New trends in polymer crystallization studies Part II. The role of transient mesophases in polymer crystallization

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NEW TRENDS IN POLYMER CRYSTALLIZATION STUDIES

PART II - THE ROLE OF TRANSIENT MESOPHASES IN POLYMER CRYSTALLIZATION

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Abstract : Studies of crystallization of polyethylene (sharp fractions) under hydrostatic pressure revealed that the previously identified mobile hexagonal phase (h) can arise as a metastable transient even in the more customary orthorhombic (o) stability regime. In fact, it was found that crystallization in the h phase controls the crystallization process even there, at least in the portion of the P-T phase diagram explored so far. Accordingly, crystallization (nucleation and growth) can only take place while in the h phase and ceases upon transformation into the o phase (occurring when the o phase is the stable one). Crystal growth includes both lateral and thickening growth. Thickening growth in particular involves chain refolding, envisaged by sliding diffusion, and can proceed to thicknesses far in excess to chain extension. All growth rates can be defined quantitatively and correlated with morphology. The above findings are raising wider issues such as : Are metastable transients necessary for polymer crystallization under all conditions, or alternatively are there at least two different modes of crystallization with a change-over unspecifiable by thermodynamics? Beyond this it raises the possibility of a new source for finite uniform lamellar thickness in the form of crystal-thickening-induced growth limiting phase inversion, an example for which has already been found in polymer trans-1,4-polybutadiene.

INTRODUCTION

The present, Part II, of the series takes its starting point from the familiar fact that polyethylene (PE) of conventional "polymeric" chain lengths is, under appropriate circumstance, capable of crystallizing in the form of extended chains. Historically it was first observed by Wunderlich and Melillo (e.g. Ref. 1) that polyethylene, when crystallised under hydrostatic pressure 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. 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 crystallization of more conventional fold length (few 10-s nm). It was then an important finding by Bassett et.al. (see e.g. Ref. 2) that PE exists in a hexagonal crystal phase (h) (as opposed to the conventional orthorhombic (o)) at elevated pressures (P), 3.3 Kbar being a triple point (Fig. 1). 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 crystallization under pressure.

The studies here reported were aiming to bridge the gap between the two hitherto separate aspects of crystallization: extended chain crystals forming under high, and folded chain crystals arising under ambient pressure. As will be seen, even if the full connection is not yet established, there are altogether new pointers arising from the recognition of the role played by the metastable state, in addition to the thermodynamically stable states embodied by phase diagrams such as Fig. 1 and shown schematically, with additional features (see below) in Fig. 2.

EXPERIMENTAL METHODS AND OBSERVATIONS

Pressure apparatus developed previously by one of us (M.H.) was used (Ref. 3), having special features not usually encountered in combination. These features are: preservation of constant pressure during volume contraction on crystallization permitting experiments which are simultaneously isobaric and isothermal, in situ optical viewing and in situ recording of X-ray diffraction patterns on visually preselected crystals. These features permitted identification of crystal phase and measurement of lateral growth rates. Subsequent electron microscopy on pressure quenched specimens, which preserves the crystal in a given optically identified state of development, then allowed determination of morphology, the measurement of crystal thickness and growth rate in the thickness direction

(thickening growth rate - see below). The observations (and measurements) were made in preselected portions of the phase diagram. (Figs. 1, 2) which subdivides into the following ranges: hexagonal (h) and orthorhombic (o) where the latter subdivides further (for our present purposes) into regions "below" and "above" the triple point Q. The materials used were specially sharp fractions of PE (from National Bureau of Standard) of $M_n = 32000$ with $M_w/M_n = 1.11$ (M_w and M_n signify weight and number average molecular weights respectively).

The crystals could be seen optically (as in preceding works e.g. Ref. 2, 3) as arising and growing in situ. Fig. 3 shows some examples where the bright streaks represent edge-on views of platelets seen in their maximum birefringence contrast between crossed polaroids. Electron microscopy on pressure quenched samples verified the single crystal nature in flat-on view of selectively extracted crystals, from the bulk sample (Fig. 4a). We see that they are lamellae, here with leaf shaped outlines (the outlines could also be circular (Ref. 4). The reason for this variation in the otherwise hexagonal crystals - see below - is presently unknown). The cross-sectional views can also be revealed by suitable etching techniques applied on the bulk sample (Fig. 4b). As seen, they have tapered shapes, inferred previously light optically; now this is directly visible and measurable from the electron micrographs.

X-ray diffraction patterns (Ref. 5), taken in situ, could identify whether the crystals were in the h or o form. A simple, so far infallible correlation was found between the optical appearance and crystal structure: uniformly bright streaks, such as A, B, C in Fig. 3a were found to be characteristic of the h form and more irregular 'blotchy' lines such as B and D in Fig. 3c to the o form. With this identification established we shall rely on the assignment based on the optical images to follow with Fig. 3 as an example.

RESULTS AND DISCUSSION

In the h stability region (Region I in Fig. 2) only h crystals were seen to form and grow as to be expected. However, and this is the salient novelty of the work, h crystals were also seen in the o stability region (Region II in Fig. 2) where they are necessarily metastable. (This finding was already implied when referring to Fig. 3c, where the h (crystal A) and o (crystal D) crystals

FIG 1: P-T phase diagram as observed by DTA.

FIG 2: Schematic P-T phase diagram including metastable and virtual phase boundaries.

are seen side by side). Even more surprisingly, it was found that crystals can form and grow only in the h form even in regions of the phase diagram where the o phase is the stable one. When in the o stability regime (Region II), at some stage of growth a growing h crystal transforms into the stable o crystal. At this stage yet another, unexpected effect was seen, namely that on h→o transformation all further growth stops.

FIG 3: In situ optical micrographs during isothermal and isobaric crystallization and melting (latter right). $P=2.82\text{Kb}$, $(\Delta T)_h=3^\circ\text{C}$. Scale bar= $50\text{ }\mu\text{m}$

The above findings are illustrated by Fig. 3, where the three consecutive frames, a), b), c) represent successive stages of crystal growth under isobaric and isothermal conditions corresponding to the o stability region in the phase diagram, just "below" the triple point Q. Crystals, A, C, D (and others not marked) are seen to grow when going from 62 to 70 mins., (Fig. 3a, b), while B is seen to have transformed into o by the above defined criterion. Growth of A and C continues in the h form up to the next frame, 95 mins (Fig. 3c), by which time D has transformed. As will be seen the previously transformed crystal B has ceased to grow further. Next, the temperature was

raised at unaltered pressure. We see (Fig. 3d) that crystals still in the $\underline{h}$ form, A, C, in Fig. 3c, have vanished, hence melted, while the transformed B and D have stayed unaltered. The sequence in Fig. 3 is therefore self-contained evidence for crystals growing in the $\underline{h}$ form, and only in the $\underline{h}$ form, i.e. not in the $\underline{o}$ form into which they eventually transform. Fig. 3 also contains the evidence of metastability of the growing crystals through the fact that those crystals which can grow are thermally less stable (melt at lower T) and vice versa.

In view of the above the metastable and virtual phase-demarcation lines in Fig. 2 acquire further significance : amongst others they define yet another region below Q, Region III, where $\underline{h}$ crystals cannot exist, and consequently no crystal of any kind, not even the stable $\underline{o}$ crystal, can form and grow.

The optical micrographs in Fig. 3 only reveal lateral growth and its cessation. Changes in thickness are just indicated, but are not measurable. This can be done from electron micrographs such as Fig. 4b. Again, crystals are seen to grow along the lamellar normal (i.e. thicken) only when in the $\underline{h}$ form; on $\underline{h} \rightarrow \underline{o}$ transformation such thickening growth, just as the lateral growth, stops. It can be deduced accordingly, that it is this arrested thickening which is the prime source of finite lamellar thickness characteristic to the $\underline{o}$ stability region (Region II). In Region I thickening proceeds unhindered within the $\underline{h}$ phase (even if not necessarily with unaltered rate) and leads to the extended chain crystals identified in earlier studies (Ref. 1, 2). To note however :

- i. Thickening, as in Fig. 4b, represents primary crystal growth with increasing crystal volume. As long as there is no layer impingement it can proceed indefinitely. Here, small layer thicknesses correspond to the chain folded state, which on increasing thickness leads to extended chains, and as we now observe, even beyond, to thicknesses which correspond to multiples of the chain length of our sharp fractions.
- ii. In all the above the principal mechanism envisaged is sliding diffusion, irrespective as to whether refolding from shorter fold lengths within the crystal or "sucking in" of new chain from the melt is involved, (see diagram Fig. 5). Such sliding diffusion has already become integral part of a theory by one of us (Ref. 6).

FIG 4a: Electron micrograph showing extracted leaf shape crystal, crystallized at $P=4.0\text{Kb}$, $(\Delta T)_h=4^\circ\text{C}$. Scale bar= $10\text{ }\mu\text{m}$

FIG 4b: Cross sectional view of crystal as in Fig 4a, showing tapered edges. $P=4.0\text{Kb}$, $(\Delta T)_h=4^\circ\text{C}$. Scale bar= $10\text{ }\mu\text{m}$
An electron micrograph of etched bulk sample.

FIG 5: Development of a crystal via chain folding to chain extension and beyond.

- iii. With lateral growth rate known from polarizing optics (such as Fig. 3) thickening as a function of time, hence thickening rate, is directly given by the cross-sectional shape, such as in Fig 4b, when expressing distance (from the growing thinnest trip) - in terms of time. Thus we acquired a direct visual measure of thickening history, including that of rates, hence also that of chain sliding diffusion.
- iv. The above kind of thickening will be drastically slowed down by face-to-face layer impingement even while in the h form. At this stage the thickening process becomes a rearrangement with constant overall crystal volume, i.e. it will represent secondary crystallization. In retrospect, this is the process which has been usually considered in past refolding studies.

Of more exhaustive growth rate studies, (Refs. 7, 8), both lateral and thickening growth here only the range of values will be quoted at a fixed pressure (~ 3.2 K bar). This is: lateral growth rates range from 2.18×10^{-2} to $65.2 \times 10^{-2} \mu/\text{sec}$. Thickening growth rates range from 7.77×10^{-4} to $5.58 \times 10^{-4} \mu/\text{sec}$. in both cases for a ΔT (supercooling) range of 4 to 10°C . It is important

to note that here it is the melting point of the h phase which needs to be taken as reference for defining ΔT

IMPLICATIONS FOR POLYMER CRYSTALLIZATION AND BEYOND

It will have been apparent that the new findings have implications on various levels. The most direct one concerns the interrelation between chain folding, chain extension and the existence of the mobile hexagonal phase. This has been the main subject of previous works on crystallization under hydrostatic pressure (Ref. 2, 3). To this we now add the quantitative determination of growth rates, including the newly recognized distinction between primary thickening growth and secondary thickening (rearrangement) by refolding, and in the former case a method of direct measurement of thickening (through cross-sectional profiles, Fig. 4b).

Beyond the above are the implications arising from the recognition of the role of the hexagonal phase in its metastable form within the orthorhombic stability regime. The new recognitions raise the question as to the connection between the happenings at high pressure and those seen traditionally under atmospheric conditions. Previously, the two were considered as separate facets of polymer crystallization distinguished by the different regions in the phase diagram such as Fig. 1. However, in view of the newly recognized metastabilities, equilibrium thermodynamics has ceased to be of unique guidance for our purpose. Thus one needs to ask how far down in P does the role of the metastable hexagonal phase extend in determining the course of crystallization in general, and lamellar thickness in particular. Specifically, does it extend down to atmospheric pressures the source of most of our previous knowledge? In other words is the h phase a necessary requirement for crystallization even there? If so, being so transient, it may possibly have remained so far undetected. In that case the "no growth" Region III could be operative even at atmospheric pressures, and it is a challenging thought how far our present data on Region III (Ref. 7-8) would extrapolate to ambient pressure conditions.

The only other alternative to a transient mobile hexagonal phase under atmospheric pressure would be a change-over in mode of crystallization in a sense that the traditionally considered mode directly into the o phase would take over as P is lowered. If so, knowing P where this occurs would be of foremost interest. In this, as before, the equilibrium phase diagram can provide no help.

On a broader level the present findings on the dominant role of the metastable phase in crystallization are leading to considerations of still wider generality the roots of which predate polymer science.

The mere fact that one tends to pass through a metastable station first in the course of change in matter of state (e.g. vapour→solid) is in itself not novel and is in fact expressed by Ostwald's "Stage Rule" dating back to 1892. 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 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 $\underline{h}$ phase could be the stable and the $\underline{o}$ phase the metastable one even in the P-T regime where normally the converse applies, i.e. a stable $\underline{o}$ and metastable $\underline{h}$ 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 $\underline{h} \rightarrow \underline{o}$ transformation will then set in beyond a certain size (lamellar thickness, fold length) as the crystal grows (thickens 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) $\underline{h}$ phase is mobile allowing for ready refolding to greater thicknesses, thus leading up to a size-induced stability inversion, in the present case to $\underline{h} \rightarrow \underline{o}$ 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 uniformly small thickness) is in fact the principle feature of a crystalline flexible chain polymer. By such an argument crystallization could start through a transient phase, which is the stable one when small (thin), but metastable beyond a certain thickness. This means, that in our polymer crystallization could, within this transient phase, start with a much reduced length, for which the chain deposition probability, hence consequent growth rate, is vastly (about exponentially) enhanced. The transient phase being mobile, thickening by chain sliding

would follow, until terminated, or drastically slowed down, by the transformation into the final, less mobile phase at or beyond a certain thickness which is characteristic of the final lamella thus created. Such a possibility is currently being tested.

Whatever the future experiments will reveal, the fact that change in crystal size, in particular thickening, can induce phase transformation through chain refolding while in an initially mobile phase, into a less mobile phase which then terminates (or slows down) this refolding, has already been conclusively demonstrated (Ref. 9). Materials and conditions were different yet still relevant. Here, the material was poly 1-4 transbutadiene which has two crystal forms, a mobile, and a less mobile even at atmospheric pressure, and the experiment was carried out not during crystallization but on the fully crystalline material. The experimental conditions were chosen so that thickening induced a transition into the less mobile phase, thus demonstrating that the coexistence temperature between the two phases is indeed crystal size, specifically, thickness dependent. It follows, that primary crystallization, if it could be monitored near the phase coexistence temperature (which in fact cannot be done with poly 1-4 transbutadiene because of the fast crystallization rates), would indeed involve a phase change with crystal growth. This would also include self-limiting lamellar thickening, hence a limiting specific lamellar thickness here by a combination of thermodynamic (size dependent phase transition) and kinetic (crystal phase determined chain mobility) reasoning. From here it is only one further step to envisage the same for the situation where the mobile phase is virtual (for P-s and T-s concerned) for the same to apply to PE and possibly other flexible polymers.

In conclusion, we have demonstrated that crystallization is initiated and controlled through the mobile hexagonal phase even when it is metastable, hence present only as a transient. This fact, definitive within our present experimental range, lends itself to projections outside and beyond this range with potentially far reaching consequences and possibilities.

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