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ON THE PHASE TRANSITIONS OF CYCLOALKANES

Hansotto DROTLOFF and Martin MÖLLER

Institut für Makromolekulare Chemie der Universität Freiburg,
Hermann-Staudinger-Haus, Stefan-Meier-Straße 31,
D-7800 Freiburg, Federal Republic of Germany

SUMMARY

Several cyclic alkanes melt in two steps. Thermograms from differential scanning calorimetry (DSC) are discussed with respect to the onset of molecular motion and the resulting degree of disorder. The cycloalkanes are clasified in three groups according to their phase transition behavior.

INTRODUCTION

The melting process of some nonpolar flexible chain molecules, low molecular weight compounds as well as high polymers, is rather complex (1). Thus, cycloalkanes can show at least one premelting transition, which reflects a more or less cooperative loss of part of the crystalline order. In general, the crystalline order can be discussed in terms of the position, orientation and conformation of the molecules. Within the concepts of statistical mechanics the occurence of any disorder results in an increase in entropy, which can be broken up correspondingly into three terms. The enthalpies and entropies of fusion can thus be discussed in terms of the onset of different molecular motions, which result in the different types of disorder.

In the present paper we report thermal data on a series of cycloalkanes C_nH_{2n} with n=12,13,14,15,16,24,36,48,72,96 and discuss the entropies of transition per methylene unit with respect to the molecular motions in the different phases.

EXPERIMENTAL

For DSC 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 equilibium conditions $\Delta H = T \Delta S$. Cycloalkanes were prepared according to ref. 2.

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RESULTS AND DISCUSSION

Table 1 gives the transition temperatures, the transition enthalpies and the transition entropies per methylene unit for the different cycloalkanes. Three groups can be distinguished within the homologous series. For $12 \leq n \leq 24$ all compounds show a solid-solid transition well below the melting transition. For $24<n<48$ only the melting transition could be observed. For $n \leq 48$ the thermal transition depends upon the crystallization conditions, i.e., whether the samples are crystallized from solution or melt.

TABLE 1

Transition temperatures, enthalpies and entropies per methylene unit for cycloalkanes C_nH_{2n}

n	T_{tr} K	ΔH_{tr} kJ/mol	ΔS_{tr} J/K·molCH$_2$	T_m K	ΔH_m J/mol	ΔS_m J/K·molCH$_2$
12	199.0	0.6	0.23	333.8	14.8	3.70
13	285.6	0.9	0.25	297.6	7.4	1.93
14	321.9	16.5	3.65	329.3	9.3	2.01
15	210.1	8.5	2.67	336.6	8.5	1.68
16	268.9	19.6	4.55	333.7	7.6	1.42
24	297.0	38.0	5.32	322.0	10.8	1.42
48	-	-	-	359.0	140.0	8.12
72^1	-	-	-	379.3	220.0	8.05
72^2	-	-	-	379.3	118.0	4.60
96^1	-	-	-	389.0	302.0	8.03
96^2	363.9	37.0	1.0	389.0	168.0	4.46

Superscripts ^{1} and ^{2} refer to the solution and melt crystallized samples respectively

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

In Fig. 1, the DSC-diagrams are shown for the above mentioned cycloalkanes. The value of $\Delta S/CH_2$ for the solid-solid transition increases considerably with molecular weight. Since the increase in entropy reflects a loss of order, there must be considerable disorder in the high temperature phases. In a first approximation it can be assumed that the cyclododecane and the cyclotetradecane molecules have primarily the same conformations in the melt, in the mesomorphic phase and in the crystal. This is in agreement with semiquantitative force field calculations of these molecules (3), 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.

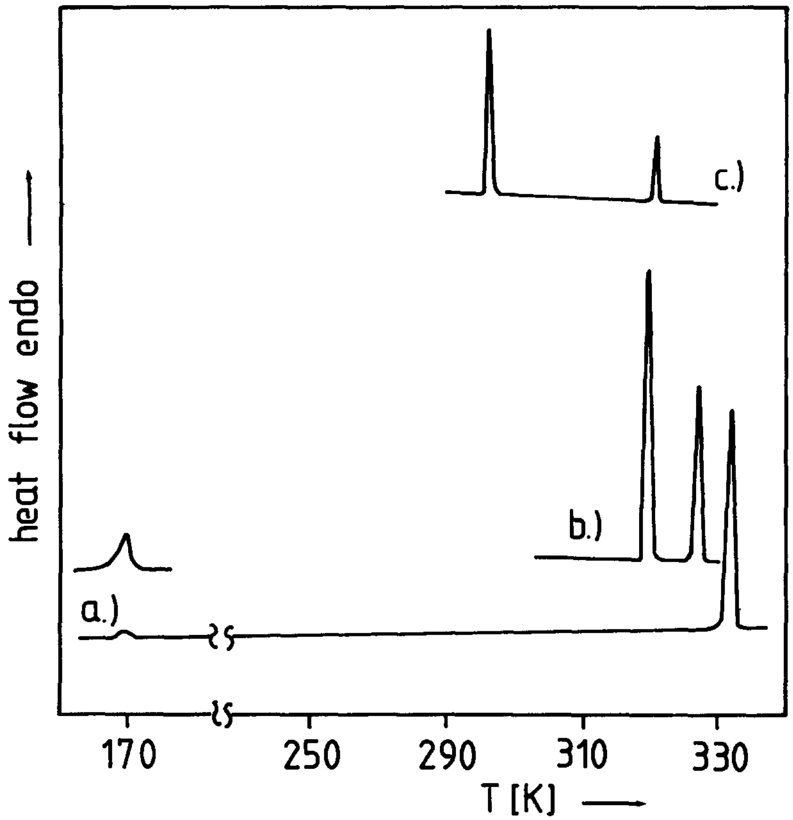

Fig. 1: DSC-Diagrams of small cycloalkanes: cyclododecane (a), cyclotetradecane (b) and cyclotetraeicosane (c)

The situation is different for cyclotetraeicosane. Due to the larger size of the ring, the molecules can assume different conformations without significant intramolecular strain. The increase in the solid-state transition entropy indicates that conformational disordering occurs in two steps: first, partially, at the solid-solid transition and then at the melt transition, where the equlibrium of the different molecular conformations is reached.

2. Medium Size Cycloalkanes, $C_{36}H_{72}$ and $C_{48}H_{96}$

No solid-solid transition could be observed for cyclotetratriacontane and cyclooctatetracontane by differential scanning calorimetry.

3. Large Size Cycloalkanes, $C_{72}H_{144}$ and $C_{96}H_{192}$

If the ring size exceeds a certain limit, the thermal behavior differs for solution and melt crystallized samples. No solid-solid transition could be observed for the solution crystallized samples. When the samples were melt crystallized, the DSC experiments showed (i) a solid-solid transition for cyclohexanonacontane and (ii) a significant decrease in the enthalpy of fusion for both compounds (see fig. 2).

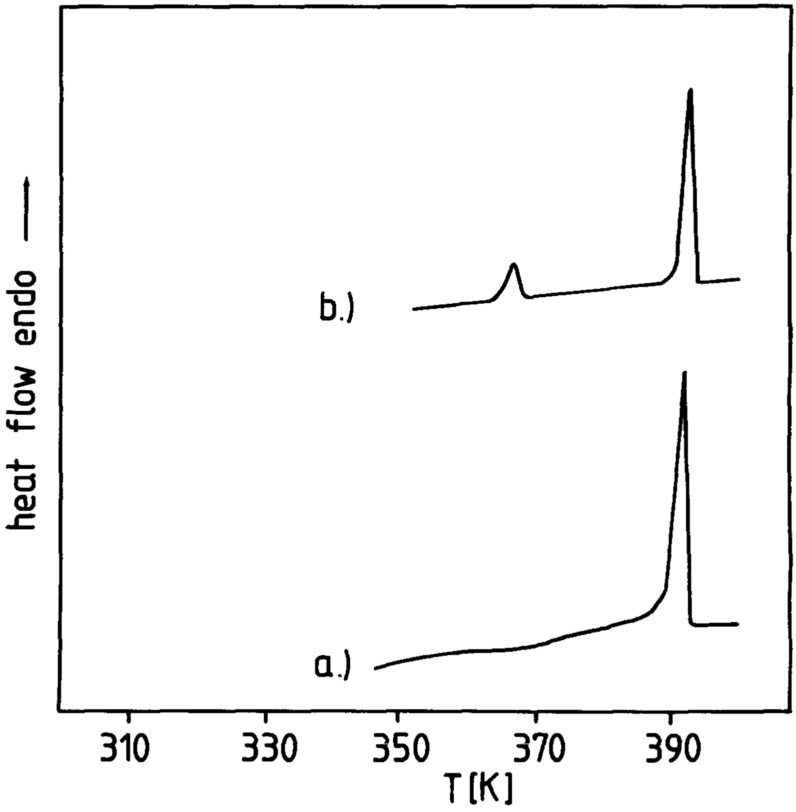

Fig. 2: DSC-Diagrams of cyclohexanonacontane crystallized from solution (a) and melt (b)

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 (4). Careful and long time annealing of the melt crystallized samples did not result in a change of the transition enthalpy. A similar decrease in the enthalpy of fusion was observed for cyclooctatetracontane. However, in this case annealing resulted in the recovery of the original value.

CONCLUSIONS

The disordering can be classified by contributions to the orientational and the conformational disorder. For the small size cycloalkanes, conformational disorder can be neglected as a factor contributing to the transition entropy. For 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 (ΔS_{tr}=33.3 J/K·mol) and cis-1,4-dimethylcyclohexane (ΔS_{tr}=48 J/K·mol). For cyclodeodecane the rather small entropy of transition indicates considerable motion already below the solid-solid transition and also little cooperativity for the onset of molecular motion. In the case of cyclotetraeicosane the comparable large entropy difference determined for the solid-solid transition reflects the onset of conformational disorder.

With increasing ring size the dense arrangement of the molecules within a crystal lattice requires more and more that the molecular conformation is that of a collapsed ring. The molecules form lamellar type crystals in which adjacent stems are connected by tight folds. Conformational interconversions and rotational motions are hindered by this restriction to a rectangular shape conformation. Conclusively no dynamically disordered mesomorphic phases could be observed for the medium size rings.

The different melting behavior of the long chain paraffines might be explained by the incompatibility of the optimal lateral packing of the stems and the minimum energy arrangement of the carbons in the folds. 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 arranged in the diamond lattice if the subcell for the stems is monoclinic. However, for a fold connecting two perpendicular planar zig-zag chains, the diamond structure is not appropriate. This implies a fold configuration with high strain energy. Hence, the folds favor the monoclinic structure while the stems favor the orthorhombic packing. It is thus indicated that the tight adjacent fold is a defect within the crystal lattice, which is of higher energy in the case of the orthorhombic polymethylene subcell as compared to the monoclinic subcell.

The size of the cycloalkanes with 72 and 96 carbon atoms is apparently such that neither of the two possible subcell structures is clearly favored. For kinetical reasons different crystallization conditions lead to different modifications. In the orthorhombic form the packing of the methylene groups in the stems adjacent to the strained folds is disturbed and not as perfect as in the monoclinic form. This could explain the different entropies of fusion found for the two modifications. In addition the strain in the folds explains the fact that the orthorhombic form clearly changes to a dynamical disordered high temperature phase. In contrast, the corresponding change seems to affect only part of the chains in the case of the monoclinic modification.

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