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Dynamics of High-Temperature Membrane Models Composed of 5-Alkoxyisophthalic Acids As Investigated by ^2H -NMR Spectroscopy

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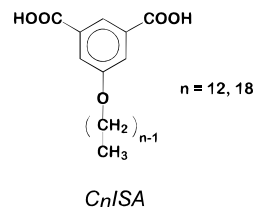
Abstract: High-temperature stable lamellar structures composed of 5-(octadecyloxy)isophthalic acid (C_{18}ISA) and 5-(dodecyloxy)isophthalic acid (C_{12}ISA), specifically deuterated in the alkyl chain ($\text{C}_{18}\text{ISA}-d_{37}$), aromatic head group ($\text{C}_{12}\text{ISA}-d_3$), or acid moieties ($\text{C}_{18}\text{ISA}-\text{COOD}$), were studied with solid-state ^2H -NMR spectroscopy. Combined with results from earlier work, it is concluded that apolar interactions between the long alkyl chains in C_{18}ISA stabilize the solid on heating until 433 K and the liquid-crystalline phase on cooling, even when contributions from the hydrogen bonds are weak. The apolar interactions between the shorter alkyl chains in C_{12}ISA are weaker, and the liquid-crystalline phase present on cooling is destabilized. The C_nISA systems thus provide promising high-temperature model membrane structures, due to the possibility of balancing the apolar interactions (alkyl chain length) and polar interactions (H-bonding of the head group).

Introduction

Structure and dynamics of biological membranes are of interest mainly because they are a vital component of the cellular architecture and serve as the “work floor” for many enzymes.¹ NMR spectroscopy of many nuclei (e.g. ^1H , ^{13}C , ^{31}P) has been applied to study the behavior of biomembranes and low-temperature model membranes.² In particular lipids have been studied with ^2H -NMR spectroscopy,³ since labeling can be performed selectively on a specific position of the lipid, and because the quadrupolar coupling in deuterium NMR is especially sensitive to molecular motions and orientations at different positions of the lipid.⁴

Various synthetic amphiphiles have been used as models for biomembranes,⁵ but most of them involve low-temperature membrane structures. The behavior of high-temperature membranes, as occur in thermophilic bacteria, is especially interesting, due to the remarkable circumstances in which they function.⁶ Also, high-temperature membrane structures are of interest as new materials.⁷ A promising new model compound

to study the structure and dynamics of high-temperature membrane structures is 5-alkoxyisophthalic acid (C_nISA), which can form both multiple hydrogen and ionic bonds (in the presence of proton acceptors) in the head group, and will have apolar (van der Waals) interactions between the variable-length tails.



Several groups have studied supramolecular aggregates based on these systems.^{8,9} It has recently been observed that C_nISAs in the range of $n = 6$ –10 form cyclic, channel-type structures of six molecules in single crystals.¹⁰ Also, single-crystal structures of C_{16}ISA and complexes of C_{12}ISA with pyrazine, pyrimidine, and ethanol have been reported.¹¹ C_{16}ISA forms a hydrogen-bonded chain of the aromatic head groups, in which the neighboring alkyl chains point alternately to opposite directions, and are interdigitated between the adjacent H-bonded chains. Also, ordered thermotropic liquid-crystalline systems can be formed, both for C_{18}ISA and its complexes with bases

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like bipyridyl and piperazine.¹² ²H-NMR spectroscopy is one of the valuable techniques used to determine whether the mobility in the high-temperature phases of the C_nISA systems is similar to that found in membranes.

In this paper, we will report variable-temperature solid-state ²H-NMR studies of C₁₈ISA, perdeuterated in the alkyl chain (C₁₈ISA-*d*₃₇) and deuterium-exchanged on the acid groups (C₁₈ISA-COOD), as well as of C₁₂ISA, deuterated on the 2, 4, and 6 positions in the aromatic ring of the head group (C₁₂ISA-*d*₃). These results will be compared to our earlier work on C₁₈ISA, deuterated in the head group,¹² and on selectively deuterated crystalline *n*-decylammonium chloride,¹³ which forms similar structures.

Experimental Section

Synthesis. The synthesis of 5-alkoxyisophthalic acids (C_nISA) from commercially available dimethyl 5-hydroxyisophthalate has been reported earlier,¹¹ and involves alkylation with different alkyl bromides and subsequent hydrolysis of the ester groups. Deuteration of the compounds has been achieved using the procedure reported by Zimmermann.¹⁴ For deuteration of the aromatic ring, we modified the procedure to a basic exchange reaction as given below. 5-Hydroxyisophthalic dimethyl ester (10 g, 0.0476 mol) was dissolved in a solution of 2.5 g of Na in 50 mL of D₂O. To this solution 2.5 g of 10% Pt/C catalyst was added and stirred in a 300-mL autoclave at 10 bar and 140 °C for 6 days. Filtration, recrystallization from water, and precipitation from a 1 N HCl solution afforded 5-hydroxy-2,4,6-trideuterioisophthalic acid as a white powder in quantitative yield.

C₁₈ISA, deuterated at the COOH positions, was obtained by repeated exchange with THF/D₂O (10:1) and evaporation. Samples for NMR spectroscopy were dried and sealed in glass tubes in vacuo.

Analysis. All samples were characterized by calorimetric measurements conducted on a Mettler DSC 30 with a heating rate of 10 K/min. Temperature-controlled polarization microscopy was performed on a Zeiss Axiophot microscope with a Linkam temperature controller TME 90. The Θ–Θ wide-angle X-ray (WAXS) data were obtained on a Siemens Kristalloflex diffractometer with a collimator width of 0.3 mm and a scintillation-based detector. The WAXS measurements were performed with the PTFE sample holder in order to prevent complexation of the acids with Cu ions of standard copper holders.

NMR Spectroscopy. ²H-NMR spectra were recorded on a Bruker CXP-300 spectrometer at a frequency of 46.07 MHz. Variable-temperature spectra were obtained with a Bruker VT-1000 unit. The two-pulse quadrupolar echo sequence¹⁵ was used with pulse lengths of 3 μs, and a delay of 20 μs between the pulses. The delay after the last pulse was adjusted so that the top of the echo coincided with a digitization point. Spectra were recorded with 1 K data points and a sweep width of 250 kHz. Some spectra were subjected to an exponential filter with LB = 1000 (C₁₈ISA-COOD and C₁₂ISA-*d*₃).

NMR Theory. The orientation-dependent frequencies in solid-state ²H-NMR spectra are described by the following equation:¹⁶

$$\nu = (\pm\delta/2)(3 \cos^2 \theta - 1 - \eta \sin^2 \theta \cos 2\varphi) \quad (1)$$

where δ is the anisotropy parameter of the quadrupolar interaction (ca. 125 kHz for C–D deuterons), η is the asymmetry parameter of the electric field gradient (EFG) tensor (usually ≈ 0 for C–D bonds), and θ and φ are the polar coordinates of the magnetic field in the principal axes system (PAS) of the C–D bond.

Since the deuterium nucleus has $I = 1$, a doublet results for each orientation with separation $\delta(3 \cos^2 \theta - 1)$, assuming an axially symmetric EFG tensor. In isotropic media, summing over all values

of θ and φ yields the well-known Pake spectrum, which contains two singularities with separation δ ($\theta = 90^\circ$), and feet with a total width of 2δ ($\theta = 0^\circ$).

Rapid motions ($\tau_c \ll \delta^{-1}$) cause a motional averaging of the EFG tensor, and averaged values $\bar{\delta}$ and $\bar{\eta}$ result, which are completely determined by the mechanism of the motion. Some formulae that are relevant for our work are collected here. Further details are given in ref 12.

For a free rotation of the C–D bond around the magnetic field on a cone with opening angle $2\theta_2$, the resulting quadrupolar coupling is:

$$\bar{\delta} = (\delta_0/2)(3 \cos^2 \theta_2 - 1) \quad (2)$$

with δ_0 being the coupling for a static C–D bond. $\bar{\eta}$ is zero for this motion.

For a 180° flip of the C–D bond on a cone with opening angle $2\theta_1$, and a simultaneous free rotation of the axis of this first cone on a second cone with opening angle $2\theta_2$ and an azimuthal angle α_2 (cf. Figure 2), the quadrupolar coupling becomes:

$$\bar{\delta} = (\delta_0/4)\{3 \cos(2\alpha_2) \sin^2 \theta_1 \sin^2 \theta_2 + (3 \cos^2 \theta_1 - 1)(3 \cos^2 \theta_2 - 1)\} \quad (3)$$

Since the molecular geometry for the deuterons in a meta position of an aromatic ring indicates a θ_1 of 60°, this relation becomes:

$$\bar{\delta} = (\delta_0/16)\{9 \cos(2\alpha_2) \sin^2 \theta_2 - (3 \cos^2 \theta_2 - 1)\} \quad (3a)$$

Also here, $\bar{\eta}$ is zero.

Results and Discussion

A. C₁₈ISA. As we have reported earlier,¹² the model compound C₁₈ISA-*d*₃ shows several transitions in DSC measurements: on second heating, endothermic peaks are detected at 330, 345, 385, and 433 K (isotropization). A recrystallization peak is seen at 368 K. On cooling, exothermic transitions appear at 418 and 325 K. Polarization microscopy revealed the presence of a monotropic liquid-crystalline phase on cooling, between 418 and 370 K.

The DSC transitions are shifted slightly for the compound with the fully deuterated alkyl chain. On second heating the first two transitions appear to coalesce at 336 K, the recrystallization occurs at 351 K, and the last two transitions are observed at 380 and 424 K. Most transitions occur 5–6 K lower compared to the nondeuterated C₁₈ISA, a phenomenon which has also been observed for polyethylene.¹⁷ On cooling, the transitions are seen at 411 and 322 K. In addition, small transitions are observed at 387 and 342 K, indicating a large structural variety in the mesophase. Compared to normal alkane behavior, these temperatures are very high.

WAXS studies have revealed that at 345 K on second heating, a transition occurs from a non-interdigitated structure to an interdigitation of the alkyl chains, which reverses itself just before isotropization.¹² The layer distances observed are consistent with a single-layered structure (see Figure 1), as present in the single-crystal structures of C_nISA ($n = 12, 14$, and 16), which are all isomorphic.¹²

Solid-state ²H-NMR studies of head group-deuterated C₁₈ISA-*d*₃ have demonstrated that the aromatic head groups become fully mobile above 385 K.¹² Thus, above 385 K, hydrogen bonding is no longer a major factor stabilizing the solid phase, which must therefore be based on alkyl–alkyl apolar interactions. This conclusion was confirmed by recording the solid-state ¹H-NMR spectrum, which showed a considerable line width up to 433 K. No macroscopic orientation was found on

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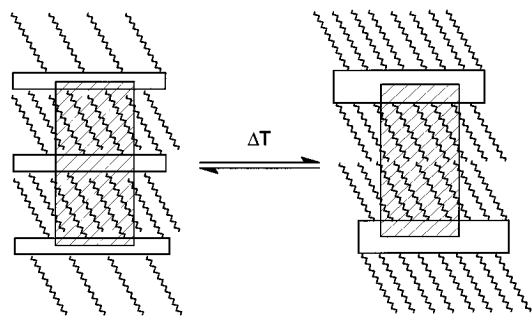


Figure 1. Schematic representation of the layered structures of C_n ISA. The aromatic head groups form a hydrogen-bonded layer, and the alkyl chains an apolar layer. The interdigitated alkyl chains on the left correspond to the low-temperature structure for $n = 12$, and the high-temperature structure for $n = 18$. The right structure with non-interdigitated alkyl chains and a reorganized hydrogen-bonded layer occurs at high temperatures for $n = 12$, and low temperatures for $n = 18$. The constant alkyl chain density is indicated by the rectangular area.

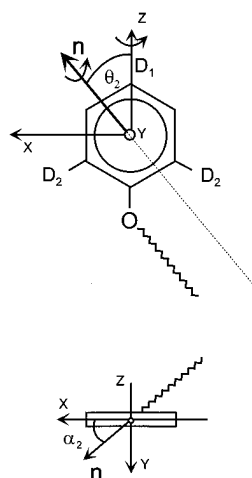


Figure 2. Schematic representation of the mechanism of motion in C_n ISA. Included is the coordinate system used for the calculation of the motionally averaged quadrupolar coupling in C_{12} ISA- d_3 . The director \mathbf{n} is located along the magnetic field, and has polar coordinates (θ_2, α_2) . The molecule rotates around the Z-axis and the director.

cooling, which prevented the determination of head group orientation. However, in combination with the results from a 1:1 complex of C_{18} ISA with piperazine,¹² it was proposed that C_{18} ISA shows a lamellar structure above 385 K, where a diffusive fast rotational motion occurs around the long molecular axis, combined with a fast phenyl ring flip (see Figure 2): The phenyl ring is tilted with respect to the director \mathbf{n} by a fixed angle θ_2 and a 180° jump occurs around the 2,5 axis of the aromatic ring, which is parallel to the C–D₁ bond. In addition to the angles reflecting the geometry of the phenyl ring the orientation of the EFG tensor associated with the C–D₂ bond must be specified by a second angle α_2 (section NMR Theory, eqs 3 and 3a), which is the azimuthal angle of the magnetic field in the principal axis system. Above 385 K for the observed coupling of the D₁ and D₂ of the C_{18} ISA the set of angles are $\theta_2 \approx 54^\circ$ and $\alpha_2 \approx 45^\circ$.

1. C_{18} ISA-COOD. In order to further check this model, the mobility of the hydrogens involved in hydrogen bonds has been probed directly by solid-state ^2H -NMR measurements on C_{18} ISA-COOD, as presented in Figure 3. At 300 K, a powder spectrum is present, characterized by an asymmetry parameter η of ca. 0.12, as is typical for deuterons in carboxylic acids.¹⁸ At higher temperatures, a small quasi-isotropic component is added, and above 390 K the complete spectrum consists of a

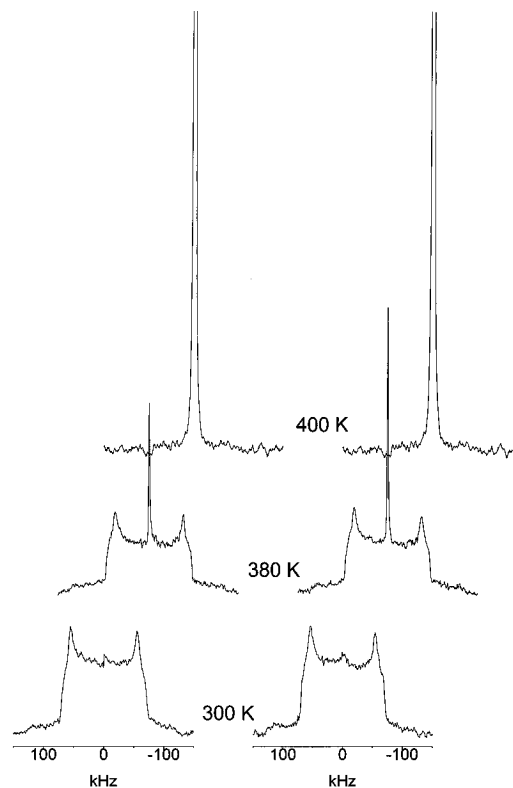


Figure 3. ^2H -NMR spectra at selected temperatures of C_{18} ISA-COOD, at heating (left) and cooling (right). The spectra are scaled to the same intensity. Therefore the peaks in the spectra at 400 K are off scale.

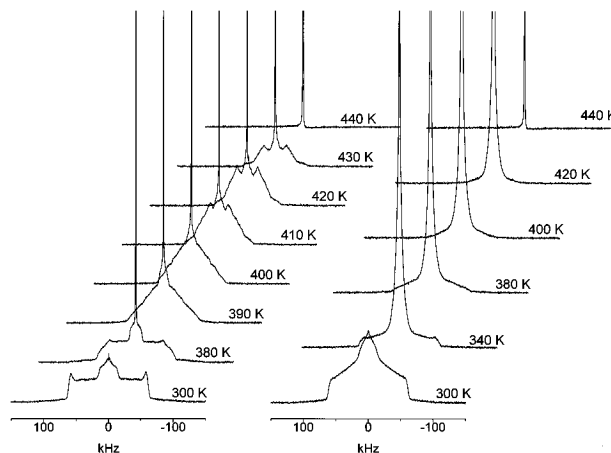


Figure 4. ^2H -NMR spectra at selected temperatures of C_{18} ISA- d_{37} , at heating (left) and cooling (right). The spectra are scaled to the same intensity. Therefore the peaks in the spectra at 340–440 K are off scale.

narrow line. On cooling, virtually the same behavior is seen in reverse. These results clearly indicate that above 390 K the hydrogen bonds are disordered and the protons move rapidly between different bonds (on a time scale smaller than 10^{-7} s). Therefore the apolar interactions must determine the high-temperature structure.

2. C_{18} ISA- d_{37} . We used the alkyl-perdeuterated system C_{18} ISA- d_{37} to obtain more insight in the orientation of the alkyl chain and its dynamic processes during heating and cooling. In the ^2H -NMR spectra of this compound, 18 subspectra always overlap. At 300 K, overlapping rigid Pake patterns and motionally averaged Pake spectra are visible (see Figure 4). The rigid Pake spectrum arises from the part of the alkyl chain close

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to the well-ordered aromatic head group, while the narrowed spectra are due to the more flexible part of the chain, further away from the head group. It should be noted that the presence of the rigid Pake spectrum indicates that crystallization of the sample has already occurred. We therefore see no changes upon heating the sample near 350 K, the recrystallization temperature. The occurrence of the recrystallization therefore depends strongly on the sample preparation (*vide infra*).

The broadest Pake components of the spectra at higher temperatures are somewhat narrowed due to small oscillatory motions in the alkyl chains. The root-mean-square (rms) value of the libration angle (β) can be calculated from the motionally averaged asymmetry parameter $\bar{\eta}$, as determined from the spectrum, via the relation $\bar{\eta} = 3\beta^2/2$, derived in Hentschel et al.¹⁹ Going from 300 to 380 K, $\bar{\eta}$ increases from 0.036 to 0.314, and concomitantly the rms angle β increases from 9° to 26°.

Upon heating, a quasi-isotropic component arises, which levels out at ca. 20% of the total integral at 360 K. Most likely, this is due to the terminal methyl group and ca. 2 adjacent methylene groups of the alkyl chain, which become more mobile (DSC transition at 336 K). This mobility is in agreement with the finding that even in the single-crystal structure of C_n ISA, the methyl group can occupy two positions.²⁰ Above 380 K, the rigid Pake spectrum is transformed into a set of overlapping narrower spectra that are not resolved. This corresponds to the solid–solid transition seen in DSC at 380 K, related to the disappearance of ordered hydrogen bonds as a dominant ordering motif. Above 410 K, all spectra assume a virtually identical shape, i.e. an overall powder spectrum with $\bar{\delta} = 49$ kHz and $\bar{\eta} = 0.34$ is present, as well as the quasi-isotropic component. At 440 K, the sample is completely isotropic. On cooling in the magnetic field, a decrease of motion occurs at 420 K, when a broad quasi-isotropic line arises, which consists of an overlapping set of motionally averaged spectra. This peak has its widest feet at ca. 60 kHz, corresponding to a value of $\bar{\delta} = 30$ kHz. This width corresponds to an order parameter for the C–D bond with respect to the director (S_{CD}) of 0.24, calculated as usual with $|S_{CD}| = \bar{\delta}/\delta_0$ (δ_0 taken as 125 kHz).²¹ Since this largest coupling is most likely due to the least mobile ether methylene group, we can calculate a segment order parameter $S_{mol} = 2|S_{CD}| = 0.48$.²¹ This high value is in agreement with the fact that no ordered hydrogen bonds are present, and that all structure in the liquid-crystalline phase must be due to alkyl–alkyl interactions. It is quite similar to the order parameters reported for methylenes near the head groups in biomembranes.^{3d} The high order of the alkyl chains is also corroborated by ¹³C CP-MAS-TOSS NMR measurements²² of C_{18} ISA, in which the chemical shift shows that the alkyl chain remains in an extended-trans conformation up to 390 K (the maximum temperature allowed by the apparatus). In contrast, we earlier found a maximum S_{mol} of only 0.28 for the ether methylene segment in a macroscopically oriented alkyl chain in related work on C_{18} ISA-*d*₃₇ complexes with piperazine,²³ where the liquid-crystalline phase is governed by hydrogen bonds. We therefore propose the existence of a macroscopically disordered but microscopically oriented alkyl chain, which is

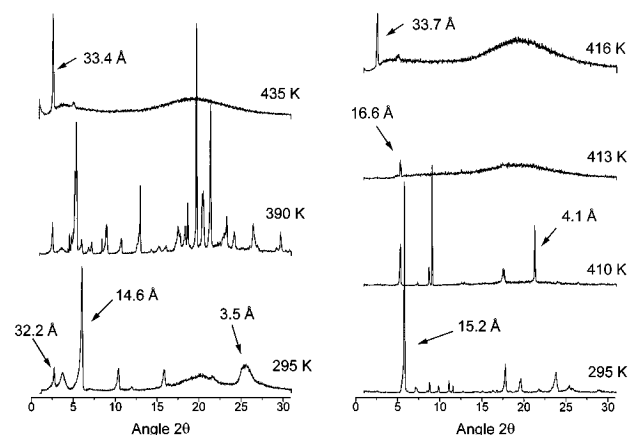


Figure 5. X-ray diffraction data for C_{12} ISA at selected temperatures during second heating (left) and second cooling (right).

oriented along the director of the liquid-crystalline phase in the case of the pure acid.

The quasi-isotropic line shows no further change until 320 K, where it becomes completely anisotropic, and forms a set of overlapping motionally averaged powder spectra. We are dealing here with an undercooled glassy situation with restricted motion or a broad distribution of correlation times. Anisotropic parts are seen already from 380 K down. Note that a tempering of the sample before the measurement might have resulted in the last spectrum as the initial one. When we reheated the sample to 350 K, the recrystallization temperature, the spectrum slowly changed to a more rigid-type spectrum over the course of 1 h. This material therefore has a characteristic time–temperature history, which should be appreciated when performing variable-temperature experiments.

The appearance of a reasonably well-defined powder spectrum for the solid on heating to 410 K, with $\bar{\delta} = 49$ kHz and $\bar{\eta} = 0.34$, is reminiscent of results on alkyl chain motions in crystalline layered structures of dodecylammonium salts reported by Jurga et al.¹³ This spectrum corresponds to an asymmetric 4-fold jump between two sets of positions that are not completely equivalent. Using the model from ref 12 for the analysis of these spectra, we conclude that the alkyl chain axis forms an angle of 15° with the bilayer normal of the lamellar solid phase, and that the four positions are populated with 23% for one set and 27% for the other set rather than 25% for 4-fold symmetry. This essentially agrees with the proposed model of fast rotation around the long molecular axis.

As was already pointed out by Jurga et al.,¹³ the spectra are very sensitive to small changes in population and angle, which explains why a strongly overlapping hump is seen between 390 and 410 K. Only at 410 K, most of the methylene groups have motions that are so similar that a seemingly well-defined spectrum emerges.

B. C_{12} ISA. In order to assess the influence of the alkyl chain length, we also studied the C_{12} ISA system. On second heating, C_{12} ISA-*d*₃ (deuterated in the 2, 4, and 6 positions of the aromatic head group) shows only an isotropization at 437 K in DSC measurements. On cooling, a small mesophase is seen between 445 and 426 K, which in polarization microscopy is identified to be liquid-crystalline in character. Apparently, the shorter alkyl chain changes the balance of stabilization between head group hydrogen bonding and apolar interactions in such a way that the liquid-crystalline behavior is destabilized.

1. X-ray Diffraction. In order to study the supramolecular organization of this compound, we performed X-ray diffraction studies of C_{12} ISA-*d*₃ on second heating and second cooling (see Figure 5). The layer spacing is given by the [100] reflection

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in the small-angle region (0° – 5°). If present, the [001] reflection in the wide-angle region (5° – 32°) shows the three-dimensional arrangement of the structure. The measurements at 295 K show after first (relatively rapid) heating and cooling a biphasic frozen-in situation with two main [100] reflections at 32.2 Å (bilayer-type ordering with non-interdigitated alkyl chains) and 14.6 Å (interdigitated chains). A [001] reflection is visible at 3.5 Å, indicating the three-dimensional spacing within the layers. The diffraction pattern also shows some other reflections, due to the heterogeneous nature of the sample. On second heating above 360 K, spontaneous recrystallization of the alkyl chains occurs, as seen from the appearance of five intense reflections in the wide-angle region. This transition was not observed in the DSC measurements, probably due to the difference in heating rate for the two techniques. Above 410 K, the alkyl chains become disordered, as evidenced by a symmetric halo. The [100] reflection corresponding with a layer distance of 33.4 Å at 435 K indicates a completely non-interdigitated arrangement. Remarkably, no [001] reflection is visible.

On cooling, a liquid-crystalline phase with disordered alkyl chains is present. Between 416 and 410 K, this liquid-crystalline phase evidently undergoes a reorganization into an interdigitated structure, characterized by a Bragg reflection at 16.6 Å. At 413 K, the correlation length is so short that virtually no reflections are seen. At 410 K, the halo of the alkyl chains has changed into a clear reflection at 4.1 Å, indicating crystallization of the alkyl chains. Below 410 K, no major changes are seen, and at 295 K a [100] reflection corresponding to 15.2 Å is observed.

2. NMR Spectroscopy. To study the molecular motions and orientation of the various phases of C_{12} ISA, we performed solid-state 2H -NMR measurements on the compound with the head group deuterated in the 2, 4, and 6 positions. As shown in Figure 6, a Pake spectrum is observed at 300 K, which goes through a T_2 -minimum at 380 K. A quasi-isotropic component is detected above 400 K, and the sample becomes completely isotropic at 460 K. On cooling in the magnetic field, a doublet arises between 435 and 420 K, corresponding to an oriented liquid-crystalline phase, as also seen in DSC. In this phase, the hydrogen bonds are present and strongly determine the mesophase structure. Below 420 K, we again see an overlapping quasi-isotropic line and a rigid Pake spectrum. Here, the alkyl–alkyl apolar interactions dominate the behavior. In the transition region, the WAXS measurements show no definite reflections, indicating a too short correlation length.

The quadrupolar coupling of 30 kHz seen in the oriented spectra can be interpreted in terms of a model we previously published¹² for head group deuterated C_{18} ISA: a 180° jump of the phenyl ring around its 2,5-axis, combined with a fast free rotation around the magnetic field axis (see Figure 2). As derived in the section NMR Theory, the quadrupolar coupling of deuteron D_1 is then described by eq 2, and that of deuterons D_2 by eq 3a. Both types of deuterons (D_1 and D_2) in C_{12} ISA show an identical coupling of 30 kHz, which occurs for an angle θ_2 between the 2,5-axis of the phenyl ring of 50° and an azimuthal angle α_2 of 33° . This orientation is very similar to that found in the complexes of C_{18} ISA with piperazine ($\theta_2 = 39$ – 42° and $\alpha_2 = 26$ – 45°).¹² This organization of the phenyl head group is very well compatible with an orientation of the

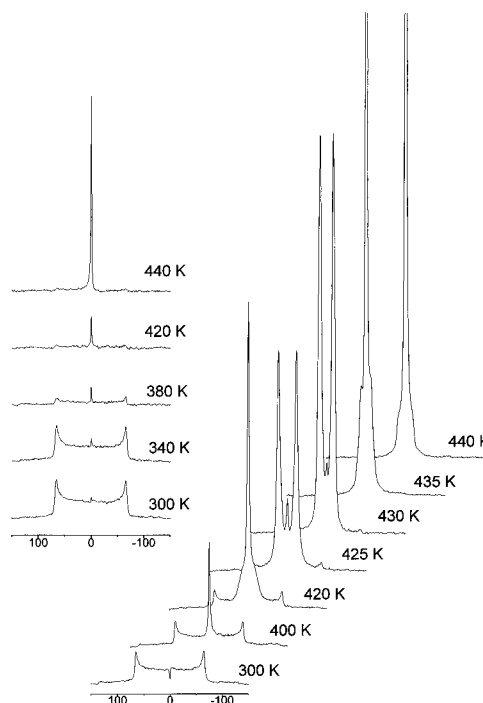


Figure 6. 2H -NMR spectra at selected temperatures of C_{12} ISA- d_3 , at heating (left) and cooling (right). The spectra are scaled to the same intensity. Therefore the peaks in the spectra at 440 and 435 K are off scale.

alkyl chains along the director, due to the ether bond angle, and therefore supports the proposed model of motion around the molecular long axis as derived for C_{18} ISA.

Conclusions

The C_n ISA systems are potential models for high-temperature membranes, since they have an adjustable balance between the apolar and polar interactions due to variation in chain length. For C_{18} ISA, a solid on heating and a liquid-crystalline phase on cooling based mainly on apolar interactions are present, while for C_{12} ISA, the apolar interactions are weaker due to the shorter alkyl chains, and a liquid-crystalline phase on cooling based on hydrogen bonds is formed. Both systems show that solid-state 2H -NMR spectroscopy is eminently suited for determining the structure and dynamics of the phases that occur, and the studies reveal that both C_n ISA compounds follow the same motional model,¹² both for the head groups and the alkyl chains. It is also confirmed that C_{12} ISA forms a lamellar structure in the single crystal lattice and in the mesophase.

As we show in related work, the mixtures of C_n ISA with various bases also lead to interesting thermotropic liquid-crystalline systems, which, however, are based on hydrogen bonding.²³ Apparently, the insertion of hydrogen bond acceptors between the head groups imposes restrictions on the alkyl chains, so that they cannot achieve an optimal packing at higher temperatures, and the apolar interactions are then weakened.

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