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THE DETECTION OF CONFORMATIONAL DISORDER BY THERMAL ANALYSIS *

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ABSTRACT

Conformational disorder in crystals is found in many molecules that possess a plurality of conformational isomers. Typical examples are linear macromolecules such as polyethylene, polytetrafluoroethylene and *trans*-1,4-polybutadiene; and small molecules such as paraffins, cycloparaffins, soaps, lipids and many liquid-crystal forming molecules. Conformational motion is often coupled with the cooperative creation of disorder. In this case a heat and entropy of transition is observed by thermal analysis. Levels of transition entropies can be estimated by assuming that most of the disorder can be traced to conformational isomerism. In case there is conformational disorder frozen-in at low temperature, thermal analysis can be used to find the glass transition of a condis crystal. An advanced thermal analysis system has been developed, and will be described, that permits a detailed interpretation of the thermal analysis traces. It is based on the establishment of high quality heat capacity for the rigid solid state (vibration only) and the mobile liquid state (vibrations and large-amplitude cooperative motion).

THE TRANSITIONS BETWEEN MESOPHASES, CRYSTALS AND GLASSES

In a recent review of thermotropic mesophases and their transitions [1] it was suggested that crystals with dynamic conformational disorder do not fit into the standard classification of mesophases as either plastic crystals [2] or liquid crystals [3]. At that time, it was proposed that a third distinct type of mesophase exists, that of the condis crystal (with dynamic conformational disorder and long-range positional and orientational order). Figure 1 illustrates schematically the various condensed phases and their interrelations. The three classical condensed phases: glass, crystal and melt, are outlined twice. Glasses and crystals are solids; the melt is a liquid. Condis crystal, plastic crystal, and liquid crystal are increasingly less solid (more liquid). The arrows on the right-hand side indicate the possible transitions between

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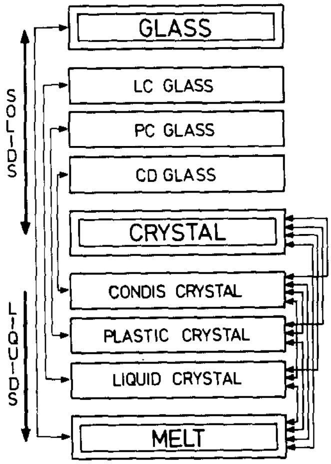

Fig. 1. Schematic diagram of condensed phases.

the phases. These are often first-order transitions, i.e. transitions involving a discontinuity in the first derivative of the Gibbs energy function, the entropy [4].

The overall entropy of fusion of a crystal, ΔS_f, can be approximately separated into the three contributions arising from positional disordering, ΔS_{pos}, orientational disordering, ΔS_{orient}, and conformational disordering, ΔS_{conf}, so that

$$\Delta S_f = \Delta S_{pos} + \Delta S_{orient} + \Delta S_{conf} \tag{1}$$

It is possible to make a first judgment of a phase classification based on the thermal analysis of the first-order transitions. Such analysis is helped by the empirical "rules" that ΔS_{pos} is generally 7–14 J K^{-1} mol^{-1} (Richards' rule) [5], ΔS_{orient} is usually 20–50 J K^{-1} mol^{-1} (based on Walden's rule) [6], and ΔS_{conf} is about 7–12 J K^{-1} mol^{-1} [7]. While ΔS_{pos} and ΔS_{orient} are referred to the whole molecule, i.e. they do not change with size, ΔS_{conf} is referred to a flexible bond (or a rigid bead), i.e. for a molecule, ΔS_{conf} is size dependent. The rather broad ranges of values indicate the approximate nature of this description. For a more precise analysis, the effects of disorder, volume change, changes in vibrational frequency, etc. would have to be detailed. Nevertheless, the empirical rules permit estimations of the various transition entropies corresponding to the arrows on the right-hand side of Fig. 1. The approximate transition entropy of 7–14 J K^{-1} mol^{-1} for the transition from the plastic crystal to the melt [2] is particularly well obeyed. The analogous transitions from the liquid crystalline phase to the melt are always much less than ΔS_{orient}, indicative of the rather high degree of orientational disorder and mobility in liquid crystals [1]. Condis crystals, finally, are expected to show variable entropies of transition from the crystal to the condis crystal and from the condis crystal to the isotropic melt, depending on the type and concentration of conformational disorder.

On cooling, the mesophases do not always follow the equilibrium path. If the ordering to the crystal can be by-passed, the liquid-like cooperative motion of the mesophases freezes at a glass transition, as is indicated on the left-hand side of Fig. 1. At these glass transitions there is no change in order and, as a result, no change in entropy. Because the liquid-like motion changes at the transition to practically vibrational motion only, there is a drop in heat capacity on vitrification. For liquid crystals, the existence of the glassy state had already been implied in the work of Vorlaender [8]. Their drop in heat capacity is practically identical to those for liquids [1]. For plastic crystals, the glassy state was first recognized by Adachi et al. [9]. The order of magnitude of the change in heat capacity at the glass transition of plastic crystals is also not much different from that of liquids. For the typical glass transition of a liquid, it was found that the change in heat capacity is approximately 10–20 J K^{-1} mol^{-1} when calculated per mole of mobile parts (beads) within the molecule [10]. As condis crystals usually show intermediate heat capacities between the solid and liquid states, their change in heat capacity on vitrification is also expected to be variable.

It seems reasonable, and has been illustrated by several examples, that molecules with dynamic conformational disorder in the liquid state also display it in the liquid crystalline and plastic crystalline states [11]. The primary way of distinguishing condis crystals from other mesophases is thus the identification of translational motion and positional disorder of the molecular centers of gravity, in the case of liquid crystals, and of molecular rotation in the case of plastic crystals.

JUSTIFICATION OF THE EMPIRICAL ENTROPY DESCRIPTION

To find an explanation for Richards' rule, one may postulate that the liquid state possesses a short-range "quasi-crystalline" structure [12]. As the temperature increases, this structure gradually changes, to become "quasi-gaseous" close to the critical temperature [12]. According to this model, the melting process can be considered as occurring in three major steps: first, the crystal lattice is expanded to give the average separation of the motifs that exists in the melt; next, the motifs are dynamically disordered; and finally, defects are introduced into the quasi-crystalline melt. Starting from a cubic close-packed crystal, Lennard-Jones and Devonshire computed the three melting stages, assuming interstitial atoms as defects [13]. For argon, an entropy of fusion of 1.70 R, or 14.1 J K^{-1} mol^{-1}, was computed that matches the experimental equilibrium value of 14.0 J K^{-1} mol^{-1} at 83.8 K. The entropy increase in going from fixed motifs in the small volume element of the crystal to the total volume of the melt (communal entropy) was earlier found to be R, or 8.31 J K^{-1} mol^{-1} [14]. The lower and upper limits of Richards' rule thus seem reasonable.

By analogy with the estimates of ΔS_{pos}, one can suggest that the empirically observed values for ΔS_{conf} are linked to the commonly used "rotational isomeric states" model of linear macromolecules [15–17]. Assuming that two to four rotational isomers become dynamically accessible on a disordering transition, and that 75% of the total entropy change is conformational, one expects an entropy gain of 7.7–15.3 J K^{-1} mol^{-1}, which is the observed range of experimental values. On the basis of atomistic calculations, a detailed rotator model was analyzed for the condis phase of flexible linear macromolecules, using a cooperative statistical treatment [18]. Both the transition from the crystal to the condis crystal and from the condis crystal to the melt could be quantitatively described as a function of pressure for polyethylene and for *trans*-1,4-polybutadiene. The overall melting of macromolecules was treated as an at least two-step transition: a conformational transition and the cooperative formation of dislocations, the latter giving rise to only minor changes in conformation [19,20]. For the condis states of polyethylene and possibly also of *trans*-1,4-polybutadiene, the two steps are widely separated at the two equilibrium transition temperatures T_{d} and T_{i} (disordering and isotropization temperatures respectively).

The orientational entropy of fusion, $\Delta S_{\mathrm{orient}} = 20\text{–}50$ J K^{-1} mol^{-1}, is based on Walden's empirical rule of entropies of irregular, rigid molecules [6]. Subtraction of the appropriate ΔS_{pos} leads to the suggested values. The separation of ΔS_{pos} and $\Delta S_{\mathrm{orient}}$ is well documented by those plastic crystals which often show ΔS_{pos} as the isotropization transition [2].

CORRELATION BETWEEN MOTION AND HEAT CAPACITY

The major motion type for the crystalline and glassy solid states is vibration. For linear macromolecules, one finds large deviations from the classical Einstein [21] or Debye [22] treatments of the heat capacity. Also, an early attempt to approximate the heat capacities with a combination of a 1-dimensional and 3-dimensional continuum to account for the anisotropy of the chain molecules [23] was, by itself, not applicable over a wide temperature range. The method that was finally successful [24,25] involves an approximation of the frequency spectrum by separation of the high-frequency group vibrations from the skeletal chain vibrations. The group vibrations are then accessible from normal-mode calculations on isolated chains, and are even transferable for polymers of similar chemical structure. The skeletal vibrations can then be approximated using the two-parameter Tarasov approach (θ_1 and θ_3) [23]. Agreement between computation and experiment has been tested for almost 100 polymers and is usually better than ±5% over the whole temperature range, starting from about 10 K [26,27]. Figure 2 illustrates the computed heat capacities of polystyrene, a polymer with 6 skeletal vibrations and 48 group vibrations per repeating

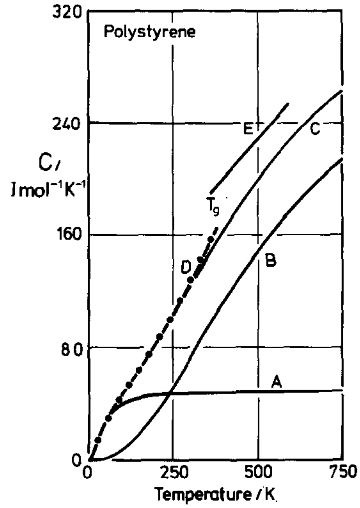

Fig. 2. Heat capacity of polystyrene. Computed heat capacities for the solid: A, skeletal contributions; B, group vibration contributions; C, total. Experimental: D (●), solid; E, liquid.

unit. At the small scale of the figure, there is hardly any difference between experiment and computation for the solid heat capacity [28].

The experimental heat capacity of the liquid is also plotted in Fig. 2 (at constant pressure, curve E) [28]. In simple cases, such as polyethylene, the heat capacity of the liquid state can be understood by introducing a heat capacity contribution for the excess volume (hole theory), and by assuming that the torsional skeletal vibration can be treated as a hindered rotator [29]. A more general treatment makes use of a separation of the partition function into the vibrational part (approximated for heat capacity by the spectrum of the solid), a conformational part (approximated by the usual conformational statistics) [15–17], and an external or configurational part. The latter has been shown to be almost completely represented by the difference in the heat capacities at constant pressure and volume [30]. The heat capacity of all polymers is thus well understood within the precision range of the experiment.

By adding the measured heats of transition to the integrated heat capacities, it is then possible to compute not only enthalpies, but also absolute entropies and free enthalpies. The change in entropy with temperature and state of matter is illustrated in Fig. 3 for the example of 1,4-polybutadienes [31]. The vibrational contributions to the entropies of the two isomers differ only slightly: $\theta_1 = 589$ K for the *cis*-isomer and 599 K for the *trans*-isomer. The sum of the entropies of the two stages of fusion of the *trans*-isomer are close to the single-step entropy of fusion of the *cis*-isomer. Also typical is the much larger accumulated vibrational entropy when compared to the transition entropy.

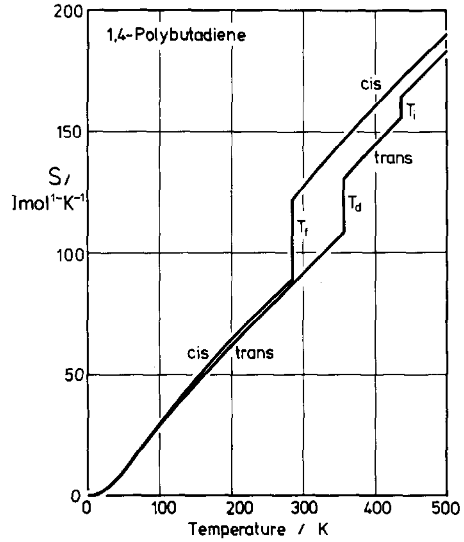

Fig. 3. Change in entropy with temperature for 1,4-polybutadiene.

In the course of the analysis of types of motion in crystals and mesophases, it became clear that large scale motion is also possible in molecular crystals. Conformational, rotational, and even diffusional motion can start considerably below the melting or disordering transition temperatures. The major tools for the determination of this motion, commonly connected only with the liquid or mesophase, are the various forms of solid state NMR [32]. In order not to lead to dynamic disorder, these larger scale motions must be jump-motions between positions of identical symmetry within the crystal. Because the intermediate in a jump-motion is present only during a negligible fraction of the total time, it can hardly be determined by most structure-analysis techniques such as X-ray diffraction and Raman or IR spectroscopy. Similarly, there are hardly any thermodynamic effects, provided the order (entropy) is little changed [33]. The changes in heat capacity when a torsional oscillator changes to a hindered rotator, for example, are gradual and usually occur over a temperature range of several hundred kelvins, so that its initial jumping from minimum to minimum in potential energy is difficult to distinguish from that of a pure oscillator [25,29]. Ultimately, this motion always leads to disordering of the crystal to mesophases or the melt.

Another large amplitude molecular motion type, first analyzed in the gas phase of pentane [34], is pseudorotation [35]. This is an internal motion which, by changing mainly torsional angles of the nuclei, interconverts conformers that are identical except for the numbering of the atoms. To visualize the motion, one may start, for cyclopentane, for example, with the molecule in the planar C_5 symmetry. This symmetry represents a local maximum in potential energy. There are then 10 puckered conformers of C_s symmetry and 10 twisted conformers of C_2 symmetry, both types having almost the same low potential energy. Interchange within a group of isomeric conformers appears as a rotation about the axis normal to the plane of the molecule, owing to the indistinguishable nature of the CH_2-groups, and has, however, no momentum about this axis. The motion actually consists of displacements parallel to the pseudo-rotation axis of corresponding groups by rotational motion about bonds.

In the crystal, pseudorotation is strongly hindered at sufficiently low temperature because of the volume restrictions resulting from the closely packed structure. On changing to the plastic crystal phase, this restriction is removed and pseudorotation is possible as in the liquid state. Larger cycloalkanes do not display a plastic crystalline state because of their larger deviation from a spherical shape. Nevertheless, these molecules show fast conformational interchange below any disordering transition temperature. This conformational interchange must occur largely within the confines of the corrugated, tubular volume available for the molecule within the crystal. Motion restricted to such a geometry can only be a concerted rotation and pseudorotation. In this case the molecule must reptate [36] along a corrugated circular path. To distinguish this type of motion from true rotation and pseudorotation, we call it "rotoreptation". As in true rotations one expects no entropy gain in rotoreptation if the motion consists of jumps between positions of identical symmetry. In this case one would not detect structure changes in the crystal.

SUMMARY

Advanced thermal analysis (ATHAS) provides considerable characterization of mesophases in general, and conformational disorder in particular. Combining thermal analysis with microscopic analysis techniques such as X-ray diffraction or solid-state NMR permits complete characterization.

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