# Investigation of Conformational Transitions in Cycloalkanes, Especially $(CH_2)_{22}$

## Hans-Peter Grossmann

Abteilung Angewandte Physik der Universität Ulm, P.O.B. 4066, 7900 Ulm, Federal Republic of Germany

## Summary

A homologous series of cycloalkanes from $(CH_2)_{14}$ up to $(CH_2)_{96}$ was investigated. With DSC measurements it was found that some of the ringalkanes additionally to the melting process undergo phase transitions in the solid state. Because of its great transition heat of the solid phase transition 27 K below the melting point $(CH_2)_{22}$ was investigated more detailed by IR- and Raman-Spectroscopy. It is shown that the intramolecular defect structure in the high temperature phase is the same as in the melt similar to the high pressure phase in polyethylene, but is not comparable to the rotator phase transition in the n-alkanes some degrees below the melting point.

## Introduction

Cycloalkanes $(CH_2)_n$ represent an appropriate model system to investigate specific defect structures in $CH_2$-chain systems, especially to study chain folding by means of infrared spectroscopy (GROSSMANN, ARNOLD, BÜRKLE, 1980) and X-ray measurements (NEWMAN, KAY, 1976; GROTH, 1979; TRZEBIATOWSKI, STROBL, 1980). Besides these spectroscopic properties one can find some interesting details in the thermal behaviour of the cycloalkanes. Several of the ringalkanes investigated undergo one or more phase transitions in the solid state (e.g. $(CH_2)_{15}$ with 2 and $(CH_2)_{21}$ with even 4 solid phase transitions). Some of them are distinguished by both a greater heat and an entropy of transition than that of the melting process. $(CH_2)_{22}$ in particular undergoes such a transition about 27 K below the melting point, so that the high temperature phase is stable in a broad temperature interval. A similar behaviour is found in $(CH_2)_{24}$.

It is interesting to ask which molecular rearrangement takes place at the transition into this high temperature solid phase having such a great transition energy and entropy. For this purpose several experiments were carried out with $(CH_2)_{22}$ as an example.

## Results

DSC measurements: Our DSC measurements were carried out with the Perkin Elmer DSC 2 of the Sektion Kalorimetrie of the University of Ulm. A detailed presentation of all thermal data (from 130 K up to the melting point), will be given elsewhere (GROSSMANN, HOEHNE). Here we report only data relevant for the purpose of this work. Fig. 1 shows the melting points of the cycloalkanes in comparison to that of the n-alkanes. The melting temperature of the n-alkanes increases stronger with molecular weight than the melting temperature of the cycloalkanes. For $(CH_2)_{96}$

(extrapolated to heating rate 0 K/min) the melting point is higher than for $C_{96}H_{194}$ (extrapolated to heating rate 0 K/min) although the $(CH_2)_{96}$ contains two fold defects already in the solid state (and therefore is more distorted) whereas $C_{96}H_{194}$ is fully extended. This is clear if one
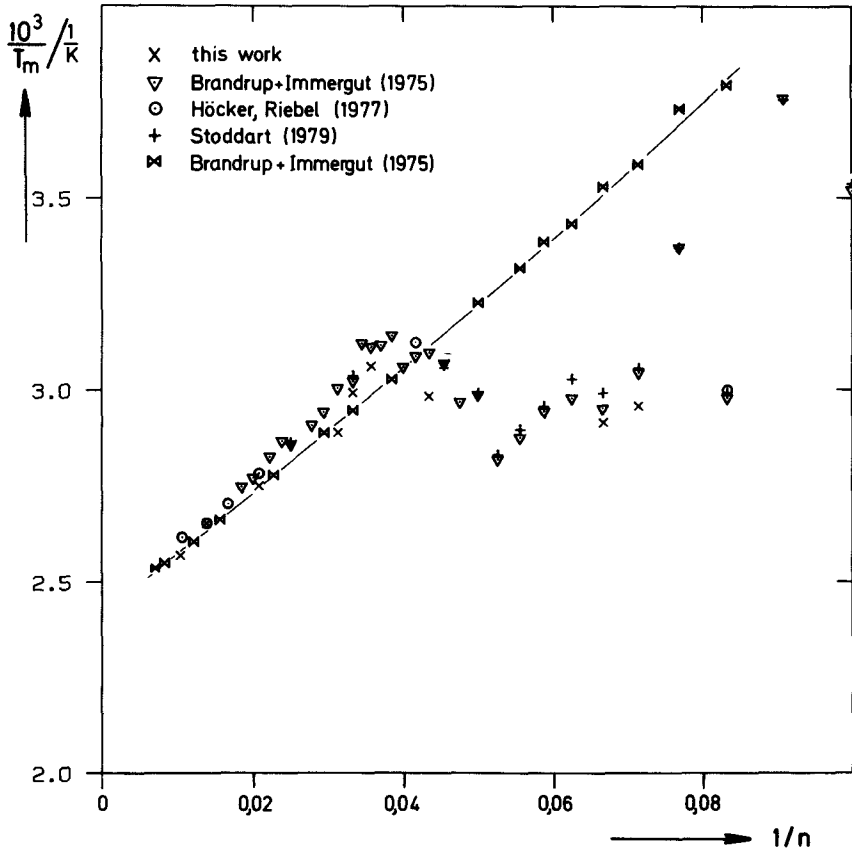


fig. 1: Melting points of the cycloalkanes (x, ▽, ⊙, +) in comparison to that of the n-alkanes ( ▷◁ ).

takes into account that the fold constraint will decrease the mobility of the cycloalkanes, which means that the transition entropy cannot increase as much as in the n-alkane molecules. In the $1/T_m$ over $1/n$ plot (fig.1) we see three groups of melting points. The cycloalkanes with high molecular weights show a linear dependence. The molecules $(CH_2)_{24}$ - $(CH_2)_{18}$ deviate clearly from the straight line, their melting temperature decreases with increasing n. Short molecules $n < 18$ behave similarly as the first group but exhibit strong scattering of data points. One could conclude that the shorter molecules $n < 18$ are subject to a relative strong ring constraint whereas the molecules with $18 < n < 24$ lie in a range inter-mediate compared to the longer molecules which exist nearly without any ring constraints. It is interesting to find that the molecules with one strong solid state phase transition (e.g. $(CH_2)_{22}$, $(CH_2)_{24}$) are from the intermediate range. Because of our special interest in these phase

transitions we now will look for the thermal behaviour of $(CH_2)_{22}$. The DSC diagram of $(CH_2)_{22}$ and $(CH_2)_{24}$ is shown in fig. 2a and 2b, respectively.

$\dot{Q}/\dfrac{mcal}{sec}$
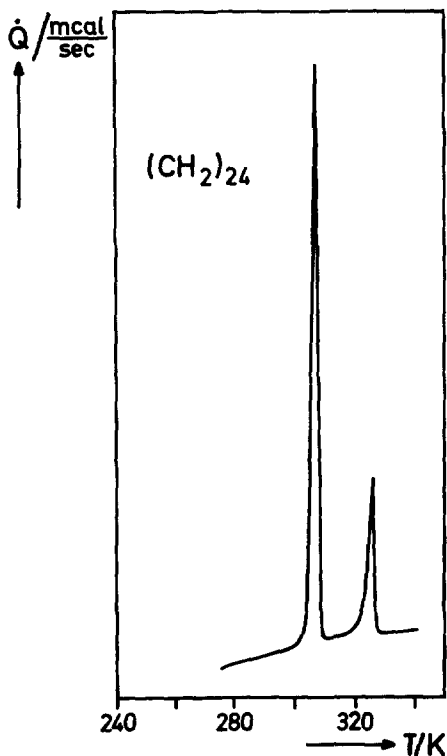
$(CH_2)_{24}$

240    280    320

T/K

fig. 2a: DSC diagram for $(CH_2)_{22}$
          (heating rate 10 K/min)

$\dot{Q}/\dfrac{mcal}{sec}$

$(CH_2)_{22}$

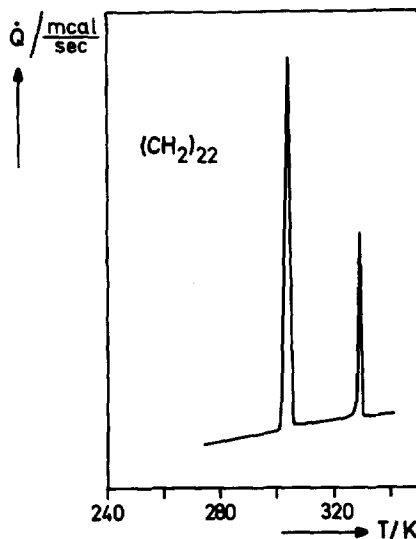240    280    320

T/K

fig. 2b: DSC diagram for $(CH_2)_{24}$
          (heating rate 10 K/min.
          An additional small
          transition is found
          below 280 K, but it
          is of no consequence
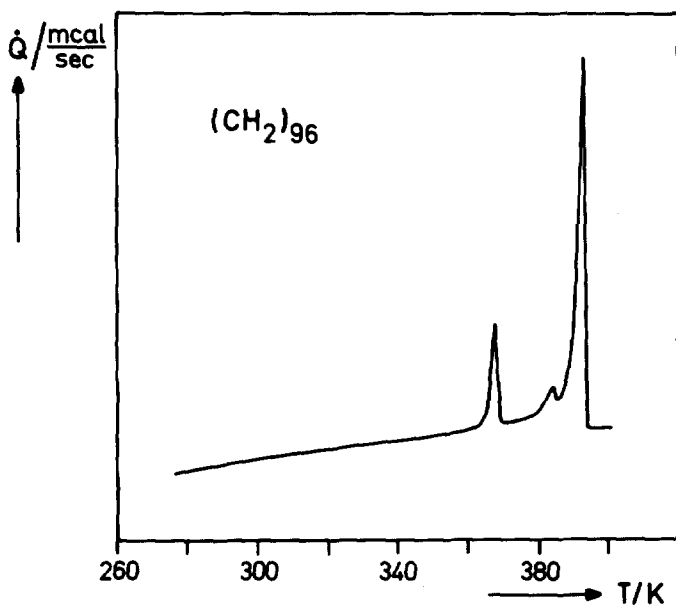          for the present
          discussion)

$\dot{Q}/\dfrac{mcal}{sec}$

$(CH_2)_{96}$

260    300    340    380

T/K

fig. 3: DSC-diagram
         for $(CH_2)_{96}$
         (heating
         rate 10 K/
         min).

The quantitative analysis of the DSC-plots gives that the heat and entropy of the phase transition at 298.5 K (extrapolated to heating rate 0 K/min) are about 4 times greater than the corresponding values of the melting process. This indicates that the transition is not the same as the rotator phase transition observed in n-alkanes some degrees below the melting points which always shows a much smaller heat of transition. Only the small transition of the longer molecule $(CH_2)_{96}$, about 20 K below the melting point (fig. 3) may be the rotator phase transition (cf. TRZEBIATOWSKI, 1980).

X-ray, IR- and Raman-Spectroscopy: In order to investigate the molecular defect structure in the high temperature phase of $(CH_2)_{22}$ we carried out some spectroscopic experiments in the different phases.

X-ray experiments: To prove whether the high temperature phase is crystalline, X-ray scattering experiments on powder samples were performed using a Guinier-de Wolff camera and Cu-$K_\alpha$ radiation. Fig. 4a shows the powder diagram of $(CH_2)_{22}$ at 296 K together with that at 313 K (fig. 4b).



fig. 4a: X-ray powder diagram of $(CH_2)_{22}$ in the low temperature phase.



fig. 4b: X-ray powder diagram of $(CH_2)_{22}$ in the solid high temperature phase.

From the smaller number of reflections in the high temperature phase one can conclude that the symmetry of the crystal increases at the phase transition. The additional occurrence of spots within the Debye-Scherrer lines indicates an increasing crystallite size. The evaluation of the line at the smallest angle yields that the longest distance of the lattice planes decreases from $11.9 \pm 0.05$ Å in the low temperature phase to $11.2 \pm 0.05$ Å in the high temperature phase. For a detailed analysis of the full crystal structure we intend to perform Weissenberg analysis on single crystals. Nevertheless our X-ray measurements show that the high temperature phase is crystalline and the long period becomes shorter.

IR and Raman Experiments: Generally defects lead to a local modification of the intra- and intermolecular interaction. This yields a variation of the vibrational spectrum which can be investigated by spectroscopic methods. For $(CH_2)$-chain molecules it is shown that many defects, e.g. rotational isomers, yield specific bands in the IR and Raman spectrum (SNYDER, 1967; SCHONHORN, LUONGO, 1969; COLEMAN, PAINTER, 1978; ZERBI, GUSSONI, 1980; HÖLZL, SCHMID, HÄGELE, 1978). Especially in the wagging region (1300 cm$^{-1}$ - 1400 cm$^{-1}$) of the spectrum, many of the partly weak bands are due to a defect specific absorption. Some of the bands cannot be assigned clearly because they are due to contributions of different defect modes (KRIMM, JAKES, 1971). Fig. 5 shows the complete IR spectra (measured with a Perkin Elmer 283 grating spectrograph) of $(CH_2)_{22}$ representative for the two solid phases and the melt. The corresponding Raman spectra are shown in fig. 6. The influence of the molecular folds in the cycloalkanes was investigated recently (GROSSMANN, ARNOLD, BÜRKLE, 1980). It could be shown that besides the well known fold band at 1344 cm$^{-1}$ the two new bands at 1442 cm$^{-1}$ and 700 cm$^{-1}$ can be assigned to the ggtgg fold defect.
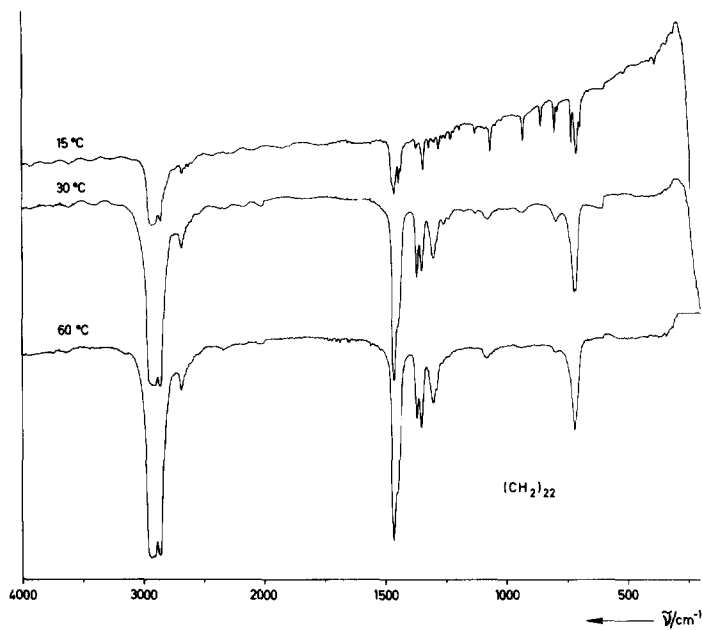
fig. 5:

Characteristic IR spectra for $(CH_2)_{22}$ in the two solid phases and the melt (15°C – low temperature solid phase, 30°C – high temperature solid phase, 60°C – melt).
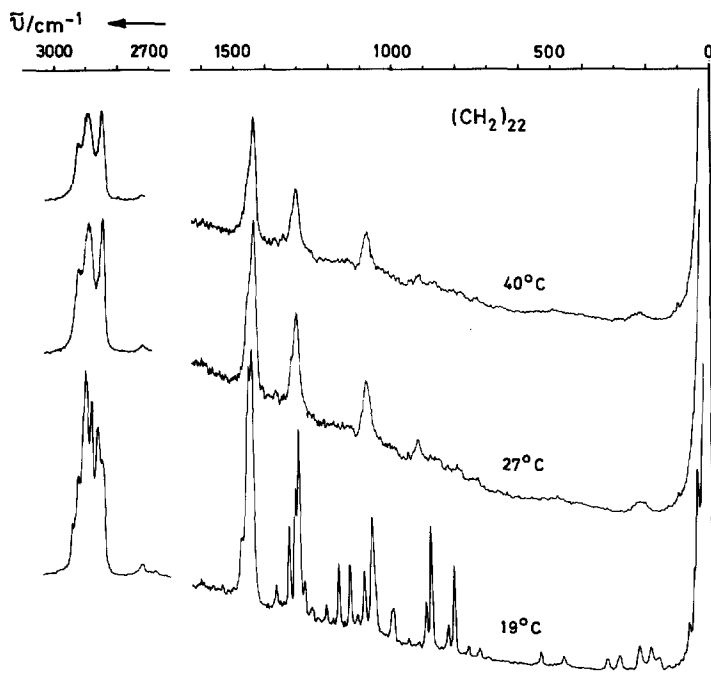


fig. 6:

Characteristic Raman spectra for $(CH_2)_{22}$ in the two solid phases and the melt (19°C – low temperature solid phase, 27°C – high temperature solid phase, 40°C – melt).

It is obvious that the spectrum in the high temperature phase resembles that of the melt whereas the low temperature spectrum has a different shape. The similarity of the defect specific part of the melt spectrum with that of the high temperature phase shows that the intramolecular defect structure of the melt is realized already in the high temperature phase. This means that during the melting process no additional rotational isomers are generated (but probably dislocations are inserted (PECHHOLD, GROSSMANN) ). To investigate single defect bands we decomposed numerically the band complexes in the rocking as well as in the wagging region of the spectra measured between 280 K and 330 K using Lorentzian-Gaussian-type functions.

Considering the positions of the IR single bands as a function of temperature it is evident that the band positions do not change at the melting point $T_m$ whereas at the transition point $T_t$ the number and position of the absorption bands change considerably. A small frequency shift of the single bands in the rocking region at $T_m$ is certainly due to the difficult fitting of the bands which are strongly overlapping in this region. In order to learn something about changes in defect concentration at the transition points, the integral intensity $I_d$ of all defect bands in the wagging part of the spectra (1200 – 1300 cm$^{-1}$) divided by the integral intensity $I_r$ of all bands in the bending region are plotted in fig. 7.
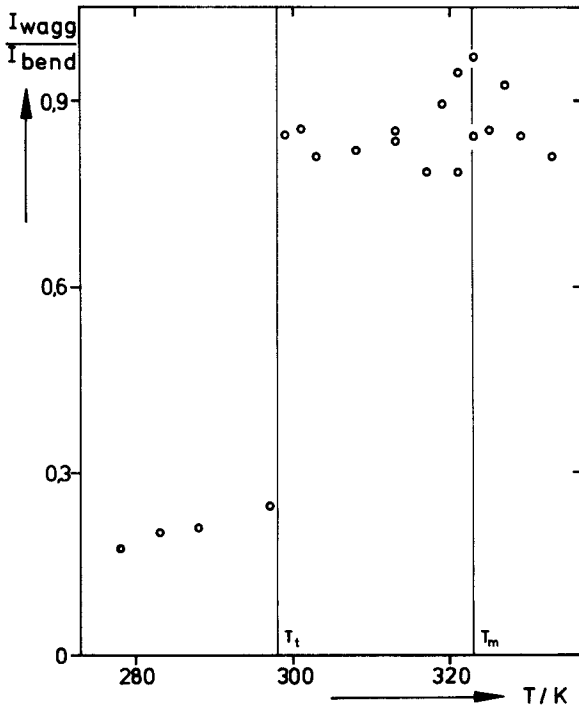


fig. 7: Integral intensity of the wagging bands as compared with the integral intensity of all bending modes.

Analogous plots one gets for the intensities of the single defect bands as shown exemplaryly for the gtg-absorption bands at 1365 cm$^{-1}$ divided by the intensity of the CH$_2$-bending absorption band at 1463 cm$^{-1}$ in fig. 8. From these experimental evidences, particularly the quantitative spectroscopic data, one can conclude that the intramolecular defect concentration increases considerably at transition point $T_t$, but does not change at the melting point. This explains the similarity of the spectra in the high temperature phase and in the melt as well as the large transition heat at $T_t$ relative to the heat of fusion at $T_m$.
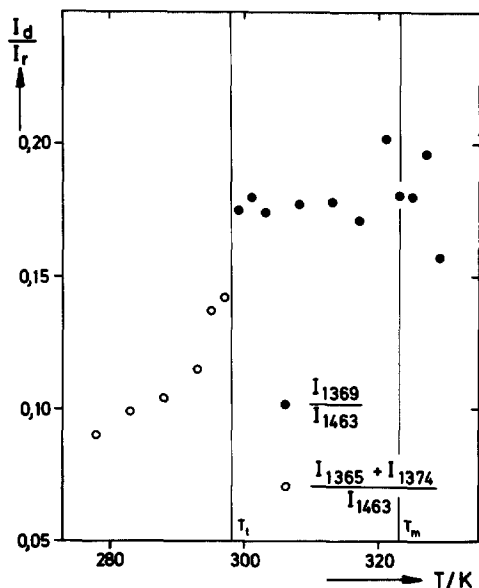
fig. 8: Integral gtg-defect absorption as compared with the integral $CH_2$-bending absorption as reference.

## Molecular Interpretation

Because of the analogy of the experimental features a comparison of the discussed solid state phase transition with the high temperature phase transition in polyethylene at elevated pressure (> 3.5 kbar) is useful. This phase crystallizes hexagonal (BASSETT, TURNER, 1972; YASUNIWA, ENOSHITA, TAKEMURA, 1976) with a greater heat and entropy of transition than the melt (LEUTE, DOLLHOPF, 1980). Recent Raman experiments show that in this solid phase the shape of the spectrum is nearly the same as in the melt (SCHWICKERT, 1980), and the FIR-measurements (LEUTE, 1981) guarantee that the intermolecular lattice modes contribute less than 15 % to the transition entropy. This means that the transition entropy mainly originates only from conformational disorder resulting from the change of the all trans chains in a 4 x 1/1 helix form with the conformation ...gt$\bar{g}$tgt$\bar{g}$... as proposed some years ago (PECHHOLD, LISKA, GROSSMANN, HÄGELE, 1976). Semiempirical atomistic calculations in the pair approximation show that this helix conformation is intramolecular as well as intermolecular stable and the high temperature phase in polyethylene consists of a mixture of about 75 % helix and 25 % trans chains which are arranged in blocks (GROSSMANN, 1977). It is this molecular model which we assume also as valid for the high temperature phase transition in the cycloalkanes investigated. The role of high pressure in the case of polyethylene here is taken over by the fold constraints. It is suggested that the two trans-parts of the molecules (between the folds) incorporate gt$\bar{g}$ defects at $T_t$ so that they are saturated with gauche-bonds. This explains the shortening of the molecule observed experimentally, the high transition enthalpy and entropy and the spectroscopic findings. For $(CH_2)_{22}$ only one gt$\bar{g}$ defect in each straight segment can be incorporated without any steric hindrance because one segment contains 6 trans positions, and direct neighbouring g-positions are forbidden as could be shown by semiempiric atomistic calculation (GROSSMANN, 1977). Nevertheless the gt$\bar{g}$ defect is not localized at only one position so that it should be very mobile. A detailed quantitative description of the high temperature phase transition (including the results of the semiempiric atomistic calculations concerning the high pressure phase in polyethylene), in particular a calculation of the transition temperature, the entropy and enthalpy, is in preparation and will be given elsewhere.

144

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