

^{13}C and ^2H NMR Study of Structure and Dynamics in Banana B_2 Phase of a Bent-Core Mesogen

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In this paper, the difficulty in orienting the B_2 phase of the banana mesogen 1,3-Phenylene-bis 4-[4-(10-undecenyloxy)-benzoyloxy] benzoate (Pbis11BB) in a relatively high magnetic field is reported based on some observations using both ^{13}C and ^2H NMR. ^2H NMR spectra recorded for the two labeled isotopomers of Pbis11BB in the isotropic and B_2 phases are shown here. Preliminary results on the deuteron spin–spin relaxation (T_2) data are reported at 61 MHz in order to underline the peculiar slow dynamics of banana-shaped liquid crystals (BLC), and these results are discussed in the framework of recent studies on similar BLC. The molecular structure and dynamics in the B_2 and crystalline phases are also studied by ^{13}C solid-state NMR techniques. The results also point to the slow dynamics in the B_2 phase of Pbis11BB. In particular, two-dimensional MAS exchange experiment has been performed to shed light on the molecular conformation structure of the five-ring banana core in the crystalline phase of Pbis11BB, and to compare with that of quantum mechanical calculations reported in the literature.

1. Introduction

Ferroelectric and antiferroelectric liquid crystals (LC) have attracted much attention in recent years. Both chiral molecules which contain chiral carbon site(s) and bent-core molecules^{1,2} can form tilted smectic layers with layer polarizations. For the latter, the so-called banana-shaped liquid crystals (BLC), chirality is believed to arise from the effective packing of bent-core molecules in the layers. The behavior of BLC in the presence of a magnetic field is particularly intriguing. The B_2 phase is one of the most interesting phases formed by these mesogens, with interesting physical properties from the technological point of view. It is a smectic phase, where molecules are perpendicular with respect to the layer layer and can pack according to different symmetry features, giving rise to chiral ferro- and antiferro-electric phases (see below). It is for this reason that we have chosen to investigate the B_2 phase of 1,3-Phenylene-bis 4-[4-(10-undecenyloxy)-benzoyloxy] benzoate (Pbis11BB).

A minor change in the substituents of the bent-core molecule (usually consisting a five ring system in the core) can drastically alter the phase behaviors in the condensed phases. For instance, the studied molecule (Pbis11BB) forms, monotropically, a B_2 phase, while a chlorine substitution in its central ring, viz. 4-chloro-1,3-Phenylene-bis 4-[4-(10-undecenyloxy)-benzoyloxy] benzoate (ClPbis11BB), shows only a nematic phase. One could “align” the ClPbis11BB sample by the magnetic field, and detailed information about the molecular and orienting properties could be achieved by using ^2H and ^{13}C NMR.³ Both 1-dimensional and 2-dimensional (2D) ^{13}C NMR have been demonstrated to be useful to study the structure of BLC.⁴ More recently

it has been shown that ClPbis11BB shows very slow dynamics both in the isotropic⁵ and nematic phases.⁶ A hypothesis about the orientation and supra-molecular arrangement of banana-shaped ClPbis11BB molecules in the bulk and under the effect of a magnetic field, has recently been proposed based on ^2H NMR and quantum mechanical calculations.⁷ From that study, it seems that in some cases banana-shaped molecules behave more similar to disklike mesogens than to rodlike ones. The factor that may determine such behaviors for the banana-shaped molecules is the size of the bent angle between the two lateral arms. Simple molecular mechanics calculations have shown that an asymmetry in the orientation of the two lateral wings with respect to the central ring is possible.⁸ Jakli et al.⁹ had found that the enantiomorphic property of Pbis11BB is likely due to the twisted conformation, and not the layer chirality. The twisted bent-core molecular shape has also been inferred by ^{13}C CP–MAS (cross-polarization magic angle spinning) spectra in other ester banana-shaped molecules which can form B_2 phase.^{10,11} The evidence given is based on the observation of doubling in the carbonyl carbon peaks in the B_2 phase of BLC P–n–O–PIMB ($n = 12$ and 14). However, Walba et al.¹² has recently challenged this evidence using the BLC P-9-O–PIMB, in which no carbon doublets were seen in its B_2 phase. It should, however, be noted that the temperature range of B_2 phase of $n = 9$ BLC is higher than those of $n = 12$ and 14 studied by Watanabe et al.¹³

The B_2 phase shows two-layer periodicity, and is composed of several subphases ($\text{SmC}_S P_A$, $\text{SmC}_A P_A$, $\text{SmC}_S P_F$, $\text{SmC}_A P_F$) resulted from different stackings of identical B_2 layers.¹⁴ Here, C_S and C_A denote synclinal and anticlinal smectic layers, while P_A and P_F represent the antiferroelectric and ferroelectric orders, respectively. The $\text{SmC}_A P_A$ subphase has already been observed as having fluid layers.¹⁴ The heterogeneity in the structure of B_2 phases has made it difficult to understand its structure and bulk properties. It is now believed that the $\text{SmC}_S P_A$ phase is

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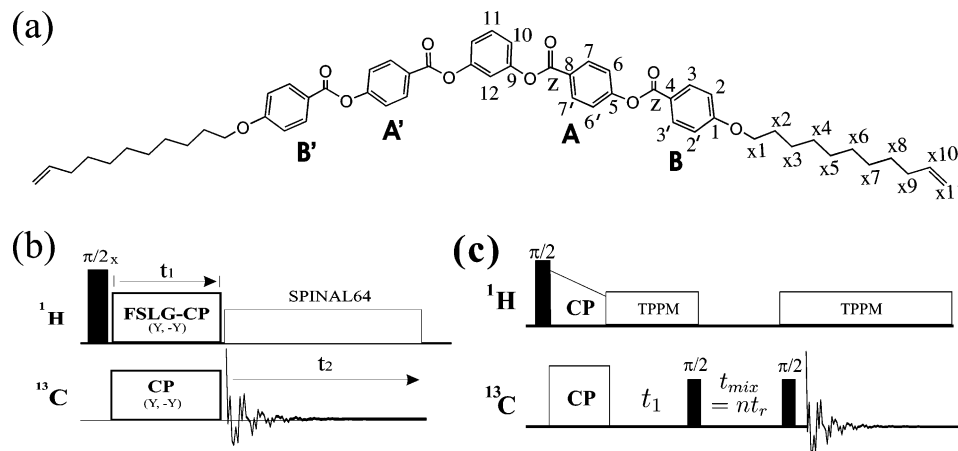
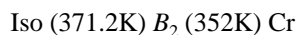


Figure 1. (a) Molecular structure of Pbis11BB together with the carbon labels. Pbis11BB-C-d₄ is fully deuterated in the central ring, while Pbis11BB-O-d₄ is deuterated at the sites 2, 2' in the lateral wings. (b) The pulse sequence used for 2D MAS SLF experiment. (c) The pulse sequence used for 2D ¹³C exchange experiment. t_r is the rotation period.

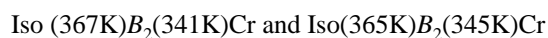
the ground state, while the $\text{SmC}_A P_A$ phase is metastable. It has also been found that the $\text{SmC}_S P_A$ and $\text{SmC}_A P_A$ phases, if they coexist in the B_2 phase, cannot be distinguished by ¹³C NMR CP–MAS spectra.¹¹ In fact, the Pbis11BB BLC is found to show difficulty in orienting in the bulk under a strong magnetic field. This is perhaps due to the small diamagnetic anisotropy $\Delta\chi_m$ introduced by their special molecular shapes.⁷ ²H NMR on two different isotopomers of Pbis11BB were used to demonstrate the inability to align the molecules in the B_2 phase. Even in the isotropic phase, our ¹³C NMR spectra showed very broad lines unless obtained with the aid of MAS. This demonstrates that the motion of this molecule was too slow⁵ in the isotropic phase to average out the dipolar couplings and chemical shift anisotropy (CSA). To support this, a deuteron T_2 relaxation study was carried out in the isotropic and B_2 phase. Since the structure of Pbis11BB cannot be obtained through studying the order parameters as in CIPbis11BB, the ¹³C study mainly focuses on the motion and conformational structure of Pbis11BB using solid state ¹³C NMR techniques. Under MAS, the ¹³C peaks from the banana-core become well resolved and can be studied as a function of temperature in the crystal and B_2 phases. In particular, both 2D MAS separated local field (SLF) and exchange experiments were used to address the assignment of carbon peaks and to shed light on the structure and motion of the banana-core. Several efforts have been pursued in order to understand the peculiar alignment behavior of banana-shaped molecules in the magnetic field on the basis of quantum mechanical and semiempirical simulation studies.¹⁵ The present study, therefore, adds another experimental example which could help in understanding this phenomenon.

2. Experimental Section

The synthesis and characterization of the nonlabeled Pbis11BB compound (shown in Figure 1a) are reported in ref 8, and its phase sequence, as detected optically by cooling, is as follows:



Two isotopomers, Pbis11BB-C-d₄ labeled on the central ring and Pbis11BB-O-d₄ labeled on the two outer phenyl rings (see Figure 1a), were synthesized for the ²H NMR study. The phase transition temperatures of the deuterated Pbis11BB-C-d₄ and Pbis11BB-O-d₄ samples, as observed from ²H NMR by cooling are, respectively:



It should be noticed that the phase transitions observed by differential scanning calorimetry (DSC) and NMR are slightly different among the three samples (the unlabeled and the two labeled ones) due to different sample purities and the deuteration effect, as observed in other liquid crystals selectively labeled in different positions.^{16,17}

The ²H NMR experiments were carried out at 61 MHz on a 9.4 T Varian InfinityPlus400 spectrometer, using a goniometric probe (5 mm) dedicated to the deuterium nucleus. For both isotopomers, samples were cooled within the magnet from the isotropic to the B_2 and then the crystal phase. The temperature was controlled within 0.2 degree and 10–30 min were allowed for thermal equilibration of the samples at each temperature. ²H NMR spectra were recorded with or without ¹H continuous-wave decoupling, either on cooling or on heating, by quadrupolar echo (QE) pulse sequence^{18,19} ($90_x - \tau - 90_y - \tau$). The 90° pulse width was 4.0 μs for Pbis11BB-C-d₄, and 4.6 μs for Pbis11BB-O-d₄. A pulse delay of 1.5 s and QE time delay τ of 18 μs were used. The number of scans varied from 400 to 6000, depending on the sample and the kind of measurements. Preliminary T_2 measurements were performed by the QE sequence with the exorcycle²⁰ phase scheme and ¹H continuous-wave decoupling. The variable time τ ranged from 18 μs to 4 ms (15 values were used). The number of scans for each τ value was 400. The ¹³C NMR experiments were carried out at 100 MHz on a 9.4T Bruker Avance 400 spectrometer with a 4 mm rotor MAS probe. Cross-polarization polarization inversion (CPPI)^{21,22} and Lee–Goldberg cross-polarization (LGCP)^{23,24} SLF experiments were performed to assign the carbon peaks. The polarization inversion interval was 60 μs , and the cross-polarization time was 2 ms. The LGCP experiment under MAS on a solid sample can be used to produce 2D–SLF spectra, from which are extracted the CH bond lengths.²⁴ Here MAS–SLF experiment used the pulse sequence in Figure 1b in order to discern various carbon sites according to the magnitudes of C–H dipolar couplings. For a simple 1D spectrum, the t_1 period (Figure 1b) was fixed. LG homonuclear decoupling had a decoupling strength of 56 kHz. The sample temperature was controlled by an airflow regulated to ca. 0.1 degree. For calibration of the sample temperature in the MAS probe at different rotor spinning rates, MAS ²⁰⁷Pb spectra of lead nitrate were used to give temperature-dependent chemical shifts and calibration curves were obtained according to the procedures described in the literature.^{25–28}

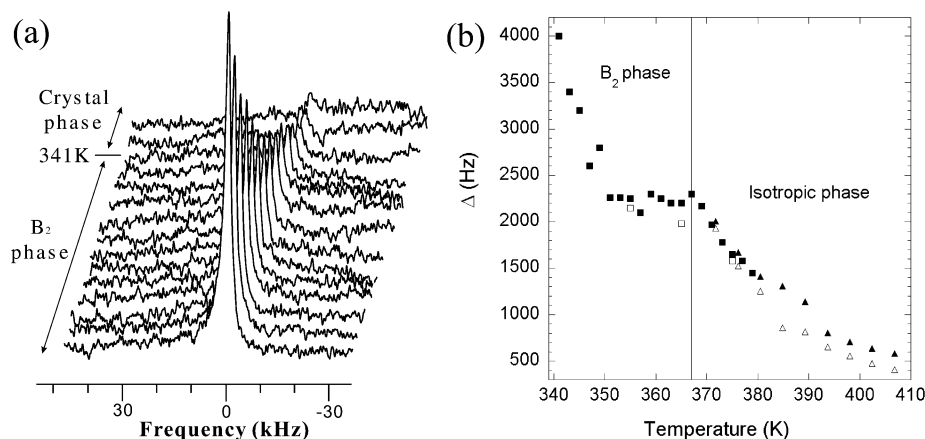


Figure 2. (a) ^2H NMR spectra of Pbis11BB-C-d₄, acquired under QE sequence and ^1H decoupling, number of scans 3000, acquired every 2 degrees from 365 K to 337 K. The B_2 –crystal transition is at 341 K. Note that the very short T_2 produces a noticeable effect in the spreading of signal under the baseline. (b) ^2H NMR line width Δ (■) measured from (a) vs the temperature. The homogeneous component Δ_{homo} as calculated from the T_2 measurements is denoted by □. ^2H NMR data (Δ) reported in ref 5 are also reproduced for direct comparison. Transition temperature is indicated with a solid line.

The ^{13}C 2D exchange experiment (see pulse sequence in Figure 1c) can be carried out on a nonenriched sample only under MAS condition, where the signal intensities are relatively high because of the line narrowing in the NMR spectrum. A ramp-CP was used to enhance the ^{13}C NMR signal. During the evolution time t_1 and acquisition time t_2 , a heteronuclear decoupling sequence (TPPM at a decoupling power of 56 kHz) was necessary in the proton channel to create narrow spectral lines in ω_1 and ω_2 dimension of the 2D exchange spectrum. Note that proton decoupling was not applied during the mixing time t_{mix} . Under slow MAS, the sidebands for different ^{13}C sites may create some cross-peaks, even when no real exchange process occurs among them. To remove these artificial peaks, one simple way is to synchronize the mixing time with the sample rotation, i.e., $t_{\text{mix}} = nt_r$, and to use an appropriate phase cycling scheme at the same time.²⁹ However, this coherence–selection scheme prevents the acquisition of pure-phase 2D spectra, thereby dramatically decreasing the spectral resolution. The frequency sign in ω_2 dimension was achieved using the STATES method.³⁰ For clarity, the magnitude calculation in ω_2 dimension was used, i.e., the intensities in the magnitude type spectrum were given by $\sqrt{I_r^2 + I_i^2}$, where I_r and I_i were the intensities obtained from the cosine modulated spectrum and sine modulated spectrum, respectively. The resulting “star” structure of the resonance peaks still limited the resolution of magnitude-type spectrum. Since the resolution was sufficient to separate most of the carbon peaks, newly developed techniques for creating pure-phase 2D ^{13}C NMR exchange spectra^{31–33} were not attempted. A recycle time of 5 s and a MAS speed of 8 kHz were used in ^{13}C NMR exchange experiments. The proton and ^{13}C 90° pulse widths were 3 and 4 μs , respectively.

3. Results and Discussion

The behavior of bulk BLC samples in a strong NMR magnet field is quite peculiar, and has been recently investigated.^{7,34} Here, a similar behavior has been observed for two differently labeled isotopomers of Pbis11BB. The difficulty of orienting the molecules in the magnetic field, when being cooled from the isotropic phase, even after spending quite a long time (more than 10 h) at temperatures higher than the clearing point, could be observed from the ^2H NMR spectra.

3.1. Pbis11BB-C-d₄. The experimental spectra as a function of temperature in the B_2 phase are reported in Figure 2a. These

spectra all show a single peak. In particular, when passing from the isotropic to the B_2 phase a significant decrease in the signal intensity of the peak is observed, until the crystal phase is reached, below 341 K. The decrease in signal intensity is, however, never associated with the appearance of any quadrupolar splittings even for extremely slow cooling, but only with a progressive broadening of the signal. This experimental observation indicates that the local directors are not aligned with respect to the external magnetic field in any preferred orientation. There are several hypotheses to explain this finding: (1) tilted banana mesophases are viscous² in comparison to common smectic mesophases. Hence, it may be difficult to orient the molecules in a bulk banana LC phase by an external magnetic field, and this may justify the fact that the same material can be oriented only in thin films, as demonstrated by electro-optical investigations; (2) the B_2 phase is also characterized by a very high degree of single-domain local order, resulting in a very different symmetry with respect to the isotropic phase: this is another factor that prevents the alignment of the molecules on entering the mesophase directly from the isotropic phase; (3) recent quantum mechanics calculations¹⁵ support previous preliminary calculations,⁷ which indicated that these molecules have a small (molecular) $\Delta\chi_m$ due to their bent shape, and also some indirect measurements of this quantity on similar BLC samples give small $\Delta\chi_m$ (1 order of magnitude less than in common calamitic compounds).³⁵

Previous ^2H NMR spectra recorded for the Pbis11BB-C-d₄ sample at a slightly different magnetic field (deuterium Larmor frequency of 58 MHz) have revealed an unusual slow dynamics in the isotropic phase.⁵ This feature is confirmed by the ^2H NMR spectra recorded with ^1H decoupling at the magnetic field corresponding to 61 MHz, further illustrating the trend of line width and spin–spin relaxation times. The line width of the observed single peak at half-height (Δ), evaluated directly from the ^2H NMR spectra, is reported in Figure 2b, as a function of temperature in both the isotropic and B_2 phases. There is a small jump of Δ at the phase transition. The experimental data obtained from a previous work in the isotropic phase are also shown in Figure 2b. To get a more reliable description of the dynamic features in the B_2 phase, the homogeneous component of the line width can be calculated by the measured T_2 spin–spin relaxation times, since T_2 is related to the homogeneous part of the ^2H NMR line width through the following relationship: $\Delta_{\text{homo}} = (\pi T_2)^{-1}$. Accordingly, the experimental Δ_{homo}

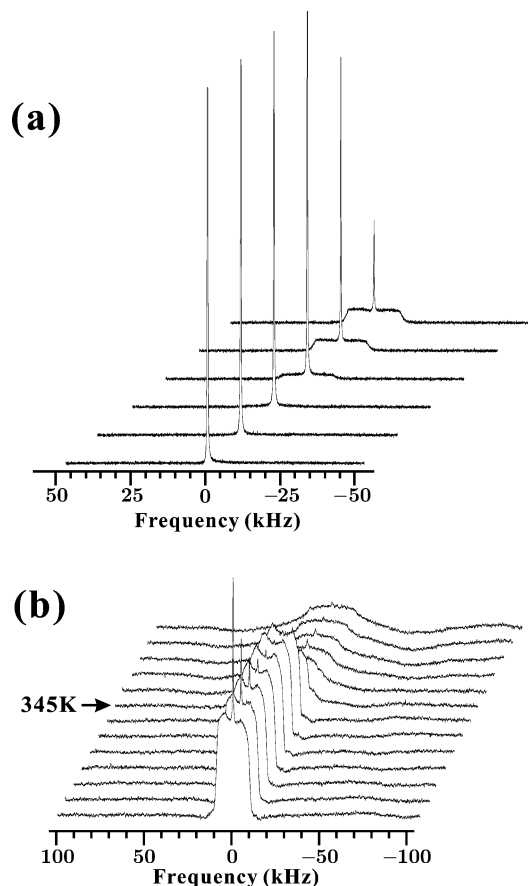


Figure 3. ^2H NMR spectra of Pbis11BB-O- d_4 , acquired using QE sequence and ^1H decoupling, (a) from 371 to 361 K with 2000 scans every 2 degrees. The B_2 phase appears at 365 K. (b) from 359 to 335 K with 5000 scans every 2 degrees. A drastic change in the deuterium line shape can be observed at 345 K (indicated by an arrow) where the sample is supposed to enter the crystalline phase.

(T) measured at some temperatures in the isotropic and B_2 phases is also shown in Figure 2b. The trend of the Δ_{homo} calculated from the spin–spin relaxation times evidences a substantial coincidence with the experimental line width Δ within the experimental error, both in the isotropic and B_2 phases. This means that the observed line broadening is mainly ascribable to the homogeneous component, indicating a dynamic nature in the line broadening. As a consequence, the motions which affect the deuterated central ring must take place on a time scale shorter than the deuteron NMR time scale $(\nu_q)^{-1} = 4 \times 10^{-6}\text{s}$, in the isotropic⁵ as well as in the B_2 phase. (here ν_q is the characteristic quadrupolar constant). Recently a molecular model has been developed to analyze the relaxation data in terms of dynamics of the central ring in the slow motion regime.⁶ The application of such model on a similar compound (CIPbis11BB) in its nematic phase, confirmed that the reorientational motion of the central ring is extremely slow ($D < 10^5\text{s}^{-1}$) in comparison with common calamitic nematic as well as smectic mesophases. We expect that similar conclusions could be drawn for the Pbis11BB compound in the viscous B_2 phase.

3.2. Pbis11BB-O- d_4 . Variable temperature ^2H NMR spectra in the Pbis11BB-O- d_4 sample are reported in Figure 3. The transition from the isotropic to the B_2 phase is more clearly seen here than for the other deuterated sample. In fact, a significant change of the ^2H NMR line shape is observed, even though there is a range of temperatures where the two phases seem to coexist. This feature has also been observed in the present ^{13}C NMR study of the unlabeled compound and can be

explained by the slow kinetics of formation and equilibration of the banana phase. However, leaving the sample at a temperature for quite a long time (1 day) did not produce any changes in the observed ^2H NMR spectra. This finding could be explained by either very slow kinetics or a thermodynamically stable situation due to the presence of impurities. In this region, from 365 to 355 K, the ^2H NMR spectra are characterized by two components: (1) an isotropic peak, probably corresponding to isotropic domains, which still exist below the clearing point; (2) a large and broad signal with a very peculiar shape, having singularities separated at about 20 kHz, a characteristic feature of this isotopomer in the B_2 phase. ^2H NMR spectra of the Pbis11BB-O- d_4 were also acquired without ^1H decoupling by cooling the sample from the isotropic phase to the room temperature. These spectra are quite similar to those shown in Figure 3. Since no single and separated quadrupolar splittings, but only a distribution of quadrupolar splittings can be observed in the B_2 phase of this isotopomer, it can certainly be asserted that the sample is not uniformly oriented in the magnetic field, confirming the substantial difficulty in orientation. Indeed the banana molecules are organized in domains which are distributed in the bulk with different orientations of different weights, giving rise to the observed distorted “Pake-like” powder pattern, likely due to the magnetic torque from the magnetic field. A hypothesis of mesophase structure has been proposed recently by Jakli et al.⁹ to interpret the optical behavior, that is, each domain is characterized by smectic layers where molecules are tilted with a very unusually large tilt angle, about 45° , with respect to the normal of the smectic layer. This finding could be useful to explain the observed spectral features here reported, although the very slow dynamics should also be taken into account to understand our observations. The spin–spin relaxation time, T_2 , is very short as noted from the FID, thus confirming that the dynamics of the lateral phenyl rings in the B_2 phase is very slow. This aspect is in agreement with what was found for the Pbis11BB-C- d_4 sample.

A complete spin–spin relaxation study on these two isotopomers is still in progress³⁶ and the analysis of the relaxation data is expected to give detailed information about the rotational diffusional coefficients for the overall molecular and internal motions, as well as to estimate the contribution of collective motions. Preliminary results³⁶ have revealed that the phenyl rings, which show very fast flip-flop reorientational motions in rodlike mesophases, feel slower motions in the banana mesophases (nematic and B_2 phase, for instance).^{6,36} The slow reorientation of the phenyl rings in the B_2 phase may also influence the spectra, producing the observed distorted “Pake-like” line shape.

3.3. ^{13}C NMR Study. To help the ^{13}C peak assignment in B_2 and crystal phases, ^{13}C NMR spectra of Pbis11BB were first recorded in the isotropic state. Two methods have been used for obtaining high-resolution spectra. One way is to dissolve the sample in CDCl_3 solvent, and to record the spectrum at room temperature using a high-resolution liquid NMR probe. Another way is to record the ^{13}C NMR spectrum with the aid of slow MAS of the sample in its isotropic phase, using a 90° carbon pulse combined with high power proton decoupling during acquisition. The recorded spectra using the two methods are shown in Figure 4. The spectra recorded using distortionless enhancement by polarization transfer (DEPT135)³⁷ pulse sequence under the same sample conditions are shown in Figure 5, in which CH peaks are positive, CH_2 peaks are negative, while quaternary peaks vanish. It is clear that spectra under these two conditions only show tiny differences. Figure 4a shows that

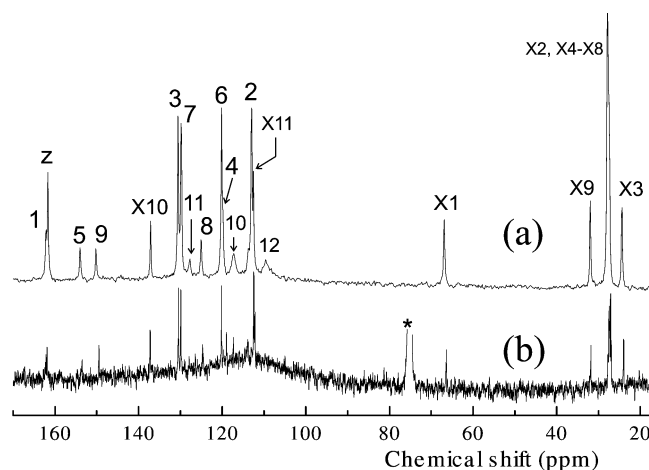


Figure 4. Typical ^{13}C NMR spectra recorded by (a) rotating the sample at the magic angle (5 kHz) at 375 K, and (b) dissolving Pbis11B in CDCl_3 at room temperature. The assignment of ^{13}C peaks are also indicated using the same labels as those in Figure 1a. The signal from CDCl_3 is indicated by star (*).

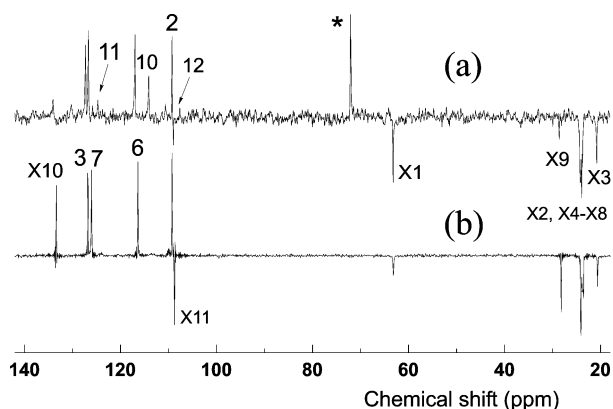


Figure 5. Typical DEPT135 ^{13}C NMR spectrum recorded by (a) dissolving the Pbis11B in CDCl_3 , and (b) rotating the sample at magic angle (5 kHz) at 375 K.

in the MAS spectrum, the ^{13}C peaks from the central ring (C_{10} , C_{11} , C_{12}) are much broader, proving that the whole molecule carries on slow motions in the isotropic solvent, while other aromatic peaks are narrowed by the fast ring flips.^{38–40} The same can be said for the DEPT135 experiments, which rely on the scalar J -coupling between ^{13}C and ^1H . The ^{13}C NMR signal survives in a DEPT135 experiment if interactions such as dipolar coupling and CSA are much smaller than the J -coupling such that the polarization can be transferred from ^1H to ^{13}C before the coherence decays away.⁴¹ It can be seen in Figure 5b that C_{10} , C_{11} and C_{12} signal under MAS are all missing in the isotropic phase, while they survive in the solution spectrum (Figure 5a). Based on the DEPT135 experiment and the carbon peak assignments in similar compounds,³ the ^{13}C peaks in the liquid state are assigned and labeled in Figures 4–5.

Figure 6 shows the typical CP–MAS ^{13}C NMR spectra recorded in B_2 and crystal phase by cooling from the isotropic phase. These spectra clearly show that some carbon peaks break into doublets in the B_2 phase and in the crystal state. The CPPI spectrum observed at 367.8 K is plotted in Figure 6b. As seen in this spectrum, one has null CH signals, negative CH_2 signals, and positive signals from quaternary carbons. The CP buildup curves in the MAS–SLF experiment show no clear dipolar oscillations for quaternary carbons (C_8 , C_4), but give similar oscillation frequencies for the protonated carbons of the phenyl groups. Thus, overlapped peaks among quaternary carbons and

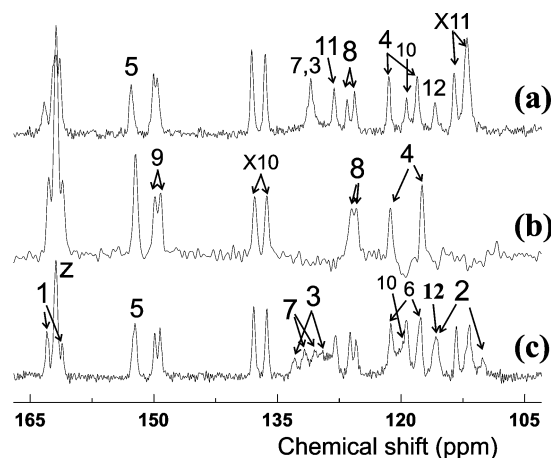


Figure 6. CP–MAS ^{13}C NMR spectrum at 367.8 K (a) and 310.4 K (c), and CPPI spectrum recorded with MAS at 367.8 K (b). MAS speed was 5 kHz. Only aromatic carbon peaks are display for clarity.

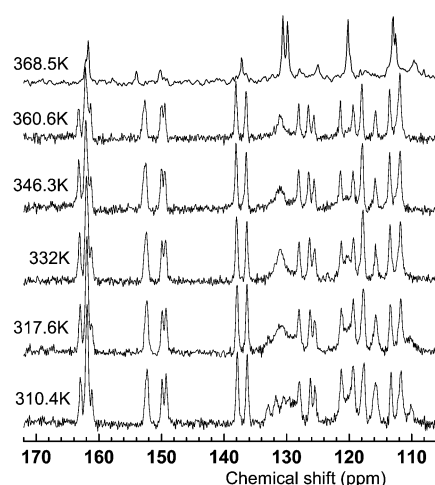


Figure 7. Some typical CP–MAS ^{13}C NMR spectra at different temperatures (MAS speed 5 kHz). Only aromatic carbon peaks are display for clarity.

protonated carbons can be clearly discriminated, such as C_6 and C_4 , in the MAS–SLF experiments. The end-chain carbon sites (e.g., X_{11}) create much smaller dipolar couplings. Based on the MAS–SLF spectra together with the chemical shifts in the isotropic state, the ^{13}C MAS spectrum in the crystal state can now be assigned as labeled in Figure 6. The CP–MAS ^{13}C NMR spectrum in the B_2 phase is shown as a function of temperature in Figure 7. These spectra clearly show the dynamic effect of ring flips at chemical shifts near 131 ppm, 120 ppm, and 111 ppm. It is observed that some carbon peaks positions (especially the quaternary C_1 , C_5 , C_8 , C_9 , and Z) show noticeable temperature dependence upon entering into the crystal phase, while the peak positions of protonated C_{10} , C_{11} , and C_{12} are relatively independent of the temperature. The temperature-dependent chemical shifts show a clear turning point at 346 K, which indicates a phase transition from the B_2 phase to the crystal phase. The detected transition temperature is about 5 K lower than that obtained from the optical observation. However it does agree with the observation by ^2H NMR. The resonance shifts introduced by the phase transition have also been observed in other liquid crystals.⁴² Besides the temperature-dependent ring flip motion, the resonance shifts may also be due to the ring current of the benzene moieties from neighboring molecules, which is the main contribution to the resonance shift from the liquid state to the solid state.⁴³ However, the sharp lines shown in our ^{13}C NMR spectra at all temperatures suggest that the

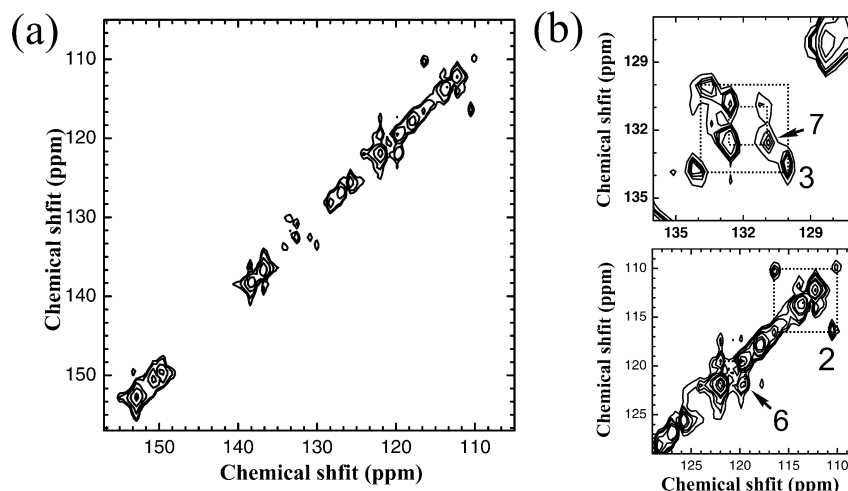


Figure 8. (a) Contour plot the ^{13}C 2D exchange spectrum recorded at room temperature (293 K) and MAS speed at 8 kHz. Mixing time was 0.1 s, and the ramp-CP contact time was 2 ms, recycle delay 5 s and 256 t_1 increment were used. 56 kHz proton decoupling was used in t_1 and t_2 intervals. (b) Expanded regions of (a) for clarity.

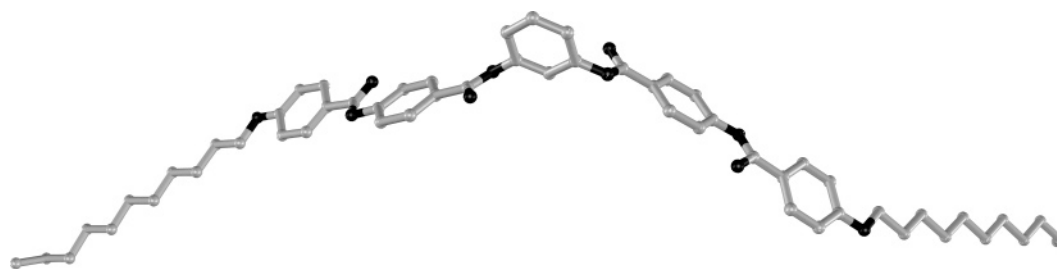


Figure 9. A schematic visualization of the backbone structure of Pbis11BB in the crystal state, in which the directions of ester groups near the central ring are uncertain.

intermolecular ring current is not a significant factor in this compound.⁴⁴ In the B_2 phase, the dynamics of the ring flip and molecular structure seem constant, or the change is small enough to render undetectable. This could account for the fact that the smectic layer thickness is almost constant in B_2 phase.⁴⁵ In principle, the transition temperature from isotropic phase to B_2 phase can be determined by the spectra recorded using CP. In our experiments, it was found that the CP ^{13}C signal intensity increased gradually with respect to the temperature when cooling the sample from 370 K, while the line shapes are similar to that observed at 367.8 K (Figure 6a). When the temperature is higher than 370 K, no ^{13}C signal could be observed since CP would not work in liquid state. The phase transition can also be determined by recording spectra using direct ^{13}C pulse excitation combined with high power proton decoupling. By cooling the sample, the ^{13}C intensities of the observed isotropic spectrum (Figure 4a) will decrease with decreasing temperature, and disappear completely at 367.8 K. These experiments indicate that our sample at temperatures between 368 K and 370 K is actually in a biphasic state of B_2 phase and isotropic phase. The transition temperature of 369 K is close to that determined by the optical method.

It is important to note that no doublets (Figure 6a) were found for carbon C_{11} and C_{12} in the central ring, while a doublet was clearly seen for C_9 besides those of other carbon sites on the lateral rings, thus ruling out the existence of two distinct conformations for the banana-core with different nearby lateral rings, i.e., $\text{R}-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{R}$ and $\text{R}'-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{R}'$. However, the observed doublets seen in Figure 6 cannot rule out one of two remaining possibilities, viz. a static core conformation structure $\text{R}'-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{R}$ or a dynamic exchange between it and its counterpart $\text{R}-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{R}'$. At the

ambient temperature, the dynamic effect if it exists would be too slow to be detected by 1D ^{13}C spectra. To find the origin of these doublets, ^{13}C NMR 2D exchange experiments were performed in the crystal state at room temperature using the pulse sequence shown in Figure 1c. The observed exchange spectrum at a mixing time of 0.1 s is shown in Figure 8a. Only the carbon sites from aromatic rings are studied. There are four pairs of cross-peaks clearly seen in Figure 8b. The exchange cross-peaks come from the very slow π flip of the phenyl rings in the crystal phase. The slow flip of the phenyl ring leads to inequivalent environments for the aromatic proton-bearing carbons, which had been observed by NMR in other polymers and liquid crystals.^{46–48} The two inequivalent protonated aromatic carbons interact differently with the esters and adjacent aromatic rings, and their chemical shifts are determined by the dihedral angle between two neighboring ring planes.^{46,49} A frequency for the ring flip at room temperature can be estimated between 10 Hz and 100 Hz from the exchange spectrum. The significant chemical shift differences (ca. 3 ppm) between carbon 3, and 3' and between carbon 6, and 6' suggest that the two aromatic rings A and B (or A', B') are in a trans-trans configuration (but the ring planes of A and B need not be coplanar), while the relatively smaller doublet of C_7 suggests that the phenyl ring A (or A') and the central ring are more close to a trans-cis configuration. The large doublet of C_2 also suggests that the alkyl chain is nearly coplanar with the attached phenyl ring. Given that a C_2 symmetry for the molecule gives a minimum molecular energy, the conformation structure of Pbis11BB in the solid state is schematized in Figure 9 based on the above information. However, quantum mechanics calculations⁵⁰ of an "isolated" Pbis11BB suggest that only the external rings (B, B') are twisted with respect to the central

ring rather than a significant twist of the rings A and A' (i.e., trans–cis configuration with the central ring), as visualized by ^{13}C NMR. Our qualitative picture may perhaps be rationalized by the packing and intermolecular interactions in the crystal phase.

In the B_2 phase, the ring flip is now fast enough to make 3, 3' and 7, 7' collapse into one single broad peak (Figure 7). However, this flip motion is still not fast enough to collapse carbons 2, 2' (or 6, 6') into one peak, it will only broaden these peaks because the splittings of these doublets are larger.⁵¹ Also the ring flip motion reduces the heteronuclear dipolar interactions of these carbons with neighboring protons, thereby causing the signals of carbon 2', 2 and 6', 6 to nearly disappear at high temperatures. Other doublets of C₁, C₄, C₈, and C₉ always appear in the NMR spectra recorded in the B_2 phase and in the crystal state. This means that these doublets must come from the asymmetric lateral wings (A, B and A', B') in the molecule, and not from the dynamic effect, since there were no cross-peaks between them in the exchange spectrum. Note that doublets introduced by crystallographic asymmetries are common in discotic liquid crystals, such as phthalocyanine, porphyrins, and their derivatives.^{43,52,53} As seen in Figure 8b, the cross-peaks of C₆ is much smaller than the diagonal peaks, and the relative intensities of the cross-peak and diagonal peak are similar for the two mixing times 0.1 s and 0.5 s (2D spectrum not shown). This indicates that the peaks of C₆ also contain C₄, which is consistent with the dipolar oscillation observed in the LGCP curves. It needs to be pointed out that, although small “cross-peaks” from the carbon X₁₁ and X₁₀ appear in Figure 8, they actually come from the “ringing” effect due to the truncation of FID in ω_2 dimension. Their intensities were dramatically smaller than the diagonal peaks and did not change for the two different mixing times. The large doublets for carbon X₁₁, X₁₂ also confirm that a twisted banana core has led to two inequivalent alkyl chains. This clearly shows that the two chains in the molecule are seriously distorted by the packing effect. The relative twist between rings A and B is still similar to that between A' and B', which can be inferred from the tiny doublet of C₅. However, the doublets of C₈ and C₉ are seen at all temperatures up to 368 K, thereby confirming that the relative position of ring A and ring A', with respect to the central ring, must remain asymmetric (see Figure 9), even in the B_2 phase, to give the asymmetry in orientation of the two lateral wings.

4. Conclusion

This NMR study has demonstrated that the B_2 phase of Pbis11BB seems not to orient in the magnetic field. The observed ^2H NMR spectra can be justified assuming that in the bulk B_2 phase, there is an isotropic distribution of domains, which do not orient in a particular direction relative to the magnetic field. Furthermore, the bent-core molecule Pbis11BB is “symmetric” in the isotropic phase, but not in the B_2 and crystal phases. In the condensed phases, Pbis11BB shows a static “twisted” molecular core with an asymmetry in the orientation of the two lateral wings. Thus, it seems unnecessary to have a mono substituent in the central ring⁴ in order to get a “twisted” molecular core like in CIPbis11BB. These two molecules, however, show different phase structures upon changing temperature, and they align differently in an external magnetic field. The motions of the bent-core molecule and of the constituent phenyl rings are slow in the B_2 phase of Pbis11BB, which are not seen in the conventional smectic LC. The observed slow exchange dynamics is derived from the existence of many “doublets” for the quaternary carbons in the entire B_2 phase,

except the carbonyl groups and C₅. The present ^{13}C NMR findings are consistent with those for the B_2 phases of Watanabe et al.,^{10,11} but are contrary to the recent B_2 phase results reported by Walba et al. We believe that the disappearance of doublets going from the low-temperature B_4 phase to the high temperature B_2 phase in a particular BLC as a clear evidence of the fluidity of B_2 phase is dangerous, especially without a due consideration of the effects of temperature-dependent viscosity and exchange narrowing. It is noted that the temperature range of the B_2 phase of P-9-O-PIMB is about 80° higher than that of Pbis11BB. A dynamic conformation exchange between R'–O–C₆H₄–O–R and R–O–C₆H₄–O–R' could exist for P-9-O-PIMB to merge the doublets giving relatively broad ^{13}C peaks. Despite the inability to find the ordering of Pbis11BB in the banana B_2 phase, the present study has shown that the solid-state ^{13}C NMR techniques can successfully elucidate the dynamics and configurational information of Pbis11BB based on high resolution ^{13}C spectra. Apart from the ring flips, the molecular core of Pbis11BB appears to show a structure relatively independent of the temperature in the B_2 phase.

The super-molecular organization of BLC in the bulk is still not well understood. The present study would justify why the behaviors in thin samples, often used for electro-optic studies, are quite different from the behavior in the bulk. The formation of smectic layers in the B_2 phase of Pbis11BB may be frustrated by the packing of the “twisted” bent-core molecules of \pm chirality, that is, the direction of the end-to-end vector of a molecule can be “up” or “down” as they are now distinct because of the twisted molecular core. The deuteron T_2 measurements can be very useful to monitor the slow dynamics in the banana phases.⁶ Both ^{13}C and ^2H NMR demonstrate slow reorientational motions for the molecule Pbis11BB in the B_2 phase, mainly due to the smectic packing and the heterogeneous phase structure. Further work is needed to address the problem of nonalignment of banana molecules in the B_2 and nematic^{7,34} phases by the magnetic field.

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References and Notes

- (1) Niori, T.; Sekine, F.; Watanabe, J.; Furukawa, T.; Takezoe, H. *J. Mater. Chem.* **1996**, *6*, 1231.
- (2) Pelzl, G.; Diele, S.; Weissflog, W. *Adv. Mater.* **1999**, *11*, 707.
- (3) Dong, R. Y.; Fodor-Csorba, K.; Xu, J.; Domenici, V.; Prampolini, G.; Veracini, C. A. *J. Phys. Chem. B* **2004**, *108*, 7694.
- (4) Dong, R. Y.; Xu, J.; Benyei, G.; Fodor-Csorba, K. *Phys. Rev. E* **2004**, *70*, 011708.
- (5) Domenici, V.; Geppi, M.; Veracini, C. A.; Blinc, R.; Lebar, A.; Zalar, B. *J. Phys. Chem. B* **2005**, *109*, 769.
- (6) Domenici, V.; Frezzato, D.; Fodor-Csorba, K.; Moro, G.; Veracini, C. A. *Ferroelectrics* **2006**, in press.
- (7) Domenici, V.; Veracini, C. A.; Zalar, B. *Soft Matter* **2005**, *1*, 408.
- (8) Fodor-Csorba, K.; Galli, G.; Jakli, A.; Demus, D.; Holly, S.; Gacs-Baitz, E. *Macromol. Chem. Phys.* **2000**, *203*, 1556.
- (9) Jakli, A.; Huang, Y. M.; Fodor-Csorba, K.; Vajda, A.; Galli, G.; Diele, S. *Adv. Mater.* **2003**, *15*, 1606.
- (10) Sekine, T.; Niori, T.; Sone, M.; Watanabe, J.; Choi, S.-W.; Takanishi, Y.; Takezoe, H. *Jpn. J. Appl. Phys.* **1997**, *36*, 6455–6463.
- (11) Kurosu, H.; Kawasaki, M.; Hirose, M.; Yamada, M.; Kang, S.; Thisayukta, J.; Sone, M.; Takezoe, H.; Watanabe, J. *J. Phys. Chem. A* **2004**, *108*, 4674–4678.
- (12) Walba, D. M.; Eshdat, L.; Korblova, E.; Shoemaker, R. K. *Cryst. Growth Design* **2006**, in press.
- (13) Imase, T.; Kawauchi, S.; Watanabe, J. *J. Mol. Structure* **2001**, *526*, 31.

- (14) Link, D. R.; Natale, G.; Shao, R.; MacLennan, J. E.; Noel, A. C.; Eva, K.; Walba, D. M. *Science* **1997**, 278, 1924–1927.
- (15) Prampolini, G.; Domenici, V.; Veracini, C. A. *Chem. Phys. Lett.*, to be published **2006**.
- (16) Catalano, D.; Cavazza, M.; Chiezzì, L.; Geppi, M.; Veracini, C. A. *Liq. Cryst.* **2000**, 27, 621.
- (17) Catalano, D.; Chiezzì, L.; Domenici, V.; Geppi, M.; Veracini, C. A. *J. Phys. Chem. B* **2003**, 107, 10104.
- (18) Powles, J. G.; Strange, J. *Proc. Phys. Soc.* **1963**, 82, 6.
- (19) Luz, Z.; Meiboom, S. *J. Chem. Phys.* **1963**, 39, 366.
- (20) Bodenhausen, G.; Freeman, R.; Turner, D. L. *J. Magn. Reson.* **1977**, 27, 511.
- (21) Wu, X. L.; Burns, S. T.; Zilm, K. W. *J. Magn. Reson. A* **1994**, 111, 29–36.
- (22) Wu, X. L.; Zilm, K. W. *J. Magn. Reson. A* **1993**, 102, 205–213.
- (23) Sinha, N.; Ramannathan, K. V. *Chem. Phys. Lett.* **2000**, 332, 125–130.
- (24) van Rossum, B.-J.; de Groot, C. P.; Ladizhansky, V.; Vega, S.; de Groot, H. J. *J. Am. Chem. Soc.* **2000**, 122, 3465–3472.
- (25) Dybowski, C.; Guenther, N. *Prog. Nucl. Magn. Reson. Spectrosc.* **2002**, 41, 153–170.
- (26) Michael, F.; Ulrich, B. *Solid State Nucl. Magn. Reson.* **1998**, 11, 231–241.
- (27) Takahashi, T.; Kawashima, H.; Sugisawa, H.; Baba, T. *Solid State Nucl. Magn. Reson.* **1999**, 15, 119–123.
- (28) McFarlane, W. *Proc. R. Soc. London, Ser. A* **1968**, 306, 185.
- (29) de Jong, A. F.; Kentgens, A. P. M.; Veeman, W. S. *Chem. Phys. Lett.* **1984**, 109, 337.
- (30) States, D. J.; Haberkorn, R. A.; Ruben, D. J. *J. Magn. Reson.* **1982**, 48, 286–292.
- (31) Hagemeyer, A.; Schmidt-Rohr, K.; Spiess, H. W. *Adv. Magn. Reson.* **1989**, 13, 85.
- (32) Boender, G. J.; Vega, S. *J. Magn. Reson. A* **1998**, 133, 281.
- (33) Ernst, M.; Kentgens, A. P. M.; Meier, B. H. *J. Magn. Reson. A* **1999**, 138, 66.
- (34) Dong, R. Y.; Zhang, J.; Fodor-Csorba, K. *Chem. Phys. Lett.* **2005**, 417, 475.
- (35) Wiant, D.; Gleeson, J. T.; Eber, N.; Fodor-Csorba, K.; Jakli, A.; Toth-Katona, T. *Phys. Rev. E* **2005**, 72, 041712.
- (36) Domenici, V.; Frezzato, D.; Veracini, C. A.; to be published.
- (37) Bendall, M. R.; Doddrell, D. M.; Pegg, D. T. *J. Magn. Reson.* **1981**, 103, 4603.
- (38) Zimmermann, H.; Bader, V.; Poupko, R.; Wachtel, E. *J. Am. Chem. Soc.* **2006**, 124, 15286.
- (39) Luz, Z.; Poupko, R.; Alexander, S. J. *J. Chem. Phys.* **1993**, 99, 7544.
- (40) Schmidt, A.; Vega, S. *J. Chem. Phys.* **1987**, 87, 6895.
- (41) Baldus, M.; Meier, B. H. *J. Magn. Reson. A* **1997**, 121, 65.
- (42) Akai, T.; Shimizu, Y. *Liq. Cryst.* **2000**, 27, 437.
- (43) Lifshitz, E.; Goldfarb, D.; Vega, S.; Luz, Z.; Zimmermann, H. *J. Am. Chem. Soc.* **1987**, 109, 7280.
- (44) Okazaki, M.; McDowell, C. A. *J. Am. Chem. Soc.* **1984**, 106, 3185.
- (45) Olson, D. A.; Veum, M.; Cady, A.; Agostino, M. V. D.; Johnson, P. M.; Nguyen, H. T.; Chien, L. C.; Huang, C. C. *Phys. Rev. E* **2001**, 63, 041702.
- (46) Brus, J.; Dybal, J.; Schmidt, P.; Kratochvíl, J.; Baldrian, J. *Macromolecules* **2003**, 33, 6448–6459.
- (47) Henrichs, P. M.; Luss, H. R.; Scaringe, R. P. *Macromolecules* **1989**, 22, 2731–2742.
- (48) Schaefer, J.; Stejskal, E.; Buchdahl, R. *Macromolecules* **1977**, 10, 384.
- (49) Henrichs, P. M.; Nicely, V. A. *Macromolecules* **1990**, 23, 3193.
- (50) Cacelli, I.; Prampolini, G. *Chem. Phys.* **2005**, 314, 283.
- (51) Gutowsky, H. S.; Saika, A. *J. Chem. Phys.* **1953**, 21, 1688.
- (52) Frydman, L.; Olivieri, A. C.; Diaz, L. E.; Valasinas, A.; Frydman, B. *J. Am. Chem. Soc.* **1988**, 110, 5651.
- (53) Kentgens, A. P. M.; Markies, B. A.; Vanderpol, J. F.; Nolte, R. J. *M. J. Am. Chem. Soc.* **1990**, 112, 8800.