

## DETECTION OF MULTIPLE NANOPHASES BY DSC

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### Abstract

Polymer molecules have contour lengths which may exceed the dimension of microphases. Especially in semicrystalline samples a single molecule may traverse several phase areas, giving rise to structures in the nanometer region. While microphases have properties that are dominated by surface effects, nanometer-size domains are dominated by interaction between opposing surfaces. Calorimetry can identify such size effects by shifts in the phase-transition temperatures and shapes, as well as changes in heat capacity. Specially restrictive phase structures exist in drawn fibers and in mesophase structures of polymers with alternating rigid and flexible segments. On several samples shifts in glass and melting temperatures will be documented. The proof of rigid amorphous sections at crystal interfaces will be given by comparison with structure analyses by X-ray diffraction and detection of motion by solid state NMR. Finally, it will be pointed out that nanophases need special attention if they are to be studied by thermal analysis since traditional 'phase' properties may not exist.

**Keywords:** DSC, glass transition, heat capacity, melting transition, nanophases, polymers

### Introduction

In thermodynamics a phase is described as a homogeneous system or subsystem of matter with a constant composition throughout [1]. Of course, thermodynamics being a macroscopic description of matter, phases must not approach atomic dimensions, since then the conditions of homogeneity and constant composition are violated. Furthermore, the thermodynamics of phases deals usually with equilibrium. Under equilibrium conditions, the relationship between the number of phases  $P$  and the number of components  $C$  is governed by the phase rule:

$$P + F = C + 2 \quad (1)$$

where  $F$  is the number of degrees of freedom (independent variables, i.e. temperature, pressure, and compositions). Treating a homopolymers as a one-component system, the number of possible phases in equilibrium is three at the triple point (constant temperature and pressure,  $F=0$ ) and two along the melting curve (constant temperature or pressure,  $F=1$ ). At constant pressure, the normal analysis condition,  $P+F=C+1$ , and only one phase can exist at different temperatures ( $F=1$ ). It is well-known, however, that many polymers are semicrystalline [2], i.e., they have at least one amorphous and one crystalline phase and, thus, violate the phase

rule and can, therefore, not be in equilibrium. The next question is naturally: Are there nonequilibrium polymer systems with three or more phases? And the answer must be affirmative. In this paper such nonequilibrium, multiple phases are discussed, and it will be shown that these phases can, in addition, be sufficiently small to be called nanophases. The phase structure governs the mechanical properties and is set during processing. The basic analysis tools for such polymer systems are: DSC for the macroscopic thermal behaviour; solid state NMR, for the detection of atomic motion; and X-ray diffraction, for phases structure studies. All must be used as a function of temperature in their 'thermal analysis' mode.

## Equilibrium considerations

Equilibrium thermodynamics is characterized by the  $H$ ,  $G$ , and  $TS$  diagram shown in Fig. 1, as example, for polyethylene. Full data sets are available through measurements on equilibrium samples and extrapolation of nonequilibrium samples to equilibrium. The ATHAS data bank contains information on some 200 polymers [3, 4]. Basic to all three curves are heat capacities,  $C_p$ , and latent heats of transition  $\Delta H = \Delta H/T_{\text{transition}}$  all measurable by calorimetry [ $H = \int C_p dT + \Sigma \Delta H$ ,  $S = \int (C_p/T) dT + \Sigma \Delta S$ ,  $G = H - TS$ ]. The heat capacity, in turn, is connected to molecular motion, while the kinetic energy of the atomic motion determines the temperature [4].

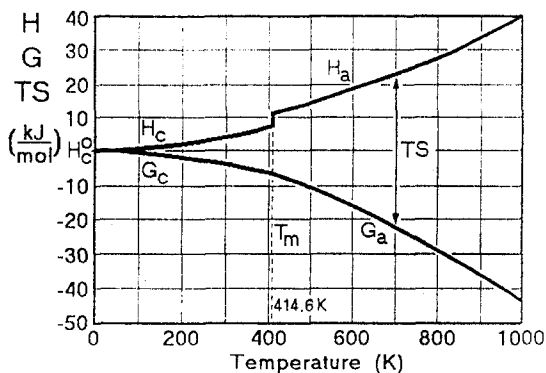


Fig. 1 Enthalpy,  $H$ , free enthalpy,  $G$  and entropy,  $S$ , of polyethylene. The entropy contribution is indicated by  $TS$ . Shown are the equilibrium states [3]

For solids, the heat capacity can be linked to the vibrational frequency spectrum, i.e. practically all heat capacity is caused by small-amplitude oscillations about the equilibrium positions of the atoms at a time scale of picoseconds ( $10^{-12}$  s) and faster, meaning that equilibrium is reached practically instantaneously [4]. For liquids, there exist additional large-amplitude motions, as in translation, rotation, and internal rotation. The latter motion is also called conformational motion and involves transitions between the different rotational isomers [5]. In the case of polymers, conformational motion is the most important large-amplitude motion. It is highly cooperative and can slow down the fast atomic motion to macroscopic time

scales. Below the glass and melting transitions, this motion usually stops and produces the typical solid properties. If this large-amplitude motion stops before an equilibrium structure has been reached, nonequilibrium structures arise, to be discussed in this paper.

The cooperative conformational motion needs commonly a larger free volume, adding potential energy to the heat capacity. This increase in potential energy is best observed at the glass transition. By changing vibrational degrees of freedom to conformations, one might expect the heat capacity to decrease because per mole of vibrators the contribution to the heat capacity should ultimately become  $R$ , the gas constant [ $8.314 \text{ J (K mol)}^{-1}$ ], while per mole of rotators the heat capacity contributions should approach  $R/2$ . The increased potential energy needed to create the larger free volume for the conformational motion causes thus the main part of the increase in heat capacity,  $\Delta C_p$  at the glass transition temperature,  $T_g$ . This increase is approximately constant when expressed per mole of mobile segments in the system [6] and can be used for an interpretation of the mobility gained at the glass transition [ $\Delta C_p \approx 11 \text{ J (K mol)}^{-1}$ ].

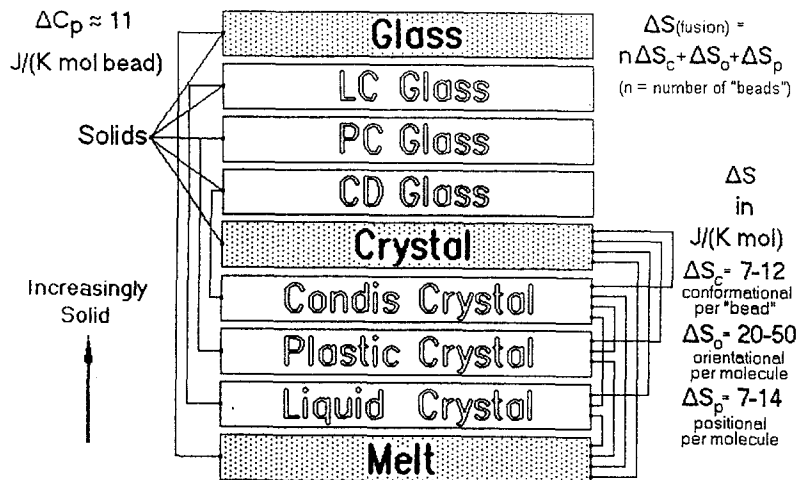


Fig. 2 Schematic of the various condensed phases and their first-order transitions (connecting lines on the right) and glass transitions (connecting lines on the left)

The entropies of transition can similarly be interpreted in terms of the disorder and motion attained or lost at a specific transition. Figure 2 shows a summary of the rules developed over the years to describe the entropy changes for the important phases and mesophases [7]. Starting from an equilibrium crystal and going to the melt, one should, by adding all entropy contributions, find a characteristic number of mobile segments ('beads') for a given polymer. This number of beads should, furthermore, agree with the number of beads identified by going from the amorphous glass of the polymer to the liquid. Based on this interpretation of the thermal properties, a quantitative study of the structure of matter is possible. It is furthermore possible to extend the equilibrium description to nonequilibrium [4].

## Size-dependence of transitions

When phase areas become smaller than about one micrometer, surface effects need to be considered. If, furthermore, the surface free energy is not at a minimum, the sample is not in equilibrium. Lamellar crystals of macromolecules are typically 5 to 50 nm thick and have two reasons for not being in equilibrium. One is that they are usually dividing a much larger sample rather than forming a single crystal, the other is that the lamellar shape is not an equilibrium shape [2]. Figure 3 illustrates the change of the melting temperature of the lamellar crystals of polyethylene as a function of thickness. All measurements were done under conditions of zero-entropy-production, i.e. the lamellae were molten such that the metastability of the lamellae matched the metastability of the supercooled melt [8]. Measurement of melting temperatures under zero-entropy-production conditions allows one, thus, to judge phase sizes.

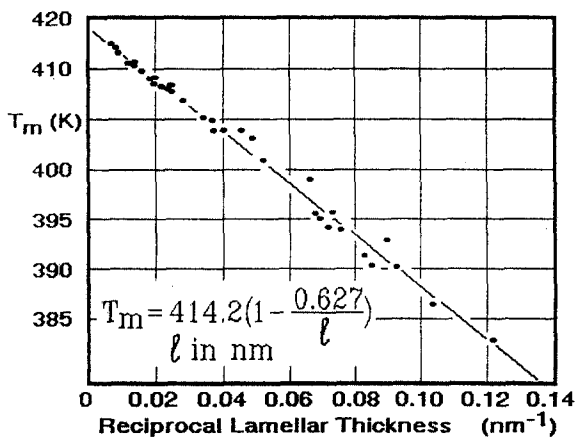


Fig. 3 Change of the melting temperature of lamellar crystals of polyethylene as a function of lamellar thickness,  $l$  [2]. (Measured under conditions of zero-entropy production [8])

The simple correlation of Fig. 3 holds strictly only if the crystal phases contain all their constituent molecules (by chain folding). As soon as larger numbers of molecules traverse the phase boundaries and are significantly restrained, additional nonequilibrium contributions to the fusion parameters are expected. Similarly, larger numbers of internal defects would need to be considered. Typical internal defects are the gauche contributions that were found experimentally as an increase in  $C_p$  before the melting point was reached [10] and could be simulated by molecular dynamics calculations [11].

The glass transition temperature is also affected by the size of the phases. One observes a broadening of the transition and a shift to lower temperatures for decreasing sizes [9]. In addition, it was found that the nature of the interface plays a role in the position and appearance of the glass transition. If molecules cross the phase boundaries, the direction of shift in the glass transition temperature depends also on the nature of the neighboring phase [9]. Finally, a local gauche-trans mobil-

ity was found to be possible below the glass transition temperature [12]. With these effects identified, one can try to identify multiple phases.

## Bulk multiple-phase structures

The first indication that the common two-phase model may not be sufficient to describe some melt-crystallized polymers was the discovery of a discrepancy in  $\Delta C_p$ . One expects a linear relationship between  $\Delta C_p$  and the heat of fusion. It was found for poly(ethylene terephthalate) that this is not so [13]. Only a certain fraction of the noncrystalline polymer would develop the large-amplitude motion, resulting in a lesser  $\Delta C_p$  than expected. The fraction of amorphous polymer that remained solid, is called the rigid amorphous fraction, RAF [14]. A typical example is shown in Fig. 4 for PEEK. The faster (poorer) the crystallization, the larger is the RAF. Since the RAF is rigid, it increases the modulus of the sample. On annealing, the RAF decreases, and the modulus of the sample should decrease, i.e. give the opposite effect as seen from the crystalline fraction which increases on annealing and, thus increases the modulus.

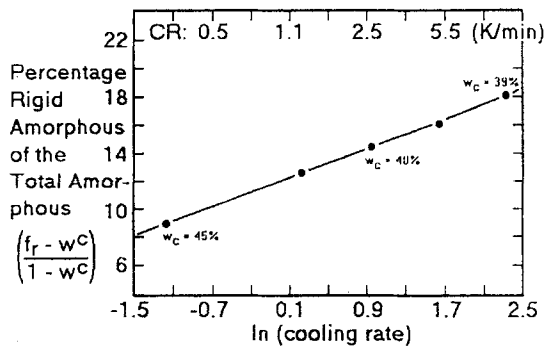


Fig. 4 Change of the rigid-amorphous fraction for poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene), PEEK as a function of cooling rate (CR). The fraction of crystallinity,  $w_c$ , changes somewhat over the chosen cooling rates [15]

Another multiple phase structure was discovered in macromolecules with sufficiently long segments of different chemical nature so that they can separate into microphases or nanophases with all molecules traversing several or many phase areas. Examples of the microphase separation are the well-known block copolymers [9]. A typical example for a nanophase separating polymer is poly(4,4'-phthalimidobenzoyl-dodecamethyleneoxycarbonyl) (PEIM-12) [16]. The repeating unit of PEIM-12 is shown below with the distinguishable carbon atoms numbered arbitrarily:

On cooling from the melt, PEIM-12 shows a two-phase layer structure that was described as a nanophase-separated material at the borderline between an amphiphilic liquid crystal and a thermotropic liquid crystal [17]. Further ordering is possible in such biphasic materials and produces multiphase structures. The lamellar superstructure is largely independent of the crystals. These types of multiphase structures complicate the thermodynamic description and help from direct analyses of the structure and motion is necessary.

## Direct measurement of structure and motion

The two-phase structure of PEIM-12 described in the last section was identified by finding two levels of mobility below the melting temperature, as shown in Fig. 5 [16]. The various peak intensities, shapes and positions can be used to interpret different mobilities of different atoms of the molecule. Together with X-ray and thermal analysis data, a full phase-structure study was possible. On quick cooling, the polymer takes on the mentioned two-phase layer structure of nanometer size. On partial crystallization, a third phase and sometimes a fourth phase appears, both in form of condis crystals (Fig. 2) with different amounts of  $\text{CH}_2$ -groups assuming crystalline *trans*-conformations.

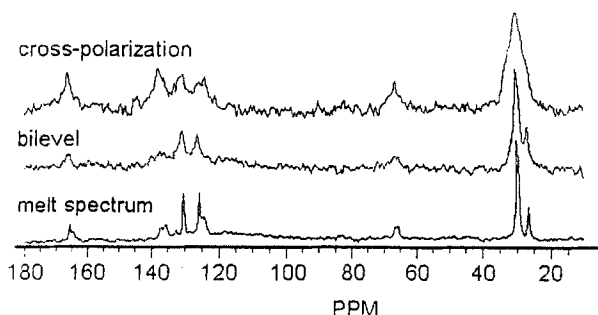


Fig. 5 NMR spectra of PEIM-12 at 393 K. The top spectrum arises from the rigid phase (crystal), the center from the mobile phase (noncrystalline, two-phase layer structure). The melt spectrum, given at the bottom as reference, was taken above the melting temperature (450 K) using also the bilevel method [16]

A second example of a multiphase structure is given by drawn fibers of poly(ethylene terephthalate). They were studied by thermal analysis and full pattern X-ray diffraction [18]. Thermal analysis identified crystallinity,  $w_c$ , and RAF from the heat of fusion and the smaller  $\Delta C_p$  at the glass transition than expected for the noncrystalline fraction ( $1-w_c$ ). Little change occurs in the RAF up to the melting region. The X-ray scattering of the sample after subtraction of the amorphous and crystalline contributions is shown in Fig. 6. Each of the fractions make up about 1/3 of the sample. The RAF gives an oriented, mesophase-like scattering pattern. Depending on the amount of draw and annealing, different degrees of order and orientation are possible and could be linked directly to mechanical properties [18].

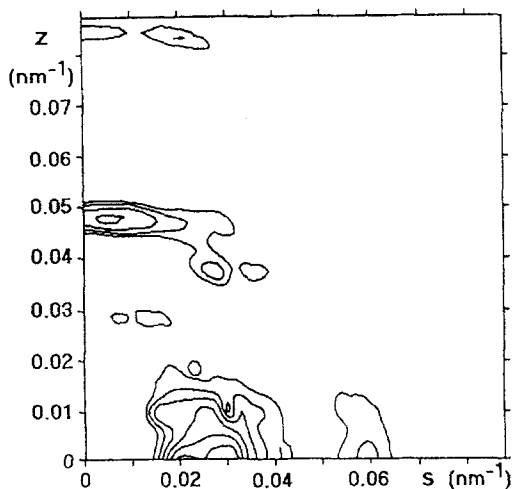


Fig. 6 Full-pattern X-ray analysis of drawn fibers of poly(ethylene terephthalate). The pattern shows the remaining intensities after subtraction of the crystalline and amorphous reflections. The spacing along the fiber axis are given by  $z$ , the equatorial direction,  $s$

Similar results, but with a much smaller amount of a mobile amorphous phase, were shown for ultrahigh-molar-mass, gel-spun polyethylene [19]. Here X-ray diffraction and solid state NMR could, together with thermal analysis, show that the crystals were not fully crystalline, despite the fact that the *trans* fraction is close to 1.0, and that there is no large amount of amorphous content, despite the fact that the heat of fusion is less than expected for full crystallization. A mobile, metastable, fully-oriented, third phase of nanometer dimension is the characteristic phase, governing, again, the mechanical properties.

In both these fiber samples the mesophases are metastable. This rather new topic of metastable mesophases was reviewed recently with special attention to the implications of the phase structures and sizes [20]. The problems of mechanical properties of drawn fibers were reviewed earlier, for example [21, 22] with models that permitted the progress summarized here for poly(ethylene terephthalate) [18] and polyethylene [19].

## Conclusions

This short summary illustrates that the description of many polymeric materials cannot be based on equilibrium thermodynamics. It is necessary to use irreversible thermodynamics. Furthermore, since irreversible thermodynamics is not limited by the phase rule, multiple-phase structures can exist and are needed to understand the structure-property-processing triangle. Finally, the phases may be smaller than the molecules, reaching ultimately nanophase dimension.

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