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The role of transient hexagonal phase in crystallization of polymers

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Abstract: Crystallization studies of polyethylene (PE) under hydrostatic pressure substantiate the earlier findings by Bassett and Turner [1, 2] that crystallization occurs initially in the hexagonal (h) phase, even within the thermodynamically stable orthorhombic (o) region. Present studies demonstrate that this is, in fact, a necessary condition for crystallization, at least in the temperature and pressure range in question; in fact, once a crystal transforms from h to o phase, further growth of crystal stops. Morphological features show that crystal growth includes both lateral and thickening growth; in the latter case the chains thicken continuously from folded to extended form and beyond. It is the thickness in a crystal which governs the phase inversion from h to o phase. Thickness dependence on phase inversion is explicitly shown in the polymer trans 1,4-polybutadiene, where the mobile h phase, similar to PE, can exist, even at atmospheric pressure.

Key words: Polyethylene; trans 1,4-polybutadiene; transient hexagonal; phase crystallization; mesophase

Crystallization of polyethylene (PE) at elevated pressures, above and below the triple point in the established P-T phase diagram [1, 2] leads to the formation of extended chain crystals [3], a consequence of the chains being in the hexagonal (h) phase. This phase is thermodynamically stable within Region I of the P-T phase diagram (Fig. 1). Volumetric and thermal measurements revealed a transient phase within the o stability regime, attributed to the h phase, which then can transform into the final stable phase (o) subsequently [2]. In subsequent works changes in the optical appearance of the crystals were attributed to such an h \rightarrow o transition [4] as observed on cooling [1].

In the present work, using a piston-cylinder type diamond anvil cell (operating both at constant temperatures and pressures, even during a phase transformation) and a sharp fraction of polyethylene ($M_w = 32\,000$ supplied by NBS), we followed crystallization in situ, optically, under isothermal and isobaric conditions. As in preceding works the crystals were seen as birefringent entities between crossed polaroids forming and growing

with time. Using the optical criterion [1, 4] for the hexagonal (h) and orthorhombic (o) crystal structures (uniformly smooth and irregular blotchy bright streaks, respectively), we could follow the crystallization in preselected regions of the phase diagram in terms of size of crystal and nature of crystal structure. In the course of this the dominant role of the h phase became increasingly apparent. Not only does it occur during crystallization, even within the o stability regime, but is a state necessary for the crystallization to start and proceed, at least within the P- and T-range examined here, even when, in the o regime, it corresponds to a metastable state.

The above can be clearly seen from Fig. 2 which demonstrates crystal growth within the o regime "below" the triple point. Here, smooth birefringent entities are seen to form and grow with time. We know from separate electron microscope work [5, 6] that these entities are isolated single-crystal layers. After a certain crystallization time (Fig. 2c) the existence of two distinct types of crystal become apparent, like crystals A and C, having a well-defined

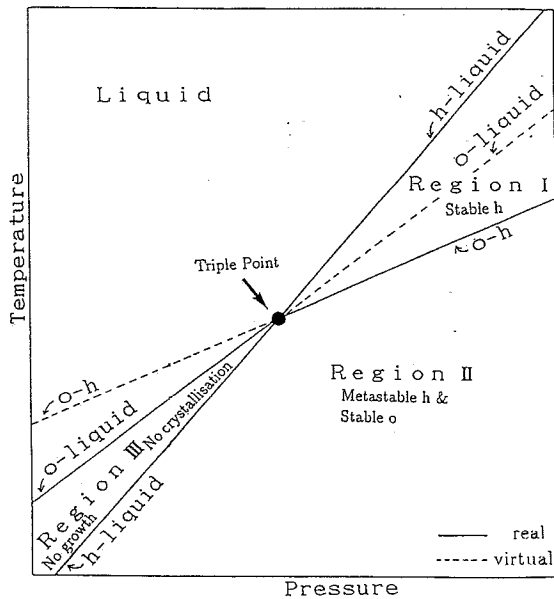


Fig. 1. Schematic P-T phase diagram including real and virtual boundaries

boundary, and crystals B and D, having distorted shape. That such crystals are indeed intrinsically different becomes evident on raising the temperature at fixed pressure (Fig. 2d). Here, crystals having well-defined boundary disappear,

crystals A and C, leaving behind distorted crystals such as B and D, which means that the former have a lower melting point. This alone provides self-contained evidence that the smooth crystals are metastable with respect to those of irregular appearance in that particular regime of the phase diagram. In situ x-ray studies [5] then revealed further that the crystals having well defined boundaries are indeed in the h form, whereas those with distorted boundaries are in the o phase, consistent with the preceding optical attribution (Fig. 2).

From the above criterion of optical distinction between h and o crystals the following conclusions may be drawn from evidence such as in Fig. 2.

- Fig. 2a shows that within the P and ΔT range concerned, even within the thermodynamically stable o phase, crystals only form and grow in the h phase initially, even within the thermodynamically stable state.
- When in the o stability regime, after certain crystallization time, a crystal initially in h phase transforms to the o phase, like crystals B and D.
- Once a crystal transforms from h to o phase it stops growing. This is seen from Fig. 2 where crystals A and C in the h phase continue to grow, whereas transformed crystals B and D stop

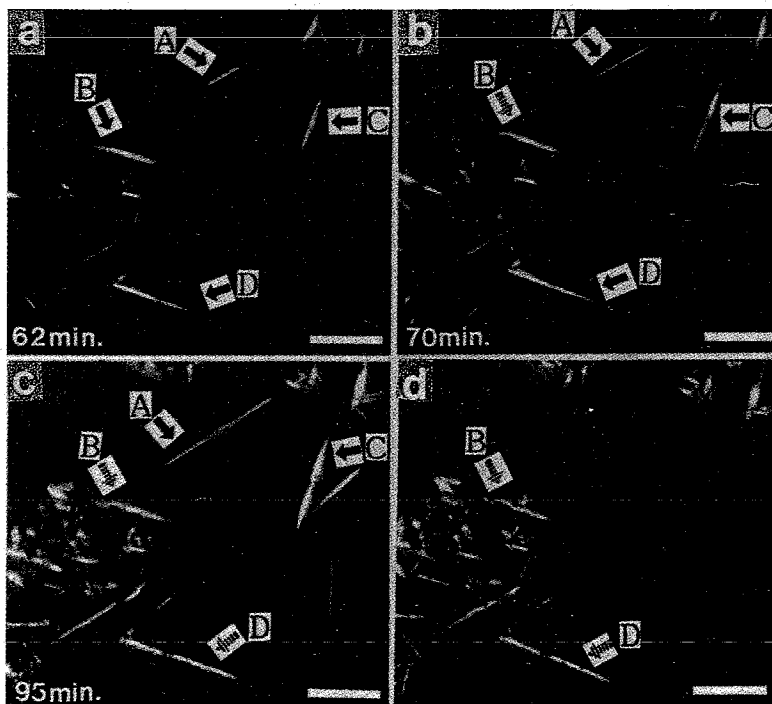


Fig. 2. In situ optical micrographs during isothermal and isobaric crystallization and melting (latter right). $P = 2.82$ kb, $(\Delta T) = 3^\circ\text{C}$. Scale bar = $50\ \mu\text{m}$

growing, at least on the time scale of the present observation.

The cross-sectional view of these crystals, as seen by transmission electron microscopy after etching and using two-stage replica technique, shows the tapered profile (Fig. 3). Since sharply fractionated PE (of chain length of about ~ 3000 Å) is used for experimentation, the tapered profile in Fig. 3 shows that, during the initial stages of crystallization, the chains are folded (~ 500 Å); they later thicken to full chain extension and even up to a few microns beyond. In the h phase thickening is feasible due to the high mobility of chains. Thus, in the h phase, simultaneous lateral and thickening growth of a crystal occurs (Fig. 3).

The mere fact that a new phase state first passes through a metastable state is, in itself, not quite unusual, and is expressed by the Ostwald Stage Rule dating back to 1898. With a reasonably appropriate choice of surface parameters [6] the situation can arise that the true thermodynamic stability conditions can invert with size. Specifically, for a PE single crystal which is sufficiently thin during the initial stages of crystallization, the h phase could be the thermodynamically stable phase. As the crystal thickens, above a critical value of lamellar thickness the initially stable h phase will no longer be thermodynamically stable. Thickening beyond the critical value of lamellar thickness will be due to kinetic reasons. Once a crystal transforms into the o phase, further thickening, along with lateral growth, becomes arrested or slows down drastically.

The fact that change in crystal size, in particular, thickening, can induce phase transformation has been successfully demonstrated on trans 1,4-polybutadiene (PTBD), Fig. 4 [8]. At ambient conditions, here, the crystals are in the monoclinic phase. With the increase of temperature, at

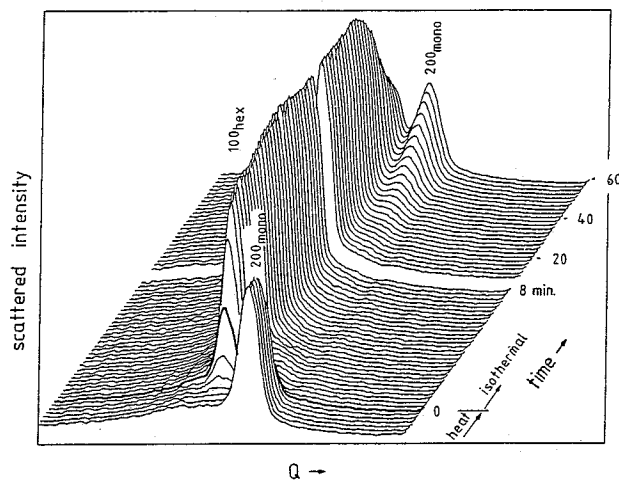


Fig. 4. Phase reversal of hexagonal to monoclinic as observed from the time-resolved WAXS

atmospheric pressure, monoclinic to hexagonal transition occurs between 60° – 85° C. This transition temperature is dependent on lamellar thickness. Chains in the h phase of PTBD are mobile, similar to that in the case of PE. The h phase here being accessible at atmospheric pressure makes PTBD an ideal case for this particular experimentation [8].

Figure 4 shows a time resolved WAXS pattern of PTBD. For the present purpose a single crystal mat of lamellar thickness 104 Å has been prepared from solution. For this thickness, monoclinic to hexagonal transition occurs at 68° C. The sample is left to anneal isothermally just above the monoclinic to hexagonal transition temperature. Once the crystals are in the h phase, they thicken. After certain isothermal annealing time, phase reversal from h to monoclinic sets in. This is indicative of the effect that, as the chains continuously extend, the initially thermodynamically stable h phase ceases to be the stable one and can undergo a hexagonal to monoclinic transition.

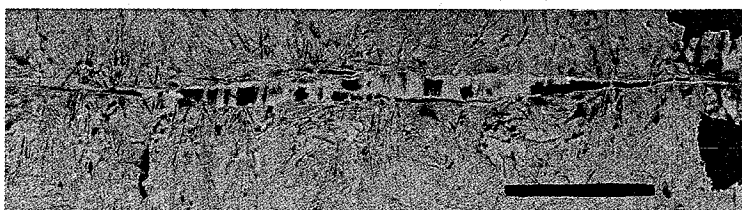


Fig. 3. Cross-sectional view of crystal, showing tapered edges. $P = 4.0$ kb, $(\Delta T) = 4^{\circ}$ C. Scale bar = 10 μ m. An electron micrograph of etched bulk sample

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