Effect of the Spacer and Aliphatic Tail Length on the Conformation of “Side-on Fixed” Liquid Crystal Polyacrylates: “SANS” Experiments

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Abstract. — The backbone conformation of two different “side-on fixed” liquid crystalline polyacrylates is studied by Small Angle Neutron Scattering experiments in the nematic phase. We observe the influence of a very large spacer and a large aliphatic extremities length on the prolate anisotropy of the polymer backbone. In both situations we find a strong decrease in the conformation anisotropy of the main chain.

Résumé. — Par Diffusion de Neutrons aux Petits Angles, nous étudions la conformation en phase nématique de la chaîne principale de deux polyacrylates en “haltère” différents. Nous observons l’influence d’un très long espaceur et de longues chaînes latérales sur l’anisotropie prolate de la chaîne polymère. Dans les deux cas nous trouvons une forte diminution de l’anisotropie de conformation du squelette polymère.

1. Introduction

“Side-on fixed” liquid crystalline polymers form a peculiar class of mesogenic polymers for which the mesogenic cores are fixed laterally to the backbone in the direction perpendicular to their long molecular axis via a flexible spacer (Fig. 1). In general these polymers are nematic [1–6].

Small Angle Neutron Scattering (SANS) is the basis technique to determine polymer conformation [7–9] specifically in liquid crystal side chain polymers [8, 9]. These “side-on fixed” polymers exhibit a global prolate conformational anisotropy in the nematic phase: the polymer backbone stretches on average on the direction of mesogenic groups [10]. This nematic

(*) The authors would like to dedicate this paper to the memory of their colleague Doctor Claude Strazielle who died on September 12th, 1995.

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Fig. 1. — Schematic representation of a “side-on fixed” polymer.

“jacketed” structure is dependent on molecular parameters. In particular it has been demonstrated that this nematic “jacketed” effect tends to be reinforced as the degree of polymerization decreases (keeping in the polymer regime): the prolate anisotropy of the global polymer conformation is weaker for the polymer with $\overline{DP}_n = 70$ ($R_{\parallel}/R_{\perp} \cong 4$) than for that with $\overline{DP}_n = 35$ ($R_{\parallel}/R_{\perp} \cong 6$) [11]. In addition, the dilution of the mesogenic content in a copolymeric homologous strongly reduces the anisotropy of the global polymer conformation [11]. We have more recently shown the influence of the spacer length of polyacrylates on the backbone conformation: the anisotropy is larger for smaller spacer length ($n = 4$ $R_{\parallel}/R_{\perp} = 6$, $n = 6$ $R_{\parallel}/R_{\perp} = 4.5$) [12].

In this paper, we aim at studying the influence of a very large spacer ($n = 11$) in order to observe if some anisotropy of the system is remained. In other way, our second goal is to study for the first time the effect of the aliphatic tails length on the polymer backbone conformation.

2. Materials

To explore the polymer backbone conformation, it is necessary to use for SANS experiments a pseudo binary system of fully protonated polyacrylate with the same one selectively deuterated on the backbone. The polymers investigated have the following general formula:

These polymers are labelled $PA_{n,m,m}$ where n is the spacer length, and m the aliphatic tails length. We study in this paper two polymers named $PA_{4,8,8}$ and $PA_{11,4,4}$.

The molecular weights of the fractionned polyacrylate samples were measured by size exclusion chromatography on line with a light scattering (SEC-LS) at the ICS (Strasbourg) from polyacrylate solutions in tetrahydrofuran. The refraction index of the solvent is $n = 1.404$ at room temperature (wavelength of light $\lambda_0 = 632$ nm). The number average and the weight average molecular weights ($\overline{M}_w$ and $\overline{M}_n$) of the polyacrylates obtained by this technique are listed

Table I. — Characterization of the polyacrylate samples by SEC-LS, Optical Microscopy and DSC. $\overline{M}_n$. number average molecular weight, $\overline{M}_w$. weight average molecular weight, $\overline{DP}_n$. degree of polymerization, I : polydispersity index. g: glassy state, N: nematic phase, I: isotropic liquid phase. * from DSC (Perkin Elmer DSC7), heating rate of 10 °C/mn.

polymer		$\overline{M}_w$	$\overline{M}_n$	$\overline{DP}_n$	I	Transition Temperatures (°C)		
						g	N	I
PA _{11,4,4}	H	130000	50500	69	2.58	23*	94	
	D	372000	76700	105	4.85	24*	92	
mixture	H,D	-	-	-	-	23*	93.5	
PA _{4,8,8}	H	235000	62200	84	3.77	28*	86	
	D	454000	93700	125	4.84	28*	89	
mixture	H,D	-	-	-	-	28*	87.5	

in Table I. The values of $\overline{DP}_n$ are deduced from these measurements and from the molecular weights M of the monomer units ($M_{PA_{4,8,8}H} = 744$, $M_{PA_{11,4,4}H} = 730$).

For each polymer, the transition temperatures were determined by optical microscopy and DSC. All these results are summarized in Table I.

3. Experimental

The experiments were performed on the SANS spectrometer "PAXY" of the Laboratoire Léon Brillouin (CEA/CNRS, CE Saclay, Orphée reactor) equipped with an XY position sensitive multidetector using a well known procedure described elsewhere [7–12]. The bulk samples have been set in an oven which is placed on the trajectory of the neutron beam. An aligned nematic phase was obtained by cooling the samples from the isotropic state under an external magnetic field of 1.4 Tesla. Under these conditions, the orientation of mesogens is achieved perpendicularly to the beam.

The incident wavelength used was $\lambda = 12 \text{ \AA}$ and the sample-multidetector distance was 2 meters. The scattering vector range explored ($q = 4\pi \sin \theta / \lambda \cong 4\pi \theta / \lambda$, where 2θ is the small scattering angle) is then:

$$3 \times 10^{-3} \text{ \AA}^{-1} \leq q \leq 6 \times 10^{-2} \text{ \AA}^{-1}$$

The linear dependence of the inverse of the intensity scattered by the backbones $I^{-1}(q)$ versus q^2 is obtained. In this range, which is the enlarged Guinier domain ($qR \leq 2$), we can write:

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

where $R_{\parallel}$ and $R_{\perp}$ are the apparent quadratic sizes of the polymer backbone in the directions parallel and perpendicular to the magnetic field.

We have also taken into account the difference in molecular weight between the labelled and the unlabelled polymer using a law derivative from the Guinier approximation [13]. This law assumes no specific interaction between labelled and unlabelled parts. This assumption is justified since the deuterated part of the $PA_{n,m,m}$ (D) is small in regard to the number of hydrogens in the macromolecules. If the component of the vector q in the direction i is noted q_i , we have:

$$I^{-1}(q_i) = A[1 + q_i^2 R_{iapp}^2][(1/(\overline{M}_{wH} \cdot \varphi_H)) + (1/(\overline{M}_{wD} \cdot \varphi_D))]$$

where A is a constant, φ_H , φ_D , are the volume fractions, $\overline{M}_{wH}$, $\overline{M}_{wD}$ the molecular weights of the hydrogenated chains and the deuterated chains respectively. R_{iapp} is the quadratic size of the deuterated chains in the direction q_i related to the real size R_{izD} of the deuterated chains by [13]:

$$R_{iapp}^2 = R_{izD}^2 [1 + \varphi_D / (\varphi_D + \overline{M}_{zD} / (\overline{M}_{zH} - \overline{M}_{zD}))]$$

In our case:

$$\varphi_D = \varphi_H = 0.5$$

Then:

$$R_{izD}^2 = 0.5 R_{iapp}^2 [1 + (\overline{M}_{zD} / \overline{M}_{zH})]$$

Moreover, we can deduce from the reference [14] the relation between $\overline{M}_z$ and $\overline{M}_w$ using a Schulz distribution. Actually, it represents our situation because of the radical polymerization using AIBN (we have a broad mass distribution). So: $\overline{M}_z = [(2I - 1)/I] \overline{M}_w$, where I is the polydispersity. In a first approximation, we can say that this formula is available even if the degrees of polymerization are important. In fact, the factor $[(2I - 1)/I]$ does not change very much for each value of polydispersity.

Therefore we obtain:

$$R_{izD} = 1.44 R_{iapp} \text{ for PA}_{11,4,4}$$

and

$$R_{izD} = 1.22 R_{iapp} \text{ for PA}_{4,8,8}$$

These corrections are slight and don't change neither the scattering shape, nor the eventual anisotropy of the backbone.

4. Results

4.1. EFFECT OF ALIPHATIC TAILS LENGTH (PA_{4,8,8}). — From the scattered intensity distribution in the XY plane of the multidetector "PAXY", we have drawn the experimental values of $I^{-1}(q_i)$ versus q_i^2 at different temperatures. For instance, Figure 2 gives these experimental values measured for PA_{4,8,8} in the nematic phase at $T = 80$ °C.

The general feature dependence of the polymer dimensions ($R_{||}$ and $R_{\perp}$) are reported in Figure 3. The error is estimated to be about 5%. In the isotropic state, the two quadratic sizes ($R_{||}$ and $R_{\perp}$) are equal to about 61 ± 3 Å. On decreasing temperature in the nematic phase, $R_{||}$ jumps to about 100 Å while $R_{\perp}$ decreases slightly to about 48 Å. The shape of this polyacrylate (PA_{4,8,8}), with long aliphatic extremities, is a weak prolate shape of anisotropy ratio ($T = 60$ °C):

$$R_{||}/R_{\perp} \cong 2.1$$

Figure 3 shows that, at $T = 40$ °C, $R_{||}$ seems to decrease whereas $R_{\perp}$ increases with respect to the values at $T = 63$ °C. A modification of the corresponding SANS pattern is shown in Figure 4. Contrary to the patterns at high temperature, the pattern at $T = 40$ °C is not an ellipsoid in the reciprocal space, so that we can't speak about a prolate shape in the real space. However, the symmetry of revolution around the magnetic field direction is conserved: we are always able to determinate the average extensions in the direction parallel or perpendicular to the field. In this situation, the parallel and perpendicular axes are not prevailing, but an angular distribution is observed. This is the signature that a proportion of polymer backbones have been tilted (with an angle of about 30°) with decreasing temperature just above the glassy transition.

Fig. 2. — Inverse of the SANS intensity (I^{-1}) plotted in arbitrary units as a function of q^2 in the nematic phase ($T \approx 80^\circ\text{C}$) of $\text{PA}_{4,8,8}$. For both $\parallel$ and $\perp$ directions, the straight lines are determined using a least square method in the enlarged Guinier domain.

Fig. 3. — Values of the components of the radii of gyration $R_{\parallel}$ and $R_{\perp}$ of the polymer backbone of $\text{PA}_{4,8,8}$ chain as function of temperature.

Fig. 4. — SANS pattern of a magnetically aligned sample ($\text{PA}_{4,8,8}$) in the nematic phase a) at $T \approx 63^\circ\text{C}$, b) at $T = 40^\circ\text{C}$. **H** is the magnetic field direction.

Fig. 5. — a) Neutron diffraction pattern of a magnetically aligned sample ($PA_{4,8,8}$) in the nematic phase ($T = 40\text{ }^{\circ}\text{C}$). The sample-detector distance is 0.95 m and the incident wavelength is $\lambda = 3.1\text{ \AA}$ (PAXY). b) X-Ray diffraction pattern of a magnetically aligned sample ($PA_{4,8,8}$) in the nematic phase ($T = 40\text{ }^{\circ}\text{C}$). The sample-detector distance is 186 mm using a $\text{CuK}\alpha$ radiation of an 18 KW rotating X-Ray generator [15]. **H** is the magnetic field direction.

In addition to SANS study, X-Ray and neutron diffraction measurements were performed for $PA_{4,8,8}$ in order to obtain complementary informations. The neutron and X-Ray diffraction pictures are shown in Figure 5.

Both neutron and X-Ray diffraction patterns present the same off axis diffuse spots centered on $2\pi/q = 28\text{ \AA}$ and with a tilt angle $\theta \cong 50^{\circ}$. These four symmetrical diffuse spots have been

Fig. 6. — Values of the components of the radii of gyration $R_{\parallel}$ and $R_{\perp}$ of the polymer backbone of $PA_{11,4,4}$ as function of temperature.

previously interpreted as strong smectic C fluctuations [16]. Nevertheless, no Sc phase has been observed up to now in homologous series of side-on fixed polymers, and such behaviour is quite unusual when large cybotactic groups exist in the nematic phase. As demonstrated elsewhere [15], we have shown that the evolution of the parameters (wavevector q and tilt angle θ) of these diffuse spots was only a function of the aliphatic tails length. An hypothetic way to explain the origin of these spots is to imagine the existence of alternated “tilted blocks” constituted of some mesogens in which the aliphatic extremities are correlated and tilted with respect to the mesogenic cores. This model seems to be in good agreement with the structural data. This unusual arrangement is strongly reinforced by the enlargement of the tails and therefore it could locally more disturb the backbone extension for $PA_{4,8,8}$ than for $PA_{4,4,4}$.

4.2. EFFECT OF THE SPACER LENGTH ($PA_{11,4,4}$). — In the same way, Figure 6 shows the temperature dependence of the backbone dimensions $R_{\parallel}$ and $R_{\perp}$ for $PA_{11,4,4}$.

This polyacrylate presents a weak temperature dependence of radii of gyration. Actually, in the isotropic phase, both $R_{\parallel}$ and $R_{\perp}$ are equal to 58 ± 2 Å, and by decreasing temperature, $R_{\parallel}$ only jumps to 64 Å while $R_{\perp}$ decreases to about 55 Å. In other words: $PA_{11,4,4}$ does not show significant backbone anisotropy ($R_{\parallel}/R_{\perp} \cong 1.1$).

5. Discussion and Conclusion

First of all, we bear in mind the influence of the degree of polymerization. In earlier study [11], the prolate anisotropy of the global polymer conformation ($R_{\parallel}/R_{\perp}$) was found stronger for a short polymer backbone. Owing to the fact that the index of polydispersity I was constant in this study, we cannot conclude on a specific influence of this parameter so far.

Taking into account that the characteristic lengths $R_{\parallel}$ and $R_{\perp}$ have to be compared with the degree of polymerization $\overline{DP}_z$, the results reported here for PA_{11,4,4} and PA_{4,8,8} and those previously obtained on PA_{4,4,4} and PA_{6,4,4} are summarized in the following table:

polymer	$R_{\parallel}/R_{\perp}$	$\overline{DP}_z^*$	I^*
PA _{4,4,4}	6	197	1.75 from Ref. [12]
PA _{6,4,4}	4.6	200	1.75 from Ref. [12]
PA _{11,4,4}	1.1	937	4.85
PA _{4,8,8}	2.1	1012	4.84

* values obtained for deuterated polymers

We recall that, keeping the same mesogenic side group and the same $\overline{DP}_z$ ($\cong 200$), the increase of the spacer length ($n = 4$ to 6) reduces the anisotropy of the backbone conformation ($R_{\parallel}/R_{\perp} = 6$ to 4.5). In the present study, from PA_{4,4,4} to PA_{11,4,4} the spacer length and the degree of polymerization increase. Qualitatively, same influence on the conformation anisotropy is expected for both parameters and consequently we observe a strong decrease in this anisotropy ($R_{\parallel}/R_{\perp} = 1.1$). Moreover, with similar degree of polymerization $\overline{DP}_z$ and polydispersity I , we observe a larger anisotropy for PA_{4,8,8} than for PA_{11,4,4}. Thus, referring to PA_{4,4,4}, we can say that the molecular modifications are certainly more efficient than the change of polydispersity.

Quantitatively, the effect of the spacer length appears more perturbative than the effect of the aliphatic extremities length. In fact, we have revealed the limit situation, that is when the spacer is sufficiently large ($n = 11$) to practically uncouple the mesogens to the backbones. As a consequence, the nematic field induced by the mesogenic rods poorly interact with the flexible chain. Such a behaviour can be compared to a solution of non liquid crystalline polymer in a nematic solvent [17]. Thus, with long spacers, whereas the mesogenic side groups tend to be oriented under an external field, the flexible backbone tends to take configuration of maximum entropy and a very weak anisotropy of the polymer conformation is detected.

At the opposite, for shorter spacers ($n = 4$ or 6), the mesogenic cores naturally impose their anisotropic order to the backbone since they are part of it. This situation corresponds to a nematic phase of N_{III} type theoretically described by Wang and Warner [18] referring to liquid crystalline side chain polymers.

More unexpected is the result for the polymer with large aliphatic extremities (PA_{4,8,8}): we observe a significant decrease in the anisotropy as m increases (even if $\overline{DP}_z$ increases from PA_{4,4,4} to PA_{4,8,8}). In that case, the interpretation is quite different since the same coupling between the mesogenic cores and the backbone is kept (the spacer length is the same $n = 4$). In other words, if we argue in terms of free energy of the backbone [18], we have *a priori* the same coupling between nematic field and entropy of the main chain. Nevertheless, it appears clearly that the increase of the length of aliphatic extremities reduces the global organization of the backbone by an effect of intramolecular plasticization and by tilted orientational correlations of the flexible extremities [15].

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