Chain folding and mesomorphic states of cycloalkanes

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(Received 4 August 1986; revised 12 November 1986; accepted 26 November 1986)

Several cyclic alkanes melt in two steps. Thermograms from differential scanning calorimetry are discussed with respect to the onset of molecular motion and the resulting degree of disorder. An attempt is made to correlate the thermal behaviour with information obtained from high-resolution solid-state nuclear magnetic resonance on molecular structure and motion. The cycloalkanes are classified into three groups with respect to their phase transition behaviour.

(Keywords: Cycloalkanes; chain folding; crystal structure; dynamic disorder; polyethylene; differential scanning calorimetry)

INTRODUCTION

Questions concerning the lamellar surface, chain folding and the crystallization and melting process of polyethylene have been discussed intensively and controversially during the last 20 years[1]. Recently, normal alkanes and cycloalkanes have been rediscovered as well defined model systems for the investigation of the crystallization of polyethylene[2-8]. Progress in this field is basically due to two reasons: the development of new synthetic routes for the preparation of monodisperse, large n-alkanes and cycloalkanes, and the availability of new spectroscopic experiments which can give detailed insight into the molecular dynamics.

Above a certain chain length, linear alkanes may form extended chain or chain-folded lamellar crystals depending on the crystallization conditions[2,3]. Owing to their cyclic structure, cycloalkanes are bound to form lamellar crystallites in which the adjacent stems are connected by tight folds. Investigation and comparison of cycloalkanes of different chain lengths can give detailed information about the formation, structure and thermodynamics of crystals in which tight folds form the lamellar interface.

In the present paper, we discuss n.m.r. and calorimetric data on a series of cycloalkanes, $(CH_2)_n$, with $n=12$, 13, 14, 15, 16, 24, 36, 48, 72 and 96. It has been recently reported[9] that some of these compounds show at least one premelting transition. Three groups have been distinguished within this homologous series: (i) for $12 \leqslant n \leqslant 24$ all compounds have a solid–solid transition into a mesomorphic phase well below the melting transition; (ii) for $24 < n \leqslant 48$ no such transition could be detected; and (iii) for $n > 48$ the phase behaviour strongly depends on the crystallization conditions. We have explained these results as the onset of different types of dynamic disorder corresponding to differences in the crystal structure.

Spectroscopic methods can give direct evidence of the molecular structure and dynamics. Solid-state n.m.r. has proven to be a powerful tool in the investigation of molecular dynamics of solids. High-resolution n.m.r. is well established as a means to evaluate molecular structures. Through the use of high-power decoupling and magic angle spinning (MAS) techniques, it is possible to obtain highly resolved spectra of solids[10]. This enables us to correlate the molecular structure to the motional state[11].

EXPERIMENTAL

For d.s.c. measurements a Perkin–Elmer model DSC-7 was used. Experiments were performed at three heating rates and extrapolated to zero to give the equilibrium transition temperatures. The instrument was calibrated with high-purity cyclohexane, gallium and indium standards. Temperature accuracy was better than ± 0.3 K. Transition enthalpies as determined by numerical integration of the transition peaks show a variation of less than 5%. The transition entropies were calculated according to the equilibrium condition $\Delta H/T = \Delta S$.

High-resolution solid-state ^{13}C n.m.r. spectra were recorded at 75.47 MHz with a Bruker CXP 300 spectrometer. A Bruker double-bearing MAS probe which was slightly modified for variable-temperature experiments was used. For the rotors, Al_2O_3 cylinders (o.d. 7 mm) with endcaps made from Macor (Corning Glass) were used. Line narrowing was achieved by high-power decoupling and magic angle sample spinning. Spinning speeds were set to 2200–3000 Hz. Two different pulse sequences were used to generate the spectra. For the spectra of the rigid molecules in the low-temperature state the usual spin-lock cross-polarization sequence was applied[12]. A 3 μs 90° pulse was employed followed by a mixing time of 1–5 ms and an acquisition time of 30 to 150 ms. The delay time between the pulse experiments was 10–100 s. The spectra of the mobile molecules in the melt and in the mesomorphic state were determined without cross-polarization (CP). A simple 90° carbon

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0032-3861/87/071200-07$03.00

pulse was applied in combination with high-power proton decoupling. Delay times long enough to allow complete relaxation were put in between the pulses. The ^{13}C signals arising from undisturbed Boltzmann equilibrium populations have intensities which represent the relative amounts of the carbons quantitatively. For the CP spectra true relative intensities are obtained when the cross-polarization times T_{CH} are short enough to allow the ^{13}C nuclei to equilibrate with the proton system and the shortest proton rotating frame relaxation time is long compared to the mixing time[13]. These conditions are well satisfied for the rigid molecules at low temperatures so the signal intensities of the low-temperature spectra represent the relative populations of the different carbon sites. Chemical shifts were determined by comparison with the methylene signal of crystalline linear polyethylene which was set to 32.81 ppm relative to TMS[14] and considered to be temperature-independent. Temperature measurements were done by means of a thermocouple directly beside the spinning rotor. These are less accurate than the d.s.c. data (±3 K). The temperature data in the figures of the spectra give the original readings. Because of the inaccuracy they do not always agree with the d.s.c. data. However, in all cases the indicated state (mesomorphic or melt) could be determined independently by T_1 relaxation data.

Cycloalkanes were prepared according to refs. 2, 15 and 16.

RESULTS AND DISCUSSION

Table 1 summarizes the transition and melting temperatures, as well as the corresponding entropies of fusion per methylene unit for the different cycloalkanes. Most of the cycloalkanes show a first-order-like solid–solid transition with considerable values for ΔH. Thus, the transition from the fully ordered crystal to the melt occurs in two steps. Above the solid–solid transition all the compounds discussed in this paper are optically anisotropic. However, under a shear stress the materials show plastic flow.

Within the concepts of statistical mechanics, an increase in entropy can be correlated with increased disorder in the system. For the fusion of a molecular crystal, disordering can be broken up into three terms: loss of positional order, loss of orientational order and loss of conformational order[17]. In a first approach, the molar loss of positional and orientational order should be approximately equal regardless of the size of the molecules*. Also, the loss of conformational order per methylene unit should be constant within the limit of large molecular weights. *Figure 1* shows a plot of the sum of the transition entropies per methylene unit, $\Delta S_f/n$, against the number n of methylene units. In a good approach this gives a measure for the total change of order between the fully ordered crystalline state and the disordered melt. The plot shows an increase in the total entropy of fusion with chain length until a limiting value of about 8.0 J K^{-1} mol^{-1} CH_2 is reached for $n \sim 48$. This is in agreement with the increasing conformational freedom. For small molecules the cyclic structure leads to severe restrictions on rotational isomerism, which corresponds to a reduced entropy of fusion. For linear alkanes the value of $\Delta S_f/n$ is nearly constant, 10.4 J K^{-1} mol^{-1} CH_2 for even- and 11.1 J K^{-1} mol^{-1} CH_2 for odd-numbered n-alkanes. The best estimate[1] of the entropy of fusion for polyethylene is 9.91 J K^{-1} mol^{-1} CH_2. Hence, there is still a difference of 2–3 J K^{-1} mol^{-1} CH_2 in the total entropy of fusion of large cyclic and linear molecules. This discrepancy cannot be explained easily by endgroup effects or conformational restrictions due to the cyclic structure. As will be discussed below, we explain this difference mainly by the fact that the tight folds in the crystals of the cyclic molecules disturb the packing of the methylene groups within the lamellae.

In the following discussion we will compare thermal and spectroscopic data in detail.

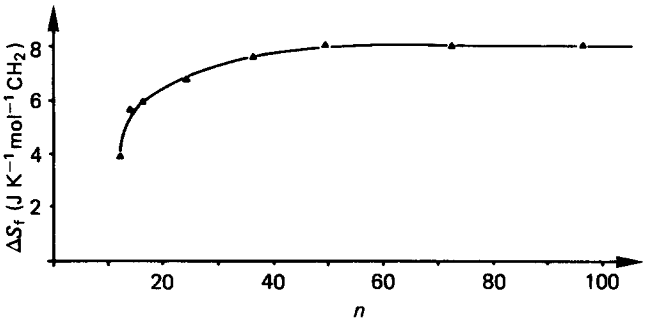

Figure 1 Plot of the sum of the transition entropies per methylene group, $\Delta S_f = \Delta S_{tr} + \Delta S_m$, against the number n of methylene groups for different cycloalkanes C_nH_{2n}

Table 1 Transition temperatures and transition entropies per methylene unit for different cycloalkanes, C_nH_{2n}

n	T_{tr} (K)	ΔS_{tr} (J K^{-1} mol^{-1} CH_2)	T_m (K)	ΔS_m (J K^{-1} mol^{-1} CH_2)	ΔS_f[a] (J K^{-1} mol^{-1} CH_2)	$\frac{\Delta S_{tr}}{\Delta S_f}$	$\frac{(\Delta S_m)_{mc}}{(\Delta S_m)_{sc}}$
12	199.0	0.23	333.8	3.7	3.93	0.06	–
13	285.6	0.25	297.6	1.93	2.18	0.11	–
14	321.9	3.65	329.3	2.01	5.66	0.64	–
15	210.1	2.67	336.6	1.68	4.35	0.61	–
16	268.9	4.55	333.7	1.42	5.97	0.76	–
24	297.0	5.32	322.0	1.42	6.74	0.79	–
36	–	–	343.0	7.60	7.60	–	–
48	–	–	362.4	7.83	7.83	–	–
48[b]	–	–	362.1	6.89	6.89	–	0.88
72	–	–	380.2	8.05	8.05	–	–
72[b]	320.1	0.20	378.1	4.60	4.60	0.04	0.57
96	–	–	389.1	8.03	8.03	–	–
96[b]	363.9	1.05	387.1	4.46	5.51	0.19	0.55

[a] $\Delta S_f = \Delta S_{tr} + \Delta S_m$
[b] Melt-crystallized samples

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* See note added in proof at end of paper

Small cycloalkanes, $C_{12}H_{24}$, $C_{14}H_{28}$ and $C_{24}H_{48}$

Figures 2–4 present the MAS ^{13}C n.m.r. spectra of cyclododecane, cyclotetradecane and cyclotetraeicosane at different temperatures. The assignment of the MAS n.m.r. spectra, as shown in the figures and in *Table 2*, was made according to ref. 11 and is given with respect to the different diastereotopic positions within the low-temperature conformation as determined by X-ray diffraction[18–20]. The drawings of the molecules give the molecular conformations determined by Dunitz *et al.*[18] for $C_{12}H_{24}$ and by Groth[19,20] for $C_{14}H_{28}$ and $C_{24}H_{48}$. For the other cycloalkanes, the molecular conformations of the monoclinic modifications are given correspondingly with the *ggagg* fold. Generally, the *ggagg* fold along the *b*-axis is well established for the monoclinic modification of the cycloalkanes[5,21].

The value of ΔS per CH_2 for the solid–solid transition, as shown in *Table 1*, increases considerably with molecular weight and reaches about 80% of the total entropy of fusion for cyclotetraeicosane. Since the increase in entropy reflects a loss of order, there must be considerable disorder in the mesomorphic high-temperature phases. The n.m.r. spectra confirm this conclusion at the molecular level. Although at low temperatures all n.m.r. spectra show several well resolved lines, in each case only one sharp resonance was observed for the mesomorphic phase. At low temperatures the conformations of the cyclic molecules are frozen with respect to the n.m.r. timescale. Different diastereotopic positions within the molecules result in resonances at different chemical shifts. At high temperatures all carbons are magnetically equivalent due to a fast exchange between the different conformational sites.

In general, an increasing fraction of *gauche* conformations results in a considerable upfield shift within the fast exchange regime[9]. As shown in *Table 3*, the upfield shift of the cyclododecane and the cyclotetradecane resonance at the melt transition is very small. The chemical shift of the mesophase signal is in good agreement with the weighted average of the low-temperature phase signals. It can be concluded that the cyclododecane and the cyclotetradecane molecules have primarily the same conformations in the melt, in the mesophase and in the crystal. This is in agreement with semiquantitative force field calculations of these molecules[22], which indicate that at room temperature only 0.06% of cyclododecane and only 1.3% of cyclotetradecane will assume a conformation different from the most stable one.

The situation is different for cyclotetraeicosane. The chemical shift average of the low-temperature spectrum differs by −0.5 ppm compared to the mesophase signal. The melt signal is shifted further upfield by 0.7 ppm. Owing to the larger size of the ring, the molecules can assume different conformations without significant intramolecular strain. Conformational disordering may occur in two steps: partially at the solid–solid transition and finally at the melt transition, where the Boltzmann equilibrium of the different molecular conformations is reached. The upfield shift of the single n.m.r. signal at the transition from the meso state to the melt indicates an increase in the amount of *gauche* conformations. The 1.3 ppm downfield shift for the average of the low-temperature state signals cf. the meso state can be explained by the changing crystal lattice[14].

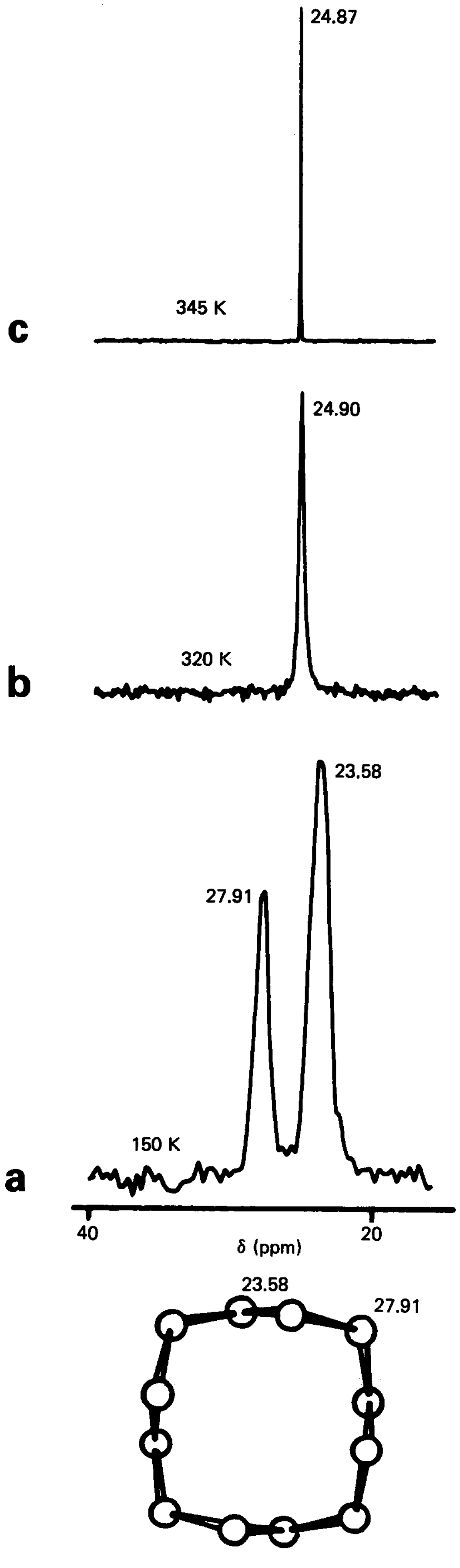

Figure 2 MAS ^{13}C n.m.r. spectra of cyclododecane $C_{12}H_{24}$ (a) in the crystalline phase, (b) in the mesomorphic phase and (c) in the melt. The drawing gives the molecular conformation as determined at −150°C by X-ray diffraction[18]

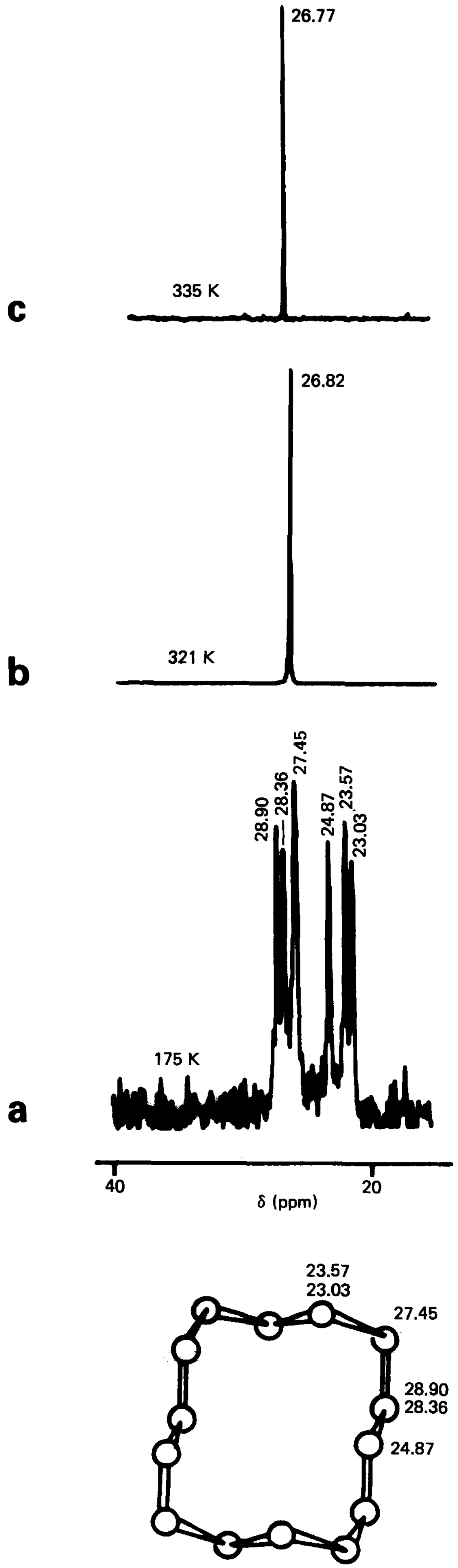

Figure 3 MAS ^{13}C n.m.r. spectra of cyclotetradecane $C_{14}H_{28}$ (a) in the crystalline phase, (b) in the mesomorphic phase and (c) in the melt. The drawing gives the molecular conformation as determined at −157°C by X-ray diffraction[19]

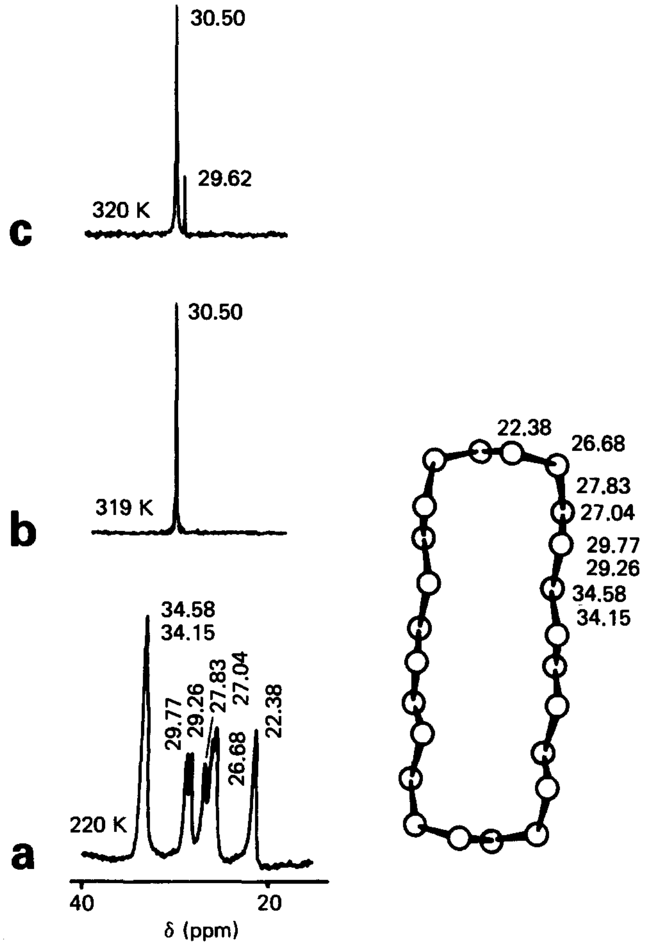

Figure 4 MAS ^{13}C n.m.r. spectra of cyclotetraeicosane $C_{24}H_{48}$ (a) in the crystalline phase, (b) in the mesomorphic phase and (c) at the melt transition, where the sample is partially molten and the upfield signal at 29.62 ppm is due to the melt, while the 30.5 ppm signal represents the methylene carbons in the meso phase. The drawing gives the molecular conformation as determined at −165°C by X-ray diffraction[20]. (Check experimental part for discrepancies in the temperature readings relative to d.s.c. data)

Similar downfield shifts have been observed for n-alkanes at the transition from the fully ordered crystal to the hexagonal 'rotator phase'[6].

Medium cycloalkanes, $C_{36}H_{72}$ and $C_{48}H_{96}$

No solid–solid transition could be observed for cyclohexatriacontane and cyclooctatetracontane by differential scanning calorimetry. Correspondingly, the n.m.r. spectra did not give any indication of motional disorder in the solid state as observed for the smaller cycloalkanes, as shown in *Figure 5* for $C_{36}H_{72}$. The signals broaden and superimpose with increasing temperature. In contrast to the smaller molecules, no narrowing of the signals was observed below the melt transition.

Large cycloalkanes, $C_{72}H_{144}$ and $C_{96}H_{192}$

If the ring size exceeds a certain limit, the thermal behaviour differs for solution- and melt-crystallized samples. No solid–solid transition could be observed for the solution-crystallized samples. When the samples were

Table 2 MAS ^{13}C n.m.r. chemical shifts of cycloalkanes (in ppm vs. TMS)

	aa.aa	*aa.ag*	*gg.aa*	*ag.ga*	*ga.ag*	*ga.gg*
$C_{12}H_{24}$	–	–	–	27.91	–	23.58
$C_{14}H_{28}$	–	–	28.90 28.76	27.45	24.87	23.57 23.03
$C_{24}H_{48}$	34.58 34.15	29.76 29.26	27.83 27.04	26.68	–	22.38
$C_{36}H_{72}$	34.65 34.36	29.30	27.82 27.41	26.59	–	22.81 22.06
$C_{96}H_{192}{}^a$	34.70	29.50	28.00 27.60	26.80	–	23.10 22.40
$C_{96}H_{192}{}^b$	32.50					

Superscripts refer to solution-crystallized (*a*) and melt-crystallized (*b*) samples

Table 3 Comparison of MAS ^{13}C n.m.r. chemical shifts of small cycloalkanes in the mesophase and in the melt (in ppm vs. TMS)

Shift^a	$C_{12}H_{24}$	$C_{14}H_{28}$	$C_{24}H_{48}$
δ_{CR}	25.02	26.23	29.2
δ_{MP}	24.90	26.37	29.7
$\delta_{CR}-\delta_{MP}$	0.12	−0.14	0.5
δ_M	24.87	26.34	29.0
$\delta_{MP}-\delta_M$	0.03	0.03	0.70

^{a}Crystalline phase (CR), mesophase (MP) and melt (M)

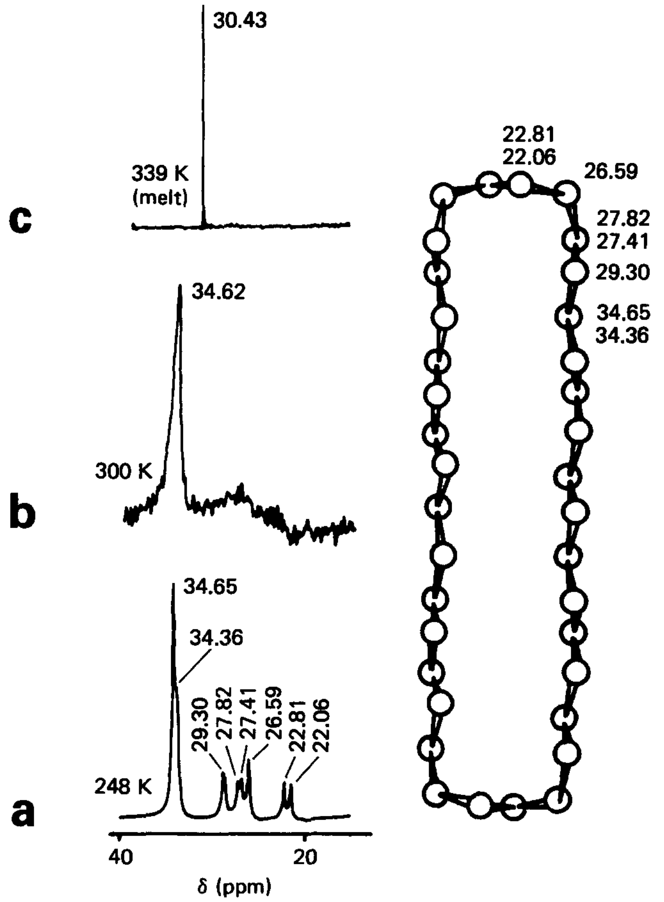

Figure 5 Temperature-dependent MAS ^{13}C n.m.r. spectra of cyclohexatriacontane $C_{36}H_{72}$

melt-crystallized, the d.s.c. experiments showed (i) a solid–solid transition and (ii) a significant decrease in the enthalpy of fusion for both compounds. X-ray diffraction data show an orthorhombic subcell for the packing of the methylene groups when the samples are melt-crystallized, while a monoclinic subcell is found for the solution-crystallized samples. The solid–solid transition can be correlated with a change to a hexagonal structure[23,24]. Only in the case of $C_{72}H_{144}$ did careful and long-time annealing of the melt-crystallized samples result in a partial recovery of the melt enthalpy of the solution-grown crystals.

Temperature-dependent n.m.r. spectra of $C_{96}H_{192}$ are shown in *Figure 6*. The room-temperature spectrum of the solution-crystallized sample shows the same signals as the spectra of the shorter cycloalkanes. This indicates a similar molecular conformation. Two parallel all-*trans* arranged stems are connected by tight *ggagg* folds. The methylene groups are packed within a monoclinic subcell[23]. Compared to the solution-crystallized sample the room-temperature signal of the melt-crystallized

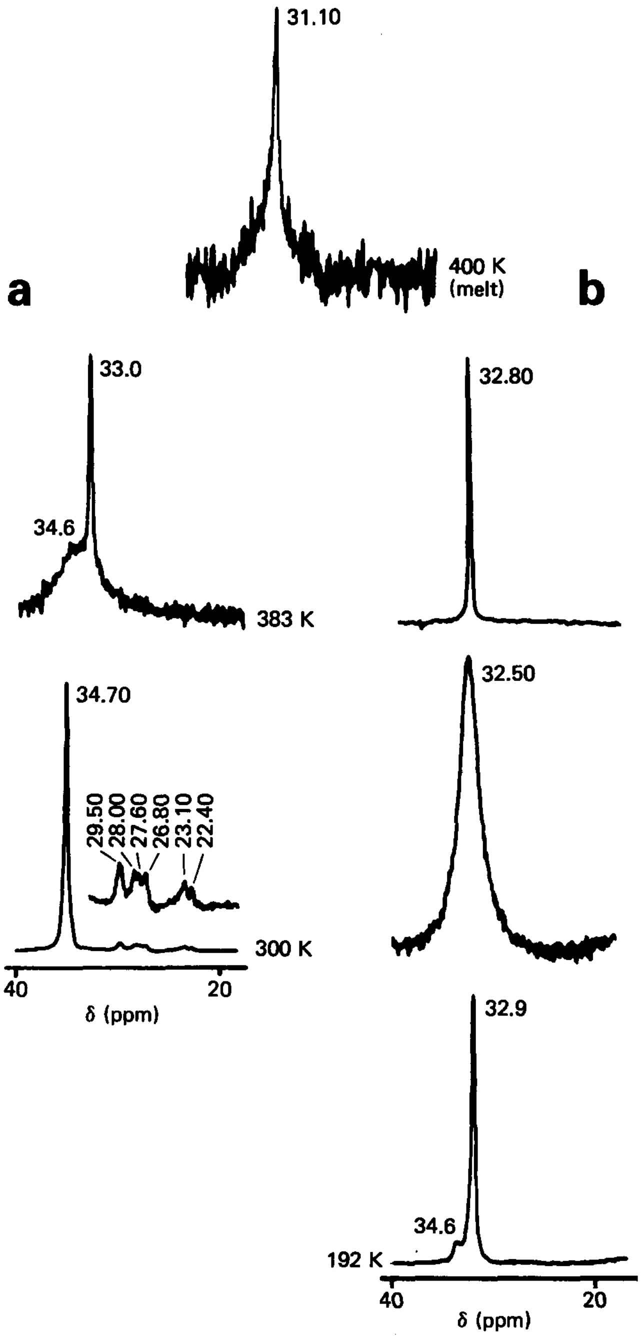

Figure 6 Temperature-dependent MAS ^{13}C n.m.r. spectra of cyclohexanonacontane $C_{96}H_{192}$: (a) solution-crystallized and (b) melt-crystallized samples

sample is shifted upfield by 1.8 ppm and is relatively broad. No discrete signals for the carbons within the fold could be observed. The upfield shift is due to the different packing of the methylene groups[19,20].

At temperatures near the melting point, sharp signals with short T_1 carbon relaxation times, typical for liquids, were observed for the melt- as well as for the solution-crystallized samples. Carbons within the folds did not give rise to discrete signals. However, for the solution-crystallized samples the high-temperature spectra always showed a signal of significant intensity at the position of the 'monoclinic' signal.

The spectra of the solution-crystallized sample at temperatures below 360 K are identical to the room-temperature spectrum. In contrast, the signal of the melt-crystallized sample broadens below 360 K and the linewidth reaches a value of $\delta_{1/2} = 190$ Hz at room temperature. At lower temperatures the linewidth decreases again until finally at 192 K the same linewidth is observed as for the solution-crystallized sample. The small downfield-shifted signal at 34.6 ppm in the 192 K spectrum is due to small amounts of monoclinic-packed methylene groups. The T_1 carbon relaxation time of the low-temperature spectrum appears to be at least several thousand seconds, comparable to crystalline polyethylene.

The n.m.r. spectra show clear evidence for molecular mobility at temperatures slightly below the melting transition. In the case of the melt-crystallized sample the broad 300 K resonance also indicates the presence of partial disorder at room temperature.

CONCLUSIONS

For the small cycloalkanes, conformational disorder can be neglected as a factor contributing to the transition entropy. Thus the solid–solid transition may be basically explained by the onset of rotational motions which result in orientational disorder. In the case of cyclotetradecane this is in agreement with the fact that the entropy for the solid–solid transition is of the same magnitude as observed for plastic crystals, e.g. cyclohexanol ($\Delta S_{tr} = 33.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$) and *cis*-1,4-dimethylcyclohexane ($\Delta S_{tr} = 48\ \mathrm{J\ K^{-1}\ mol^{-1}}$). The rather small entropy of transition of cyclododecane and cyclotridecane may be due to either little cooperativity for the onset of molecular motion or to less disorder in the intermediate phase. The latter explanation is in agreement with the relatively large melting entropy of cyclododecane and the high molecular symmetry. In the case of cyclotetraeicosane the relatively large entropy difference, determined for the solid–solid transition, reflects the onset of conformational disorder.

With increasing ring size, the formation of lamellar-type crystals, in which pairs of adjacent stems are connected by tight folds, is essential for the arrangement of the molecules within a crystal lattice[5]. Conformational interconversions and rotational motions are hindered by this restriction to a rectangular shape conformation. Consequently no dynamically disordered mesomorphic phases could be observed for the medium-sized rings.

The different melting behaviour of the long-chain alkanes might be explained by the incompatibility of the optimal lateral packing of the stems and the minimum energy arrangement of the carbons within the folds. The formation of a low strain fold is the most important factor for the crystalline packing of small molecules. Long, linear methylene chains tend to crystallize with an orthorhombic subcell to minimize the lateral packing energy of the chains. Folds with a minimum number of closure atoms can be fairly perfectly arranged in the diamond lattice only if the subcell for the stems is monoclinic[5,21]. The diamond structure is not appropriate for a fold connecting two perpendicular planar zig-zag chains. This implies a fold configuration with high strain energy for the case where the methylene groups of the stems are packed in an orthorhombic subcell. Hence, the folds favour the monoclinic structure while the stems favour the orthorhombic packing.

The size of the cycloalkanes with 72 and 96 carbon atoms is apparently such that neither of the two possible subcell structures is clearly favoured. For kinetic reasons different crystallization conditions lead to different modifications. The equilibrium state is clearly the monoclinic modification, which is formed by slow crystallization from dilute solution, while rapid crystallization, especially from the melt, results in the orthorhombic modification.

Thus, the tight adjacent fold may be regarded as a defect of rather high energy within the orthorhombic crystals of the polymethylene chains. As a consequence the packing of the methylene groups adjacent to the strained folds is severely disturbed. The cycloalkanes packed with a monoclinic subcell are also not free of strain. X-ray diffraction[5,18] as well as differences in the MAS ^{13}C n.m.r. spectra of the crystalline phase clearly show some distortion of the dihedral angles. This indicates that the tight adjacent fold can also be regarded as a defect in the monoclinic subcell. However, the defect is of higher energy in the case of the orthorhombic subcell than in the case of the monoclinic subcell.

Looking at the fold as a lattice defect, we can explain that for $(CH_2)_{72}$ and $(CH_2)_{96}$ the entropy of fusion of the monoclinic modification is about $2\ \mathrm{J\ K^{-1}\ mol^{-1}\ CH_2}$ smaller than the entropy of fusion of linear alkanes or polyethylene, while that of the orthorhombic modification is about $6\ \mathrm{J\ K^{-1}\ mol^{-1}\ CH_2}$ smaller. For both modifications the packing of the methylene groups adjacent to and in the folds is not perfect. The disorder is considerably higher for the orthorhombically packed molecules. Owing to the higher strain the orthorhombic form changes completely to a dynamically disordered high-temperature phase, while only parts of the chains of the monoclinic modification become disordered. The 'monoclinic' resonance in the high-temperature MAS ^{13}C n.m.r. spectra of the solution-crystallized cyclohexanonacontane and cyclodoheptacontane thus originates from the inner part of the lamellae which is still nearly perfectly packed, although the outer part is already dynamically disordered.

Two spectroscopic studies on long-chain alkanes reported before have to be mentioned explicitly within the context of this work. Grossmann *et al.*[7] published i.r. data on a similar series of cycloalkanes. In agreement with the data reported in this paper the i.r. spectra show different types of folds for the melt- and the solution-crystallized $C_{72}H_{144}$ and $C_{96}H_{192}$ samples. Owing to the different timescale of the i.r. experiments, dynamic disorder as observed in the n.m.r. spectra could not be detected. Moreover, no distinctive data on the complex phase behaviour and the corresponding temperature dependence of the i.r. spectra were reported. For the chain length dependence of the intensities of the i.r. bands assigned to the folds the authors report significant differences for the larger and the small cycloalkanes. This might be explained if one considers that the smaller cycloalkanes are at room temperature in the mesomorphic state, while the larger molecules still give fully ordered crystals. More recently a comparative MAS ^{13}C n.m.r. study on polyethylene and a cyclic alkane, $C_{64}H_{128}$, has been reported[8]. Although the resolution of the cycloalkane spectra is poor, they clearly show signals of the *ggagg* fold for the monoclinic modification. The authors compare these signals with the spectra of melt- and solution-crystallized polyethylenes and give conclusions concerning the adjacent re-entry fold in polyethylene. Our experiments on the orthorhombic modifications of the long-chain cycloalkanes gave no discrete signals for the tight conformation, although a tight fold should certainly exist in this case. With regard to the differences of the tight folds between the antiparallel stems of the orthorhombic modification and the tight folds which connect the parallel stems of the monoclinic cycloalkanes we discussed in this paper, such a comparison may lead to incorrect results.

We believe that the picture of a highly strained adjacent fold for an orthorhombically packed polymethylene chain and the corresponding dynamic disorder is of direct relevance for polyethylene crystals. However, it remains to be determined to what extent the tight adjacent 'orthorhombic' folds as found for the cycloalkanes is comparable to the folds within a polyethylene crystal. In a following paper we shall report i.r. data which give evidence that polyethylene single crystals as crystallized from solution contain primarily the same type of fold as orthorhombic cycloalkanes.

ACKNOWLEDGEMENT

This research was supported by the Deutsche Forschungs-Gemeinschaft within the SFB 60.

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NOTE ADDED IN PROOF

It can be shown that the ΔS contribution from the change in orientational order depends on the symmetry of the molecular structure. Even within the series of the cycloalkanes the symmetry of the crystal conformation changes with the molecular weight. So in certain cases the contribution of the orientational disorder can differ with the size of the molecules. This is observed in the case of $C_{12}H_{24}$ and $C_{14}H_{28}$. (H. Drotloff, H. Rotter, D. Emeis and M. Möller, manuscript submitted to *J. Am. Chem. Soc.*)