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Dependence of the Stereoregularity on the Structure and the Conformation of Side-Chain Liquid Crystalline Polynorbornenes of Various Spacer Lengths

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ABSTRACT: We use the neutron scattering properties to characterize the influence of the stereoregularity on the nature of the liquid crystalline phase and on the polymer conformation of a series of stereoregular side-chain liquid crystalline polynorbornenes (SCLC-polynorbornenes) with various spacer lengths. It is demonstrated that *trans*-SCLC-polynorbornenes with short spacer lengths display a nematic phase and a prolate main-chain conformation whereas long spacer lengths favor the smectic phase and an oblate main-chain conformation. This smectic structure is no more stable at low temperature, making a spectacular smectic-reentrant nematic transition appear. For identical spacer lengths, a high population of trans configurations favors the emergence of the nematic phase and a prolate main-chain conformation. In contrast, a majority of cis configurations produces the smectic phase and an oblate main-chain conformation. An equirepartition of cis and trans is at the origin of a smectic−nematic reentrance. This reentrant nematic phase reveals moreover a very peculiar conformation since the main-chain anisotropy is inverted from small to large scales.

I. Introduction

The stereoregularity in polymers is known to play a determinant role on the glass transition temperature, the solubility, or the crystallinity.[1] However, there has been much less concern about its impact on the liquid crystalline properties. In particular, the influence of the main chain stereoregularity on the conformation of comblike side-chain polymers, subject of this present study, remained completely unexplored. The very first works on stereoregular LC-side-chain polymers are due to Frosini et al.;[2] however, no effect of the tacticity except a temperature shift similar to that already observed in conventional PMMA[3] was noticed. Later, Duran and Gramain[4.a,b] and then Nakano et al.[4.c] reported also a shift in the isotropization temperature and suggested that the occurrence of a smectic or a nematic phase may depend on the ratio of iso/syndiotactic bonds and even involve a change in the main-chain conformation.[4] These first studies were carried out on polymers made of polyacrylate or -methacrylate main-chains.

Recently, a new synthetic route opened by Schrock et al.[5] has been developed on the basis of ring opening metathesis polymerization (ROMP). This method drives to the construction of a rigid backbone made of norbornene units (1,3-cyclopentylene−vinylene units). A first series of SCLC-polynorbornenes consisted of main-chains substitued by one mesogenic group per monomer unit. Another class of SCLC-polynorbornenes was then synthesized on the basis of 2,3-disubstitued norbornenes.[6] The presence of the double bond in the repeating unit gives rise to two types of *Z*- and *E*-configuration of the double bond. Since each side-chain moiety can be grafted either in cis or in trans configuration onto the cyclopentylene ring, this gives rise to further variations of the structure. All polymers investigated in this paper had a 2,3-trans substitution at the 1,3-pentylene units. Therefore, we decided to use cis and trans for the configuration of the double bonds. The use of different well-defined ROMP initiators allows one to control the rate of cis and trans double bond populations. Because of the nonequivalence of the bonds linked to each cyclopentylene in 1,3-position, the tacticity can also be varied. It has been established, using ^{13}C NMR techniques, that the cis configuration is associated with an isotactic bond distribution whereas the polymer of trans configuration is atactic.[7]

The present study is restricted to LC-polynorbornenes containing two liquid crystal moieties per repetitive unit (Chart 1). The structure of the mesophase and the conformation of the norbornene chain is examined on a series of stereoregular SCLC-polynorbornenes. To characterize the influence of the stereoregularity, two parameters have been tested: the length of the spacer and the proportion of trans and cis double bond contents on the conformation and on the structure of SCLC-polynorbornenes.

We will first describe the influence of the length of the alkyl chain spacer $-(CH_2)_n-$ on a series of LC-polynorbornenes displaying the trans double bond configuration. These polymers are characterized by a trans content of about 80%.[7] The effect of stereoregularity is then tested for the polymers with two distinct spacer lengths $n = 6$ and $n = 11$. Three stereoregular species containing a high content of cis, a high content of trans, and an equipopulation of cis and trans, *respectively*, will be compared for each spacer length. The content of cis configuration is about 78% for the cis polymer whereas the equipopulation corresponds to the conversion rate of 55%.

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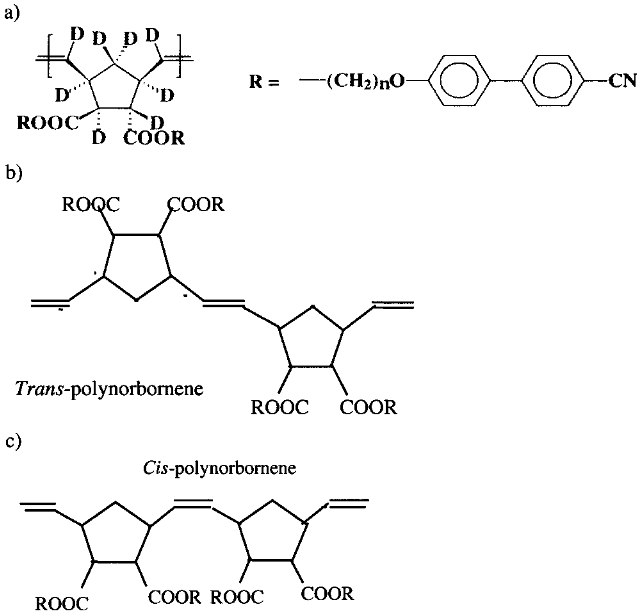
Chart 1. (a) Chemical Formula of the Deuterated Polymer (Eight Hydrogens Have Been Substituted by Deuterium; (b) Representation of the *trans*-Polynorbornene Configuration; (c) Representation of the *cis*-Polynorbornene Configuration



II. Experimental Section

The conformation of the SCLC-polynorbornene and in particular of its main-chain is determined in situ by small-angle neutron scattering (SANS) on mixtures of hydrogenated polymers and polymers specifically deuterated on the main chain (Chart 1). To provide the form factor associated to the main-chain conformation, two series of polynorbornenes, as similar as possible in molecular weight and stereoregularity, have been synthesized via ROMP (with molybdenum carbene complex as initiator) of the corresponding liquid crystal monomers[6,7] (as the fully hydrogenated isotope and the one deuterated onto the main chain, respectively. Disklike samples (15 mm diameter, 1 mm thickness) were prepared containing either the fully hydrogenated polymer or a 1:1 mixture of fully hydrogenated polymer and of polymer deuterated on the main chain alone. The mixture was prepared by dissolution of both polymers and evaporation of the solvent (chloroform). The neutron measurements were achieved on aligned monodomains obtained by slowly decreasing the temperature from the isotropic phase down to the glassy state under a magnetic field of 1.4 T. The same alignment process was applied for each sample, ensuring that a monodomain sample is obtained.

The scattered beam was collected onto the plane of the 2-dimensional spectrometer (PAXY of the Lab. Léon Brillouin) using two settings to cover the small angle range corresponding to the Guinier domain ($qR_g \leq 1$) and the large angles (diffraction). The small angle range was obtained with a wavelength $\lambda = 10$ Å and a sample-multidetector distance $d = 2$ m; the scattering range explored to measure the form factor of the polymer main-chain was 0.01 Å^{-1} $< q <$ 0.1 Å^{-1} (where q is the scattering vector defined by $q = (4\pi/\lambda)\sin(\theta/2)$ with θ being the scattering angle). For the diffraction measurements, the distance and the wavelength were switched down to $d = 1$ m and $\lambda = 5$ Å to access a larger scattering range reaching 0.1 Å^{-1}. The data were normalized and the (incoherent and electronic) backgrounds removed.

Under the Guinier conditions ($qR \leq 1$), the signal $S(q)$ scattered at small angles by an equimolar mixture of hydrogenated and deuterated polymers is proportional to the form factor $P(q)$ associated to the main-chain part of the polymer. In the present case, an extra-scattering, is superposed to $P(q)$ at very small angles ($q <$ 0.015 Å^{-1}). The existence of a similar extra-scattering on fully hydrogenated sample indicates that its origin is likely due to the contribution of Mo catalyst traces which provides a sharp interface scattering. This interface signal can be easily modeled by an isotropic power law $\epsilon(q) \alpha 1/q^{3.5}$. The total scattering $S(q) = (M_w/4m^2)P(q) + \epsilon(q)$, where m is the monomer mass, M_w the polymer weight average, N the Avogadro number and K the scattering contrast, is modeled by a 2-dimensional fit.[8] The form factor $P(q)$ is expressed by a 2-d Lorentzian function:

$$P(q) = 1/\langle 1 + (R_x^2 q_x^2 + R_y^2 q_y^2 + R_z^2 q_z^2)\rangle$$
$$\text{with } R_g^2 = R_x^2 + R_y^2 + R_z^2$$

If we choose O_x as the axis parallel to the magnetic field then $R_x = R_{\parallel}$ is the component of the radius of gyration R_g of the polymer main-chain following the director of the phase. O_y and O_z correspond thus to the perpendicular directions: $R_y = R_z = R_{\perp}$ (only one component of the radius of gyration is measured; the other one is equivalent for symmetry reasons). The 2-dimensional fit presents a huge advantage, allowing one to avoid the systematic error introduced by the use of masks of defined widths, and increases also considerably the statistics. After calibration of the incident neutron beam, the scattered intensity is normalized following the method described in ref 9, allowing the determination of the weight average molecular weight M_w of the isotopic mixture.

Table 1. Molecular Weights (M_n) and Polydispersity (I) of the Hydrogenated and Deuterated Homologues of *trans*-Polynorbornenes Determined by Gel-Permeation Chromatography−Light Scattering on Line (ICTOS-Graz)

	trans-polynorbornene 100% H		*trans*-polynorbornene 100% D	
n	M_n	$I = M_w/M_n$	M_n	$I = M_w/M_n$
4	38 100	1.12	34 600	1.34
5	41 400	1.17	53 900	1.24
6	49 600	1.14	52 492	1.30
7	41 200	1.47	34 800	1.33
8	36 800	1.69	63 000	1.15
9	45 300	1.37	39 000	1.47

Table 2. Molecular Weights and Polydispersities of the Two Stereoregular Species (a, trans, and c, cis) and of the Cis/Trans Mixture (c) determined by GPC−Light Scattering on Line for the 100%H Polymer[10] and Deduced from Absolute Calibration of the SANS Signal Following the Procedure Reported in Ref 9 for the H/D Mixtures

	polynorbornene 100%H[10]		polynorbornene H/D mixture
n(**a**,**b**,**c**)	M_n	$I = M_w/M_n$	M_w
6**a**	see Table 1	see Table 1 for $n = 6$	/
6**b**	61 300	1.52	70400
6**c**	61 300	1.10	79200
11**a**	189 000	1.39	158000
11**b**	77 700	1.20	82200
11**c**	91 400	1.19	98600

III. Influence of the Spacer Length on the Conformation and the Structure of Trans Stereoregular SCLC-Polynorbornenes

The evolution of the main-chain conformation of LC-polynorbornenes as a function of the temperature is examined for a series of 6 polynorbornenes characterized by six different spacer lengths: $-(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_6-$, $-(CH_2)_7-$, $-(CH_2)_8-$, and $-(CH_2)_9-$. The ROMP catalyst employed for the polymerization provides a high content of trans double bond configuration. The stereospatial distribution of the side chains with respect to the main chain is random; i.e., the polymer

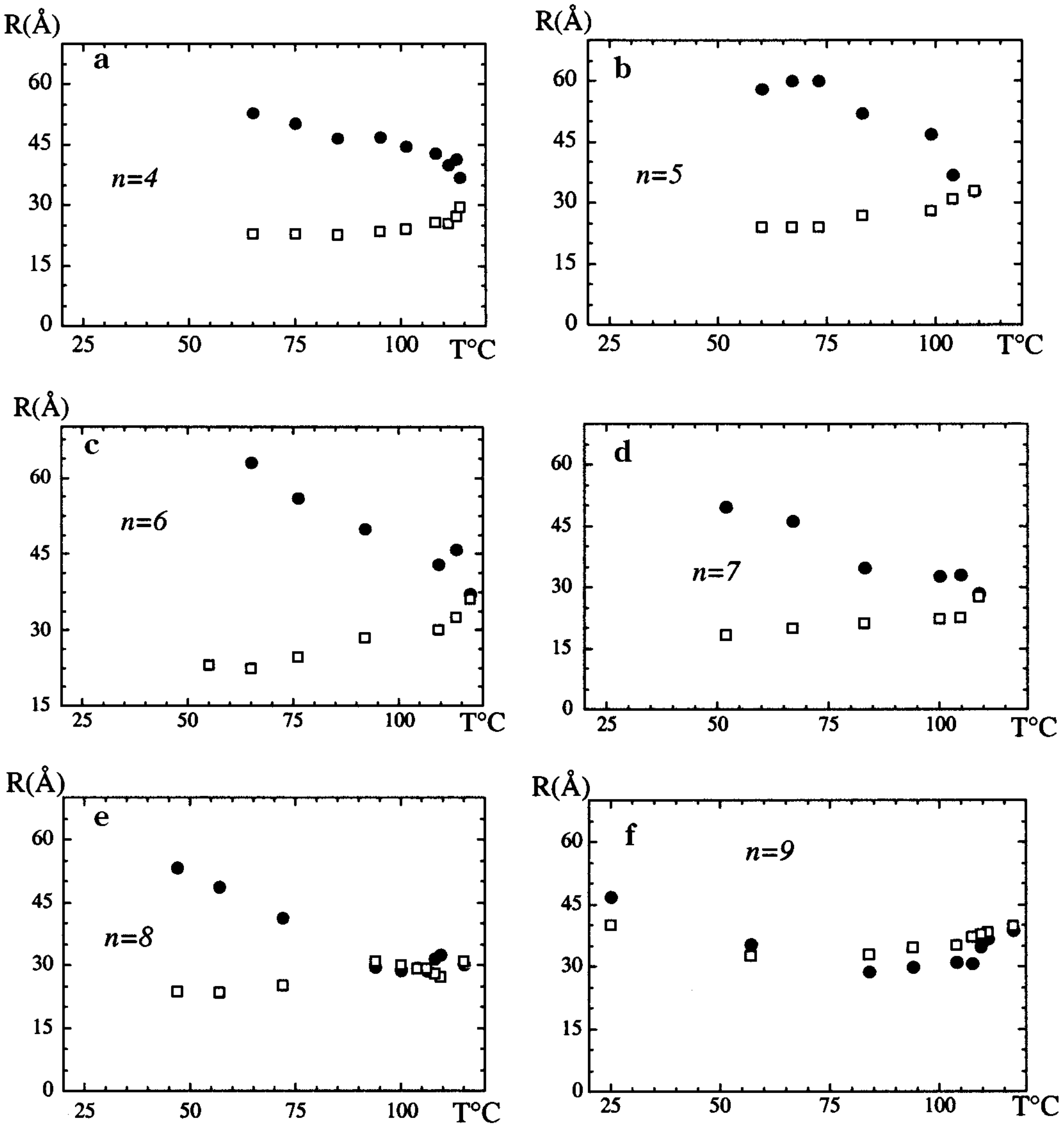


Figure 1. Evolution of the main-chain anisotropy of a series of trans polynorbornenes with different spacer length $-(CH_2)_n-$ as a function of the temperature: (a) $n = 4$; (b) $n = 5$; (c) $n = 6$; (d) $n = 7$; (e) $n = 8$; (f) $n = 9$. $R_{\|}$ and $R_{\perp}$ are indicated by ● and □, respectively, and are determined within 5% accuracy.

is atactic. Following the description of the thermotropic properties reported by Ungerank at al,[6,10] the emergence of the smectic phase is supposed to occur for spacer lengths longer than $-(CH_2)_7-$. The polymers with shorter spacers display a simple nematic phase. The appearance of the smectic phase by increasing the spacer length is not specific to SCLC-polynorbornenes but corresponds to a general rule in thermotropic liquid crystals. However, in the case of SCLCPs of flexible main chains (me(th)acrylate, siloxane main chains), the appearance of the smectic phase occurs with a simultaneous anisotropic reduction of the chain entropy, resulting in a microsegregation of the main chains between the mesogenic layers.[11] The rigid norbornene backbone does not present many degrees of freedom with respect with its low polymerization degree; this reduced entropy case could contrast with the previous situation of microsegregation. This conformational question is here developed and discussed.

Parts a−f of Figure 1 display the evolution of the main-chain conformation of SCLC-polynorbornene of spacer lengths from $n = 4$ to $n = 9$ as a function of the temperature. The conformation is determined in terms of extensions of the main-chain radius of gyration $R_{\|}$ and $R_{\perp}$ following the mesophase director and the normal to the director, respectively. Two main categories of evolutions of the main-chain anisotropy can be distinguished:

- The first category concerns the trans LC-polynorbornenes with spacer lengths from $n = 4$ to $n = 7$. The evolution of the main-chain anisotropy is presented in parts a−d of Figure 1. In the isotropic phase, no anisotropy is observed. For these spacer lengths, a simple nematic sequence has been identified by DSC and microscopy,[6] and is here confirmed by the absence of any structure at large scattering angle (absence of smectic correlations). In the nematic phase, these polymers present all a prolate main-chain conformation ($R_{\|} > R_{\perp}$). In this geometry, the main-chain trajectory is mostly parallel to the director; i.e., parallel to its own mesogens. The prolate anisotropy can be considered as the shape favored by the symmetry of the nematic phase. This situation was also observed in case of SCLC-polyacrylates presenting exclusively a nematic mesophase.[11] With decreasing temperature, the average anisotropy of the norbornene main chain increases

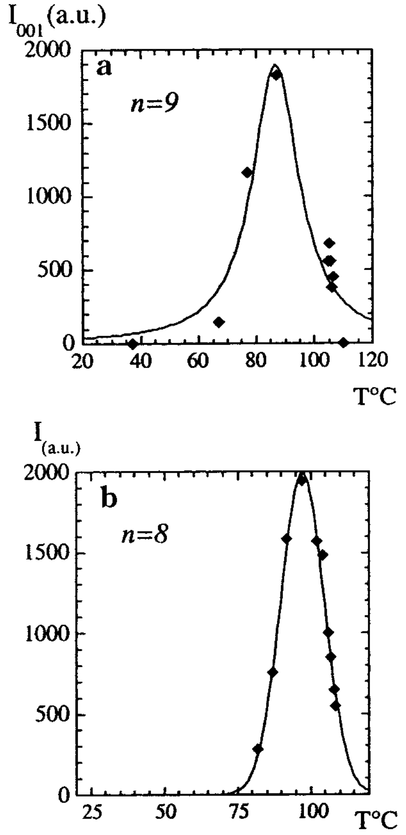


Figure 2. Variation of the intensity of the 001 smectic reflection as a function of the temperature for the trans LC-polynorbornene (100% D species) with the spacer: (a) $n = 9$; (b) $n = 8$.

regularly in agreement with the increase of the nematic order parameter. It corresponds to a rapid alignment of the main-chain along the director ($R_{\parallel}$ reaches at low-temperature twice the value obtained in the isotropic phase) and a smoother decrease of the perpendicular extension ($R_{\perp}$ is reduced only of a factor 0.75). No singularity can be noticed in the scattering pattern.

- The second category displays a more complex behavior; it concerns the trans LC-polynorbornenes from spacers $n = 8$ to $n = 9$ (Figure 1, parts e and f). A 001 smectic reflection is identified at large scattering. For the polymer of spacer $n = 9$, the smectic layer distance is about $d \cong 36 \pm 0.5$ Å. Compared to the extended mesogen length (24.5 Å), it indicates a partially bilayered smectic phase which corresponds to the overlap of the biphenyl groups. Figure 2a corresponds to the variation of the 001 smectic reflection vs temperature for the polymer with $n = 9$. The smectic phase temperature range corresponds actually to an interval smaller than what was deduced from DSC data and microscopy observations.[6] The smectic structure appears immediately below the isotropic phase and exists down to 65 °C only. Within this temperature interval, the main-chain conformation corresponds to an oblate shape. This is in agreement with the scheme of main-chains more or less confined between mesogenic layers. Below 65 °C, no smectic structure is detected anymore and a prolate main-chain conformation takes place revealing the reentrance of the nematic phase.

The change of main-chain conformation (from oblate to prolate) is thus an efficient indicator of a mesophase change (smectic to nematic respectively). The SCLC-polynorbornene of spacer $n = 9$ displays thus the following mesophase succession:

$$T_g - 31\ °\text{C} - \text{N(Re)} - 65\ °\text{C} - \text{S(Ad)} - 112\ °\text{C} - \text{I}$$

The increase of the spacer length is known to be a parameter which stabilizes the smectic interactions which is precisely what is observed here. This phenomenon is induced by the reinforcement of the interaction between the alkyl parts and should drive the system toward a monolayer smectic structure. The experiment shows that the resulting smectic phase is, in contrast, partially bilayer. This means that the dipolar interactions, mainly due to the cyano group, are stronger than the segregation interactions. By decreasing the temperature, the competition between antagonistic smectic modulations is enhanced (probably between the dipolar and the segregation forces). Because of the inability to condense either in the one or the other modulation, a rentrant nematic phase occurs. This nematic phase does probably not have the same origin as those displayed in the first category with smaller spacer lengths ($n = 4-7$).

In agreement with this argumentation, a reduction of the spacer length (from $n = 9$ to $n = 8$) should lead to a progressive reduction of the smectic interval and to the reappearance of the high-temperature nematic phase.

The complete scenario is effectively reproduced by the polymer with the spacer $n = 8$ (Figure 1e). By decreasing the temperature from the isotropic phase, the polymer main-chain adopts a prolate shape, then a quasi-isotropic shape slightly oblate, and finally a strong prolate anisotropy. By neutron diffraction, the smectic phase is identified and the intensity of the 001 reflection measured (Figure 2b). The smectic phase corresponds to a temperature range of 106−80 °C. The layer distance is $d \cong 40 \pm 1$ Å. Compared to a mesogen length of 23.6 Å, it indicates also a partially bilayered smectic structure.

The successive main-chain conformations displayed by the SCLC−polynorbornene of spacer $n = 8$ are thus in agreement with the following phase succession:

$$T_g - 39\ °\text{C} - \text{N(Re)} - 80 \pm 5\ °\text{C} - \text{S(Ad)} - 106\ °\text{C} - \text{N} - 115\ °\text{C} - \text{I}$$

It is interesting to note that the smectic phase corresponds to a very slightly oblate shape (Figure 1e). This weak anisotropy can be explained by the soft structure of the S_{Ad} phase much less constraining than a monolayer structure.[11,12] In the following, we will exploit the diffraction patterns to build a detailed scheme of the polynorbornene main-chain distribution in the mesophase organization.

A first piece of information can be already obtained by the examination of the smectic reflections. The comparison of the smectic intensities displayed by the H/D isotopic mixtures the polynorbornenes with spacers $n = 8$ and $n = 9$ reveals that the 002 smectic reflection is much higher than the 001 one (Figure 3). This result obtained on two different polynorbornenes indicates that it is not due to a structure factor anomaly. The structure of the smectic phase is more complex than a simple modulation. In a first approximation, since the main chains correspond to a strongly labeled site (eight hydrogens have been substituted with deuterium), an intense 002 reflection could indicate that the main chains form two sublayers within one mesogenic layer.

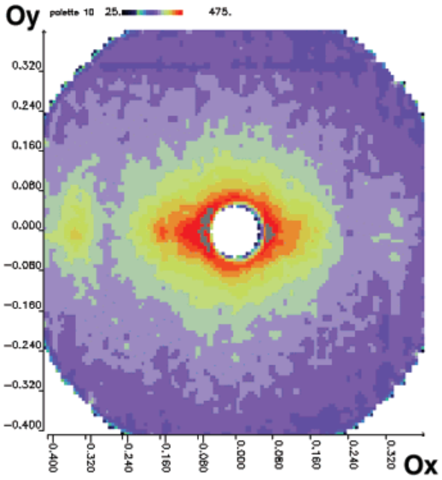


Figure 3. Neutron scattering pattern obtained at large angles (λ = 5 Å, d = 2 m) at 57 °C for the mixture of fully hydrogenated *trans*-polynorbornene of spacer $n = 9$ with its homologue deuterated at the main-chain cyclopentylenes. The director is horizontal.

In the case of the polymer of spacer $n = 9$, the diffraction patterns have been measured on the deuterated polymer and the H/D isotopic mixture, respectively. From the comparison of these patterns, the exact profile of distribution of the main-chains along the director can be deduced.[13]

The smectic modulation can be described as a Fourier series

$$\rho(z) = \rho_0 + \sum_l F_{00l} \times \cos\left(\frac{2\pi}{d} lz\right)$$

with d the period of the modulation, z the director axis, and ρ the density of the coherent scattering length. In the reciprocal space, the different $F_{00l}{}^2$ correspond to the intensity of each reflection *00l*. In the present case, two profiles of coherent scattering lengths associated to the H/D mixture and to the homogeneous deuterated samples are respectively determined. After normalization to the same number of scatterers, the profiles are subtracted from each other to obtain the scattering length variation specifically associated to the main-chains. The profile of the distribution of the polynorbornene main chains of spacer $n = 9$ is presented in Figure 4, and corresponds to the following equation

$$\rho_{\text{main-chain}}(z) = \rho_{\text{D}}(z) - \rho_{\text{H}}(z) = 2(\rho_{\text{D}}(z) - \rho_{\text{H/D}}(z))$$

$$\rho_{\text{main-chain}}(z) = F_{001}{}^{\text{D}} \cos\left(\frac{2\pi}{d} z\right) + F_{002}{}^{\text{D}} \cos\left(\frac{4\pi}{d} z\right) - 2\left(F_{001}{}^{\text{H/D}} \cos\left(\frac{2\pi}{d} z\right) + F_{002}{}^{\text{H/D}} \cos\left(\frac{4\pi}{d} z\right)\right)$$

where

$$F_{001}{}^{\text{D}} = 1, \quad F_{002}{}^{\text{D}} = 0.63, \quad F_{001}{}^{\text{H/D}} = 0.32, \quad F_{002}{}^{\text{H/D}} = 1.17$$

The presence of three maxima in the plot of the density distribution ρ (Figure 4) indicates a double occupancy; i.e., the main-chains not only are present on both sides of the smectic layer but also are present right in the middle of this one. This implies that at least in part the norbornene main chains share the same zone as the biphenyl rings (see Figure 4). The double layer packing has been already observed in the case of a side-chain polyacrylate and was explained by symmetry arguments since the spacer length was in that case, as long as the hard core (phenyl benzoate).[13] In the present case, the biphenyl group size (≈7 Å) is smaller than the spacer length (13 Å for $n = 9$**)**, and the S_{Ad} structure contains thus large alkyl overlapping zones. The insertion of sublayers is only stabilized by the alkyl overlap which explains the relatively low proportion of sublayers. The double main-chain confinement seems thus to be rather a normal solution for the main-chain packing.

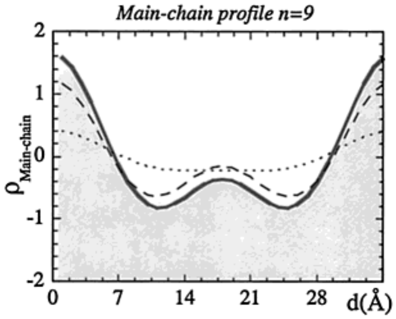


Figure 4. Distribution of the density of coherent scattering length associated with the main chains (bold line delimited the shaded area) along the director (along one smectic period) for the SCLC-polynorbonene of spacer $n = 9$ at 87 °C. The profile indicates three maxima: two on both extremities indicating the main-chain confinement between the mesogenic layers and an additional one in the middle of the layer. The dotted line and the dashed line correspond to the density of coherent scattering length associated to the polymer mixture and to the polymer deuterated on the main-chain alone, respectively.

A second streaking feature is the anisotropy displayed by the main chain in the high-temperature nematic phase. The SCLC-polynorbornene of spacer $n = 8$ presents a high temperature nematic phase followed by a smectic phase. In contrast with usual SCLCPs, the polynorbornene main chain adopts a prolate shape whereas usual LC-polyacrylates or polymethacrylates usually exhibit an oblate main-chain shape because of the influence of the smectic interactions;[11] the oblate conformation observed for poly(meth)acrylates results from a nonnegligible effect of confinement of smectic fluctuations. Compared to usual SCLCPs, two structural parameters differ. First, using the wormlike chain model ($R_g{}^2 = (Lb/6)(1 - (3b/L)(1 - 2b/L) - 3b^3/4L^3)$), where L is the length of the macromolecule supposed to be monodisperse and b the statistical unit), an estimation of the flexibility of the main chain can be carried out through the b value and on the basis of several *trans* LC-polynorbornenes (n = 4, 6, 7, 9) since it can be supposed to be roughly independent of the spacer length. b value is about 90 ± 15 Å for LC-polynorbornenes against 20 Å for a SCLC-poly(meth)acrylate chain.[14b] This rigid main chain points out the question as to how such a rodlike conformation can successively adopt a prolate and an oblate shape as has been observed for long spacer species. Actually, the comparison of the polymer size to the statistical unit indicates that the main chain has almost no entropy. In this case, the term of main-chain orientation with respect to the director is probably more appropriate than main-chain conformation. Local smectic fluctuations are not strong enough to bend the nematic prolate main-chain anisotropy.

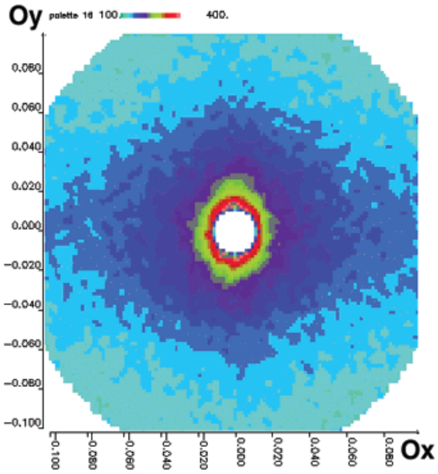


Figure 5. Small angle scattering pattern ($\lambda = 10$ Å, $d = 2$ m) displayed at 25 °C by the aligned trans polynorbornene with the spacer $n = 9$ (isotopic mixture). The director is horizontal. The form factor shows a singular inversion from small to large scattering vectors.

Second, looking back at the architecture of the molecule, two main interactions appear: the one associated to the mesogens belonging to the same cyclopentylene unit which is probably the strongest since spaced of only 1.5 Å (intra) and the one between mesogens of different cyclopentylenes (inter). On these geometrical considerations, the liquid crystalline transition should very likely be achieved in steps corresponding to the enthalpy of the distinct interactions. Otherwise, the equilibrium of the phase itself implies the participation of mesogens belonging to other different chains and/or a tilt of the main-chain to establish an average interaction distance. In such cases, the decoupling role of the spacer is crucial to compensate the main-chain rigidity.

The examination of the form factor displayed by the polymers with spacers $n = 8$ and $n = 9$ contains useful information in agreement with the previous analysis. Figure 5 presents the shape of the scattering shown by the polymer of spacer $n = 9$ at 25 °C, i.e., 40° below the reentrant nematic-smectic transition ($n = 8$ displays similar scattering). This spectacular scattering arises from opposite local and global main-chain anisotropies. In the smectic state, for enthalpic reasons, the main-chains are driven to separate from the side-chains and to occupy a reduced space between mesogenic layers. The cohesion of the smectic structure is optimized when the planes of the cyclopentylene are oriented perpendicular to the director. On Figure 5, at large angles, the scattering indicates that main chains are locally perpendicular to the mesogens. The local structure is thus reminiscent of the smectic organization. It can be supposed that the persistent smectic sites correspond mostly to the cyclopentylene unit. The strong coupling (intra-interaction) binding the two side-mesogens is conserved as long as the side groups remain perpendicular to the cyclopentylene plane (smectic geometry). At small angles, the scattering indicates that the global main-chain orientation is in contrast, parallel to the mesogen direction. The apparent antagonism can be explained by the architecture of the norbornene chain, which consists of a succession of a rigid part (double bond) and the cyclopentylene unit carrying the mesogens which is free of rotation around the axis parallel to the double bond. Using Dreiding models, it can be shown that the cyclopentylene planes can be oriented perpendicular to this double bond axis. The set forms a kind of tilted cyclopentylene column carrying mesogen pairs translated of about 5 Å from each other along the director. In this geometry, the whole shape becomes elongated parallel to the director, allowing the development of simultaneously a nematic interaction and local persistent sites formed by the cyclopentylene units, keeping a local main-chain/side-chain perpendicular orientation due to the late smectic interaction. A final rotation of the cyclopentylene plane (low temperature state) orients the entire molecule parallel to the director in agreement with the symmetry of a nematic phase.

IV. Influence of the Cis/Trans Content on the Conformation and the Structure of SCLC−Polynorbornenes

The influence of the cis/trans double bond content has been tested on two series of LC−polynorbornenes with different spacer lengths, either $n = 6$ or $n = 11$. For each spacer species, three types of population (characterized by NMR[7]) are studied; (a) the high trans content which corresponds to an atactic polymer, (b) the statistical trans/cis content, and (c) the high cis content population which presents a syndiotactic structure. For each population, the hydrogenated polymer and its homologue deuterated onto the main chain have been synthesized via ROMP using the specific Schrock catalyst giving rise either to the a, b, or c stereoregular species following the procedure exposed by Ungerank et al.[7]

Let us first examine the influence of the stereoregularity on the behavior of the polymer of spacer $n = 11$. Figure 6 displays the evolution of the main-chain conformation of the three stereoregular species a−c as a function of the temperature. The study of the small angle scattering shows that the three species display the same type of behavior; i.e., the extension of the main-chain is reduced along the director whereas the perpendicular dimension keeps almost the same value. The main chains are thus oriented perpendicular to the director whatever the trans/cis double bond content. The observation at large angles, indicates the presence of the 001 smectic reflection which is consistent with the existence of a smectic phase already identified by the fanlike texture observed by microscopy.[7] The smectic layer distance remains almost constant for the three polymers, (a) $d = 42.5$ Å, (b) $d = 43.5$ Å, and (c) $d = 41.5$ Å, and is thus independent of the stereoregularity of the chain.

The impact of the stereoregularity of the main-chain will be evidenced on the other polymer presenting a shorter spacer length of $n = 6$. The conformation and the structure have been determined on the three stereoregular species. The same convention has been taken: species (a) denotes the polynorbornene with a high trans content, the (b) species is a statistical trans /cis double bond content and the third species (c) corresponds to the high cis polymer, which is in addition syndiotactic considering the orientation of the cyclopentane rings).

Figure 7 displays the evolution of the main-chain for the three types of SCLC−polynorbornenes of spacer length $n = 6$ as a function of the temperature.

- Figure 7a is given as reference (identical to Figure 1c): we remind the reader that a high *trans* double bond content (stereoregular species a) produces, on the poly-

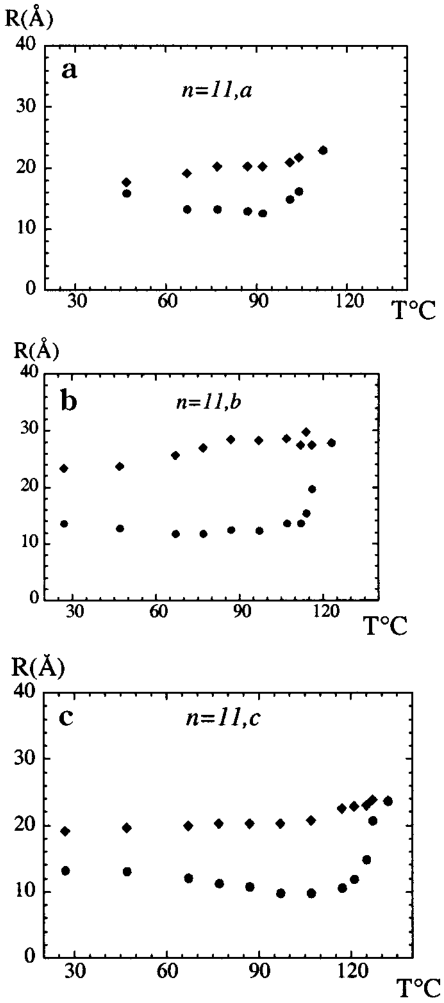


Figure 6. Evolution of the main-chain anisotropy of three different stereoregular species of the LC-polynorbornene of spacer $n = 11$ as a function of the temperature: (a) the high trans double bond content polymer (atactic); (b) the statistical trans/cis double bond polymer; (c) the high cis double bond polymer (with syndiotacticity). $R_{\parallel}$ and $R_{\perp}$ are indicated by ● and □, respectively, and are determined within 5% accuracy.

mer of spacer $n = 6$, a prolate main-chain conformation and a wide nematic phase.

- The introduction of a statistical trans/cis double bond content (polymer *b*) induces a new behavior displayed on Figure 7b. By decreasing the temperature, the main-chain of the polymer of spacer $n = 6$ adopts successively an oblate shape and a prolate shape. The analysis of the texture of the b species by optical miscrocopy revealed a smectic phase instead of a nematic phase for polymer a.[7] The observation at large angles confirms the presence of a smectic reflection corresponding to a layer distance of 35 Å, within a temperature interval from 114 (isotropic phase) to 75 °C. Below this temperature, the absence of smectic reflection together with the appearance of the prolate shape indicates the formation of a reentrant nematic phase. A simple change of stereoregularity has thus completely modified the phase diagram. Instead of the previous nematic phase, the statistical trans/cis-polynorbornene of spacer $n = 6$ presents this phase succession:

$$T_g - 48\ °\mathrm{C} - \mathrm{N(Re)} - 75\ °\mathrm{C} - \mathrm{S(Ad)} - 117\ °\mathrm{C} - \mathrm{I}$$

Below 75 °C, the appearance of the nematic phase (N(Re)) leads to an inversion of the main-chain conformation which executes a 90° reorientation from the smectic phase (the main chain is in average perpendicular to the director) down to the reentrant nematic phase (the main chain is oriented parallel to the director). This evolution gives rise to a spectacular scattering pattern when the two orientations coexist since the local scale is inverted compared to the global orientation of the main chain. This feature is illustrated on Figure 8. In a way similar to that for the highly trans polymer with spacer $n = 9$ (Figure 5), the nematic order first takes place at the large scale, without destroying the local smectic interaction. By decreasing the temperature, the phase installs itself at a more local scale driving the main-chain and the mesogen parallel to each other. Compared to the usual LC-polymers such as LC-poly(meth)acrylate, the rigidity of the main chain is at the origin of the partial persistence of the local smectic modulation. A characteristic distance $\xi = 2\pi/q^*$, where q^* points to the value of the scattering vector at the anisotropy inversion, can be determined. Figure 9 displays the ξ evolution as a function of temperature. ξ

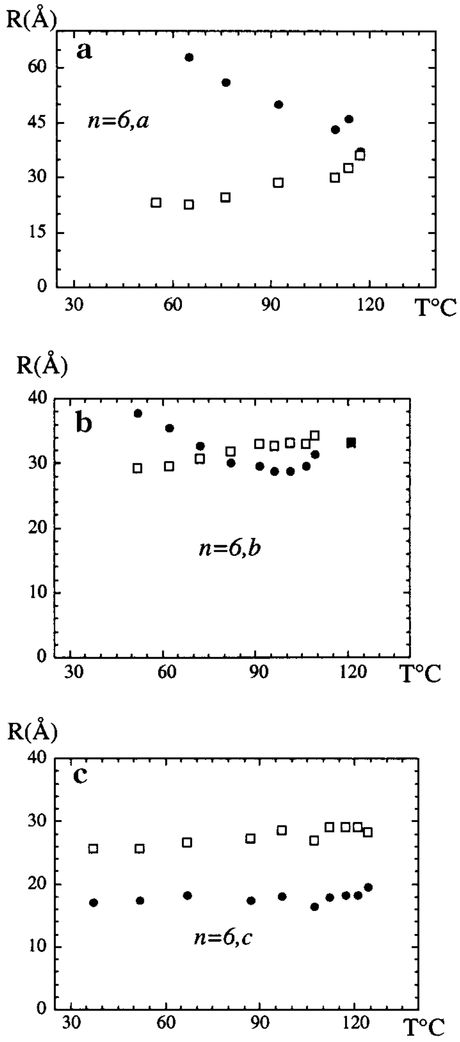


Figure 7. Evolution of the main-chain anisotropy of three different stereoregular species of the LC-polynorbornene with spacer length $n = 6$ as a function of the temperature: (a) the high trans double bond content polymer (atactic) (identical to Figure 1c); (b) the statistical trans/cis double bond polymer; (c) the high cis double bond polymer (with syndiotacticity). $R_{\parallel}$ and $R_{\perp}$ are indicated by ● and □, respectively, and are determined within 5% accuracy.

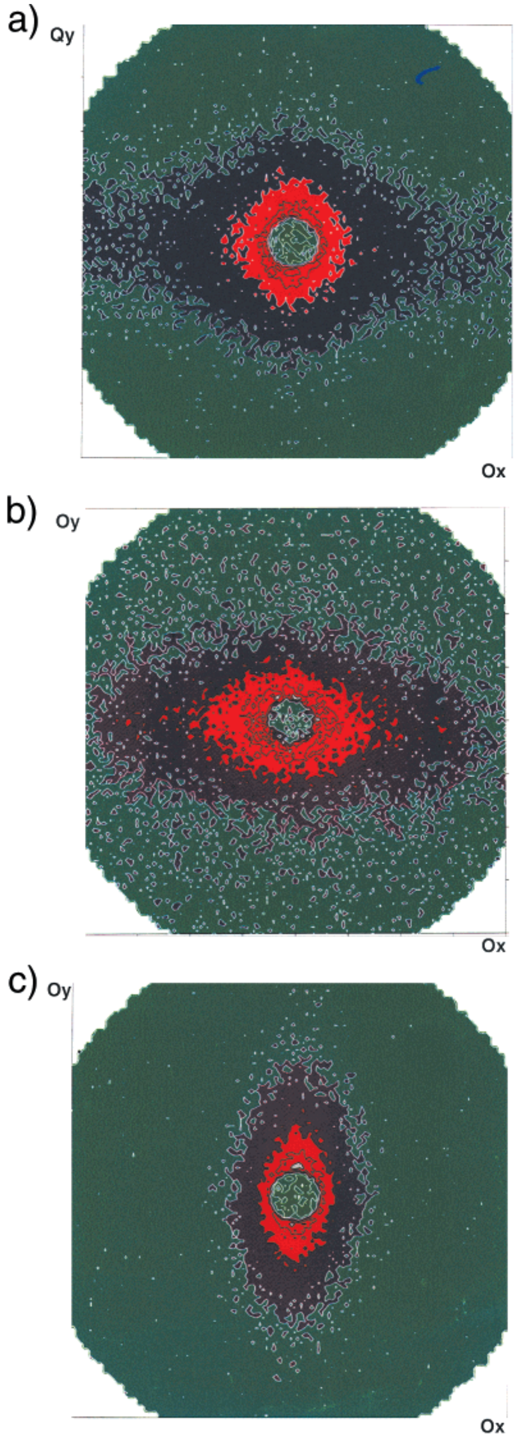


Figure 8. Small angle scattering patterns ($\lambda = 8$ Å, $d = 2$ m) displayed by the *cis/trans*-LC-polynorbornene with a spacer $n = 6$: (a) in the smectic phase ($T = 100$ °C); (b) in the reentrant nematic phase ($T = 60$ °C); (c) at low temperature ($T = 25$ °C) in the reentrant nematic phase. The director is horizontal. The evolution from a to c illustrates the progression of the 90° reorientation from large to small scales.

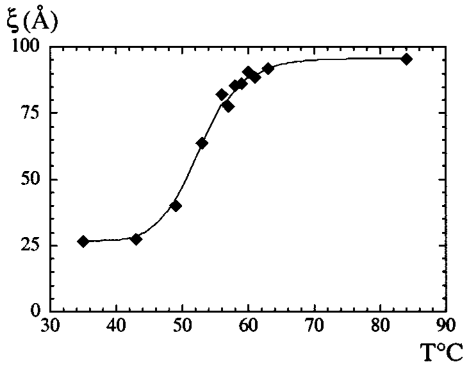


Figure 9. Evolution of the critical distance ξ(Å) as a function of the temperature.

can be considered as the upper limit under which the nematic field does not act, i.e., the smallest nematic correlation length. It seems that the nematic tendency is preexisting at high temperature (>90 °C) since ξ reaches a plateau corresponding to an upper limit of $\xi_{max} \cong 100$ Å instead of infinitely increasing. This correlation length decreases strongly below 60 °C and reaches another plateau at low temperature corresponding to $\xi_{min} \cong 25$ Å which fits approximately with the mesogen length. The lower limit is thus reached.

The similarity between the *cis/trans*-polynorbornene of spacer $n = 6$ and the *trans*-polynorbornene of spacer $n = 9$, leads to the conclusion that an increase of the spacer length produces the same effect as the introduction of the *cis* stereoregularity. A further increase of the cis double bond content should thus drive the system toward an increase of the stability of the smectic phase. This is precisely what is observed on the *cis*-polynorbornene (c species).

- Figure 7c displays the evolution of the main-chain anisotropy of the high cis content polynorbornene (of spacer length $n = 6$) vs temperature (polymer *c*). A clear oblate conformation is observed as soon as the isotropic phase is down to 30 °C.

From the observation of the texture, a smectic phase has been identified in the whole range of temperatures:

$$T_g - 46\ °\mathrm{C} - \mathrm{S(Ad)} - 140\ °\mathrm{C} - \mathrm{I}$$

X-ray measurements carried out at room temperature (the neutron structure factor does not allow one to detect easily the smectic reflection) confirm the existence of a smectic phase with a layer thickness of 35 Å. This value is the same as the one observed in the *cis/trans*-polynorbornene. As for the polymer of spacer $n = 11$, no influence of the stereoregularity (and tacticity) can be noticed on the layer thickness which remains the same for both b and c species of the Polynorbornene of spacer $n = 6$. This feature is coherent with the assumption of cyclopentylene planes oriented perpendicular to the director, in this configuration they do not contribute to the smectic layer distance.

Through the behavior study on polynorbornene, interesting information on how the formation of a new phase takes place can be drawn. The reentrant nematic phase is first established on a large scale and then extends itself on a monomer scale resulting in a singular scattering where local and global anisotropies are opposed. A generalization can be attempted for the usual smectic SCLCPs. For these SCLCPs, the main-chain extends itself along the director via rodlike crossings (layer hopping model[14a]). Following the scaling laws,[14b] each new crossing increases the parallel main-chain extension by a step equivalent to the smectic layer thickness. The extrapolation at large molecular weight should correspond surprisingly to the pattern observed here at the reentrance: the main chain is prolate at large scale and remains oblate at local scale. Another possibility would be when the energy cost for a crossing defect is lower than the cohesion energy of the smectic layer. This second case of local/global inversion could

Table 3.

(a) Mesophase and Main-Chain Conformation Anisotropy Displayed by the *trans*-Polynorbornenes As a Function of the Number of Methylene Units (n) in the Spacer Length

$n = 4$ trans	T_g − 62 °C − N − 114°C − I prolate
$n = 5$ trans	T_g − 27 °C − N − 109 °C − I prolate
$n = 6$ trans	T_g − 23 °C − N − 118 °C − I prolate
$n = 7$ trans	T_g − 46 °C − N − 113 °C − I prolate
$n = 8$ trans	T_g − 39 °C − N(Re) − 80 ± 5 °C − S(Ad) − 100 °C − N − 115 °C − I prolate oblate prolate
$n = 9$ trans	T_g − 31 °C − N(Re) − 65 °C − S(Ad) − 112 °C − I prolate oblate

(b) Influence of the Trans/Cis Rate on the Mesophase Sequence and the Main-Chain Conformation for Polynorbornenes with Spacers $n = 6$ and $n = 11$, Respectively

$n = 6$ trans	T_g − 23 °C − N − 118 °C − I prolate
$n = 6$ trans/cis	T_g − 48 °C − N(Re) − 75 °C − S(Ad) − 117 °C − I prolate oblate
$n = 6$ cis	T_g − 46 °C − S(Ad) − 140 °C − I oblate
$n = 11$ trans	T_g − 19 °C − S(Ad) − 118 °C − I oblate
$n = 11$ trans/cis	T_g − 21 °C − S(Ad) − 132 °C − I oblate
$n = 11$ cis	T_g − 18.5 °C − S(Ad) − 149 °C − I oblate

correspond to the NMR observation carried out by Hempel et al. on SCLC−polysiloxanes.[15]

V. Summary of the Spacer Length Influence and the Stereoregularity Dependence on the Mesophase and the Main-Chain Anisotropy Type

Table 3 summarizes the mesophases and the corresponding main-chain anisotropies displayed vs spacer lengths and stereoregularities by the series of LC-polynorbornenes examined here.

VI. Conclusions

In Table 3, in contrast with Frosini et al.[2] which observe no dependence of the ordering with the stereoregularity on flexible backbones, here the influence is clearly stated on rigid backbones demonstrating the interest of a conformational study until now neglected in stereoregular SCLCPs.

The liquid crystalline properties of these SCLC−polynorbornenes are based on strong local nematic interactions. However, we have shown that long spacer lengths or high cis configuration content, reinforce the smectic field, at high temperature (n = 8−9, n = 6b), or in the whole temperature range (n = 11(a,b,c), 6c), and drives in all cases to a confinement of the main-chains between the mesogenic layers which appears as an oblate conformation. The invariance of the smectic layer thickness whatever the stereoregularity, suggests that the cyclopentylene planes are oriented perpendicular to the director. The decrease of the temperature reinforces the nematic character making appear a very peculiar scattering pattern when the nematic reentrance takes place (n = 6b, n = 8, 9) which reveals a main-chain reorientation from a perpendicular to a parallel orientation. In contrast, SCLC-polynorbornenes with short spacer lengths or high trans double bond contents, display uniquely a nematic phase. In this nematic phase, the main-chains are oriented parallel to the director respecting the symmetry of the phase.

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