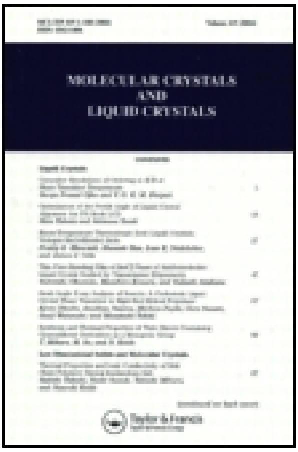

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Small Angle Neutron Scattering (Sans) Studies on "Side-On Fixed" Liquid Crystal Polymers

F. Hardouin [a], N. Leroux [a], L. Noirez [b], P. Keller [b], M. Mauzac [a] & M. F. Achard [a]

[a] Centre de Recherche Paul Pascal, Université Bordeaux I, Av. A. Schweitzer, F-33600, Pessac, France

[b] Laboratoire Léon Brillouin, CEA - CNRS/CEN Saclay, F-91191, Gif sur Yvette, France

Version of record first published: 24 Sep 2006.

To cite this article: F. Hardouin, N. Leroux, L. Noirez, P. Keller, M. Mauzac & M. F. Achard (1994): Small Angle Neutron Scattering (Sans) Studies on "Side-On Fixed" Liquid Crystal Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 254:1, 267-282

To link to this article: http://dx.doi.org/10.1080/10587259408036081

Mol. Cryst. Liq. Cryst. 1994, Vol. 254, pp. 267–282
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Printed in the United States of America

SMALL ANGLE NEUTRON SCATTERING (SANS) STUDIES ON "SIDE-ON FIXED" LIQUID CRYSTAL POLYMERS

F. HARDOUIN+, N. LEROUX+, L. NOIREZ*, P. KELLER*, M. MAUZAC+, M. F. ACHARD+
+ Centre de Recherche Paul Pascal, Université Bordeaux I, Av. A. Schweitzer, F-33600 Pessac, France
* Laboratoire Léon Brillouin, CEA - CNRS / CEN Saclay, F-91191 Gif sur Yvette, France

(Received: February 7, 1994)

Abstract Small angle neutron scattering experiments were carried out on liquid crystalline "side-on fixed" polymers in order to draw the main features of the backbone conformation in the nematic phase of these systems. At low temperature, the main chain exhibits a high prolate anisotropy which corresponds to a large extension of the polymer and, such anisotropy depends on the chemical structure of the liquid crystalline "side-on fixed" polymers.

INTRODUCTION

"Side-on fixed" liquid crystalline polymers form a peculiar class of mesomorphic side chain polymers. In these compounds the mesogenic groups are laterally attached to the backbone via a flexible spacer (Figure 1) instead of a longitudinal connection ("side-end fixed") in the case of conventionnal liquid crystalline side chain polymers.

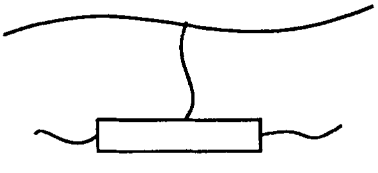


Figure 1 Schematic representation of the "side-on" fixation.

From the last two decades, it is well known that the longitudinal attachment of the rod-like mesogenic groups in the "side-end fixed" mesomorphic polymers induces predominantly smectogenic mesophases and that they exhibit the same wealth of polymorphism as conventional low molar mass thermotropic liquid crystals (nematic, smectic A, smectic C, smectic B, ...). At the opposite, the "side-on fixed" liquid crystalline polymers generally promote only the nematic state [1,2,3].

The determination of the polymer conformation in these two classes of mesomorphic side-chain polymers has aroused considerable interest in recent years and has been the subject of extensive experimental and theoretical studies. The problem is as follow : the backbone alone which is a flexible or semi-flexible chain has the natural tendency to keep a random coil conformation, but an anisotropic order is imposed by the mesogenic pendents. This antagonism raises two fundamental questions : what about the influence of the mesophase on the backbone conformation and is there an universal answer ?

Especially small angle neutron scattering (SANS) on mixtures of unlabelled and labelled polymers is well adapted to solve experimentally the problem at the scale of the polymer sizes. Indeed the mixtures of all hydrogenated liquid crystalline polymers with the corresponding partially deuterated liquid crystalline polymers produce a signal at small angles from which the conformation of a single chain can be deduced.

By means of this technique previous studies emphasized general features for "side-end fixed" polymers : whatever the nature of the chain (polymethacrylate, polyacrylate, polysiloxane) if the compound presents only a nematic phase (without smectic phase), the backbone conformation is slightly prolate and the average direction of the polymer backbone is the same as the mesogenic orientation, as long as the spacer length allows it [4-9]. In that case, the mesophase organization can be depicted by the nematic phase of N_{III} type (prolate shape) described in the Wang and Warner theory [10] (Figure 2).

With a smectic A phase at lower temperature than the nematic phase, the polymer backbone adopts a global oblate conformation in the smectic phase [11-18] : the backbone is confined between the liquid crystalline layers. In this latter case, a weaker oblate shape is observed in the nematic phase due to the existence of smectic A fluctuations , and this nematic phase can be described by the N_I phase (oblate shape) of the Wang and Warner theory (Figure 2). Moreover, qualitatively and quantitatively, the nature of the smectic phase (S_{A1}, S_{Ad}) and its organization, even at the scale of fluctuations in the nematic phase, affects the oblate anisotropy of the backbone conformation.

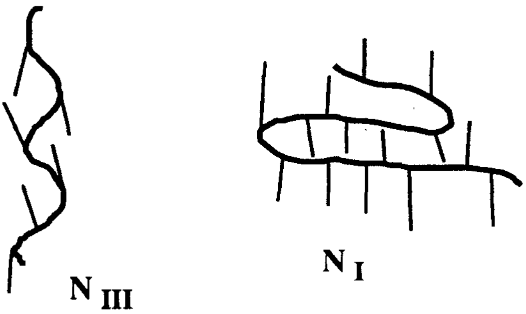


Figure 2 Schematic representation of the N_{III} and N_I phases described in the theory of Wang and Warner [10].

In this paper we report an overwiev about informations given by SANS studies on various "side-on fixed" liquid crystalline polymers aligned in the bulk under an external magnetic field and by this way, we intend to draw the main features of the experimental results on the influence of the chemical and mesomorphic structures on the backbone conformation in the nematic phase of these systems.

PRINCIPLE OF SMALL ANGLE NEUTRON SCATTERING

As yet mentionned, the small angle neutron scattering (SANS) technique is a convenient method to determine the polymer conformation at the scale of the backbone sizes [19-20]. The fundamental parameter is the transfer wave vector $\underline{q}$ where $\underline{q} = \underline{k}-\underline{k_0}$ where $\underline{k_0}$ and $\underline{k}$ are respectively the incident and scattered wave vectors. In static experiment, the norm of $\underline{q}$ (q) is given by the Bragg relation where θ is the scattering angle : $q = 4\ \pi/\lambda\ \sin\theta/2$.

At small angles, the q values are calculated from the approximation : $q \approx 2\ \pi\ \theta/\lambda$. Thus, the scattering intensity in the θ direction is directly q dependent : $I(\theta) = I(\underline{q})$. The small angle neutron scattering intensity can be written as proportional to the coherent scattering function S(q) (through a flux factor K) : $I(q) \approx K\ S(q)$.

Considering n polymers with the same size, roughly, this coherent scattering function corresponds to an interchain scattering function (called the form factor) plus an interchain term : $S(q) = n\ S_1(q) + n^2\ S_2(q)$. In an homogeneous medium (without concentration fluctuations) if the incompressebility hypothesis is valuable, no central scattering is observed : $S(q) \approx 0$.

In contrast, using the labelling method, a mixture of n_D partially deuterated polymers and $(n - n_D)$ fully protonated polymers make the coherent scattering function a non zero signal related to the contrast ($K_{D/H}$), which depends on the pair correlation functions only of the deuterated polymers : $S(q) = K_{D/H}\ [\, n_D\, S_1(q) + n_D^2\, S_2(q)\,]$.

In this condition, the coherent scattering function and thus the intensity correspond to the form factor of the polymer : $S(q) = K^2_{D/H}\ \Phi\ (1-\Phi)\ S_1(q)$ with $\Phi = n_D/n$ and then, $I(q) = \Phi\ (1-\Phi)\ S_1(q)$. Therefore, a mixture of fully protonated and partially deuterated polymers in equal parts ($\Phi = 0.5$) maximizes the intensity.

Besides if the polymer backbone is the deuterated part, the coherent scattering will be representative of the backbone conformation. On the other hand, if this is a part of each mesogenic side-group which is deuterated, the coherent scattering at low q-values will correspond to the global conformation of the polymer (including the mesogenic group).

The analysis method to determine the size of one chain is based on the expression of the form factor S_1 which is $S_1(q) = \sum_{i,j} < e^{iq(r_i - r_j)} >$. In the Guinier domain ($qR \leq 1$, where R is the characteristic length of the polymer), at low q range, S_1 can be expressed by the first term of a limited serie : $S_1(q) = 1 - q^2R^2$.

In an uniaxial symmetry of a nematic phase or smectic A phase, the radius of gyration Rg is : $Rg = R_{//}{}^2 + 2\, R_{\perp}{}^2$ where the characteristic lengths parallel and perpendicular to the director are provided from the classical Zimm plots :

$I^{-1}(q_{//}) = I^{-1}(0)\ (1 + q_{//}{}^2\, R_{//}{}^2)$ with $q_{//}\, R_{//} \leq 1$

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

From these sizes, three geometries for the polymer conformation can be distinguished :

$R_{//} / R_{\perp} = 1$	random coil
$R_{//} / R_{\perp} < 1$	oblate shape
$R_{//} / R_{\perp} > 1$	prolate shape

If we have to take into account the difference in molecular weight of the labelled and unlabelled polymer we apply an extension of the Guinier approximation. R_{iapp} ($i = //$ or $\perp$) which is an apparent quadratic size in the direction q_i, is induced by the molecular weights difference between the two polymers. It is related to the real size R_i of the labelled chains by [18,20] :

$$R_{iapp}{}^2 = R_i{}^2\ [1 + \Omega_D / (\Omega_H + M_D / (M_H - M_D))]$$

where Ω_H and Ω_D are the volume fractions, M_H, M_D the molecular weights of the hydrogenated chains and the deuteriated chains respectively.

In our case, we have : $\Omega_D = \Omega_H = 1/2$

Then we get : $R_i^2 = 1/2\ R_{iapp}^2\ [1 + M_D / M_H]$

This relation primarily established for isotropic systems can be important but does not change neither the scattering shape nor the type of backbone anisotropy. In any case, this scattering law supposes that no specific interaction occurs between labelled and unlabelled species. This is experimentally checked by following the extrapolated intensity at the origin ($q = 0$).

EXPERIMENTAL PROCEDURE

The experiments have been performed on the SANS spectrometer "PAXY" of the Laboratoire Léon Brillouin (CEA-CNRS, CEN Saclay, Orphée reactor) using a procedure reported elsewhere [4,6,11-16,18]. The bulk sample is put in an oven (with a temperature stability of 0.2°C) which is placed in the neutron beam and between the poles of an electro-magnet (Figure 3).

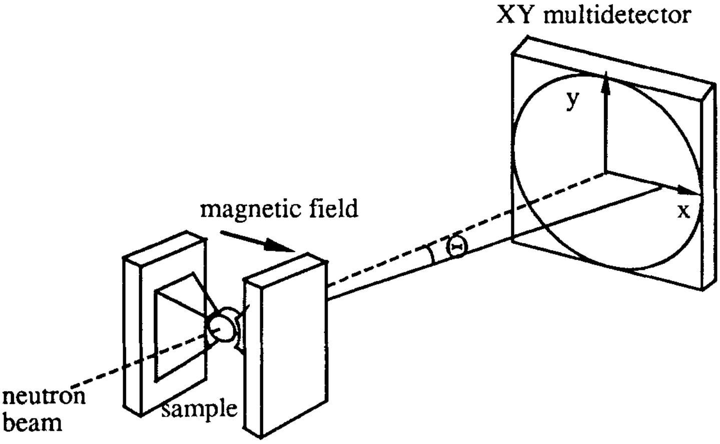
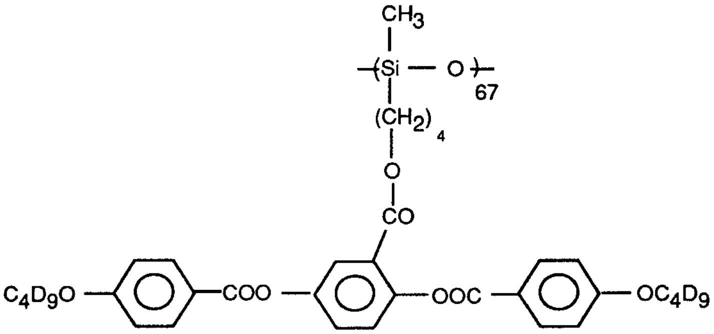


Figure 3 Schematic representation of the SANS experimental set up.

A monodomain of nematic can be obtained by cooling down from the isotropic state under a magnetic field of 1.4 Teslas. The orientation is produced perpendicularly to the neutron beam and the scattered intensity is collected on the plane of a bidimensionnal XY multidetector. Typically, the range of the scattering vector q usually choosen is between : $0.008\ Å^{-1} < q < 0.1\ Å^{-1}$ for a sample-multidetector distance of 2m and using an incindent wavelength $\lambda = 10$ Å.

DETERMINATION OF THE GLOBAL CONFORMATION IN THE NEMATIC PHASE OF "SIDE-ON FIXED" LIQUID CRYSTAL POLYSILOXANES

The SANS experiments were first performed on "side-on fixed" homopolysiloxanes with deuterated tails on the mesogenic side-groups which have the following general formula [3,21-24] (labelled P4,4,4):



In the nematic phase at low temperatures, though $R_\perp$ decreases only slightly, one finds a large extension of $R_{//}$ with a highly anisotropic prolate shape [22-24] ($R_{//} / R_\perp = 4$) (Figure 4).

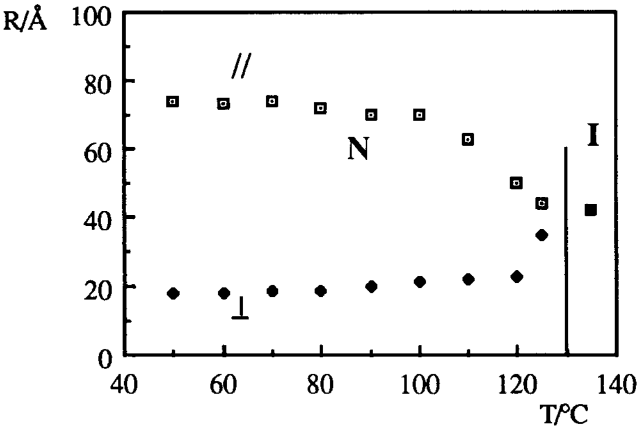


Figure 4 Quadratic size in parallel ($R_{//}$) and perpendicular ($R_\perp$) directions to the magnetic field as a function of temperature for the "side-on fixed" polysiloxane P4,4,4 100% $\overline{DPn} = 67$.

A tentative representation corresponds to a flexible polysiloxane chain which is strongly streched along the nematic director (i-e the magnetic field). Therefore at the scale of the chain dimensions , a strong "jacketed" nematic system is revealed at low temperature in a "side-on fixed" polysiloxane P4,4,4 with a rather short spacer (4 methylenic groups) (Figure 5). This result is the experimental confirmation of the molecular argument of Qi-Feng Zhou and al [2].

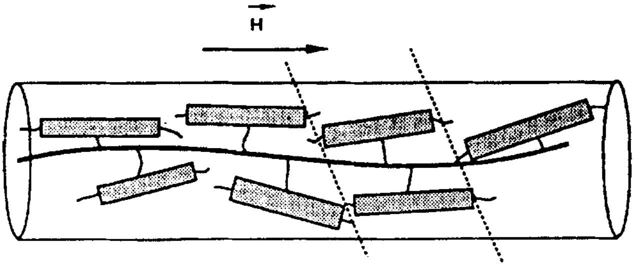


Figure 5 Tentative representation of the jacketed nematic effect on the extension of the backbone in "side-on fixed" polysiloxanes.[22]

At the opposite of the anisotropic effects previously reported in "side-end fixed" polymers, the effect of the molecular weight is quantitatively strong for the "side-on fixed" systems. Indeed, a decrease of the polymerization degree (of half) reduces the absolute value of the gyration radius $R_{//}$ (Figure 6), but the striking feature is that the "jacketed" effect is more efficient since the saturated anisotropy ratio increases from 4 to 6 due to the decrease of $R_{\perp}$ [23].

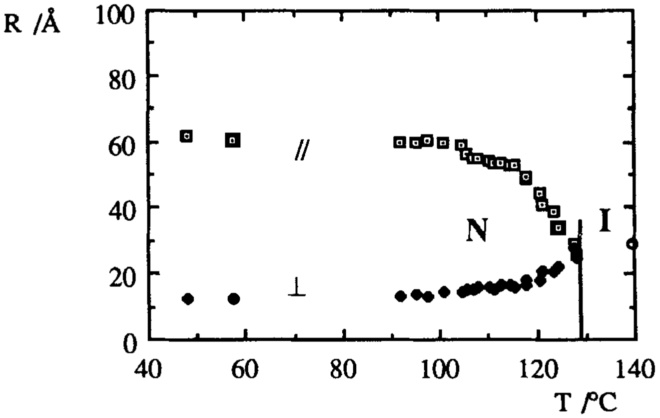


Figure 6 Quadratic size in parallel ($R_{//}$) and perpendicular ($R_{\perp}$) directions to the magnetic field as a function of temperature for the "side-on fixed" polysiloxane P4,4,4 100% $\overline{DPn} = 36$.

Generally, a fall in $\overline{DPn}$ tends to decrease the glass transition temperature (Tg) as well as the isotropic-nematic clearing temperature (T_{IN}) but, in the case of "side-on fixed" polymers, it is balanced by the opposing influence of the increase of the global anisotropy of the polymer (see table 1).

Table 1 Phase transition temperatures (°C) for the homopolysiloxanes P4,4,4. g : glassy state, N : nematic phase, I : isotropic liquid phase, from DSC (Perkin Elmer DSC 7), (heating rate of 10 K / mn).

Homopolysiloxanes	g		N		I
P4,4,4 ($\overline{DPn}$ = 67)		36		130	
P4,4,4 ($\overline{DPn}$ = 36)		39		129	

In other words, we suggest that the persistence length should be here chain-length dependent with a non monotonous evolution. In addition, we notice that the prolate shape is very much stronger than that observed in the nematic phase of some "side-end fixed" polyacrylates : $R_{//} / R_{\perp} \approx 1.5 - 1.8$.

DETERMINATION OF THE GLOBAL CONFORMATION IN THE NEMATIC PHASE OF "DILUTED SIDE-ON FIXED" LIQUID CRYSTAL COPOLYSILOXANES

Now we focus our interest on statistical copolymers unlead homopolymers, with similar chain length ($\overline{DPn}$ =30, referring to the previous homopolysiloxane with a low polymerization degree) and with the proportion 30% of substitued mesogenic moiety (using the same "side-on" liquid crystalline group as the previous experiments) and 70% of dimethylsiloxane units (Figure 7) [21,23,24].

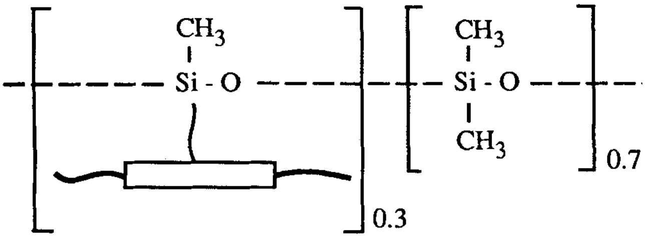


Figure 7 Schematic molecular structure of a "side-on fixed" copolysiloxane with 30% of mesogens deuterated on the tails and 70% of dimethylsiloxane units.

Table 2 Phase transition temperatures (in °C) for the polysiloxanes P4,4,4. g : glassy state, N : nematic phase, I : isotropic liquid phase, from DSC (Perkin Elmer DSC 7), (heating rate of 10 K / mn).

Polysiloxanes	g	N	I
P4,4,4 ($\overline{\mathrm{DPn}}$ = 36) 100%	39	129	
P4,4,4 ($\overline{\mathrm{DPn}}$ = 30) 30%	13	77	

In that case, the main feature obtained from SANS experiments is that the prolate shape of the polymer conformation is drastically reduced : the value of the copolymer anisotropy at saturation is about $R_{//} / R_{\perp} \approx 1.2$ (Figure 8) (compared with the $R_{//} / R_{\perp} \approx 6$ for the homopolymer with the same length of the main chain).

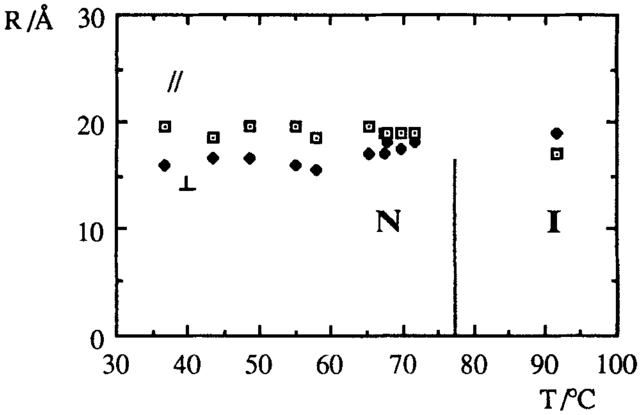
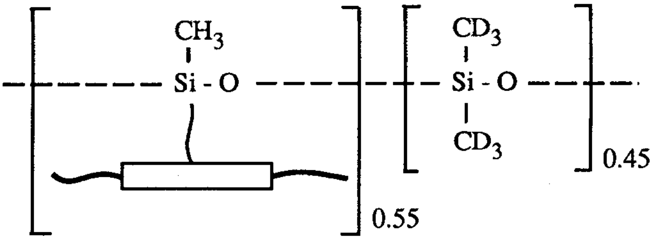


Figure 8 Quadratic size in parallel ($R_{//}$) and perpendicular ($R_{\perp}$) directions to the magnetic field as a function of temperature for the "side-on fixed" polysiloxane P4,4,4 30% $\overline{\mathrm{DPn}}$ = 30.

In such "diluted side-on fixed" mesomorphic copolysiloxanes, the strong increase of the flexibility creates therefore a loss of anisotropy and a weakeness of the nematic field.

DETERMINATION OF THE BACKBONE CONFORMATION IN THE NEMATIC PHASE OF DILUTED SIDE-ON FIXED LIQUID CRYSTALLINE COPOLYSILOXANES

Diluted copolysiloxanes can be deuterated in the main chain. These recent studies are based on new statistical copoly(hydrogenomethyl-dimethyl)siloxanes with perdeuterated dimethylsiloxane units [25], used as precursor backbone which are substitued by the same "side-on" mesogenic groups as the previous experiments. The investigated copolymer which is labelled P4,4,4 55%, presents a polymerization degree of about 55. It can be schematically representated by the following structure :



Thus, the deuteriation of the polymer inside the main chain allows the direct determination of the backbone conformation. The temperature dependence of $R_{//}$ and $R_{\perp}$ are reported in Figure 9.

The SANS experiments carried out on this system revealed that the backbone anisotropy is yet pronounced at low temperature in the nematic phase : $R_{//} / R_{\perp} \approx 2.7$ at saturation. However, we notice that at low temperature, $R_{\perp} \approx 30$Å is greater than what can be expected for a fully extended chain and this difference suggest elbows formation in the nematic phase.

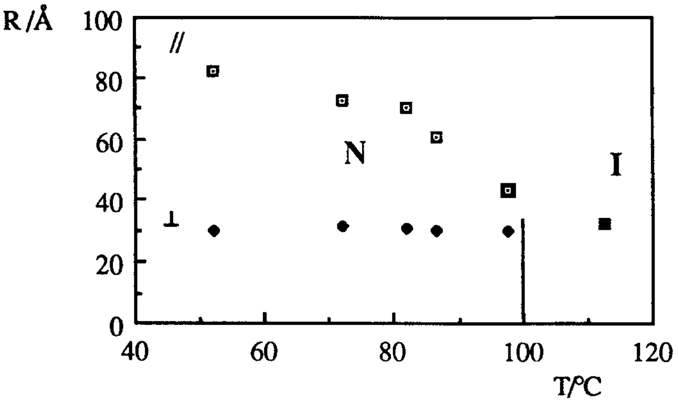


Figure 9 Quadratic size in parallel ($R_{//}$) and perpendicular ($R_{\perp}$) directions to the magnetic field as a function of temperature for the "side-on fixed" polysiloxane P4,4,4 55% $\overline{DPn} = 55$.

In addition, if we compare the thermodynamic properties of the four polysiloxane systems reported here (see table 3), we notice that undoubtly, decreasing the amount of mesogens leads to lower restriction of the polymer in the nematic phase and that the polymer anisotropy appears directly connected to the isotrope-nematic entropy change and to Tg.

Table 3 Phase transition temperatures (in °C), enthalpy transition ΔH_{IN} (g/mol), entropy transition ΔS_{IN} (g/mol/K) and saturated value of the anisotropy ($R_{//} / R_{\perp}$) for the polysiloxanes P4,4,4. g : glassy state, N : nematic phase, I : isotropic liquid phase, from DSC (Perkin Elmer DSC 7), (heating rate of 10 K / mn).

Polysiloxanes	$\overline{DPn}$	g		N		I	ΔH_{IN}	ΔS_{IN}	$R_{//} / R_{\perp}$
P4,4,4 100%	67		36		130		2.2	3.2	4
P4,4,4 100%	36		39		129		3.4	5.3	6
P4,4,4 55%	55		24		99		1.7	1.7	2.7
P4,4,4 30%	30		13		77		0.7	0.5	1.2

Thus, the "jacketed" effect is observed whatever the location of the deuteriation. Even if it is difficult to quantitatively compare backbone anisotropy with global polymer anisotropy, we can claim that for a given short spacer, the "jacketed" effect is more marked increasing the proportion of the mesogenic side groups and finally, if the "jacketed" effect is strong, it depends significantly on the polymerization degree (Figure 10) [25].

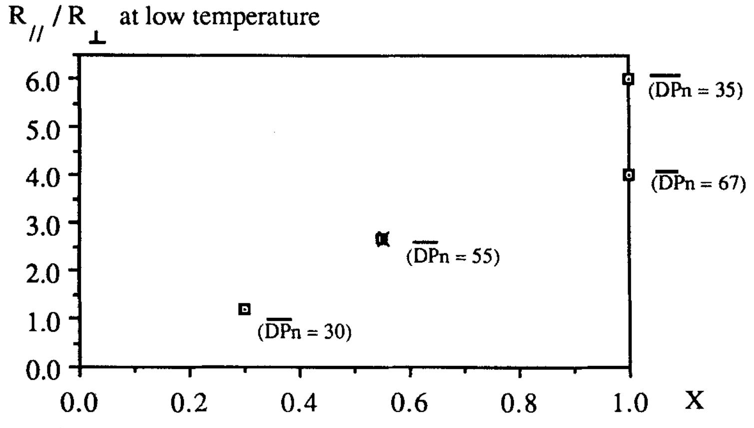


Figure 10 Anisotropy of the "P4,4,4, X" polymer as a function of X where X is the proportion of the "side-on fixed" mesogens. (• : labelled on the aliphatic tails ; x : labelled in the main chain).

DETERMINATION OF THE BACKBONE CONFORMATION IN THE NEMATIC PHASE OF "SIDE-ON FIXED" LIQUID CRYSTALLINE POLYACRYLATES

In this last part, we describe SANS experiments on "side-on fixed" homopolyacrylates which are deuterated within the main chain [26] to specify the conformational anisotropy of the polymer backbone in the nematic phase in new systems, changing here the type of the flexible main chain but keeping the same mesogenic unit (Figure 11).

We have selected two spacer lengths : 4 and 6 methylenic groups. These polyacrylates have practically similar polymerization degree ($\overline{\mathrm{DPn}}$ ≈ 80) and index of polydispersity (I ≈ 1.8). The transition temperatures are listed in table 4.

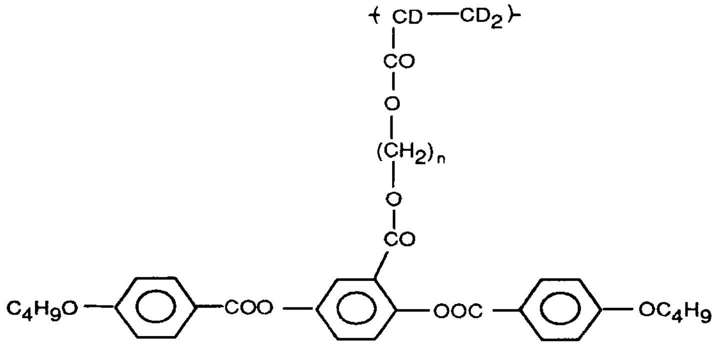


Figure 11 Formula of the "side-on fixed" polyacrylates PA n,4,4 (n = 4 and 6).

Table 4 Phase transition temperatures (in °C) for the polyacrylates PA n,4,4 (n = 4 and 6). g : glassy state, N : nematic phase, I : isotropic liquid phase, from DSC (Perkin Elmer DSC 7), (heating rate of 10 K / mn).

Polyacrylates	g		N		I
PA 4,4,4		40		116	
PA 6,4,4		28		105	

The extension of the backbone for the polyacrylate system with short spacer is shown on the figure 12 : R// strongly increases in the nematic phase [26]. Thus, the "jacketed" nematic effect is verified in "side-on fixed" polymers whatever the type of the polymer main chain (polyacrylate or polysiloxane). Especially, if we compare the homopolymers polysiloxane P4,4,4 ($\overline{\mathrm{DPn}} \approx 70$) and the polyacrylate PA 4,4,4 ($\overline{\mathrm{DPn}} \approx 80$) which possess the same mesogenic side group, the same spacer length and comparable degree of polymerization, we notice that the anisotropy is smaller for the polysiloxane than for the polyacrylate :

$$R_{//}/R_{\perp} \approx 4 \quad < \quad R_{//}/R_{\perp} \approx 6$$

Polysiloxane Polyacrylate

This difference might be an artefact due to the different labelling positions (in the tails of the mesogenic side groups or in the main chain), or it could correspond to a problem of characterization denoting a difference in the mass dispersity of these two systems, but it could also reveal an intrinsic difference in the persistence length which plays a role on the "jacketed" effect.

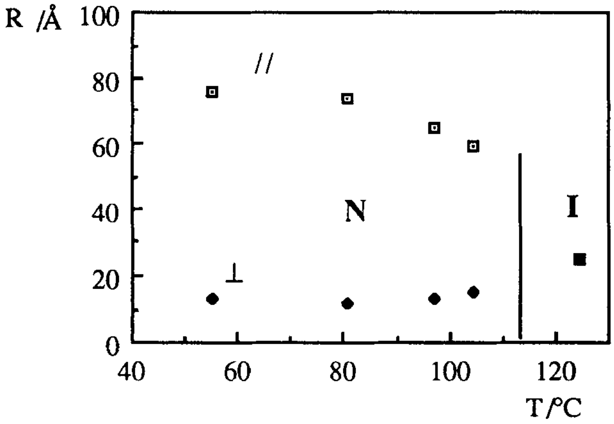


Figure 12 Quadratic size in parallel ($R_{//}$) and perpendicular ($R_{\perp}$) directions to the magnetic field as a function of temperature for the "side-on fixed" polyacrylate PA 4,4,4.

For the PA 6,4,4 a large extension of $R_{//}$ is also evidenced in the nematic phase (Figure 13). Quantitatively these recent experiments reveal for the first time that in the nematic phase, the anisotropy of the backbone conformation of "side-on fixed" liquid crystalline polymers increases by decreasing the spacer length. Indeed the saturated values at low temperature are $R_{//}/R_{\perp} \approx 4.5$ for PA 6,4,4 and $R_{//}/R_{\perp} \approx 6$ for PA 4,4,4. The prolate conformation of the polymer main chain is then reinforced by the crosscoupling via the spacer, so that smaller is the spacer, larger is the nematic "jacketed" effect.

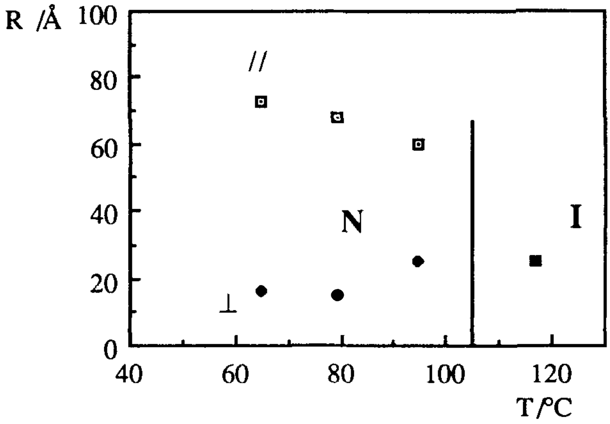


Figure 13 Quadratic size in parallel ($R_{//}$) and perpendicular ($R_{\perp}$) directions to the magnetic field as a function of temperature for the "side-on fixed" polyacrylate PA 6,4,4.

Moreover, we notice that, due to similar degree of polymerization, the radius of gyration in the isotropic phase is the same for both polymers.

CONCLUSION

We have reported an overview about informations given by SANS studies of "side-on fixed" polymers in order to determine, at the scale of the chain dimension, the influence of different molecular parameters on the shape of the polymer backbone in the nematic phase.

The nematic phase primarily imposed by the mesogenic side groups is reinforced by the "jacketed" effect which corresponds to a large extension of the polymer backbone with a highly anisotropic prolate shape. Such a supra nematic organization in side chain liquid crystalline polymers, can be described as the nematic phase of N_{III} type from the Wang and Warner theory.

This large main chain extension in "side-on fixed" liquid crystal polymers in the nematic phase looks like the behaviour observed by SANS for thermotropic segmented main chain polymers but in this latter case, the mesogenic rigid moities naturally impose the backbone anisotropy since they are part of it [27-30].

Moreover, the opportunity in mesomorphic side-chain polymers to get either contribution or non-contribution of the main chains to the orientationnal order parameter should lead to some distinct physical responses justifying the classification between nematic phase of N_{III} type and nematic phase of N_I type.

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