is in the glassy nematic state the angle seems to reach a plateau.

Moreover, on overexposed patterns (at 30 °C), diffuse spots located on the meridian can be detected at small angles with an average distance $d = 26.5$ Å. At 70 °C, these diffuse spots are no longer observed.

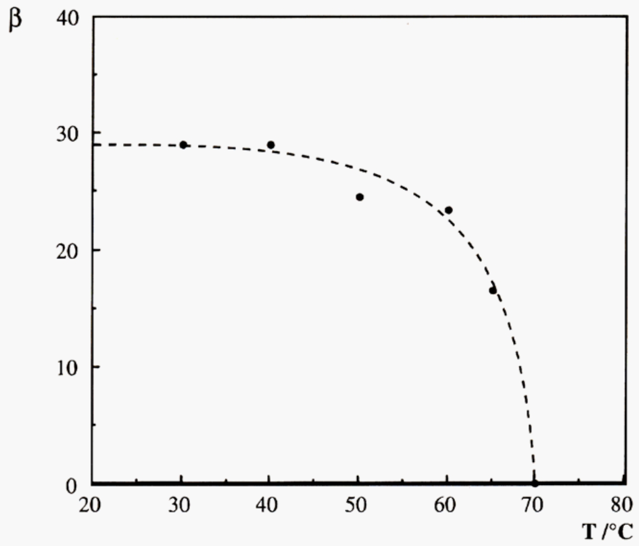

Figure 3. Tilt angle (β) versus temperature from X-ray data at wide angle.

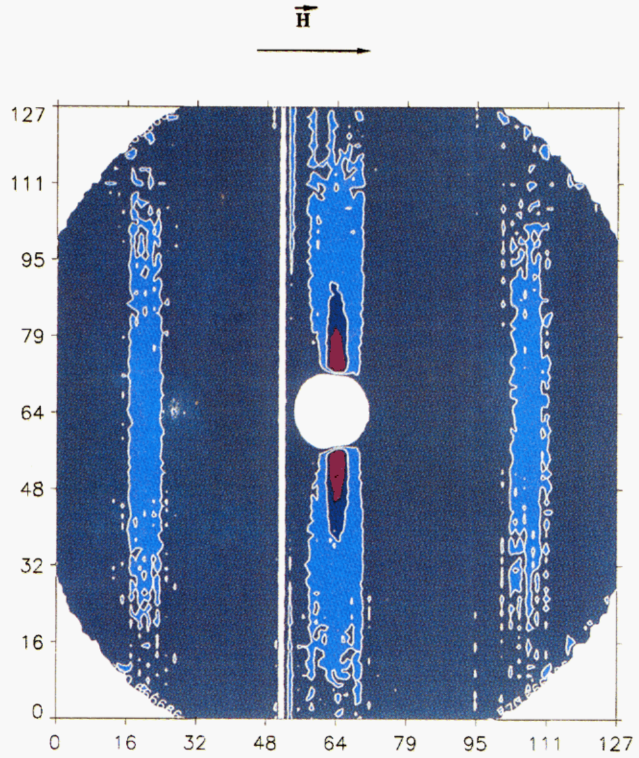

Figure 4. Scattering pattern of the 50D/50H polyether sample in the oriented nematic phase at 86 °C. $l = 3.5$ Å, $D = 1.4$ m. H indicates the direction of the magnetic field. Let us notice the strong anisotropy of the scattering in the smallest q region and the diffuse lines at larger q perpendicular to the field. The vertical white line is due to a defect on the detector.

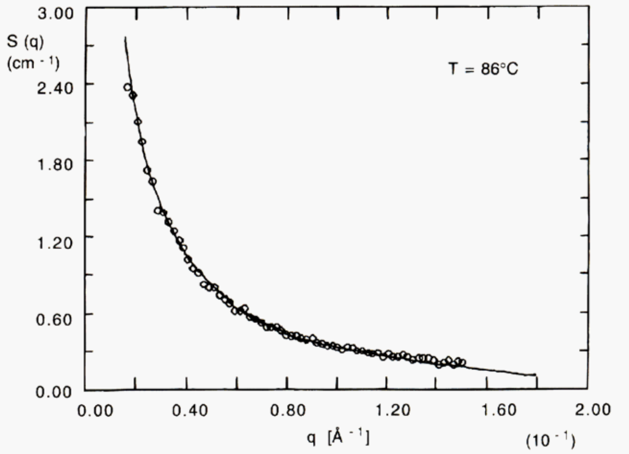

Figure 5. Absolute scattering intensity in the intermediate vector range of the 50D/50H polyether sample in the unoriented nematic phase at 86 °C. The full line corresponds to the form factor of randomly distributed cylinders ($R = 9.5$ Å and $M/2H = 46$ Da·Å^{-1}; see text in section 3.1).

Table 1. Results of the Fit of the Scattering Data to a Cylinder Model in the Intermediate q Range[a]

T (°C)	R (Å)	$M/2H$ (Da·Å^{-1})	$\bar{m}/d$ (Da·Å^{-1})
63	7 ± 2	39 ± 2	
86	9 ± 2	46 ± 2	471/25.6 ≈18
90.5	10 ± 2	48 ± 2	

[a] R and $M/2H$ are the radius and the linear density of the cylinder and $\bar{m}/d$ is the linear density of the monomer.

3. Chain Conformation in the Nematic Phase at High Temperatures ($T > 70$ °C)

In the nematic phase the chain conformation of the polyether is very anisotropic (see Figure 4). This means that the chain size parallel to the nematic director is much greater than the perpendicular one and confirms the results obtained on the polyesters of comparable molecular weights.[6,9,10,14,15,20] In such a case, the determination of the small chain dimension is easy in the q range, but the large chain dimension is not measured directly from the scattering curves even in the smallest accessible q range. Consequently, in order to study the conformation of the main-chain polyether, we have proposed a simple model to calculate the chain form factor of these very anisotropic polymers:[14,15,20] a cylinder, in which the polymer chain is lying. Only two parameters, the height $2H$ and the radius R, are required to describe a cylinder. As already mentioned above, the small sizes can be obtained quite easily, but another method is to determine R from the scattering at large q ($qH \gg 1$) in the unoriented nematic state. Furthermore, in this unoriented state, the average of the scattering intensities in all the q directions improves the accuracy of the measurements. We can then study the effect of the temperature on this R value.

3.1. Results in the Unoriented Nematic Phase.

The scattering by the 50/50 sample is obtained in the intermediate q range ($0.017 < q < 0.15$ Å^{-1}) at three temperatures (63, 86, and 90.5 °C). In this q range, the scattering intensity of randomly oriented cylinders can be expressed as follows:[23]

$$I(q) \propto k\frac{\pi M}{2Hq}\exp(-q^2R^2/4) \qquad (2H)^{-1} \ll q \le R^{-1} \quad (3)$$

where $M/2H$ is the linear density of the cylinders. A typical example of experimental data and the corresponding fit to eq 3 are shown in Figure 5. The comparison with the cylinder model seems rather good and the results of the fits are listed in Table 1. The values of R and $M/2H$ obtained increase with increasing temperature, showing that the anisotropy of the cylinder shape decreases slightly with increasing temperature. Let us compare the values of $M/2H$ thus obtained with those of the linear density of the monomer $\bar{m}/d$. This latter is calculated from the mean molecular weight of the monomer repeat unit ($\bar{m} = 471$ Da) and the monomer length d. This parameter is deduced from the diffuse lines observed on the scattering pattern of the oriented sample (see Figure 4). These lines, perpendicular to the nematic director, are due to longitudinal

Table 2. Parameters of the Chain Conformation and Results of the Fits to a Cylinder Model for the Polyether in the Oriented Nematic Phase[a]

	exptl results in the Guinier range		params of the cylinder model				no. of hairpin wires
T (°C)	$R_\perp$ (Å)	M_w	R (Å)	$R_\perp$ (Å)	P_2	$2H$ (Å)	$n_H = L/2H$
63	21 ± 3	18 000	10 ± 2	19.2 ± 1.0	0.94	330 ± 20	1.82
86	19 ± 1	21 500	10 ± 2	17.2 ± 1.0	0.95	320 ± 20	1.87
90.5	21 ± 1	21 000	10 ± 2	21.0 ± 1.0	0.92	310 ± 20	1.93

[a] n_H is the ratio of the calculated length of the fully extended polyether chain ($L \approx 23.5 \times 25.6 = 600$ Å) and the measured cylinder length ($2H$).

interferences between the repeat units of the same chain. The Bragg distance corresponding to the length of the repeat units is $d = 25.6 \pm 0.5$ Å, which matches the value for fully extended local conformations, as found by ^{2}H-NMR experiments.[19] The values of the linear densities $M/2H$ (between 39 and 48 Da·Å^{-1}) are a little more than 2 times that of the monomer (see Table 1). These measurements lead to about 45/18 ≈ 2.5 wires of a chain in the cylinder. This result is confirmed from the comparison of the radius of the cylinder (7−10 Å) to the value of 4.7 Å obtained from the X-ray diffraction. The numbers of wires are comparable to those obtained for the polyesters[16] with a similar degree of polymerization.

3.2. Results in the Oriented Nematic Phase. The scattering experiments on the oriented 50/50 sample have been performed at 63, 86, and 90.5 °C in the small q range ($7.9 \times 10^{-3} < q < 6.7 \times 10^{-2}$ Å^{-1}). By using the Zimm approximation, the data obtained in the direction perpendicular to the nematic director are fitted to the following equation:

$$I_\perp^{-1}(q) = I_\perp^{-1}(0)(1 + q^2 R_\perp^{\,2}) \qquad qR_\perp < 1 \tag{4}$$

According to this equation we have obtained the average distance of inertia $R_\perp$, and according to eq 2 we can also measure the weight average molecular weight $\bar{M}_w$ of the polymer chains. A similar fit of the data in the parallel direction shows that the Guinier condition $qR_\parallel < 1$ is not fulfilled. This means that the chain dimension in this direction is too large to be determined by this method. The same problem was also encountered with the polyesters.[15,16] The results are listed in Table 2. The values of the molecular weights are in very good agreement with those already measured in the isotropic phase, except at the lowest temperature (63 °C) at which these values are slightly lower (10%). The values of $R_\perp$ are rather constant in the studied temperature range. As a matter of fact, the same values of $R_\perp$ are obtained at 63 °C and at 90.5 °C. These surprising results are probably due to smectic fluctuations observed at the lowest temperature for this polyether. Nevertheless, this effect is weak and may be neglected in the following discussion.

A more complete description of the chain conformation needs the determination of the chain dimension in the parallel direction. In order to calculate this parameter, we have adjusted the experimental data with the cylinder model in the parallel and perpendicular directions simultaneously. The form factor of the cylinder is[23]

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

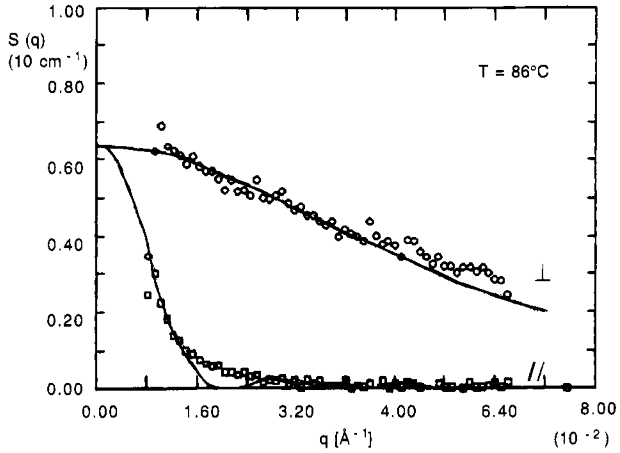

Figure 6. Absolute scattering intensity $I(q)$ measured in the direction parallel (□) and perpendicular (○) to the magnetic field as a function of the scattering vector q in the smallest vector range for the 50/50 polyether sample in the oriented nematic phase at 86 °C. The full lines are calculated curves of a well-oriented cylinder of 320 Å length and 10 Å radius, $P_2 = 0.95$ (see text in section 3.2). The chain conformation is composed of one hairpin.

where $J_1(x)$ is the Bessel function of the first order and β is the angle between the scattering vector q and the main axis of the cylinder. The distribution chosen for β around the nematic direction is the Maier−Saupe distribution:[24]

$$P(a,\beta) = A\mathrm{e}^{a\cos^2\beta} \qquad A^{-1} = 4\pi\int_0^{\pi/2}\mathrm{e}^{a\cos^2\beta}\sin\beta\,\mathrm{d}\beta \tag{6}$$

The orientation of the cylinder is described by the order parameter P_2:

$$P_2 = 4\pi\int_0^{\pi/2}\frac{(3\cos^2\beta - 1)}{2}P(a,\beta)\sin\beta\,\mathrm{d}\beta \tag{7}$$

Finally, the scattering data are fitted with the following functions:[25]

$$I_\parallel(q) = I(0)\int_0^{\pi/2}P(a,\beta)\,F(R,2H,\beta,q)\sin\beta\,\mathrm{d}\beta \tag{8}$$

$$I_\perp(q) = I(0)\int_0^{\pi/2}P(a,\beta)\,F\left(R,2H,\frac{\pi}{2} - \beta,q\right)\sin\beta\,\mathrm{d}\beta \tag{9}$$

where $I(0)$ is the value obtained for $I_\perp(0)$. The results of the fits ($2H$, R, and P_2) as a function of the temperature are given in Table 2. A typical example of the fits in both directions is shown in Figure 6. The fits are not very good in the parallel direction, but are much better in the perpendicular one. In the parallel direction, the experimental curve gives no oscillation. It is mainly due to a distribution of the hairpin positions in the chains, which leads to a polydispersity of the cylinder length (see ref 16). This effect is increased by the usual polydispersity of the chains molecular weight. Nevertheless, the values of $2H$ obtained are very large, about 320 Å, and seem to slightly decrease with increasing temperature. The R values determined from the fit in the perpendicular direction are similar to those obtained in the unoriented nematic phase. They remain constant (≈10 Å), about twice the lateral distance measured by X-ray. The order parameter of the cylinder P_2 does not change; it is very high, lying in between 0.92 and 0.95. All these results show that the cylinders are very long and have very weak fluctuations of orientation around the nematic director, in good agreement with the NMR results.[19]

The values of $R_\perp$ measured using eq 4 are 2 times greater than those of R (≈10 Å). It is due to the fluctuations of orientation of the cylinder which, even though very weak, give a contribution of 2H in the determination of the $R_\perp$ value. This can be estimated using the small q expansion of eq 9:

$$I_\perp(q) \propto 1 - q_\perp^{2}\left(\frac{4H^2\langle\cos^2(\pi/2-\beta)\rangle}{12} + \frac{R^2\langle\sin^2(\pi/2-\beta)\rangle}{4}\right) \quad (10)$$

$$q_\perp R \ll 1,\ q_\perp H\cos(\pi/2-\beta) < 1$$

where the brackets indicate an average using the Maier–Saupe distribution. For $P_2 = 0.95$, $2H = 330$ Å, and $R = 10$ Å, we find a calculated value of $R_\perp$ of 19 Å, in very good agreement with that of 21 Å experimentally found (see Table 2). This confirms that the condition $q_\perp H\cos(\pi/2-\beta) \leq 1$ is well fulfilled.

It is now possible to determine the number of hairpins from comparison of $2H$ with the total length L of the fully extended chain. The latter is obtained from the monomer length (d = 25.6 Å, already measured by neutron diffraction) and the number[26] average degree of polymerization ($\overline{DP}_n \approx 23-24$): $L = 23.5 \times 25.6 \approx 600$ Å. In Table 2, we have reported the number of hairpin wires, $n_H = L/2H$, thus estimated. No significant effect of the temperature on this value is observed. The chain conformation is composed of scarcely two wires, confined in a long and thin cylinder. Thus in the nematic phase the polyether chains have, on average, only one hairpin.

4. SANS Studies below 70 °C

As shown by X-rays, below 70 °C, smectic C fluctuations appear, increasing with decreasing temperature down to 30 °C. These fluctuations are also observed by SANS. The corresponding phenomenon is the splitting of the highly anisotropic central scattering to an "X" pattern with $\beta = 30°$ at room temperature (Tr), as shown in Figure 7. Since the X pattern is the form factor of one mean chain, it means that the whole cylinder is tilted with the same angle as observed by X-rays (Figure 3).

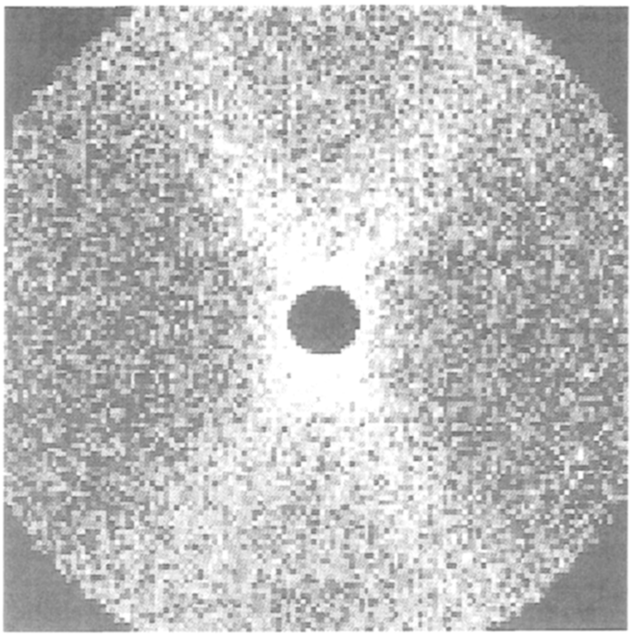

Figure 7. SANS pattern obtained with the sample $\beta = 30°$ at room temperature. The q scale is given by $q = 0$ at the center of the X and by $q = 0.072$ Å^{-1} at one extremity of a branch.

Since it is difficult to fill the space with cylinders of different orientations, it is easier to accept the idea that a given orientation corresponds to a "grain" of smectic C fluctuations. In each "grain" the layers are perpendicular to the magnetic field and the cylinders have the same tilt angle as the mesogens. Moreover, each branch of the "X" has been fitted to the cylinder model by using the procedure of section 3.2. The results are $R = 15 \pm 5$ Å and $2H = 280 \pm 10$ Å. They correspond to a cylinder quite similar to that obtained at high temperatures without splitting. This indicates that the whole extended chain is tilted since the length of the cylinder is roughly not modified. At 63 °C the scattering curve shows no splitting but a weak smearing of the extremities of the central scattering, roughly compatible with the X-ray data at 65 °C (see Figure 2).

A second sample studied by SANS at room temperature gives $\beta = 15°$. Additional neutron diffraction experiments performed on this sample show that the two diffuse lines observed at high temperatures (Figure 4) become crescents at room temperature. The meridian width of this crescent is 2 times greater than that of the instrumental resolution. This last result is consistent with the existence of smectic fluctuations at low temperatures in the nematic phase shown by X-rays. The layer thickness is 24.6 Å at room temperature, to compare with 25.6 Å determined at high temperatures from the diffuse lines observed with both samples. Let us notice that the ratio of 24.6 and 25.6 is cos 15°, confirming the tilt of the mesogens in the layers.

The difference between the values $\beta = 30°$ and $\beta = 15°$ of the two samples is probably connected to the thermal alignment process. On the other hand, we have no explanation for the difference between the values of 26.5 and 24.6 Å obtained by X-ray and neutron diffraction, respectively, for the periodicity corresponding to the crescent at room temperature. It is difficult to believe that these experiments can give an error of 10%. We believe that this error may be due to the difference between the structure factors which are technique dependent.

5. Conclusion

From SANS measurements performed on a mixture of labeled and unlabeled polymers TPB-10 together with the possibility of aligning the polymer samples TPB-10, it is concluded that the chain conformation in the nematic phase is well described by a model of a homogeneous and very well oriented cylinder. This cylinder is on average composed of two very confined and extended wires forming one hairpin defect (Figure 8). The local chain conformations are fully extended, in agreement with the finding of ^{2}H-NMR experiments[19] and the theoretical predictions of Yoon and Flory.[27]

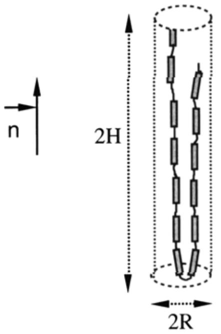

Figure 8. One-hairpin defect on the chain with two wires confined in a long ($2H$) and thin ($2R$) cylinder. The arrow indicates the nematic director n.

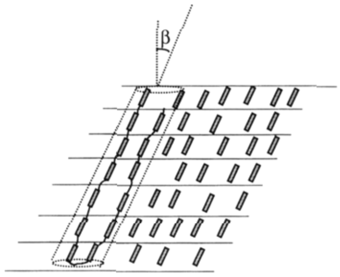

Figure 9. Smectic C fluctuation indicating that the whole chain is tilted with the same angle as the mesogenic units.

Additional X-ray and neutron diffraction measurements on TPB-10 suggest that there is no smectic fluctuations in the high-temperature nematic range ($T > 70$ °C), whereas smectic C cybotactic clusters occur at low temperatures. In this latter situation, combining our SANS results with X-ray and neutron diffraction data, we find that the whole extended chains follow the tilt of the mesogenic units in the layering order of each "grain" of smectic C fluctuations (Figure 9).

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