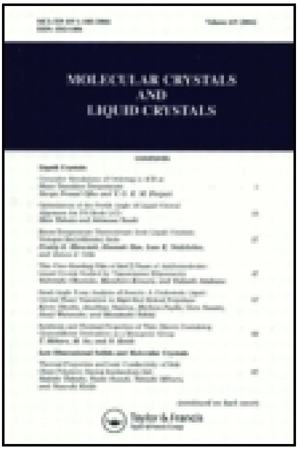

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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To cite this article: Gerhard Kögler , Hansotto Drotloff & Martin Möller (1987): Molecular Motion of Solid Cycloalkanes, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 153:1, 179-189

To link to this article: http://dx.doi.org/10.1080/00268948708074534

Mol. Cryst. Liq. Cryst., 1987, Vol. 153, pp. 179-189
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Printed in the United States of America

MOLECULAR MOTION OF SOLID CYCLOALKANES

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Abstract: Cycloalkanes with 12 to 96 methylene groups show solid-solid transitions of high cooperativity. Although the molecules are highly flexible and do not contain mesogenic units as it is typical for liquid crystals, they form a mesomorphic phase. In this mesomorphic state, fast molecular motion with correlation times smaller than 10^{-8} s is observed by ^{2}H-NMR. The molecular structure is characterized by dynamic conformational disorder. In addition slow conformational interconversion is evident below the phase transition. Thus, jump type interconversion processes which do not result in disordering occur in the fully ordered crystal. At the phase transition, the increase in the specific volume and the onset of additional molecular mobility results in the formation of a partially disordered, fluid structure.

INTRODUCTION

Flexible chain molecules, such as polytetrafluorethylene, trans-1,4,-polybutadiene, poly-p-xylylene, polydiethylsiloxane, polypropylene, the phosphazenes, n-alkanes and cycloalkanes show solid-solid transitions from an ordered crystal to a state of intermediate order /1/. The molecules form lamellae crystallites. Typically, the extended chains within the lamelae are packed hexagonally in the high temperature phase. This implies, that the extended chains adopt a cylindrical shape, irrespective of the molecular structure. For the rotator phase of n-alkanes, this hexagonal symmetry can result from fast rotation of the entire molecule around it's long axis /2/. However with high molecular weight samples, chain folding and the resulting reentry of the molecule in the lamellae crystallite prevents rotation of the entire molecule. In this case, axial symmetry around the stems in the crystallite must be the result of complex segmental molecular motions.

Adjacent stems in the lamellae crystallites of cycloalkanes have to be connected by two folds because of the ring structure. Thus the cycloalkanes represent well defined model compounds for the investigation of the solid state structure and dynamics of nonpolar flexible polymers. In the present paper, the phase behavior of partially deuterated cycloalkanes determined by differential scanning calorimetry (DSC) will be discussed in relation to the molecular motion observed by solid state ^{2}H-NMR-spectroscopy at various temperatures. Recently we reported about MAS ^{13}C-NMR spectra of cycloalkanes with 12 to 96 methylene groups /3,4/. In case of the smaller cycloalkanes, the results clearly showed the onset of conformational interconversion below the disordering transition. For all compounds we observed fast exchange of the methylene groups between the different sites of the cycles in the mesomorphic state.

EXPERIMENTAL PART

Synthesis, purification and crystallization of the partially deuterated samples cyclododecane ($C_{12}H_{24}$-d_6), cyclotetradecane ($C_{14}H_{28}$-d_2), cyclotetraeicosane ($C_{24}H_{48}$-d_8), cyclooctatetracontane ($C_{48}H_{96}$-d_{16}), cyclodoheptacontane ($C_{72}H_{144}$-d_{32}) and cyclohexanonacontane ($C_{96}H_{192}$-d_{32}) has been achieved according to the procedure described by Schill /5/ and Anet /6/.

For experimental details of the DSC investigations see ref. /7/.

^{2}H-NMR spectra were obtained on a Bruker CXP 300 spectrometer operating at 46.073 MHz. The quadrupole echo sequence was employed with 20 to 60 µs delay between 90° pulses (3 µs) and 3 to 15 s recycle time. Spectra are acquired with a 833 kHz spectra width, accumulating from 300 to 3000 scans.

RESULTS AND DISCUSSION

THERMAL ANALYSIS OF THE CYCLOALKANES

Table I summarizes the transition temperatures and transition entropies of the different cycloalkanes. Three groups can be distinguished:

1. Small cycloalkanes with 12,14 and 24 C-atoms show a thermal transition prior to melting. The transition entropy increases considerably with increasing molecular weight.

2. Intermediate size cycloalkanes e.g.$C_{48}H_{96}$ do not show a phase transition below the melting point.

3. The thermal behavior of large cycloalkanes with 72 and 96 C-atoms depends upon the crystallization conditions. Only melt crystallized samples show a solid-solid transition. In addition, the DSC experiments show a significant decrease in the entropy of fusion (see Table I). X-Ray diffraction data exhibit two different modifications: Solution crystallized samples present a monoclinic subcell, while within the melt crystallized samples, the methylene groups are arranged orthorhombically. The solid-solid transition corresponds to a change from orthogonal to hexagonal packing /8/.

TABLE I: Transition temperatures and transition entropies of partially deuterated cycloalkanes.

n	T_{tr} K	ΔS_{tr} J/K·mol	T_m K	ΔS_m J/K·mol
12	200.1	3.36	332.5	48.7
14	319.1	49.0	327.5	28.2
24	299.5	129.6	323.0	34.6
48	-	-	362.5	380.4
72[1]	-	-	381.2	640.3
72[2]	352.8	80	381.0	306.0
96[1]	-	-	391.2	810.1
96[2]	362.4	110	389.5	462.1

1) solution crystallized
2) melt crystallized

^{2}H-NMR SPECTROSCOPY

Solid state ^{2}H-NMR of powder samples give the well known "pake" spectrum with a quadrupole splitting of $\Delta\nu_{xx}$=125 kHz. Fast molecular motion with a correlation time $\tau<10^{-8}$ s leads to an averaging of the quadrupole interactions, resulting in decreased line widths. Molecular motion with correlation times $\tau>10^{-4}$s are slow within the time domain of the ^{2}H-NMR spectrum and can not be observed by a change of the resonance line. The line shape and the line width are determined by the type of the molecular motion. In the intermediate range 10^{-4}s $>\tau>$ 10^{-8} the averaging is not complete and the ^{2}H-NMR resonances depend on the type of molecular motion as well as on the rate /9/.

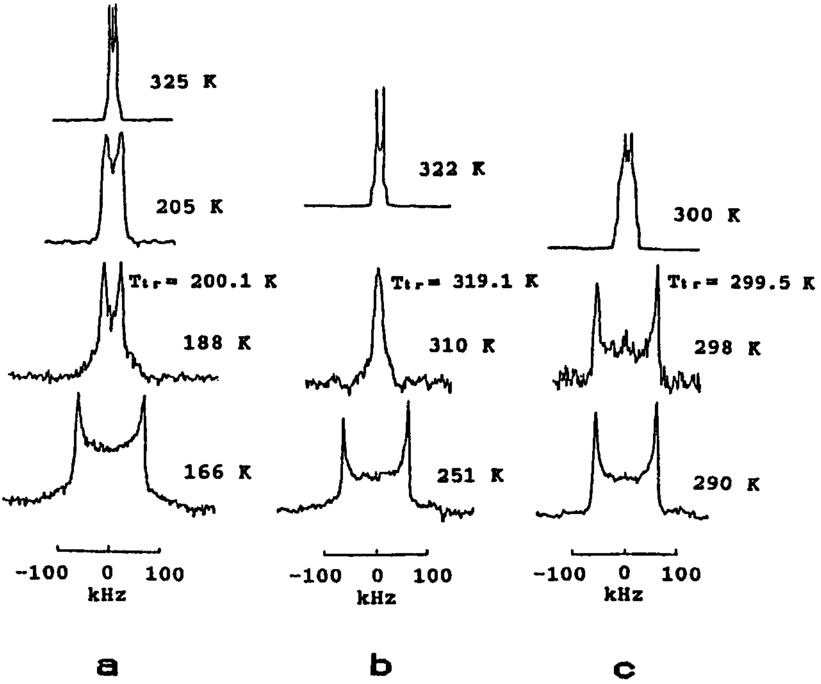

FIGURE 1. ^{2}H-NMR spectra of a: $C_{12}H_{24}$-d_6, b: $C_{14}H_{28}$-d_2 and c: $C_{24}H_{48}$-d_8 in dependence of the temperature.

Fig. 1 shows the ^{2}H-NMR-Spectra of the small cycloalkanes at different temperatures. At low temperatures, a broad "pake" spectrum with $\Delta\nu_{xx}$=125 kHz, is observed. Considerable signal narrowing already occurs below the phase transition in the spectra of cyclododecane and cyclotetradecane, only small effects can be observed below the solid-solid transition of cyclotetraeicosane. In the mesophase, cyclododecane and cyclotetradecane show the same axially symmetric ^{2}H-NMR line shape and line width of $\Delta\nu_{xx}$=16 kHz and $\Delta\nu_{zz}$=32 kHz. For cyclododecane, signal narrowing clearly occurs in two steps, as it can be shown by T_2 measurements. The first narrowing process already occurs below the solid-solid transition and results in a line width of about $\Delta\nu_{zz}$=60 kHz. Increasing the temperature further leads to the axially symmetric spectrum with $\Delta\nu_{xx}$=16 kHz.

For cyclotetraeicosane the ^{2}H-NMR resonance in the mesophase is much broader and not axially symmetric ($\Delta\nu_{xx}$=12, $\Delta\nu_{yy}$=33 and $\Delta\nu_{zz}$=45 kHz). It is a one component spectrum in the region of the fast exchange for $\tau<10^{-8}$. $C_{24}H_{48}$ forms lamellae crystallites where adjacent stems are connected by two tight folds /10/. The one component spectrum in the mesophase indicates a fast exchange between the conformationally different sites within the ring. Thus, fast translational diffusion of the methylene groups between the folds and the stems must occur.

Cyclooctatetracontane does not show a solid-solid transition. Also, the ^{2}H-NMR spectra, presented in fig. 2, do not show any significant narrowing below the melting point. The sharp resonance line in the middle of the spectrum near the melting point can be assigned to parts of the sample which are already molten, due to crystal imperfections or small impurities.

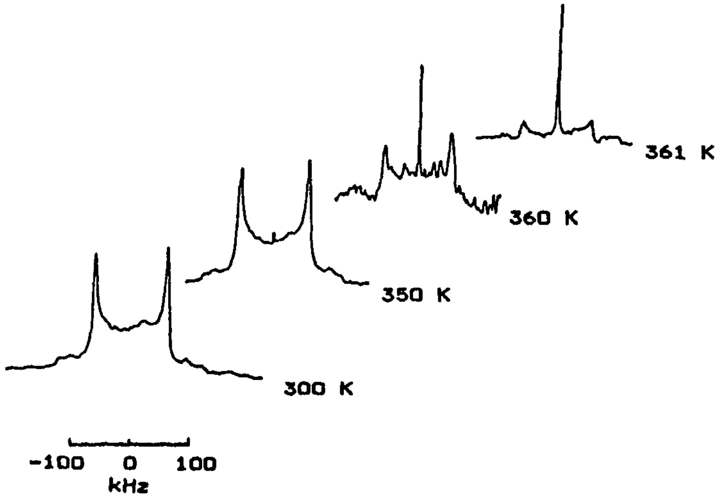

FIGURE 2: ^{2}H-NMR spectra of $C_{48}H_{96}$-d_{16} in dependence of the temperature.

In Fig. 3, the ^{2}H-NMR-Spectra of melt and solution crystallized cyclodoheptacontane (at 375 K) and cyclohexanonacontane (at 385 K) are compared. At low temperatures (not shown), the ^{2}H-NMR line width of both modifications of the two compounds is 125 kHz. At high temperatures the spectra of the two modifications are significantly different. This observation is consistent with the thermal behavior, as only the melt crystallized samples undergo a solid-solid transition.

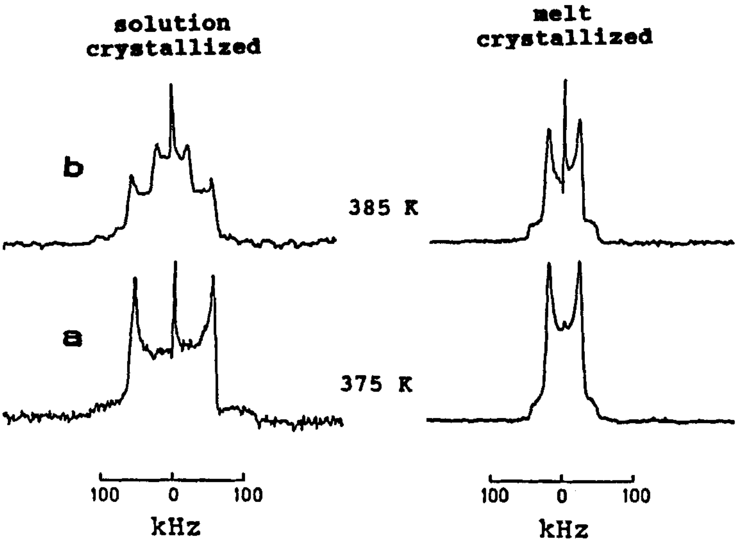

FIGURE 3. ^{2}H-NMR spectra of the solution and melt crystallized samples of a: $C_{72}H_{144}$-d_{24} at 375 K and b: $C_{96}H_{192}$-d_{32} at 385 K

Within the high temperature phase, the spectra of the melt crystallized samples of both compounds are narrowed to a nearly axially symmetric spectrum with a total line width $\Delta\nu_{zz}$ of about 100 kHz. The onset of the narrowing is already evident below the phase transition. We observed a strong dependence of the line shape from the delay time between the two 90° pulses of the quadrupole echo experiment. Thus, the molecular motion has not yet reached correlation times $\tau<10^{-8}$s, which is the condition for a fast exchange.

The signals of the solution crystallized samples are not narrowed significantly until melting. However an additional superimposed narrow signal with a width of about 100 kHz is shown at 385 K in the solution crystallized cyclohexanonacontane spectrum. This narrow portion is comparable to the signal of the hexagonal modification, observed for the melt crystallized sample at the same temperature. No similar narrowing has been observed for the solution crystallized $C_{72}H_{144}$-d_{24}. For $C_{96}H_{192}$-d_{32} the effect may be explained by polymorphism. Due to imperfections in the crystal, parts of the sample convert to the same hexagonal form as observed for the melt crystallized sample.

As a result, four groups of cycloalkanes can be distinguished based on their dynamic behavior:

1. Cyclododecane and cyclotetradecane show the same ^{2}H-NMR line shape and line width in the mesophase, indicating the same type of motion in the mesophase. For both compounds, the narrowing of the signal is already evident below the solid-solid transition. The observations are in agreement with corresponding MAS ^{13}C-NMR experiments /4/. For $C_{14}H_{28}$ we could show the onset of a pseudorotation type motion below the melting point and the onset of an additional jump like rotation around the axis parallel to the ring plane at the transition to the mesophase. The superposition of the two motional processes explain the strong narrowing in two steps to an axially symmetric spectrum.

2. Cyclotetraeicosane shows a much broader resonance line within the mesophase whose shape is not axially symmetric. In spite of the fact, that the molecules form lamellae crystals, the spectrum in the mesophase is a one component-spectrum in the

fast exchange region, indicating a fast diffusion of the methylene groups from the fold to the stems and reverse.

3. Cyclooctatetradecane does not show motional narrowing of the ^{2}H-NMR spectra below the melting point. Thus the structure seems to be rigid.

4. Cyclodoheptacontane and cyclohexanonacontane give mesophases only if crystallized from the melt. Motional narrowing of the resonance line is observed in the mesophase. Line shape and line width are identical, hence both compounds undergo the same type of molecular motion. Consistent with MAS ^{13}C-NMR data, the line narrowing can be explained by dynamically disordered conformational state. Within the restriction to a cylindrical space, the molecular segments undergo conformational interconversion processes with rates of about 10^{-6}-10^{-7} Hz. As a result of the fluid structure, the intermolecular friction is low or neglegible. Thus translational diffusion processes of the methylene groups through the lamellae becomes possible. The observation appears of great importance for the extended chain crystals. The observed mass transport through the lamellae could easily explain the not yet fully understood high rates of the lamellae thickening within the hexagonal phase of polyethylene /11/.

ACKNOWLEDGEMENT

The authors gratefully thank Prof. B. Wunderlich for valuable stimulating discussions, A. Hasenhindl for technical assistance, and C. Pugh for editorial help. This research was supported by the Deutsche Forschungs Gemeinschaft within the SFB 60.

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