

Morphology of polymers

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Abstract - A survey is presented on the principles of polymer morphology. The major portion is concerned with placing existing observational material in wider perspectives, not featuring elsewhere, while the concluding parts invoke new material such as is pointing to new trends in the subject also beyond the confines of polymer science. The main emphasis is on the interrelation between thermodynamical and kinetical factors in phase transformations as generating and determining the morphology of the resulting phases. Special attention is being given to two-fluid separation in solutions and to crystallization, and to the interrelation between the two, where both can pertain. Within the subject of crystallization the essentials and consequences of chain folding are being presented together with the relation between chain folding and chain extension as emerging in ongoing works. In the latter context the importance of phase size is emerging as a factor not only determining thermodynamic stability per se but also the stability sequence, including the possibility of sequence inversion, of the different phases an issue of potential generality. The important role of metastable phases, true and size determined, and the hierarchical nature of the morphology is a connecting thread throughout.

INTRODUCTION

Under "Morphology" I shall be concerned with the physical organization of macromolecules. This, as I hope to show, is important scientifically for the understanding of macromolecular behaviour and for technological and practical applications, as for a polymer of a given chemical constitution it is the determining factor of physical properties. This subject is more than merely describing, shapes and sizes. It includes in the more generalized sense what is normally termed crystal structure, even if I shall not be writing here about crystal structures as such, and it encompasses the organizational capabilities of macromolecules in wider generality; also it lies at the cross road of the kinetics and thermodynamics of phase transformations. The outcome is a kaleidoscopic variety of structure features most profitably viewed as forming hierarchical systems in terms, not only of their dimensions, but also in terms of their genesis.

I shall confine myself to synthetic polymers in this article. Here, in contrast to natural polymers, the morphological features are in principle at least within our control; namely we can create them, influence them and shape them to our design. Also with synthetic polymers we can come closer to the physicist's abstraction of a string of beads in an attempt to discern the fundamental behaviour of long chains as such, as distinct from the effect of specific chemical influences, all important as their are in their own right. In pursuing this search for fundamentals I shall frequently refer to some of the simplest compounds even amongst the synthetics, to polyethylene in particular. Except for the last section most of the factual material to be referred to here will not be new in itself, yet I believe, placed in a perspective not presented so far.

THERMODYNAMICS, KINETICS AND METASTABILITY

The ultimate origin of the morphological features to be discussed lies in the fact that the thermodynamically stablest state is virtually never achieved. For a single component system in complete thermodynamic equilibrium, at a given temperature (T) and pressure (P), we would have a single phase (at all except along the coexistence line in the PT phase diagram) where the only morphological feature is the bounding surface of the macroscopic sample : thus we would have a liquid (melt) as bounded by the containing, vessel, or a macroscopic single crystal bounded by appropriate crystallographic facets. Similarly, in the case of an immixible (or partially mixible) two-component system, we would have two clearly separated macroscopic phases and no other morphology. The fact that a crystalline sample is always polycrystalline and that in a multiphase sample the phases are always finely divided, in other words that we have a morphology at all, is a reflection of the fact that thermodynamic equilibrium has not been achieved. This is true for materials in general, but a fortiori so for polymers of our concern. One obvious reason is the high viscosity of polymeric systems and the consequent sluggishness by which it adjusts itself to altered conditions of equilibrium. This factor combines with the large multiplicity in the organizational possibilities of which the long chains can avail themselves : the ones they will choose will then be determined more by kinetic than by thermodynamic factors. In other words the system will choose the pathway along which, the required change in phase can proceed fastest. Salient example of the latter is the chain folded crystallization of flexible chains : here the stablest state would be that of the fully extended chain, nevertheless the crystals can form and grow fastest by chain folding, where the fastest pathway determines the frequency of folding (the fold length, see later).

It follows that a polymeric material, as we have it, is nearly always in a metastable state. It follows further that there can be many stages in metastability, and correspondingly many metastable states. Now, it often happens that metastable states are favoured kinetically, i.e. they form faster than the corresponding stable states. The latter is long standing experience expressed in Ostwald's Law of Stages, dating from 1892, which states that a transformation from one stable phase to another will proceed through metastable states whenever such states exist. This law, while supported by ample experience, however, has remained purely empirical, and as such has currently fallen in oblivion. We shall demonstrate below that in certain instances at least, such as have direct applicability to polymers, it can be given more rigorous foundation.

Metastable states themselves can exist on various levels, particularly in polymers. Such a state is e.g. a supercooled liquid which is kinetically unable, or is slow, to crystallise. In polymers it can coexist with the crystal in a partially crystalline sample, the basis of the so-called "amorphous - crystalline two-phase structure" in most thermoplastics. Then the crystals themselves can exist with different crystal structures. As at any given T or P only one structure can be stable it follows that in cases where there are several crystal structures at a given T and P, all but one must be metastable. The scope of metastability is widened still further with the possibility of mesophases such as liquid crystals. Polymers in particular are prone to form mesophases and in many instances there can be near continuity between such phases and the crystal phase proper. Kinetic preference then can often lead to liquid crystals which are metastable ("monotropic" liquid crystals) greatly enriching the canvas of possible metastabilities and their interrelations.

To all the above we now add a further factor which hardly ever features in consideration on phase relations. This is the size dependence of a given phase, i.e. that a phase of small dimensions is less stable than the same phase of infinite dimension for which phase diagrams are usually constructed. Of course it is familiar that small crystals melt and small droplets boil at lowered temperatures etc., and that this depression of transition temperature is expressed by the well known Thompson-Gibbs relation. What however is not normally considered is the fact that the same applies also for transitions, to, from and between metastable phases, and that the degree of depression for a given size change is different for the different phases. It may therefore happen that stability regimes invert with size. In other words, a phase that is metastable with respect to another phase at a

given P and T in case of infinite extension of the phases, may become the stable one as the sizes are reduced. As limitation in size is one manifestation of morphology, we see here a link between thermodynamics and morphology through the concept of metastability, and underlying all, with the kinetic pathway of the phase transformation. To be again specific, small size could make the metastable phase the stable one, compared to the phase that is stable for infinite size. In the case that the phases are able to grow the relative stabilities could then invert during the growth process itself, and in this way what originally has started as a stable phase for small sizes could become metastable after passing a particular critical dimension.

Examples for some of the above possibilities and interconnections will be quoted below. Here we merely add that smallness in size has special significance for polymers where for small phase sizes the dimension of the phases can become comparable with that of the molecule itself.

For the present purpose I shall start with multicomponent systems where the segregation of components creates its own morphology which I shall term "Phase Morphology". Following this I shall proceed to phase transformations, in the present case crystallization, within a given single component system itself, which I shall term "Crystal Morphology".

PHASE MORPHOLOGY; TWO-FLUID SEPARATION

In what follows we shall consider two-component fluid systems as examples, and amongst those where one component is a small molecular compound and the second a polymer, a system normally considered as a "solution". A further extension of it of great practical topicality is the system where both fluids are polymers; in present usage these are termed "blends". Such "blends" display all the features of "solutions" plus many more, but this area cannot be accommodated within the present article.

Confining ourselves to solutions we consider first liquid-liquid (L-L) demixing without crystallization. Such is represented by familiar demixing curves as in Fig. 1, here displaying an upper critical temperature. Some polymers are too irregular to crystallize (e.g. atactic polythylene, a-PS); they will stay liquid throughout. Small molecular solvents usually crystallize, but this normally occurs at very low temperatures, out of range of most pertinent situations. In cases of high melting solvents where solvent crystallization comes within range, a variety of eutectic and cocrystallization features arise between polymer and solvent with corresponding enrichment of the morphological tableau (e.g. ref.1), which again cannot be accommodated within the present article.

In Fig. 1 the coexistence line is highly asymmetric. Such an asymmetry is inherent to polymer-solvent systems and reflects the asymmetry in size and that of the consequent interchangeability of polymer and solvent molecule. Lowering the temperature provokes

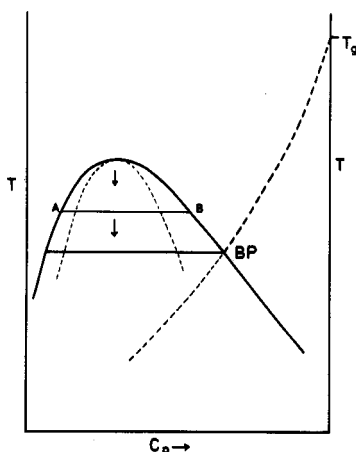


Fig. 1 : Schematic phase diagram, for a polymer in solution showing liquid-liquid phase separation intercepted by vitrification. (T_g)

L-L phase separation in the usual manner with compositions corresponding to the lever rule construction along tie lines. The sluggishness of the process due to high polymer viscosity alone will ensure that separation into two liquid layers of appropriate composition will not proceed to completion, hence a more or less permanent dispersion, hence phase morphology will result. However, this effect is often much accentuated by a further factor, vitrification, stabilizing transient phase morphologies, to which we now turn.

Most polymeric liquids "freeze in" below a certain temperature, the glass transition temperature T_g . T_g does not represent a thermodynamic transition (although this issue has been under much debate in the past) but a temperature signalling the very rapid rise of viscosity, hence it does not normally feature in phase considerations. Even so its inclusions in phase diagrams is, in my view, highly desirable because it indicates the temperatures and concentrations where genuine phase transformations are arrested, or are made impossible in practice. It follows that the system below T_g will be metastable. This, in view of the above, applies on several levels: the glassy solid itself will be metastable because it possesses excess volume, enthalpy etc, even within the liquid phase stability regime. It will become multiply metastable when passing into regimes of other phases, into which it is prevented to transform due to restricted molecular mobility.

The significance of T_g for L-L phase transformation was recognised by Berghmans in connection with physical gelation², but the implications are wider³. In Fig. 1 T_g is presented as function of concentration (c) of polymer. As seen, T_g for pure polymer is depressed on addition of solvent, an effect commonly known as plasticization. It will be apparent that the T_g v.c. line will intersect the L-L phase line at a point I termed BP (Berghmans Point).

To illustrate the significance of this intersection consider a solution of a given concentration as it is being cooled. On crossing the phase line it will separate into a solvent-rich and polymer-rich phase of composition defined by the two end-points of the tie lines corresponding to the temperature which pertains at the particular stage of cooling. When this end point situated at the site of higher concentration reaches the BP point the corresponding concentrated phase vitrifies and further phase separation ceases at that T value. This also means that the state of phase dispersion prevailing at the instant of vitrification is preserved, imparting to the sample a corresponding "phase morphology". If the polymeric phase is connected at that stage, either through isolated molecules linking vitrified particles, or through microscopic phase continuity we then have a gel. In fact, as recognised by Berghmans, this is the simplest form of physical gel formation, independent of any molecular specificity. The detailed morphology will depend on the starting concentration. At low concentrations the vitrified polymer-rich phase will be the dispersed phase with the fluid, solvent-rich phase as a matrix. For long enough molecules (at an otherwise "low" polymer concentration) there will be molecular connectedness between the glassy particles, hence a gel. In the absence of molecular connectedness we have a latex suspension, which nevertheless, if sufficiently concentrated, can form ramifying aggregates and eventually gels through adhesive contact (Fig. 2). For high enough initial solution concentration, there will be particle-matrix inversion giving rise to a continuous glass with dispersed droplets within. Intermediate concentrations yield glassy foams, closed or open, according to whether at the high or low polymer concentration side of this intermediate concentration range.

The above relation between initial solution concentration and morphology represents a well documented qualitative trend. For quantitative considerations there is yet another factor which overrides what otherwise would be a matter of straightforward percolation statistics. This is the mode of phase separation, namely, whether it is nucleation or spinodally generated. Fig. 2 is a typical result of separation through nucleation. If phase separation occurs within the spinodal regime of the phase diagram (within the dashed lines in Fig. 1) then the resulting morphology, as arrested by vitrification, will be quite different: it will form a bicontinuous interpenetrating network of the two phases even at

very low polymer concentrations, below the percolation threshold of mutual phase continuity (Fig. 3). As seen from Fig. 3 here the polymer rich-phase forms a kind of connected girder structure continuous throughout the macroscopic sample.

It should be obvious from the above excerpts from a much wider field that phase morphology originating through the combined influences of thermodynamic and kinetic factors can profoundly affect structure and consequent properties of materials. Understanding and consequent control of the above factors should lead to purposeful design of membranes and porous structures in particular. Further, when applied to "blends", i.e. to bi-(or multi) component systems, where the "solvent" is also a polymer, the same consideration should facilitate design of materials for structural purposes.

RELATION BETWEEN PHASE AND CRYSTAL MORPHOLOGY

Before discussing crystal morphology itself, first its relation to phase morphology will be introduced. For this we extend a phase diagram as in Figure 1 to include crystallization. For a single component system the "phase diagram" is a simple temperature scale denoting the L-C transition, i.e. the melting point T_m , (which in Fig. 4 is the right hand side ordinate); above T_m the material is liquid, below crystalline. For a two-component system say solution, in the simplest case of complete miscibility above and immiscibility below the melting (T_m) (or rather dissolution temperature (T_d)), the phase diagram will be as in Fig. 4, (with freezing of the solvent at high dilution - in simplest case a eutectic - at the lowest temperatures omitted). Cooling such a solution, yields the usual solution crystallized product. At the highest dilutions the precipitating solid polymer can be in the form of isolated crystals, the so called polymer single crystals, which form the basis of all polymer crystallization studies. As known, in the simplest form they are isolated lamellae containing the chains in a folded conformation (Fig. 5, 6). At all but the highest dilutions the precipitate will consist of lamellar aggregates of increasing compactness and complexity as the concentration is increased (Fig. 7). At the highest concentrations and in single component melts they will, in general, give rise to spherulites with their characteristic appearance (Maltese cross and often concentric banded extinction features) under crossed polars in the optical microscope (Fig. 8). These features, at the large scale end of the crystalline structure hierarchy are radially arranged and growing lamellar aggregates (the source of the Maltese cross), often with uniform helicoidal progression of these lamellae along radial directions (the source of the banding).

I shall return to some aspects of the basic crystallization process and associated morphology in the next chapter. Here, I rather pass on to the situation where two-fluid separation and crystallization combine. A corresponding phase diagram for a bicomponent polymer-solvent system is shown by in Fig. 9. At the high c side the situation is similar to the one discussed above: total miscibility above a certain T (T_d) and precipitation of solid below. On the left hand side we have two-fluid separation, in this case as drawn for an upper critical temperature. As the temperature is lowered there is, as for Fig. 1, separation into solvent-rich and polymer-rich fluid phase defined by tie points A and B. On progressive lowering of temperature, points A, B "slide" downwards along the phase line until the "invariant" line A^* , B^* , C^* is reached. Here thermodynamically crystallization can occur, i.e. precipitation of a concentration as C^* (practically 100% polymer) within the polymer-rich phase of composition B^* . It will proceed with unaltered concentration until that phase is consumed and the concentration of the whole remaining solution will be as in A^* , i.e. corresponding to the dilute solution along the invariant line. On further lowering of T crystallization will then proceed in the same way as from a totally miscible solution, in the present case confined to the dilute concentration in terms of polymer.

Of special interest for the present are the consequences for the morphology. Namely, the crystal morphologies will now develop within the confines of the phase morphology. The phase morphology will be represented by the state of dispersion the system attains when the temperature reaches the line $A^* B^* C^*$. If this phase is a set of globules the

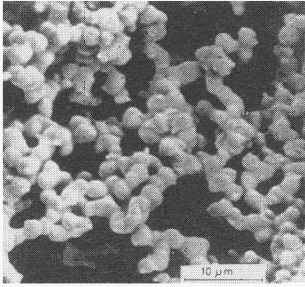


Fig. 2

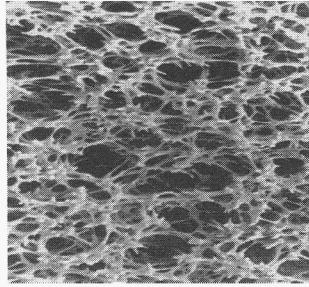


Fig. 3

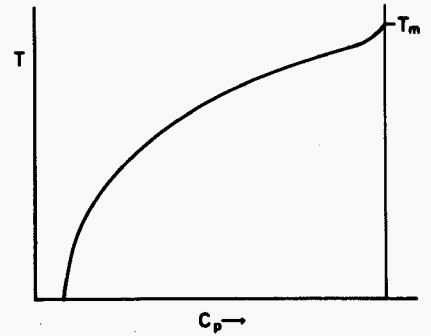


Fig. 4

Fig. 2 : Phase separated and vitrified a-PS globules forming a gel through adhesive contact. Phase separation is through nucleation. SEM micrograph.

Fig. 3 : As Fig. 2 but with phase separation through spinodal mechanism at the appropriate concentration. 2000x

Fig. 4 : Schematic liquid-solid (crystal) phase diagram for a fully miscible polymer solution.

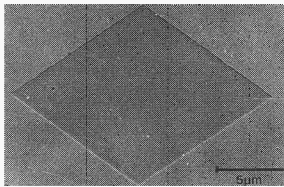


Fig. 5

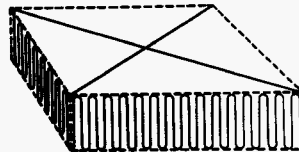


Fig. 6

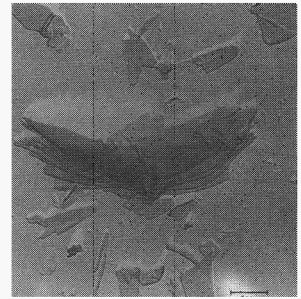


Fig. 7

Fig. 5 : Lamellar single crystal of polyethylene as forming from solution, Electron micrograph (6).

Fig. 6 : Diagram showing chain folding in a polymer single crystal as in Fig. 5., (also indicating sectorization : distinct sectors by fold plane direction, see ref. 4).

Fig. 7 : Splaying aggregate of lamellar crystals of polyethylene extracted from melt crystallized interior (12).

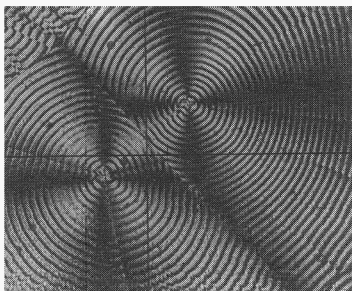


Fig. 8

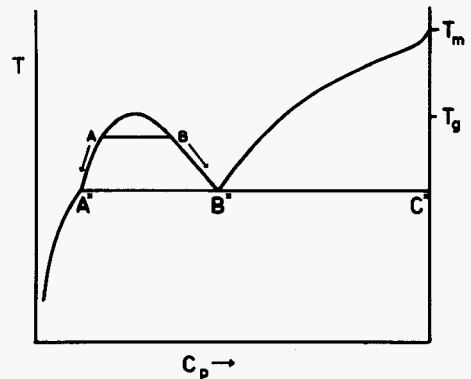


Fig. 9

Fig. 8 : Spherulites in a melt crystallized polymer. (Poly hexamethylene adipate) Polarizing optical micrograph. (13) 200x.

Fig. 9 : Schematic phase diagram showing liquid-liquid phase separation plus crystallization from solution.

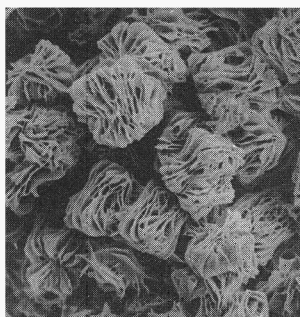


Fig. 10 : Crystalline lamellae within liquid-liquid phase segregated phase morphology. Poly 4-methyl-pentene 1 in amylacetate. (14) SEM micrograph 1000X.

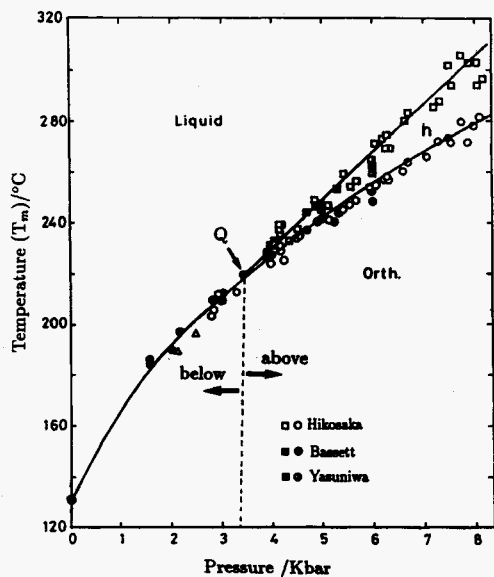


Fig. 12 : PT phase diagram for polyethylene displaying hexagonal phase regime (h) and triple point. Measurement points by authors indicated.

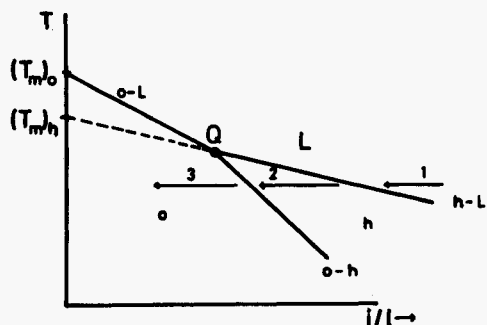


Fig. 15: Schematic melt-crystal "phase diagram" displaying size (l) dependence with a cross-over of stability regimes as it might pertain for polyethylene (see text).

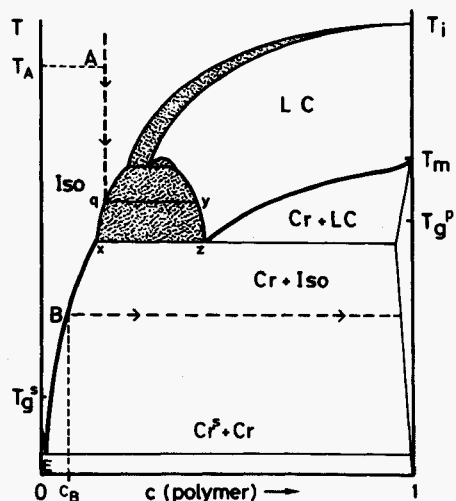


Fig. 11 : Schematic phase diagram of a hypothetical liquid crystal forming polymer which can be both thermotropic and lyotropic, i.e. can form biphasic solution.

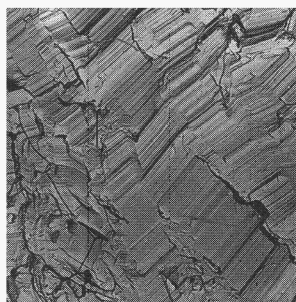


Fig. 13



Fig. 14

Fig. 13 : Extended chain type morphology in polyethylene crystallized under pressure. Fracture surface, replica (7) 26000X.

Fig. 14: Cross section (EM replica of fracture surface) of an isolated lamellar single crystal growing from the melt under elevated pressure (9) 1000X.

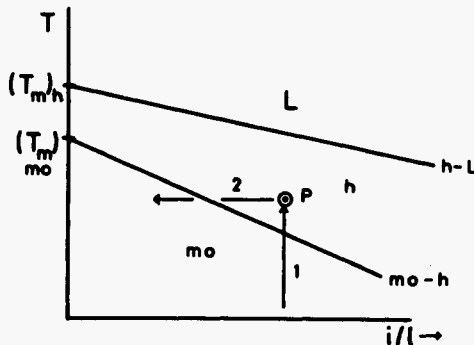


Fig. 16 : As Fig. 15 but for the cases where both crystal phases are stable for all sizes, as pertains for poly 1-4 transbutadiene. An experimental pathway is indicated. (11)

lamellae, and aggregates thereof, will develop within these globules, as e.g. in Fig. 10 which is a clear example of the combination of phase (globule and crystal (lamellae and aggregates) morphologies. Clearly, by considering the potential variety of phase morphologies (Figs. 2 and 3 are examples for a non-crystalline polymer) the possible combinations are endless. If both components are crystallizable within the temperature range in question (as e.g. with solvents of melting points in the range of the polymer melting point, or what is practically more important, when the second component is also a polymer, the case of blends), the variety of phase conditions and corresponding morphologies will become even further enhanced.

The canvas widens further when the polymer has several crystal modifications, and particularly when it can exist as liquid crystal. There is no scope to enlarge on this in the present paper and in any event the subject area is still in a state of rapid development. Here I only add the simplest phase diagram (Fig. 11) which can be expected for a two-component system with one component a low molecular weight solvent and the other a polymer capable of forming both liquid crystal (LC) and crystal (C). As above, the pure polymer ($c = 1$) is represented by the right hand side ordinate. Such a system (termed "thermotropic") on cooling transforms into LC phase first at T_i and subsequently into crystal at T_m . It is readily seen from the foregoing, that the crystal morphology will be greatly influenced by the preceding phase morphology in the LC state, thus that now we can have a two stage morphological hierarchy, an LC phase morphology plus a crystal morphology even in a single component system. On adding a solvent component (a system termed "lyotropic") we can have again two-fluid separation, but now between the isotropic solution and a solvent containing the LC phase, the so called biphasic behaviour of lyotropic liquid crystals, of which Fig. 11 is possibly the simplest case. (As it is, a full phase diagram such as in Fig. 11 - also proposed by Papkov - has not yet been observed in practice, only portions of it in a given system, because in existing materials it has not been possible to cover the full concentration and temperature range so far). The enhanced multitude of morphological possibilities arising from the combination of phase and crystal morphologies will again be apparent.

Finally as in Fig. 1 vitrification can intervene in all the possibilities raised above. T_g can be located anywhere below T_m (or T_d) and will arrest (or prevent) any of the phase transformations including crystallization. (It is marked arbitrarily in Figs. 9, 11)

In all the above we were discussing phase transitions as occurring along the respective phase line on cooling. As known, this is not always so as the systems often supercool. In polymers this is more so than usual. They always supercool and, what more, this supercooling is usually different for the different kinds of phase transition. Thus, here kinetics dominates more than usual and may even override the thermodynamic sequence with temperature. In particular, the supercooling required for crystallization can be particularly massive allowing metastable phases to appear which otherwise would lie deeply buried beneath the phase lines denoting maximum stability. This means a still further, vastly increased multiplicity in morphological possibilities.

CRYSTAL MORPHOLOGY

Chain folded crystallization—general

As already implied by Fig. 5 crystals of flexible polymers are lamellae, constituted of regularly and periodically folded chains (Fig. 6). Originally this was totally unexpected. It was based on straightforward observation coupled with quite simple deductions therefrom. Crystals such as in Fig. 5 could be seen directly as precipitating from solution. The molecular orientation was simply established from electron diffraction which, in the knowledge of the crystal structure, reveals that the chains are perpendicular to the lamellar surface. As the lamellae are 100 or a few 100Å-s thick and the chains thousands and tens of thousands of Å long, they cannot be accommodated within the thickness of the lamellae in an extended form. Hence it follows that they must be folded over many

times as represented in an idealised form in Fig. 6. Thus we have a rather unique situation where a crystal dimension, the lamellar thickness, corresponds to a molecular parameter the fold length (to be denoted ℓ). It follows that the subject of crystal morphology, concerned with shapes and sizes, and that of crystal structure, concerned with the position and arrangement of molecules, here became closely linked.

In all the above the fold length ℓ , readily determinable, as it is equivalent to the crystal thickness, has an all important part to play. It was found to be uniquely dependent on the crystallization temperature (T_c), or rather on the supercooling (ΔT where $\Delta T \equiv T_m - T_c$), where in first approximation, $\ell \propto 1/\Delta T$. However, ℓ once established through primary crystallization, may increase further subsequently on heat annealing, or even during later stages of crystallization (secondary crystallization). This subsequent increase in ℓ involves a refolding process of the chains while in the solid (or partially solid) state. The sum total of these and other experimental facts form the basis of the theories setting out to describe and explain chain folded crystallization in quantitative terms. This is a very large subject beyond the scope of this article. Here only that much will be stated that the thermodynamically stablest form is the crystal with fully extended chains which, however, is not attained due to kinetic factors, which in turn leads to chain folding. Or putting it in more concrete terms, the initial deposition of the chain along a crystal face in a fully extended form is a highly improbable and also energetically highly unfavourable event, even if it leads to a state of maximum stability in the end. Folding over of the chains in the course of their deposition occurs faster and hence will determine the course of the crystallization. Further, it can be shown, that there is always a narrow range of favoured ℓ -s which then will impart the lamellar character with uniform lamellar thickness to the crystal morphology. These chain folded lamellar crystals with thicknesses appropriate to a given supercooling are thus the ones which form fastest even if they do not correspond to the thermodynamically stablest state. In fact they represent metastable states in their own right, the main source of metastability being the small crystal size (thickness), which here is not a simple transitory state, but is in effect locked in through the very nature of the crystal growth process itself.

For more details on chain folded lamellar crystallization I need to refer to some of the reviews (4,5,6) I shall lift out one aspect only which presently promises to have many forward looking consequences and which also links up with the main theme of this article i.e. interaction between thermodynamics, kinetics and morphology including issues relating to metastability. The subject to be discussed specifically further centres on the relation between chain folding and chain extension which in polyethylene is made accessible through studies of crystallization under high pressure.

Chain folding v. chain extension and some recent trends

The origin of the subject lies in crystallization studies of polyethylene under hydrostatic pressure. As Wunderlich and colleagues observed first ⁽⁷⁾ polyethylene, when crystallised above 3.3 Kbars (precise value is of later origin) differed from the familiar plastic; it was hard and brittle and of near 100% crystallinity by conventional criteria. Morphologically, the samples had a highly stratified structure with chains perpendicular to the stratification (Fig. 13). It was inferred from the scale of the stratification, which was 0.1 - several μm , that the chains must be in an extended, or at least not too numerous folded conformation, which by the morphological evidence of tapering crystal edges must have been attained by refolding subsequent to an initially chain folded crystallisation of more conventional fold length (few 100-s \AA). It was then an important finding by Bassett (see ref. 8) that PE exists in a hexagonal crystal phase (h) (as opposed to the conventional orthorhombic (o)) at elevated pressures, 3.3 Kbar being a triple point for PT phase diagram (see Fig. 12). This hexagonal phase is highly mobile (we currently attribute liquid-crystal characteristics to it) which facilitates refolding to longer fold lengths and ultimately to full chain extension while in this phase, which is the origin of the "extended chain type" texture observed in crystallisation under pressure.

In a recent extension of this work individual crystals were viewed growing while under pressure in preselected portions of the phase diagram. Also simultaneously X-ray diffraction patterns were recorded. Further, the electron microscopic fine structure was examined, at selected stages of development of crystals⁽⁹⁾. Fig. 14 is a cross section of an isolated layer formed and grown at elevated pressure where growth had been interrupted by pressure quenching and internal structure exposed by cutting and suitable etching. It is wedge shaped. The chains are perpendicular to the wedge surface. At the tip the wedge is $<500\text{\AA}$; this is much thinner than the molecule is long (3000\AA in this case) hence the chains there must be folded. At the centre the wedge is much thicker ($3\ \mu\text{m}$) than the chain length, hence there the chains must be extended and stacked (and interleaved) on top of each other. Hence growth starts with chain folding and proceeds both laterally and in the thickness direction. If in the hexagonal phase regime then growth along the thickness direction proceeds towards chain extension and beyond without any discontinuity in the growth process giving rise to the extended chain type crystal as in Figs. 13, 14. This is in contrast to the usual experience with crystallization in the orthorhombic regime where such thickening growth does not occur at all, or stops at a particular stage of chain extension, giving rise to the by now more familiar chain folded lamellae discussed previously.

Current work is throwing new light on the relation between chain folded and chain extended crystals as differentiated above. In particular, three important observations were made: i) crystal growth always starts in the mobile hexagonal (h) phase even in the orthorhombic (o) stability regime of the PT phase diagram, where the h phase is thus metastable, at least around the triple point examinable by our in situ pressure experimentation. ii) Within the o phase regime this metastable h phase transforms into the stable o phase at some observable stage of growth. iii) On transformation all growth, lateral and thickening growth, stops (or slows down drastically). The latter in particular is locking in the prevailing crystal thickness (together with the corresponding chain folded conformation if in that thickness regime).

The above has many potential consequences, both forward looking and retrospective. While of major influence on the present issue, the mere fact that a new phase state first passes through a metastable station in the course of change in matter of state (e.g. vapour \rightarrow solid, liquid \rightarrow solid) is in itself not quite unusual and is in fact expressed by Ostwald's "Stage Rule". A further intriguing possibility arises when considering the effect of phase size on the phase diagram. Namely, with appropriate (and reasonable) choice of surface parameters the situation can arise that the true thermodynamic stability conditions can invert with size. Specifically, for a polyethylene crystal that is thin enough (to home in on the case of our interest, the argument in principle is more general) the h phase could be the stable and the o phase the metastable one even in the P-T regime where normally the converse applies, i.e. stable o and metastable h phase for an infinite size crystal. If and when this is the case, true metastability need not even be involved to account for the observation of a metastable phase appearing first. In fact, here the metastable phase will, in its diminutive form, be the stable phase, with an inversion of phase stability on growth; an accompanying $h \rightarrow o$ transformation will then set in beyond a certain size (lamellar thickness, fold length) as the crystal grows (thickness for the present purpose). While the occurrence of the above is a general possibility (being one manifestation of the "Ostwald Stage Rule", here rather founded on equilibrium thermodynamics) it acquires special significance for polymers such as polyethylene. Here, below the triple point, the initial (and for infinite sizes metastable) h phase is mobile allowing for ready refolding to greater thicknesses thus leading up to a size induced stability inversion, in the present case to $h \rightarrow o$ transformation, which then in turn arrests (or drastically reduces) the thickening which has brought the newly formed phase into being with the effect of limiting the final thickness of the lamellae. The latter (i.e. lamellae of uniform small thickness) is in fact the principal feature of a crystalline flexible chain polymer.

As all new phases have to form and grow, and go through all sizes in the process, we feel that the above scheme has the potential of wide ranging applicability, which in the case of polymers acquires special significance due to the enhanced chain mobility and consequent thickening capability, in the metastable phase.

It can be readily shown ⁽¹⁰⁾ that the condition for cross-over of phase stability with crystal size is

$$\frac{\sigma'}{\Delta H'} < \frac{\sigma}{\Delta H} \dots\dots\dots 1)$$

where σ and ΔH are surface free energies and heats of fusion respectively, where σ' and $\Delta H'$ pertain to the metastable phase (in the present case of polyethylene the h phase) and the σ and ΔH to the stable phase (in polyethylene the o phase) as referred to infinite phase sizes. (In lamellar polymer crystals σ' and σ are essentially the basal plane, hence fold surface free energies). In that case a cross-over will occur for a particular critical phase size ℓ_{cr} (lamellar thickness in present situation). It can be shown ⁽¹⁰⁾ that ℓ_{cr} is inversely proportional to the supercooling, which in this case is defined with respect to the h \rightarrow o transition temperature pertaining for infinite phase size, with a proportionality constant which depends on the thermodynamic parameters (or rather their differences) of the two phases involved. As in polyethylene condition under 1) can be shown to pertain, crystallization could start with the transient h phase, with a much reduced length compared to what would be the stable one for the o phase, for which in turn the chain deposition probability, hence consequent growth rate, is vastly enhanced.

The process is represented thermodynamically by Fig. 15. This is a temperature v. size ($1/\ell$) "phase diagram" for a liquid (L) - solid system the latter having a metastable (here h) and stable (here o) variant. As seen, for small enough size (large $1/\ell$), more specifically beyond a "triple point" Q, h has a stable domain. Consider crystal formation at a T corresponding to the horizontal arrows denoting the process of growth. Along arrow (1) the new phase is subcritical. It becomes stable by reaching large enough size, ℓ , (for polymers lamellar thickness) to enter the h regime (arrow (2)), which for that small ℓ is actually the stable phase. On continued growth (which for our polymer is thickening of lamellae) we cross the o-h phase line and the crystal can convert to o, the phase of ultimate stability (arrow (3)). By the results quoted above further growth will stop or slow down, locking in the corresponding crystal size (ℓ) as a permanent feature of the final texture.

Thermodynamically, the feasibility of the above scheme is beyond query. Whether it is actually operative in any given system depends on the numerical parameters, both thermodynamic and kinetic, involved, which would require individual attention for each system. We certainly can quote one example of size determined phase transition in the course of lamellar thickening, the principal ingredient of the scheme in Fig. 15. This is on a polymer, poly-trans 1-4 butadiene, which has a stable mobile crystal phase for infinite phase size even at atmospheric pressure. Here the T v. $1/\ell$ "phase diagram" is as in Fig. 16, i.e. without any cross-over with size. The size dependence could in fact be demonstrated on chain folded lamellar crystals as follows. A preparation of chain folded crystals, already grown to thickness ℓ , was heated to point P along pathway 1, when it changed from immobile phase mo (here monoclinic) to the mobile h phase. On holding at P the crystals were thickening rapidly (arrow 2), until at sufficiently large ℓ the mo-h phase line is reached and crossed, when the system was observed to revert to the initial mo phase, the stable phase for infinite size at that temperature⁽¹¹⁾.

At this, I think forward looking point I need to end the present survey, in which I have tried to provide a glimpse into the rich and varied subject of polymer morphology with, what I hope, perspectives extending beyond the confines of polymer science.

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