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The influence of the liquid-to-solid transitions on the changes of macromolecules from disorder to order[☆]

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ABSTRACT

When crystallizing macromolecules, one needs to recognize that they are sufficiently long to connect neighboring phases. This coupling between the phases is the reason that on ordering, practically all polymers develop a globally metastable, semicrystalline structure, consisting of multiple phases with different degrees of mobility. The ordered and amorphous phases are separated by nanophases of strained segments of molecule of nanometer dimensions, consisting of rigid-amorphous fractions, RAFs, which soften, above, within, or below the often very broad melting range of the ordered phases. Thus, ordering of a melt of macromolecules causes significant changes in the remaining amorphous phases. A summary of the various phases is given in terms of their structures, molecular vibrations, and large-amplitude motion as they influence the glass and order-disorder transitions. This is followed by a description of the limits of the classical nucleation theory of crystals when applied to macromolecules. Discussed in detail are the problems in primary and secondary nucleation which arise from the presence of RAFs. Special macromolecular nucleation processes that needed to be considered are the self-nucleation on cooling from above the melting temperature or on heating from above the glass transition temperature, and the molecular nucleation causing molar mass segregation on ordering. Finally, the glass transitions of the phases of various sizes and degree of order are discussed on hand of selected, pertinent examples.

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1. Introduction

1.1. Flexible, linear macromolecules

The understanding of *the influence of the liquid to solid transitions on the changes of macromolecules from disorder to order* has to overcome many difficulties which arose from the efforts to attempt to describe macromolecular systems on the basis of models developed and tested for the crystallization of small molecules. The ordering process for small molecules can be described by three major steps: (1) Nucleation, which creates an initial surface for the ordering and subsequent growth. (2) Diffusion of the ordering motifs to this surface, governed by the mobility within the liquid state. (3) Continued growth from the amorphous phase onto the crystal or incompletely ordered mesophase. These three steps were initially described by motion of simple, close to spherical motifs across the phase boundaries. For macromolecules, these steps are followed by limited improvements within the new, ordered phase until a metastable state is reached [1].

To describe the *ordering of flexible, linear macromolecules*, one must first consider the molecular size. For example, the much studied linear polyethylene, PE $(CH_2-)_x$, has typical lengths varying in length x from 10^3 to 10^6, or a molar mass from 14,000 to 14,000,000 Da, and an extended-chain zigzag length from 127 nm to 127 μm (with a fixed diameter of less than 0.5 nm). At sufficiently high temperature, their backbone is flexible due to conformational changes caused by internal rotations about the C–C-bonds. In the melt, the CH_2-groups of these molecules assume the shape of random coils, *macroconformations* with a root-mean-square distance from the center of gravity from 4 to 213 nm, respectively [2,3].

A compact crystal of a single PE molecule of $x = 10^6$ would fill a cube with ≈30 nm sides, a size which is in the microphase range. When not folded into a compact volume, such large molecules can cross many phase boundaries and connect the phases with covalent bonds. Their ordering begins in one part of the molecule and influence the residual molecule and the surrounding amorphous phase. The restrictions which are thus created, limit the ordering to a *semicrystalline, metastable state*, common in macromolecules. Furthermore, the amorphous phase surrounding the ordered phase

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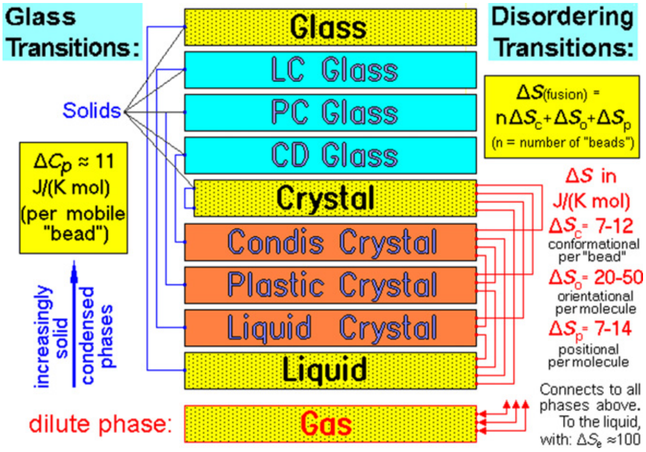

Fig. 1. The 10 different types of phases. The glass transitions are marked by the connecting lines on the left, the disordering transition, on the right.

is frequently separated into mobile and rigid amorphous fractions, MAFs and RAFs, respectively, with different glass transition behaviors [4].

The large number of possible *intramolecular* conformations of an amorphous macromolecule determines its entropy of fusion, ΔS_f. In contrast to the ΔS_f of macromolecules, the ΔS_f of small molecules is caused by *intermolecular* attainment of disorder based on translational motion and, if the molecular shape permits, rotational motion of the whole molecule, described by the well-known Richards' and Walden's rules for ΔS_f, first published in 1897 and 1908, respectively [5].

Equilibrium crystals of macromolecules would require an assembly of a large number of extended-chain molecules. Instead, it was discovered in the 1950–1970s that there exists a *chain-folding principle* [2, Section 3.2.2.1] which typically causes to 5–50 nm thin lamellae. Even crystals of single molecules of poly(oxyethylene), POE, and isotactic polystyrene, iPS, have fold lengths determined by the kinetics of crystallization [6,7] and not the ratio of surface free energies of the fold to side surfaces (usually 10/1) which would minimize the crystal free energy [1, Fig. VII.1].

Chain extension of the folded-chain crystals occurs on annealing after crystallization, but is usually limited [1,2]. Extended-chain crystals could be produced for some polymers of lower molar mass such as for POE [8], from more mobile and less dense mesophases, such as are known for PE to exist at high pressure [9], or by simultaneous crystallization and polymerization [10]. An example of the latter is poly(oxymethylene), POM, grown from crystalline trioxane [3, Fig. 3.104].

Before discussing the details of crystal and molecular nucleation (Sections 2 and 3) and the influence of the glass transition on nucleation and crystallization (Section 4), a brief definition of the basics of phases, semicrystalline macromolecules, and the glass transitions in the various phases of macromolecules is given, concentrating on results from calorimetric experiments.

1.2. The phases of matter

A recently completed arrangement of the all *possible phase types* is given in Fig. 1 [11]. In this scheme, a *solid* is defined as a phase below its glass transition, as first proposed in 1963 [12]. The different phases are characterized by their structure, as marked in the center column and commonly derived from X-ray diffraction. The dotted boxes represent the four classical phase types: gas, liquid, crystal, and glass. Between liquid and crystal there are three possible mesophases: (1) liquid crystals, LC (liquid phases with some orientational order, based on rigid mesogens of linear, lath-like, or disc-like shape within the molecules); (2) plastic crystals, PC (small molecules, rotatable within the crystal to produce orientational disorder); and (3) condis crystals, CD (with some intramolecular, conformational disorder). The mesophases have large-amplitude intermolecular or intramolecular mobility, i.e., they have a glass transition temperature, T_g, below which they are solids, as indicated by the vitrified liquid which represents the common Glass, the upper three mesophases (glasses of the LC, PC, or CD phases). Even macromolecular crystals may have glass transitions [13] and, then, are solid only below T_g. All glass transitions are marked on the left sides of the phase boxes of Fig. 1. The connecting lines link the phases of the same structure, but different, cooperative, large-amplitude motion.

In the right column, the *disordering transitions* are marked. These transitions are characterized by an increase in entropy, measurable by calorimetry in terms of the corresponding latent heat, extrapolated to the equilibrium temperature for the transition. The entropy of transition from the crystal to the liquid phase, the melt, is expressed by the listed information for $\Delta S_{(fusion)}$. The empirical ranges of contributions from the three large-amplitude motions involved in fusion are given below. The orientational, 'o' (rotational), and positional, 'p' (translational), contributions are normalized to molar mass, while the conformational contribution, c (intramolecular, hindered rotational), is normalized to a *bead size*, determined by the molecular segments involved in the conformational motion. For flexible macromolecules, orientational, and positional disorder are negligible relative to $n\Delta S_c$. The 'bead' is of similar size as is needed to establish the heat capacity change ΔC_p at the glass transition. The indicated ranges of entropy can be estimated from the empirical *Trouton's rule* for evaporation, ΔS_e, and for fusion, by *Richard's rule*, ΔS_p, and *Walden's rule*, $\Delta S_o + \Delta S_p$. A similar *rule for conformational disordering* is listed as ΔS_c [5,14].

After establishing the thermodynamic description of the phases, it is now necessary to recognize the change of properties when decreasing the *size of a phase*. Fig. 2 illustrates a useful separation of nanophases from microphases, and furthermore, macrophases. *A macrophase* (or bulk phase) is so large that the surface has little influence on its thermodynamic functions, enthalpy, H, entropy, S, and free enthalpy, G (or Gibbs function).

Thermodynamically, the ordered phases should be growing preferentially by adding mobile motifs to interfaces with a lesser surface free energy and thus determine the shape of the phase. The preferred lattice planes of lowest surface free energy, thus, fix the equilibrium crystal form (*Wulff construction* [2, Fig. III.4]).

A smaller phase is the *microphase*. Its surface effect is sufficient, for example, to significantly lower the melting temperature,

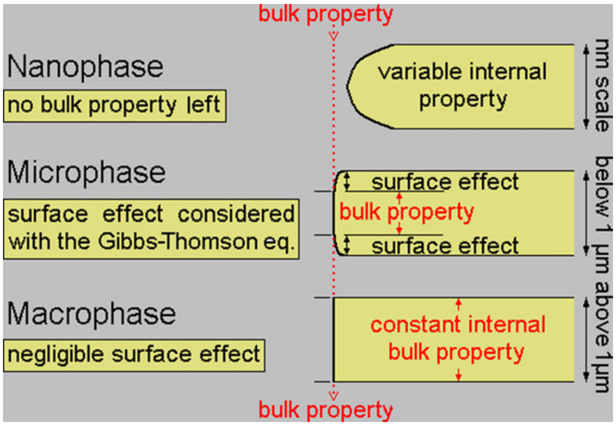

Fig. 2. The characteristics of different phase sizes. From top to bottom, the drawings on the right represent a cross-sections through lamellar phases of increasing thickness.