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# Conformational Transition and Melting in Polyethylene and Model Systems

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## Summary

It is shown, that melting of chain molecules can be described as a double process:
1) a conformational transition, where the "liquid" molecule conformation is created and
2) the "real" melting caused by the cooperative insertion of dislocations, 3-dimensionally arranged in dislocation walls.
This melting concept is shown to be valid in atomic crystals as well as in low molecular crystals and in polymers, too.

Considering the phase transitions of monoatomic crystals from low temperatures up to the melting point one obtains in several cases (besides the melting) one or more displacive transitions (change in lattice symmetry) with a smaller latent heat and entropy as compared to that of the melting A similar behaviour is also found in molecular crystals, e.g. for the rotator phase transition in n-alkanes (up to $C_{38}H_{76}$) or some cycloalkanes (fig. 1).

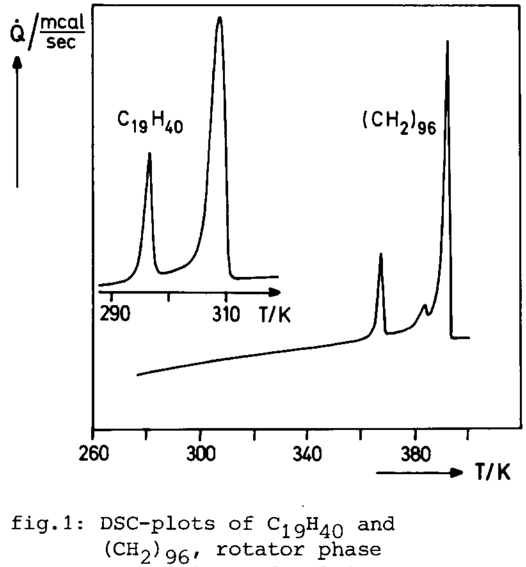

fig.1: DSC-plots of $C_{19}H_{40}$ and $(CH_2)_{96}$, rotator phase transition and melting.

Conformational transition: In some polymer systems however there are found solid-solid phase transitions (u) with remarkably greater transition quantities than those of the melting (m) (fig. 2): For linear PE the transition u occurs only under high pressure (> 3.5 kbar) with $\Delta H_u / \Delta H_m = 2.5$ at $p = 5$ kbar, $\Delta H_u = 4$ kJ/mol $CH_2$ and leads to the well known hexagonal high temperature phase (BASSETT, TURNER 1974; LEUTE, DOLLHOPF 1981). In the case of e. g. trans - 1,4 - PBD however, the high temperature phase is already stable at 1 bar with $\Delta H_u / \Delta H_m = 2.3$, $H_u = 2.2$ kJ/backboneatom (BAUTZ et al. 1981). The relative great values of the transition quantities ($\Delta S_u$, $\Delta H_u$) suggest the supposition that this displacive

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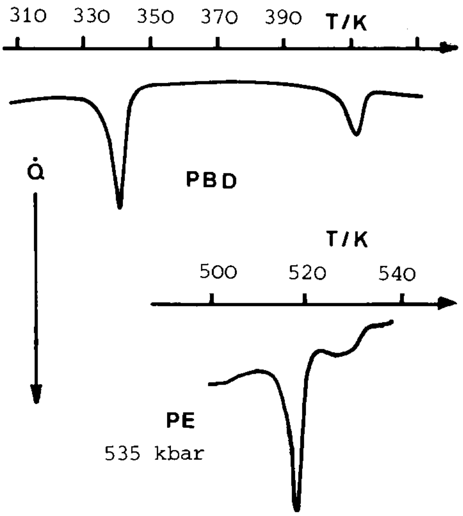

fig.2: High temperature phase transition and melting of PBD (BAUTZ et al. 1981) and PE (BASSETT, TURNER 1974).

phase transitions are associated - besides the change in lattice symmetry - with a significant change of the intramolecular chain conformation (conformational transition). Based on the semiempirical atomistic calculations of intramolecular stable PE-helices it was suggested (PECHHOLD et al. 1976; GROSSMANN 1977) that in the high temperature phase of PE the chains are in 4 x 1/1 helix conformation (··$gt\bar{g}tgt\bar{g}t$··) for about 70 % and in all trans conformation only for 30 % , each forming lateral blocks. The phase transition itself can be described quantitatively within the framework of a cooperative pair theory, taking additionally into account the surface energies of the trans and helix blocks.

In order to prove experimentally the idea of cooperative formation of intramolecular conformational disorder at the transition point it is near at the hand to investigate appropriate model systems which we found to be the cycloalkanes $(CH_2)_{22}$ and $(CH_2)_{24}$. This systems exhibit a strong solid-solid phase transition with $\Delta H_u/\Delta H_m = 3.5$, $\Delta H_u = 1.6$ kJ/$CH_2$ about 25 K below the melting point (fig. 3).

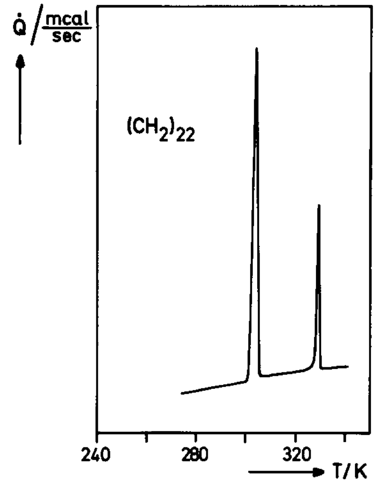

fig.3: DSC-plot for $(CH_2)_{22}$. A similar plot is also found for $(CH_2)_{24}$ (GROSSMANN 1981).

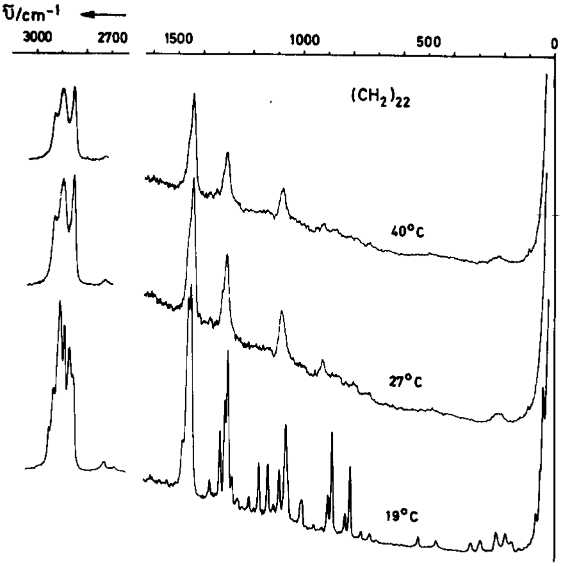

fig. 4: Raman spectra of the different phases of $(CH_2)_{22}$.

For the purpose of characterizing the conformational state detailed Raman and IR-spectroscopic measurements in the different phases were carried out. The results can be summarized as follows (GROSSMANN 1981):

a) The shape of the Raman spectra in the high temperature phase as well as the infrared spectra are largely similar to that of the melt and differ significantly from the spectra in the low temperature phase (fig. 4).

b) The quantitative analysis of the integral absorbance in the conformational specific wagging region of the infrared spectra (1300 - 1400 $cm^{-1}$) exhibit a strong increase of g-bands at the transition temperature but no change at the melting point (fig. 5).

This also holds for the gtg rsp. gtḡ absorption at about 1369 $cm^{-1}$. Semiempirical atomistic calculations of different possible defect conformations of the $(CH_2)_{24}$ molecule show evidence for the insertion of two kinks (gtḡ) per molecule at the transition point. It could be shown that these kink defects are stable and the defect energies depending on their localisation are about 12 - 16 kJ/mol. In combination with the contribution of the interlamellar gap this value is comparable to the transition enthalpy (GROSSMANN et al. 1982).

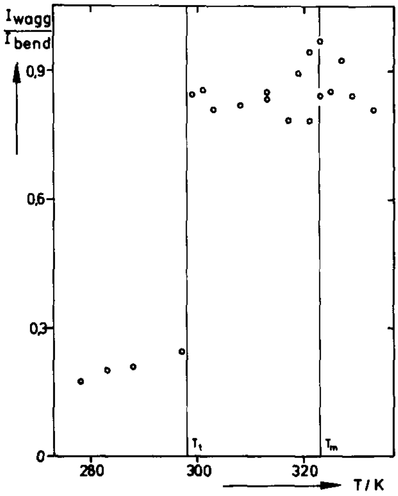

fig.5: Integral wagging absorption in $(CH_2)_{22}$.

Concerning the Raman spectra for linear PE under high pressure recently it was found that the melt spectra are similar to those of the high temperature phase (SCHWICKERT 1980; WUNDER 1981). This means also that melting is not caused by insertion of intramolecular chain defects.

Melting: Comparing the entropy of fusion $\Delta S_m/k$ per Segment for PE (less any contribution of conformational transition) extrapolated to p = 1 bar ($\Delta S_m/k = 1.3$) or for trans-1,4-PBD ($\Delta S_m/k = 1.2$) with the values for fcc- or hcp atomic lattices, the agreement is conspicous. The nearly constant $\Delta S_m/k$ values for all elements of the same lattice type suggest a general melting mechanism: a cooperative increase of the number of dislocations which are (from energetical grounds) arranged in 3-dimensional stacks of dislocation loops forming tilt boundaries (PECHHOLD et al. 1982). Taking lines of atoms (atomic dislocations) perpendicular to the tilt boundaries as statistical elements, a quantitative treatment of this model within the scope of a cooperative pair theory and the cluster-entropy-hypothesis (CEH) can be carried out. For this purpose the Gibbs free energy of a crystal containing dislocations has to be calculated as function of the concentration of atomic dislocations and pairs of differently displaced atoms. Minimizing this function one gets after some calculations the equilibrium Gibbs free energy $(\Delta g/kT)|_{eq.}$ which has a sharp bend at the melting point (first order transition, fig. 6). The derivative of $(\Delta g/kT)|_{eq.}$ yields the transition entropy $\Delta S_m/k = \Delta H_m/kT_m = 1.03$ for the fcc-lattice and $\Delta S_m/k = 0.79$ for the bcc-lattice. The relating experimental values are a little higher because of vibrational contributions. Further derivation gives the excess contribution to the specific heat in good approximation. Calculating the average energy

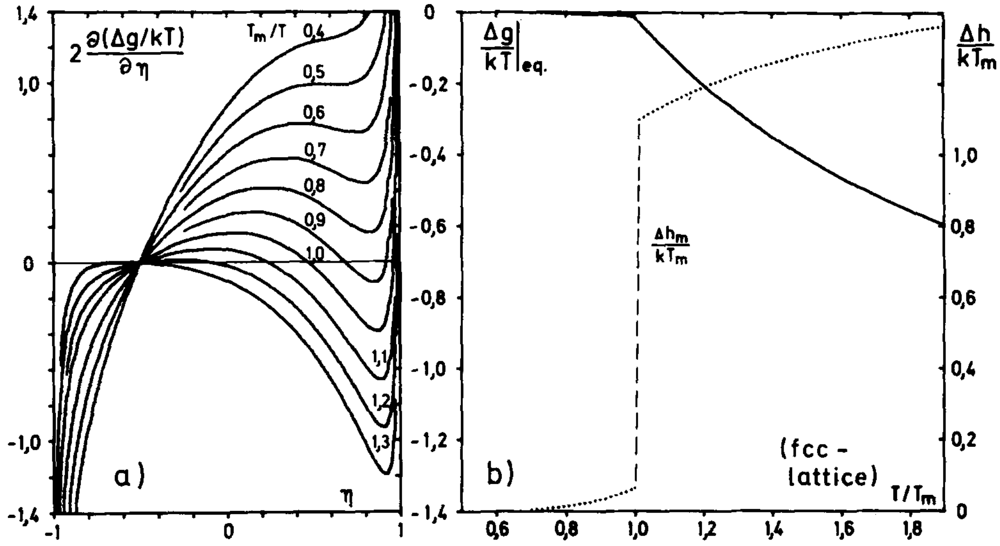

fig.6: a) Derivative of the excess Gibbs free energy (fcc-lattice) as function of the order parameter $\eta$ ($\eta \approx 1$ crystalline state, $\eta = -1/2$ melt).
b) Equilibrium excess Gibbs free energy.

of a dislocation in a fluctuating wall, as assumed in this theory, one can derive Lindemanns formula. The theoretical values e.g. for PE and PBD ($Gd^3/kT_m \approx 22$) are in good agreement with the experimental values, taking the lattice shear modulus $G(T_m)$ from extrapolation to the melting point ($Gd^3/kT_m = 21$ for PE and for PBD too). The contribution of the dislocations to the volume effect $\Delta V_m/V$ as well as to the thermal expansion coefficient can be calculated in terms of the anharmonic dilatation of the dislocation structure.

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