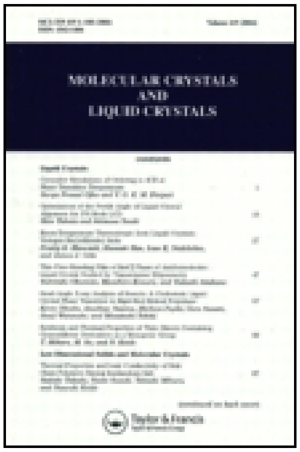

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Condis Crystals of Small Molecules I. The Concept and Limitations

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Condis Crystals of Small Molecules
I. The Concept and Limitations

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The concept of condis crystals (conformationally disordered crystals) is displayed as it applies to small, flexible molecules. Nematic liquid crystals are shown to be always conformationally disordered. Smectic liquid crystals, particularly in the more ordered polymorphs, need reexamination relative to their condis character. Plastic crystals of flexible molecules present a special problem since they may have varying degrees of conformational and orientational freedom. The transition into the condis state on increasing the temperature is shown to be either gradual or abrupt.

I. INTRODUCTION

Several years ago we surveyed the large knowledge on mesophases of small and large molecules.[1] Out of this work resulted a comprehensive, systematic description of mesophases in terms of three major types: 1. the long-known liquid crystals, characterized by rod- or disc-like mesogens which permit liquid-like motion while retaining orientational order;[2] 2. the well-described plastic crystals, characterized by close to spherical mesogens which are able to attain rotational motion in the crystals without losing positional order;[3] and 3. the newly-proposed condis crystals (short for conformationally disordered crystals) which consist of flexible molecules, able to change between different conformations within the crystal.[1] For each of the mesophases a corresponding metastable glassy state (LC-, PC-, and CD-glass, respectively) was suggested. These glasses are solid with mesophase disorder frozen on cooling below the glass transition temperature.

The condis state proved particularly important for the description of crystals of macromolecules with high conformational mobility, such as trigonal polyethylene (stable at elevated pressure),[1] trigonal trans-poly-1,4-butadiene,[4] or trigonal polytetrafluoroethylene.[5] Already at the time of writing of the review it became likely that some small molecules are perhaps better described as condis crystals. Examples mentioned at that time included linear and macrocyclic alkanes, 2,3-dimethyl butane, cyclohexanol and cyclohexane.[1] In the present series of research publications we would like to explore the concept of condis crystals of small molecules. The major questions to be addressed will be: do condis crystals of low molecular weight exist? is the change from rigid, fully ordered crystal to condis crystals a first order transition or can it occur continuously over a wider temperature range? and, what is the difference between a liquid crystal or a plastic crystal which also shows conformational mobility and a condis crystal? Naturally we would like to answer the first question with yes. Perhaps also not surprising (at least after some experimentation and thought), it seems that both continuous and sharp transitions into the condis state are possible. Finally, the plastic and liquid crystalline motion can probably sometimes be separated from the conformational mobility. The materials used as major examples are the prior analyzed N,N′-bis(4-*n*-octyloxybenzal)-1,4-phenylene diamine[6] (OOBPD), known for its many liquid crystalline polymorphs and several cyclosilanes which had not been described in detail before.

In this first paper, the general concept is to be described. The second paper deals specifically with OOBPD studied by thermal analysis, x-ray diffraction, and optical microscopy. The third paper deals with the cyclosilanes and their calorimetric analysis. The fourth, with the solid state NMR study of cyclosilanes. This broad study became possible by cooperation between three laboratories specializing in hot stage microscopy (Mettler), solid state NMR (University of Freiburg), and thermal analysis (RPI).

2. CONFORMATIONAL DISORDER IN LIQUID CRYSTALS

Liquid crystals, especially in their nematic polymorphs, are characterized by close to liquid-like motion. Thermodynamically this manifests itself in a change in heat capacity on vitrification which is similar to that of amorphous liquids and a surprisingly small entropy difference from the isotropic melt. Kinetically one finds a relative ease of transition into the nematic liquid crystal phase from the isotropic melt (low supercooling).

Although a reasonable body of thermodynamic data about liquid crystal transitions has been collected over the years,[7] data on glass transitions are somewhat limited. A survey of the literature came up with heat capacity data for LC-glass transitions of five small molecules, seven macromolecules with mesogens in the side-chain, and four macromolecules with mesogens in the main-chain.[1] All 16 data combined showed an average of 13 J K^{-1} mol^{-1} heat capacity increase at the glass transition when heating from the LC-glass to the liquid crystal. The molar reference unit in this calculation is the "bead," defined as a flexible part of the molecule. For example, a mesogen would make a single, very large bead, and each CH_2-, O- or similar group would be an additional bead. The average number of beads of the 16 small and large liquid crystal molecules or repeating units was seven. For isotropic liquids, the average increase in heat capacity at the glass transition is 11 J K^{-1} mol^{-1}.[8] For large beads this value may increase to perhaps 23 J K^{-1} mol^{-1}. From this observation we draw two important conclusions: 1. The long range motions in isotropic liquids and liquid crystals are similar, since on freezing both give a similar change in heat capacity. 2. At the glass transition *all* long range molecular motion stops, not only that of the mesogen. If only the mesogen long range motion would freeze, the expected change in heat capacity at the glass transition would be 11–23 J K^{-1} mol^{-1} for the whole molecule or repeating unit, instead of the observed 93 J K^{-1} mol^{-1}.

A thermodynamic analysis can also be made using the transition from the liquid crystalline state to the isotropic melt.[1] For this transition one expects for full orientational disordering of a rigid, nonspherical molecule an entropy of disordering ΔS_i of about 20 to 40 J K^{-1} mol^{-1}.[9] In a survey[1] of 11 small liquid crystalline molecules ΔS_i was found to be 2 ± 1 J K^{-1} mol^{-1}. Macromolecular liquid crystals with the mesogen in the side chain showed a ΔS_i of 7 ± 5 J K^{-1} mol^{-1} (28 examples) and with the mesogen in the main chain ΔS_i

was 15 ± 7 J K^{-1} mol^{-1} (67 examples). These entropies of disordering are given per mole of molecule or repeating unit. The three classes of liquid crystals had 4 ± 2, 9 ± 4, and 15 ± 5 beads per molecule or repeating unit, respectively; the bead being chosen, as above, as the mobile subunit. These observations let us draw two additional conclusions: 3. The flexible portions of the liquid crystalline molecules participate very little in the creation of liquid crystalline order, although side chain and, even more so, main chain macromolecular liquid crystals have a somewhat larger ΔS_i. 4. The orientational order of the mesogen is far from complete, otherwise ΔS_i would have to approach 20–40 J K^{-1} mol^{-1}.

Two further observations are of importance for the distinction of thermal analysis data on liquid crystals from other mesophases: 5. The liquid crystals to isotropic liquid transitions are usually close to reversible for both small and large molecules, i.e. nucleation of the liquid phase from the isotropic phase is much easier than nucleation of a crystal (and condis or plastic crystal). 6. The isotropic liquid to liquid crystal transitions are easily brought to completion, in contrast to at least macromolecular crystals (and condis crystals) where partial crystallinity is commonly observed.

These six observations in conjunction with the definition of a condis crystal, given in the Introduction, make it clear that all flexible beads in a liquid crystal are conformationally disordered. The degree of disorder in the nematic liquid crystals approaches that of the liquid. The questions which remain concern the increasing conformational order and three-dimensional crystallization of the mesogen on going from nematic liquid crystals to smectic liquid crystals of increasing order. In particular, it may be possible in OOBPD that the mesogen takes on a fixed position, while the octyloxy groups still are able to have partial conformational freedom. Such a crystal would not be a smectic liquid crystal any more, but would have to be classified as a condis crystal. In the second paper of this series the various polymorphs of OOBPD will be discussed.

3. CONFORMATIONAL DISORDER IN PLASTIC CRYSTALS

Plastic crystals are well defined as long as the molecules are inherently rigid such as is the case for N_2, CO, CCl_4, etc. In these cases the mesophase disorder and mobility can involve only molecular orientation. In all these plastic crystals the entropy of transition to the isotropic melt is in the range of 7 to 14 J K^{-1} mol^{-1}, the same range as derived for the fusion of spherical molecules (rule of Richards).[3,9] Thermodynamically one finds thus practically full positional order for the plastic crystals and no remaining orientational order since the latter should substantially increase the entropy of transition to the isotropic phase.

The description of plastic crystals becomes more complicated if the molecule is flexible, i.e. may possess more than one rotational isomer. In this case there may be conformational *and* orientational disorder. Potentially one may have two stages of transition into the mesophase, that of the achievement of conformational disorder and that of orientational disorder.

Some information about the thermal properties of flexible molecules which have been described as plastic crystals is available through adiabatic calorimetry.[10–13] For 2,3-dimethylbutane, cyclohexane, and cis-1,4-dimethylcyclohexane the rigid crystal phase can be avoided and glass transitions measured which show in all cases a change in heat capacity not much different from amorphous liquids. One expects thus that the mesophases are basically condis crystals and it still needs to be established whether rotation of the whole molecules, as required for a plastic crystal, takes place. The residual entropies at 0 K were too small to support fully random conformational isomers and orientational positioning.[11] The sum of the transition enthalpies (and entropies) of the disordering transition to the mesophase and the transition to the isotropic melt are often too small to account for all disordering in these transitions.[11] It was thus suggested for plastic, as well as condis and liquid crystals, that possibly a portion of the disordering occurs outside of the transition region.

All these points are to be addressed in the subsequent publications of this series using thermodynamic arguments as well as direct measurements of the motion by solid state NMR.

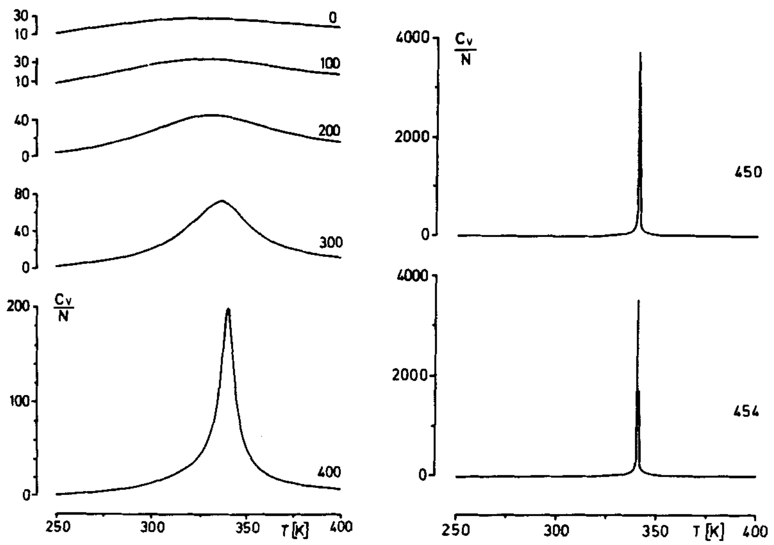
4. TRANSITION INTO THE CONDIS STATE

The basic motion of a molecule to change conformations is rotation about a chemical bond. Within a crystal this motion may need cooperative conformational changes of neighboring molecules or parts of the same molecules. As this cooperation increases, the change from the rigid crystal without conformational disorder to the condis crystal acquires the nature of a first order transition. Hydrocarbons which permit hindered rotation about the C—C-bonds may provide the examples.

The (hindered) rotational behavior of a methyl group —CH_3 connected to a hydrocarbon residue illustrates the gradual acquisition of conformational freedom. Its energy levels and statistical thermodynamics have been long established.[14] At low temperature, the torsional C—C bond heat capacity contribution is zero. As the torsional oscillation becomes excited, the heat capacity increases towards the limit of an oscillator (R). As increasing rotation become possible, the heat capacity drops to that of a rotator (R/2). The entropy stays close to zero at low temperature until the torsional oscillation begins, and then it increases, first more slowly than the entropy increase of a free rotator, then more rapidly. Ultimately, the hindered rotator approaches at high temperature the entropy of the free rotator.[14] If we look at polypropylene, the calculated torsional oscillation frequency of its CH_3-group is about 200 cm^{-1}.[15] With a hindering potential of about 10 kJ/mol, a narrowing of the NMR signal over a wide temperature range has been seen below 130 K,[16] indicative of gradual initiation of hindered rotation or tunneling. The conformational freedom is in this case acquired without a sharp transition.

An example of cooperative acquisition of conformational freedom is represented by some *n*-paraffins and polyethylene.[1] The detailed review of the motion during the multiple paraffin transitions, in particular in tritriacontane, as revealed by x-ray diffraction, Raman, and IR spectroscopy, dielectric relaxation and neutron scattering, was published recently.[17] Of interest here is the transition into the so called "rotor phase" which occurs at 341 K with a heat of transition of 29.3 kJ/mol for $C_{33}H_{68}$ (melting at 345 K, 79.5 kJ/mol). After the transition, the molecule is shortened from its all-trans conformation through the introduction of intrachain kinks. Estimates of 0.5 gauche(+)-trans-gauche(−) kinks per chain have been made. These kinks represent conformational isomers and possess inter- and intrachain mobility.[17] Even larger concentrations of such conformational isomers are found, judging from the heats of transition, in cyclotetracosane and trigonal polyethylene, the latter being stable only at elevated pressure.[1]

An attempt to rationalize the paraffin behavior was presented by Baur.[18] The key to the theory is the evaluation of the number of different arrangements of the conformationally disordered chains at constant energy. This value is needed for the calculation of the partition function. The solution is closely related to the two-dimensional Ising model with external field. In the condis crystal the equivalent effect of the external field on the dipoles of an Ising crystal is the



Heat capacity as a function of cooperativeness curves after Ref. 18.

excess energy of the rotational isomers. Since the model cannot be solved exactly, Baur used the Bragg-Williams and the quasichemical method for analysis. The figure shows the change in heat capacity as a function of temperature as the introduction of rotational isomers becomes increasingly cooperative. The cooperation is expressed by the excess energy parameter listed in the figure. It represents the energy difference between the asymmetric fully-ordered-chain rotational-isomer-chain pairs to the symmetrical pairs of rotational-isomer-chains. As this parameter reaches the critical value 454, the transition becomes of the first order. As this parameter approaches zero, the transition is as broad as expected for an isolated hindered rotator with rotational isomers of different energy. Depending on the excess energy parameters one can thus expect a gradual or an abrupt transition from the rigid, fully ordered crystal to the condis crystal. The temperature (or temperature range) of this transition depends, in addition, on the rotational isomer and crystal energy parameters.

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