Observation of Hairpin Defects in a Nematic Main-Chain Polyester

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The conformation of a main-chain liquid crystalline polyester in its oriented nematic phase has been determined by small-angle neutron scattering. The data are fitted by a model of rigid cylinder with orientational fluctuations. For a low degree of polymerization (~9) the chain is almost completely elongated in the direction of the nematic field. For a polymer 3 times longer, the existence of two hairpins is shown at high temperature; this number decreases with decreasing temperature.

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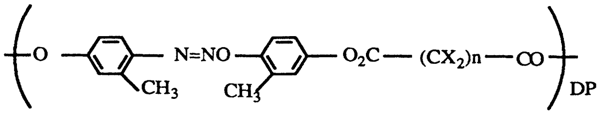
Liquid crystalline polymers (LCPs) have generated much interest in the recent years both because of the challenge of understanding such systems and because of their important technological applications in high modulus fibers, nonlinear optics, synthetic membranes, and electronic devices. A main-chain LCP is a linear link of repetitive units that may, but often does not, possess intrinsic mesogenic character. The liquid crystalline character of the main-chain LCP is a property of the chain backbone. For a semiflexible main-chain LCP in its nematic phase, the tendency to follow long-range orientational order of the nematic phase enters into competition with the random conformation necessary to maximize the polymer entropy. Depending upon the chain molecular weight M, two possible chain conformations have been predicted by de Gennes [1]: For low M values the chain adopts a linear conformation essentially parallel to the nematic director whereas for high M values it can present hairpin defects where the chain executes a contour reversal (180°) with respect to the director. The number of hairpins is an exponential function of the temperature. Statics and dynamics of hairpins in wormlike chains have been developed [2] by Warner and co-workers and a precise temperature dependence of the chain size has been predicted: The chain size increases with decreasing temperature [3]. From a practical point of view the existence of hairpins can play an important role in the rheology and in the nonlinear dielectric and optical properties of main-chain LCPs. We report, for the first time, on the experimental observation of the hairpin conformation by small-angle neutron scattering (SANS) associated with wide-angle x-ray scattering (WAXS). The crucial problem is to determine the dimensions of one chain in the direction parallel and perpendicular to the nematic director. It has been resolved by SANS using for the chain a cylinder model. WAXS has been used to measure the monomer length and the monomer orientational order of the polymer in the nematic phase. The existence of the hairpins is deduced from the comparison of the height of the cylinder to the total length of the chain.

SANS allows the determination of the conformation of one chain from a melt of 50% deuterated (D) chains dispersed in protonated (H) ones [4]. Here the difficulties lie in finding soluble nematic polymers (in order to obtain the H and D chain mixture from a solution) with a nematic phase in a low-temperature range ($T < 200°\mathrm{C}$). A rather good candidate is the following mesomorphic polyester



where DP is the degree of polymerization, X is either H or D, and n is the spacer length. This polyester was first synthesized [5] and widely studied by Blumstein and Blumstein [6]. This group has obtained the first SANS results [7] and shown that these chains are very extended in the nematic phase. Nevertheless, quantitative interpretation of their data is difficult since the authors did not mention anything concerning the transesterification reaction. This reaction occurs during the preparation of a homogeneous polyester sample by annealing in the isotropic phase. Higgins and co-workers and Weiss and co-workers have undertaken the conformation study of LCP by SANS using as a sample another polyester [8,9], in which the transesterification was a major problem [8].

The transesterification reaction [10] is a random scission of the carboxyl groups $(\mathrm{C{=}O}){-}\mathrm{O}{-}$ of the polyester and a recombination of subchains induced by heating. This leads to a sample made of H chains, D chains, and partial D chains. Neutron scattering intensities of such samples are very difficult to interpret in the low scattering vector range [11] where the size of the chain is obtained. The conservation of the mean molecular weight of the D (or H) chains or of the intensity scattered at zero q value during the SANS experiment is the proof of negligible effects of transesterification. Evaluation of M_W can be achieved from an absolute intensity calibration of the SANS experiment [12]. This procedure was recently used by our group to carry out systematic studies [13] of this chemical reaction with different polyesters ($n = 8$, 10, and 11) following the theory of Benoît, Fischer, and Zach-Mann [14]. As a result, a method has been developed to prepare and study samples where the effects of the transesterification reaction are negligible. This method consists of preparing the homogeneous polyester sample in the crystalline phase near the crystalline-nematic transition and keeping the measuring time in the isotropic phase less than 1 h.

Here we report the results of the conformational study of the polyester with spacer length $n=10$ conformation in the nematic phase for two samples: A sample DP28 is obtained from a half and half mixture of H chains ($M_w=14900$; $M_w/M_n=1.16$; $99<T_{NC}<108°\mathrm{C}$; $152<T_{IN}<158°\mathrm{C}$) and D chains ($M_w=16100$; $M_w/M_n=1.18$; $99<T_{NC}<108°\mathrm{C}$; $152<T_{IN}<159°\mathrm{C}$). M_n and M_w are the number and weight average molecular weights, respectively, T_{NC} the range of transition temperature from nematic to crystalline phases, and T_{IN} that from isotropic to nematic phases—of course no measurements were made in these biphasic temperature ranges. The second sample (DP7-11) is prepared from a mixture of H chains DP=7 ($M_w=4080$; $M_w/M_n=1.36$) and D chains DP=11 ($M_w=5920$; $M_w/M_n=1.17$). Note this short polymer sample has a bimodal distribution of short chains. The transition temperatures of this mixture are ($80<T_{NC}<95°\mathrm{C}$; $132<T_{IN}<145°\mathrm{C}$).

The polymer (DP28) in the nematic phase was first studied by wide-angle x-ray scattering in order to determine the length and the nematic order parameter of the monomer.

A sample of $\simeq 5$ mg in a capillary glass tube ($\varnothing=1.5$ mm) was aligned by a magnetic field of 1.7 T and studied *in situ* in the oven of the x-ray setup. This setup, already described [15], uses the point focused x-ray beam ($\lambda \mathrm{Cu}K_\alpha=1.541$ Å) issued from a doubly bent graphite monochromator.

On the one hand, the x-ray diffraction pattern (Fig. 1) shows the wide-angle diffuse ring at $q\sim 2\pi/4.5$ Å^{-1} (q is the scattering vector of modulus $4\pi\sin\theta/\lambda$ where 2θ is the scattering angle) classically due to lateral interferences between mesogenic cores. The intensity distribution along the ring indicates that the mesogenic cores are oriented parallel to the magnetic field. More precisely, this intensity distribution can be exploited to derive the nematic order parameter S according to published methods [16,17]. The value $S=0.85\pm0.09$ was thus obtained [18] at 140 °C. In the whole temperature range of the nematic phase, the S value only increases by 10% with decreasing temperature.

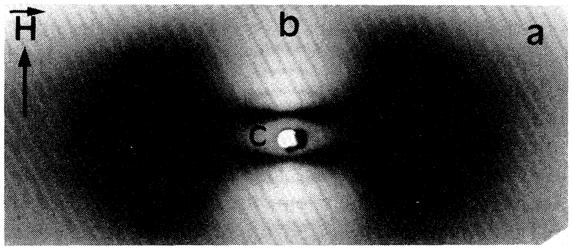


FIG. 1. X-ray diffraction pattern of a magnetically aligned sample of the long polymer in the nematic phase. H is the magnetic field direction (sample film distance 60 mm). (a) Wide-angle diffuse ring, (b) diffuse lines, and (c) diffuse spots due to unimportant smectic-C fluctuations (see Ref. [6]) superimposed on the first diffuse line.

On the other hand, the x-ray diffraction patterns also show 4 orders of diffuse lines perpendicular to the director (see Fig. 1). These diffuse lines arise from longitudinal interferences between monomers belonging to the same polymer chain [19,20]. The resulting distance $d=24.5\pm0.5$ Å appears as the length of the monomer. Comparison of this value to the length (25.2 Å) measured on stereomodels in the most extended configuration shows that the spacer $(\mathrm{CH_2})_{10}$ is almost completely elongated. This last result is quite independent of the temperature. Similar results were obtained with a polymer DP=15. They are extrapolated to the short polymer DP=7-11.

The SANS measurements were performed on the PAXY spectrometer at LLB (Orphée Reactor, Saclay). The wavelength used was 10 Å and the distance between the sample and the multidetector (128×128 cells of 5×5 mm^2) was 3.0 m. The scattering vector range was $7.9\times10^{-3}\leq q\leq 6.7\times10^{-2}$ Å^{-1}. The sample was oriented *in situ* in an oven with a magnetic field of 1.4 T. The scattering was extremely anisotropic. The cells of the same q modulus were regrouped by rectangular sectors of eleven cells in the direction parallel and eight cells in the direction perpendicular to the magnetic field. This gives us the primary scattering intensities $I_\parallel(q)$ and $I_\perp(q)$, respectively.

The data treatment is carried out using the classical procedure. The background is determined from the weighted sum of the incoherent intensity delivered by a sample of H polymers and of D polymers. Absolute calibration is obtained from the direct determination of the number of neutrons in the incident beam [12]. This allows us to obtain the scattering cross section $S(q)$ in cm^{-1}.

The data of $S_\perp(q)$ are easy to interpret as a function of the radius of gyration $Rg_\perp$ using the Zimm representation [21]

$$S_\perp^{-1}(q)=S_\perp^{-1}(0)(1+q^2Rg_\perp^2/3),\quad qRg_\perp<1\,. \tag{1}$$

The $S_\perp^{-1}(0)$ values are very close to the corresponding ones measured in the isotropic phase which give the correct molecular weights. For example, we have obtained the radius of gyration $Rg_\perp=23\pm1$ Å for the sample DP28 at $T=135$°C and $Rg_\perp=13.5\pm0.5$ Å for the sample DP7-11 at $T=124$°C. For $S_\parallel(q)$ a similar relation

$$S_\parallel^{-1}(q)=S_\parallel^{-1}(0)[1+q^2Rg_\parallel^2/3],\quad qRg_\parallel<1 \tag{2}$$

is used. But $S_{\parallel}^{-1}(0)$ which should be equal to $S_{\perp}^{-1}(0)$ is found to be much lower. This result, already obtained by d'Allest *et al.* (see Fig. 3 in Ref. [7(a)]) means that the condition $(qRg_{\parallel} < 1)$ necessary to use Eq. (2) is not fulfilled experimentally. Thus, in this direction, it is not possible to determine $Rg_{\parallel}$ using the Zimm approximation without data in a smaller q range. This indicates a very elongated conformation. Unfortunately, the corresponding low scattering intensity does not allow us to work in a smaller q range.

The best way to obtain the parallel dimension of the chain is to try a fit of the data of the two directions with a model. The simple model adopted here for the chain is that of a cylinder of length $2H$ and of radius R; its form factor is [22]

$$F(\beta) = \left[\frac{\sin(qH\cos\beta)}{qH\cos\beta} \frac{2J_1(qR\sin\beta)}{qR\sin\beta} \right]^2 , \qquad (3)$$

where $J_1(x)$ is the Bessel function and β the angle between the scattering vector and the axis of the cylinder. There is a certain orientational distribution for this cylinder, i.e., the angular distribution of β in the nematic phase. The distribution chosen for β is assumed to be the Maier-Saupe distribution [23] (without real reasons but for simplicity):

$$\begin{aligned} &P(a,\beta) = Ae^{a\cos^2\beta} , \\ &A^{-1} = 4\pi \int_0^{\pi/2} e^{a\cos^2\beta} \sin\beta \, d\beta . \end{aligned} \qquad (4)$$

Finally the scattering data were fitted with the following functions:

$$S_{\parallel}(q) = S(0) \int_0^{\pi/2} P(a,\beta) F(\beta) \sin\beta \, d\beta , \qquad (5)$$

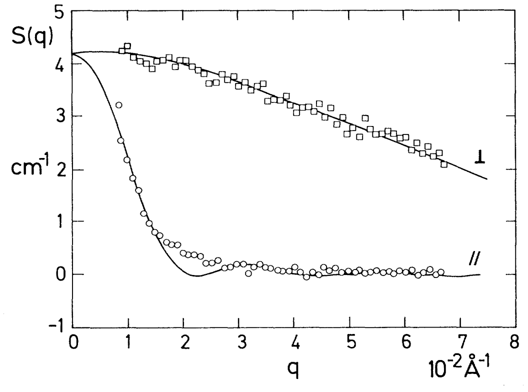


FIG. 2. Absolute scattering intensity recorded in the directions parallel (∥) and perpendicular (⊥) to the magnetic field as a function of the scattering vector q. The data are the response of a main chain of 28 monomers. The solid lines are simulated curves of a cylinder of 280 Å in length and 12 Å in radius (see text). This result shows the existence of two hairpins in the chain conformation.

$$S_{\perp}(q) = S(0) \int_0^{\pi/2} P(a,\beta) F\left(\frac{\pi}{2} - \beta \right) \sin\beta \, d\beta , \qquad (6)$$

where $S(0) = S_{\perp}(0)$ is an experimental datum. The adjustable parameters are $2H$, R, and a; *a priori,* they intervene in both directions because of the orientational fluctuations. Fortunately, the chains are very elongated in the ∥ direction; thus a precise value of $2H$ can be deduced from $S_{\parallel}(q)$ alone. This value of $2H$ is introduced in the fit of $S_{\perp}(q)$ but a difficulty lies in the correlations of the a and R values. However, this problem is not relevant to the hairpin existence which is derived mainly from the $2H$ value.

Figure 2 shows the fits of experimental data to Eqs. (5) and (6) for the long polymer at 135 °C, the higher temperature in the nematic phase. The fits are quite good and lead to $2H = 280 + 10$ Å, $R = 12 \pm 2$ Å, and $a = 50$, corresponding to a very high value of the nematic order parameter P_2 of the cylinder $P_2 = 0.97$. Since the total length L of the polymer is $28 \times 24.5 = 686$ Å the chain presents (686/280) 2.45 hairpins on the average. [Rigorously, the hairpin number is $n = (L/2H) - 1$, and $L/2H$ represents the arm number of hairpins. $L/2H$ is used here because it has been shown to be a crucial parameter in the theoretical discussion [1].] A schematic representation of the chain conformation is given in Fig. 3. At the lower temperature in the nematic phase $T = 116$ °C these values become $2H = 320 \pm 10$ Å, $R = 8 \pm 3$ Å, and $a = 87$ $(P_2 = 0.98)$. Thus the mean hairpin number (686/320=2.1) decreases with decreasing temperature. As regards the correlations of the R and a values, a complementary measurement of R has been made in the unoriented nematic phase at $T = 135$ °C where the scattering cross section [22]

$$S(q) \sim \frac{M}{2qH} \exp\left(-\frac{q^2R^2}{4} \right), \quad (2H)^{-1} \ll q \leq R^{-1}$$

yields R directly. The corresponding value of 11.5 ± 0.5 Å is in very good agreement with that of 12 Å deduced from the fits and gives us confidence in our results. The absence of oscillations in the experimental curve $S_{\parallel}(q)$ can be explained by a distribution of cylinder length due to the distribution of hairpin's positions along the chain.

For the short polymer (DP7-11) at 124 °C the fits give $2H = 180 \pm 10$ Å, $R = 5 \pm 3$ Å, and $a = 50$ $(P_2 = 0.97)$. Thus this polymer is almost completely elongated along the director. Here also the experimental curve $S_{\parallel}(q)$

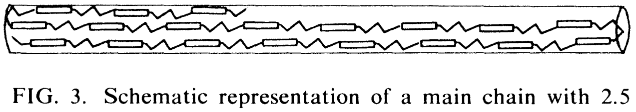


FIG. 3. Schematic representation of a main chain with 2.5 hairpins on the average. The cylinder is the model used to fit the experimental data.

does not present oscillations but in this case it is a consequence of the bimodal distribution of H and D polymers.

The orientational fluctuations of the whole polymer are very weak relative to those of the monomers. This striking result is obtained comparing the nematic order parameter of the monomer $S=0.85$ measured by x-ray diffraction to $P_2=0.97$ obtained for the cylinder from the fit.

In conclusion, we can say that the conformation of the short polymer corresponds to a totally elongated polymer with very little orientational fluctuations. The conformation of the long polymer is explained with two hairpins but their arms are extremely elongated and closely packed in a cylinder of about 20 Å in diameter (see Fig. 3). The mean number of hairpins is a decreasing function of temperature, but the variation observed in the present experiment is too weak to test the theoretical models [1,2], in which an exponentially decreasing function of temperature for the hairpin number is predicted.

A main question concerns the possibility of a drastic change in local conformation required by a hairpin. Since, in the isotropic phase, the polyester ($n=10$) shows [18] the characteristic behavior, $S(q)\sim q^{-2}$, in the wide q range (0.016 to 0.16 Å^{-1}), of a Gaussian coil and not that of a wormlike chain [$S(q)\sim q^{-1}$], this striking result can be explained by a Gaussian conformation of the chain due to the high flexibility of its spacers. As a consequence, the energy penalty paid by the spacer participating in the hairpin structure is perhaps not too high.

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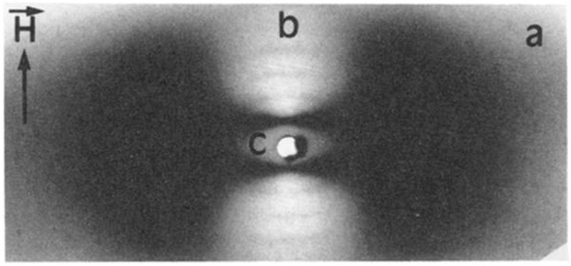

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