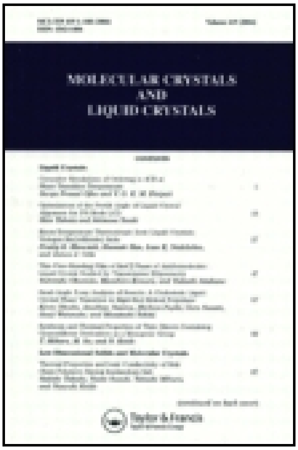

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Deuterium NMR Investigation of the Influence of Molecular Structure on the Biaxial Ordering of Organosiloxane Tetrapodes Nematic Phase

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In order to contribute to the understanding of the origin of biaxial nematic ordering in tetrapodes, a deuterium NMR study was performed on mixtures of monomers from organosiloxane tetrapodes with a deuterated nematic probe. Contrary to the tetrapode system previously studied, which exhibits a biaxial nematic phase, the results for monomers are compatible, within the experimental error, with uniaxial nematic ordering in the whole nematic range. The data are in agreement with the conjecture that the nematic biaxial behaviour is related to hindering of the mesogenic units' rotational movements, arising from interdigitation and connection to the central silicon core.

Keywords: biaxial nematic phase; dendrimers; deuterium NMR; organosiloxane tetrapodes

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INTRODUCTION

Recent studies revealed the biaxial character of the nematic phases of a number of thermotropic liquid crystalline systems [1–8]. Among those, organosiloxane tetrapodes present the highest asymmetry parameter and exhibit the nematic phase in very broad thermal domains including room temperature. These results encourage the research on these compounds as promising systems for technological applications.

Tetrapodes are a particular case of dendrimers, which are molecules with a branching structure resulting from a sequence of repetitive synthetic steps. The number of steps in the dendrimer "growth" defines the so-called dendrimer generation. For high generation numbers, n, the dendrimers tend to adopt a globular shape due to space-filling conditions [9]. On the other hand, for lower generations (usually for $n < 5$), the flexibility of the dendrimer "branches" gives rise to a noticeable shape flexibility characteristic of the dendritic molecules. If mesogenic units, typical of liquid crystalline molecules, like elongated aromatic cores, are connected to a dendritic core, this shape flexibility can be combined with special orientational properties, giving rise to very rich polymorphisms [10]. Yet, contrary to polymers (which result also from flexible, repetitive molecular structures), dendrimers are monodispersed systems as a consequence of its special synthetic process.

Liquid crystalline organosiloxane tetrapodes are a particular case of generation 0 dendrimers, with four mesogenic units (composed by aromatic core and aliphatic chains) linked to a central siloxane core by siloxane flexible spacers. These systems exhibit different polymorphisms and physical properties, depending on the specific structure of the aromatic cores, the chains and spacers length, and also the type of linkage (side-on vs. end-on) between the mesogenic units and the dendrimer core [11,12]. Recently, a nematic biaxial phase was observed in one of these compounds by means of optical measurements, IR and NMR spectroscopy, and also dynamic light scattering [4–6]. These studies indicate that the appearance of the biaxial nematic order in tetrapodes of laterally attached mesogenic units as in side-on polymers is related to the hinderance of reorientation movements due to the linkage of the mesogenic rigid units to a dendrimeric core or the polymer chain [2,4,7]. In order to investigate this effect, molecular order investigations by deuterium NMR were performed in the nematic phase of the monomers, which compose the organosiloxane tetrapodes that present the biaxial nematic ordering (Fig. 1a). These monomers are composed by the mesogenic

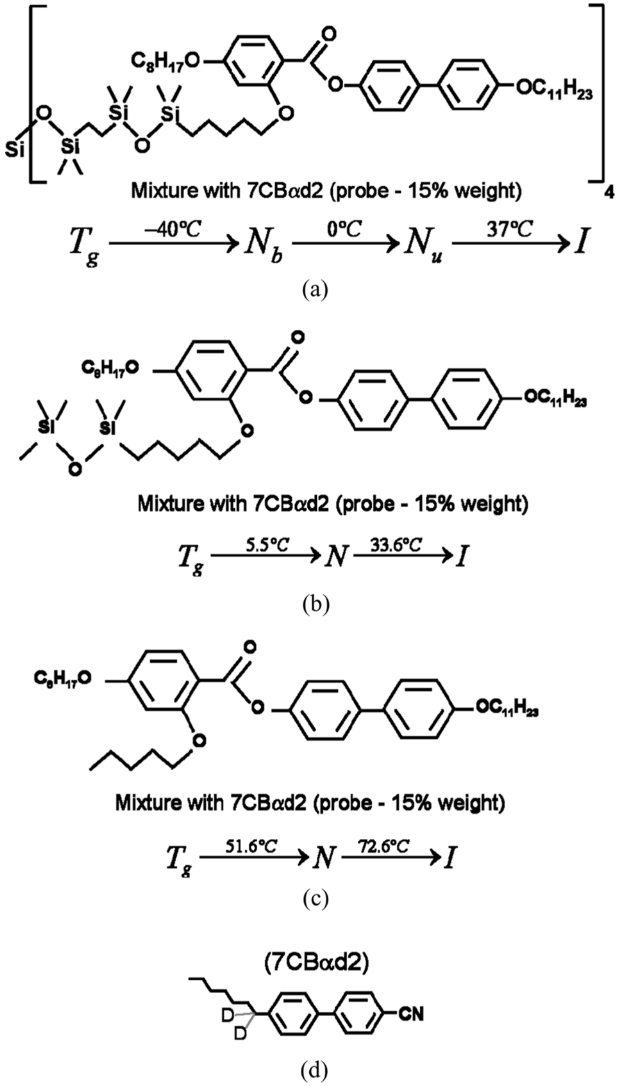


FIGURE 1 Molecular structures and phase sequences of organosiloxane tetrapode (a) which exhibits the biaxial nematic phase and the corresponding substituted (b) and non-substituted (c) monomers (for the mixtures with deuterated liquid crystal 7CBαd2 – (d)).

units and part of (in the non-substituted monomer – Fig. 1c) or all (in the substituted monomer – Fig. 1b) the spacer which connect the monomers to the dendritic siloxane core. It is important to notice that, apart from the bond, which connects each of the monomers to the dendrimer core, the systems now under investigation are chemically similar to the tetrapode. Of course, these apparently subtle differences are in fact major and determinant causes resulting in dramatic changes in transitions temperatures and other properties of the materials. Therefore, the study of the monomers is clearly expected to be important in bringing together additional evidence regarding the origin of biaxial nematic order of the dendrimers.

When the samples to be investigated are not deuterated, which was the case for the tetrapodes presented in reference [5], a deuterated probe is used. If the probe is appropriate, it will experience the ordering of the host system as verified for the studied tetrapodes. In this study, for comparison purposes, the same probe at the same concentration as used in the measurements performed with the tetrapode, was mixed with the monomers. It is worthwhile to notice that a nematic probe is expected to pack preferentially with the mesogenic units of the tetrapodes due to the amphiphilic effect which will favour the aromatic cores of the probe to align with those of the host molecules [13]. The fact that the same probe was used, at precisely the same concentration, reinforces the chemical analogy between the monomer systems and the tetrapode material as studied previously by deuterium NMR. The molecular structure of this probe is presented in Figure 1d. The phase sequences in Figure 1, are obtained for the mixtures of the tetrapodes or the monomers with the probe at a 15% mass concentration. Again, it should be noticed that the remaining and crucial difference (as shown by the experiments) between tetrapodes and monomers systems is the connection between the mesogenic units and the central siloxane dendritic core. Finally, the use of two different monomers, (the substituted one with the exact chemical structure of a complete dendrimer arm and the other (non-substituted) closer to the “bare” mesogenic unit) allows for the analysis of the effect of the lateral substitute in the ordering properties of the corresponding nematic mesophases.

For this investigation ^{2}H NMR spectra were collected both on static aligned samples and samples rotating around an axis perpendicular to the static NMR magnetic field, $\mathbf{B}_0$. The simulation of the spectra allows for a description of the director’s spatial distribution under rotation in the studied system. The comparison of these results to those obtained for the corresponding tetrapodes contributes to a clarifying discussion of the hypothesis which connect the origin of the nematic biaxial ordering of the tetrapodes to the corresponding molecular structure [5].

EXPERIMENTAL TECHNIQUE: DEUTERIUM NMR

In general, the ordering of a liquid crystalline system may be observed through the measurement of a second rank tensorial physical property. In the case of deuterium NMR, this physical property is the average electric field gradient (AFG) tensor, associated with a C-D covalent bond (in the case where the deuterium is chemically linked to a carbon atom). In a uniaxial nematic phase, one quantity ($V_{zz} = V_{\parallel}$, and $V_{xx} = V_{yy} = -V_{\parallel}/2$) will be enough to define the AFG tensor in its principal frame, being the director, ***n***, coincident with the z direction. Contrary, on a biaxial phase, the tensor components V_{xx} and V_{yy} will be different. Therefore, a second quantity will be needed to fully determine the tensor in its principal frame and two secondary directors (***l*** and ***m***) will be defined by the x and y directions, respectively. The crucial physical parameter, which is determined by deuterium NMR, is the so called asymmetry parameter given by:

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \tag{1}$$

where the x, y and z axis are assigned in such a way that $|V_{zz}| > |V_{yy}| \geq |V_{xx}|$. This parameter, which is zero in a uniaxial phase and different from zero in the biaxial case, may be obtained, through a ^{2}H NMR experiment, from the measurement of the quadrupolar splitting, given by:

$$\delta\nu = \frac{3}{4}\nu_Q\left[\left(3\cos^2\theta - 1\right) + \eta\sin^2\theta\cos 2\varphi\right] \tag{2}$$

where θ and φ are the angles which define the orientation of the static magnetic field in the principal frame of the AFG tensor, ν_Q is the averaged quadrupolar coupling constant and η is the asymmetry parameter.

For a sample constituted by an aligned nematic monodomain, the ^{2}H NMR spectrum is given by a pair of lines separated by a splitting given by Eq. (2). In the case of a powder sample formed by multiple nematic domains with different alignment directions with respect to $\mathbf{B}_0$, the spectrum is given by:

$$G(\nu) = \int_{\Omega}\left[L(\nu - \delta\nu/2) + L(\nu + \delta\nu/2)\right]P(\Omega)d\Omega \tag{3}$$

where $\delta\nu$ is given by expression (2), L is a function representing the line shape and $P(\Omega \equiv (\theta, \varphi))$ defines the distribution of the directors' orientations with respect to the static magnetic field.

The simpler NMR experiment that can be used to determine the asymmetry parameter, and therefore the type of nematic ordering (uniaxial vs. biaxial) is based on the analysis of spectra obtained from static aligned samples rotated of different angles (generally 0° and 90°) with respect to the static magnetic field [5]. This method may be used only when the sample is sufficiently viscous to withstand the magnetic torque, so that the director stays long enough at a given angle in order for the spectra to be collected. This was the case for the tetrapodes [5] but not for the monomers. In the present case, an alternative method [14,15], also used recently by Samulski and co-workers in the study of the biaxial nematic phase of bent-core mesogens, was employed [1]. In this case, a two-dimensional powder sample is obtained by rotating the sample about an axis perpendicular to $\mathbf{B}_0$ at a speed higher then the speed limit for achieving a constant director orientation relative to $\mathbf{B}_0$. The shape of the spectra of the two dimensional powders, in the uniaxial and biaxial nematic phases, respectively, are characteristic of the types of nematic ordering and constitute a signature that can be obtained by deuterium NMR [14]. In this work ^{2}H NMR spectra were collected both for static aligned samples and continuously rotating samples. The spectra were simulated using expressions (2) and (3), as discussed in more detail in the following sections. These spectra were obtained, for different temperatures, on a BRUKER AVANCE II 300 spectrometer equipped with a BRUKER B-E30 electromagnet operating at a magnetic field strength of 2.3 T corresponding to a deuterium resonance frequency of 15.1 MHz. A quadrupolar echo sequence was used with a pulse spacing of $\tau = 17\,\mu$s, a $\pi/2$ pulse length around 5 μs and the following phase sequence $(\pi/2)\mathrm{x} - \tau - (\pi/2)\mathrm{y} - \tau -$ echo. The spectra presented correspond to the accumulation of 8192 free induction decay (FID) signals, separated by a delay time of 1.0 s while the sample was rotating at a speed of 1.3 Hz.

RESULTS AND DISCUSSION

As referred before, two nematic systems, corresponding to the mixtures of the substituted and non-substituted monomers with the deuterated probe were investigated. The phase sequences of these systems are presented in Figures 1b and 1c, respectively. The spectra of aligned static samples, at temperatures of 285 K for the substituted monomer and 300 K for the non-substituted monomer, are presented in Figures 3a and 4a, respectively. The black (thin) solid line corresponds to the experimental data and the red (thick) solid line to the simulation. When the main director is aligned with the static NMR magnetic field, $\mathbf{B}_0$, the angle θ is zero and the value of the average quadrupolar coupling constant ν_Q is straightforwardly obtained from the splitting of the aligned static sample (see expression 2).

The simulation also gives the line-width of the NMR lines corresponding to a nematic mono-domain.

The value of the asymmetry parameter, η, crucial for the investigation of the possible biaxial ordering, can be obtained experimentally from the

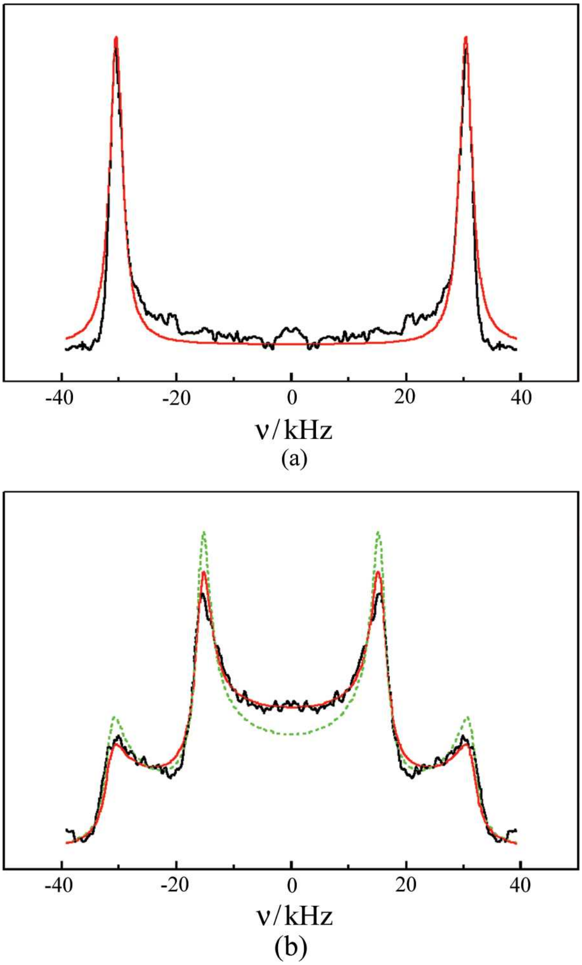


FIGURE 2 Spectra of aligned static sample (a) and rotating sample (b) for the substituted monomer mixed with deuterated probe 7CBαd2 at a temperature of 285 K. Black (thin) solid line: experimental data; red (thick) solid line: simulation with partial alignment distributions of the directors, in the plane perpendicular to $\mathbf{B}_0$ (in the case of rotating samples); green dashed line: simulation with uniform distribution of the directors in the plane perpendicular to $\mathbf{B}_0$.

simulation of spectra asynchronously collected from samples continuously rotating with respect to an axis perpendicular to $\mathbf{B}_0$. For low enough rotation speeds, the director tends to realign homogeneously with $\mathbf{B}_0$ and, in the permanent regime, a single pair of lines is obtained. This single pair of lines corresponds to a nematic mono-domain rotated of some angle θ with respect to $\mathbf{B}_0$. In order to obtain, as wanted, a two dimensional powder in the plane perpendicular to the rotation axis, the sample must be rotated at a speed higher then the critical speed determined by the magnetic field and the rotational viscosity, γ, of the nematic sample [1]. This situation is easily controlled experimentally, as the spectrum of the powder sample is typical [14] and dramatically different from the single pair of lines obtained at the low speed regime. The spectra for the rotating samples, at temperatures of 285 K for the substituted monomer and 300 K for the non-substituted monomer, are presented in Figures 2b and 3b. The simulation of these spectra, using expressions (2) and (3) and considering for $P(\Omega)$, a uniform distribution of nematic domains with directors in the plane perpendicular to the rotation axis is shown as a green dashed line. As it may be verified in these figures, the spectra simulated considering the ideal two dimensional powder don't fit the experimental data accurately. The fits presented, (green dashed line) were obtained for $\eta = 0$. This value results from the fact that the splitting between the "inner" peaks of the spectra is (within the experimental accuracy) half of the splitting corresponding to the "outer" ones. This is the signature of the uniaxial nematic phase [14]. Further, it was verified that the introduction of a different value for the asymmetry parameter did not contribute to the attainment of better fits. This is quite clear, as the introduction of a non zero value of η would change the position of the inner peaks of the spectra and not in the relative amplitudes of these peaks as would be necessary to improve the quality of the fits. In these simulations the discussions presented in [16] by Galerne and in [16,17] by Madsen and Samulski was taken into account and it was verified that the introduction of an angle ψ corresponding to an eventual out of plane deviation of the director was also inadequate to explain the experimental data. On the other hand, it was verified that the fits are significantly improved if partial director realignment within the plane perpendicular to the rotation axis is considered (as shown in Figs. 2b and 3b respectively). This partial realignment, resulting from the effect of the magnetic torque during the rotation process, may be expressed by Eq. (4).

$$P(\Omega) = [1 + C_1\cos(2\theta) + C_2\cos(4\theta) + C_3\cos(6\theta)] \tag{4}$$

The results of the fits considering this correction are plotted in Figures 2b and 3b as solid red lines. The corresponding non-uniform (red solid line)

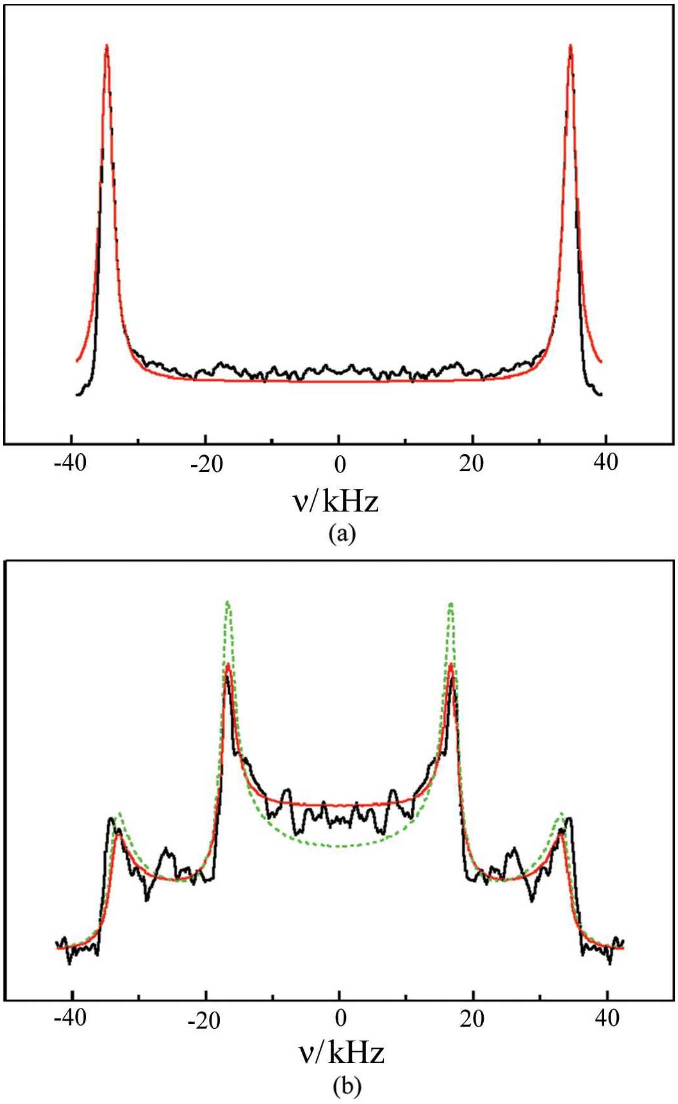
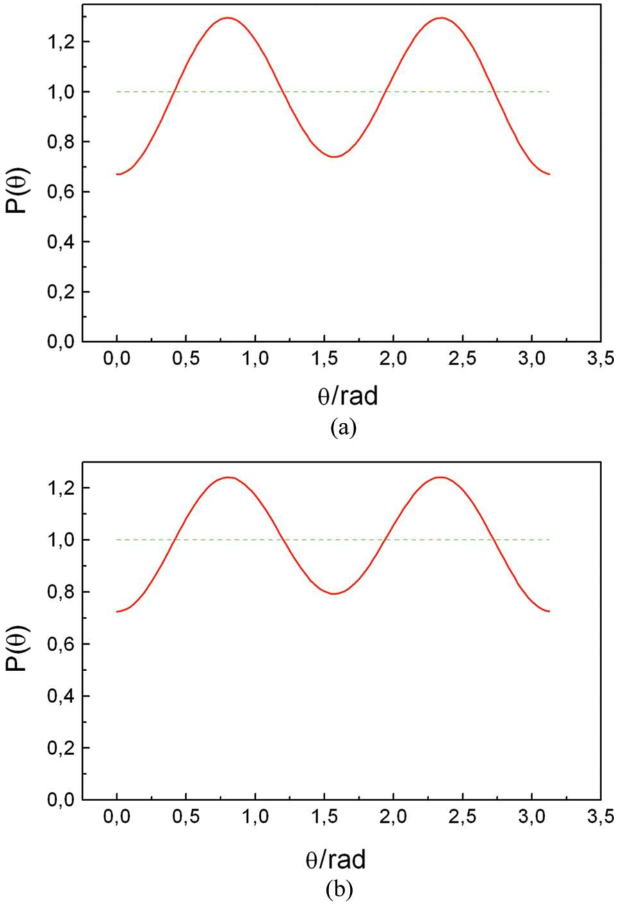


FIGURE 3 Spectra of aligned static sample (a) and rotating sample (b) for the non-substituted monomer mixed with deuterated probe 7CBαd2 at a temperature of 300 K. Black (thin) solid line: experimental data; red (thick) solid line: simulation with partial alignment distributions of the directors, in the plane perpendicular to $\mathbf{B}_0$ (in the case of rotating samples); green dashed line: simulation with uniform distribution of the directors in the plane perpendicular to $\mathbf{B}_0$.



(a)

(b)

FIGURE 4 Partial alignment distributions of the directors, in the plane perpendicular to $\mathbf{B}_0$, resulting from the simulation of spectra obtained from the rotating samples of the substituted (a) and non-substituted (b) monomers.

vs. uniform (green dashed line) distributions are presented in Figures 4a and 4b, respectively, for the substituted and non-substituted monomers. These distributions show minima for $\theta = 0$, $\theta = \pi/2$ and $\theta = \pi$, corresponding to the stability conditions of molecular alignment associated with the magnetic torque. The $\theta = 0$ and $\theta = \pi$ minima are equivalent due to the inversion symmetry of the director. The fact that the minimum at $\pi/2$ is higher that the $\theta = 0$ (or $\theta = \pi$) is due to the difference of stability in these two situations: stable equilibrium for $\theta = 0$ (or $\theta = \pi$) and unstable equilibrium for $\theta = \pi/2$.

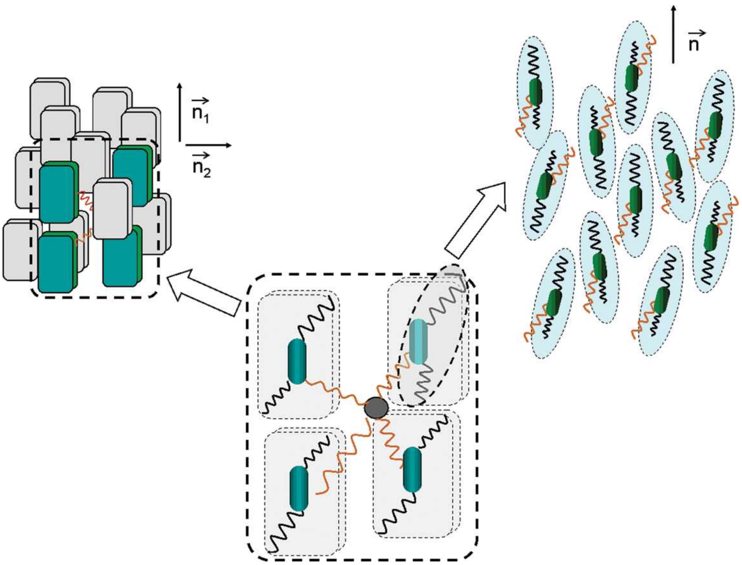


FIGURE 5 Schematic representation of the structures of the biaxial nematic phase formed by the tetrapodes (left) and of the uniaxial nematic phase formed by the monomers.

The results are similar for all the temperatures in the nematic phases of both systems. As the biaxial order is favoured by lower temperatures, several measurements were done at the lowest accessible temperatures corresponding to a supercooling condition of the nematic phase. All the measurements are compatible within the experimental error with a zero value for the asymmetry parameter.

CONCLUSION

Contrary to the tetrapodes' case, the deuterium NMR spectra obtained for the corresponding monomers, both with and without the lateral siloxane group, are compatible (as far as the present experimental conditions can show) with an uniaxial nematic mesophase. It is important to notice that, especially in the case of the substituted monomer, (apart from the central siloxane connection between the four monomers) the mesogenic units are perfectly identical to those which constitute the tetrapodes. Therefore, the previously stated hypothesis, that the biaxial ordering exhibited by the organiosiloxane tetrapodes is strongly conditioned by the lateral attachment between mesogenic groups, is clearly favoured by the present study. As pointed out in [5], the connection of the tetrapodes arms to the dendrimer core gives rise to a phase structure where interdigitation of the mesogenic units plays an important role. As previously observed for nematic polymers [2,7], the side-on link to the dendrimer core has the effect of constraining the rotations of the individual mesogenic units, thus explaining the appearance of the biaxial nematic ordering for low enough temperatures. A schematic representation of the biaxial nematic phase of the tetrapodes is presented in Figure 5. On the other hand, the monomers, which have the same exact chemical structure of the dendrimer arms but are free to rotate around the long molecular axis (because they are not interconnected to a dendrimer core) present uniaxial ordering in their whole nematic temperature range (see Fig. 5).

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