

Morphological Implications of the Interphase; Linking Crystalline and Amorphous Regions in Semi-Crystalline Polymers

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Summary: In semi-crystalline polymers, a range of morphologies can be obtained in which a chain may traverse the amorphous region between the crystals or fold back into the crystals leading to adjacent or non-adjacent re-entry, depending on the molecular architecture and crystallization conditions. This causes topological variations on the crystal surface, thus affecting the mechanical properties. In this communication, we will address how the morphology on the crystal surface plays a prominent role in drawability. Materials chosen are branched polymers.

Introduction

The semi-crystalline structures often formed by crystallizable polymers are known to consist of thin crystalline lamellae separated by amorphous regions. For crystallization from the melt, where the conditions are far from equilibrium, the polymer chains must achieve a regular conformation from the highly entangled melt and align parallel to each other to form thin plate-like lamellae, the entanglements being confined to the amorphous regions. It is still unclear whether the polymer chains do actually disentangle or merely that during crystallization, entanglements are pushed to the surface. However, independent of the mechanism involved, the molecular structure of the amorphous region strongly depends not just on the chemical nature and inherent shape of the polymer, but also on the crystallization conditions either in the quiescent state or obtained during flow. Experimental efforts to decouple the mechanical properties of polymers from the crystalline and amorphous fractions have not been particularly successful because of the dependence of the molecular organization in the amorphous region upon the crystallization conditions.

Moreover, a third structural component, an interphase of intermediate order, could exist between the amorphous and crystalline phases, as has been proposed both theoretically and

experimentally, which means that a sharp demarcation line between the amorphous and crystalline phases is unlikely. This added complication is necessary if one considers that the chains emerge at the crystalline surfaces with a high degree of molecular alignment. These chains must either fold back into the crystallite, whether by adjacent re-entry, or must reside in the amorphous matrix.

Crystallization of the interphase in branched alkanes

Normally, for linear polymers it is anticipated that extended chain crystals are thermodynamically the most favorable, and ultimately given an example of linear polyethylene, it is shown that chains within the folded chain crystals tend to move along the c-axis via chain sliding diffusion to attain a thermodynamically stable morphology. However, the possibility of chain diffusion within the crystal lattice cannot be realized normally when the molecular structure changes from linear to branched, in particular, where the side branches cannot be incorporated within the crystal. To gain a better insight the phase behavior of the butyl branched alkane $C_{96}H_{193}CH(C_4H_9)C_{94}H_{189}$ has been investigated at elevated pressures. In this model compound a well-defined morphology is expected where the chains are adjacent reentrant, due to the enhanced chain mobility along the c-axis at elevated pressures and temperatures. If we envisage the folding of a single molecule, then the branch, which occurs exactly after 96 C-atoms and is followed by 94 C-atoms, will lie almost in the middle of the fold. Variations in the crystal structure have been followed in-situ with WAXD. Detailed study are reported in references [1-2].

Upon crystallizing from the melt at 3.8kbar, crystal formation occurs directly in the orthorhombic phase, Figure 1a. The orthorhombic (110) and (200) reflections gain intensity with increasing supercooling. A weak monoclinic reflection appears at approximately 148°C. With subsequent cooling at ~ 70°C, a relatively broad and weak new reflection appears next to the monoclinic reflection. The

appearance of the new reflection is followed by a sudden drop in the intensity of the orthorhombic reflection and a simultaneous increase in the intensity of the monoclinic reflection. The presence of the new reflection becomes more evident with further cooling. The (110) and (200) orthorhombic peaks show a sudden shift to higher angles implying a densification of the orthorhombic crystalline lattice with the appearance of the monoclinic reflection and the new reflection. Detailed study show that after the appearance of the new reflection at $\sim 70^\circ\text{C}$, a dramatic decrease along the a axis of the orthorhombic unit cell occurs together with a sharp decrease along the b axis. Densification of the orthorhombic unit cell ($\rho = 1141\text{kg/m}^3$ at 4.0kbar, 25°C) occurs too.

Definite assignment of a phase to the new reflection is not straightforward as only one reflection is observed; for the present it has been termed a pseudo-hexagonal phase as its spacing is close to that of the hexagonal phase in polyethylene ($d=4.16\text{\AA}$ c.f. $d_{100\text{hex}}(\text{polyethylene})=4.2\text{\AA}$).

Sample as crystallized under pressure shows appearance (or disappearance) of the new reflection, contraction (or expansion) of the orthorhombic lattice on increasing (or releasing) pressure at room temperature, see Figure 1b. Crystallographic changes on compression or release of pressure are similar to the one observed on melt crystallization at the elevated pressures.

Crystallization of the interphase in ethylene-octene copolymers; parallels with the ultra-branched alkane

In recent years, ethylene-1-octene copolymers with densities between 870 and 910 kg/m^3 have attracted considerable academic and industrial interest. One of the main characteristics of these copolymers is that they are 'homogeneous' copolymers, that is, these polymers do not display any differences in comonomer distribution along the chains other than the differences related to statistical fluctuations. Detailed studies are reported elsewhere [2-3].

On crystallizing the 5 mole % of ethylene-octene copolymer at approximately 3.8kbar, similar to the branched alkanes, around 200°C crystallization preceded directly via the orthorhombic phase without the intervention of the anticipated hexagonal phase as would be anticipated in linear polyethylenes at these high pressures and temperatures. At $\sim 100^\circ\text{C}$, see Fig. 1c, the d values for (110) and (200) orthorhombic reflections are 4.08\AA and 3.71\AA . When the sample is cooled below 100°C , a

new reflection adjacent to the (110) orthorhombic peak appears at $\sim 80^\circ\text{C}$. The position of the new reflection is found to be 4.19\AA and so corresponds to the new phase. No change in the intensity of the existing (110) and (200) reflections is observed, however intensity of the amorphous halo decreases, which suggests that appearance of the new reflection ($d = 4.19\text{\AA}$) is solely due to the crystallization of a non-crystalline component. On cooling further as the new reflection intensifies, the (110) and (200) orthorhombic reflections shift gradually. However, at $\sim 50^\circ\text{C}$, the (100) monoclinic reflection appears with a concomitant decrease in the intensity of the (110) orthorhombic reflection and a sudden shift in the Bragg d values of the orthorhombic reflections. These results indicate a solid-solid phase transition at 50°C of a large amount of crystals, from the orthorhombic to monoclinic phase. At room temperature it can be seen that the new reflection is much more intense than the (110) orthorhombic reflection and a corresponding secondary new reflection is observed at $d=3.78\text{\AA}$ see Fig. 1c.

If one considers the ratio of the two new reflections ($4.19\text{\AA}/3.78\text{\AA} \approx 1.108$) and compares their intensities, it can be concluded that this phase resembles an orthorhombic phase (for linear polyethylene, $d_{110\text{ ortho.}}/d_{200\text{ ortho.}} \approx 1.111$). However, the d values for the new reflections are higher when compared to the conventional d values for the orthorhombic phase and do not match exactly with the known monoclinic or triclinic phase in linear polyethylene. Keeping this in mind and assuming no change along the c -axis, the unit cell dimensions for the new orthorhombic phase at 3.8kbar and room temperature (25°C), were calculated to be $a = 7.56\text{\AA}$, $b = 5.03\text{\AA}$ and $c = 2.55\text{\AA}$. The unit cell volume was found to be approximately 96.97\AA^3 and the density 960kg/m^3 . This is the first time that this type of orthorhombic phase has been observed in polyethylene. Compared to the conventional orthorhombic phase, the density of the new orthorhombic phase is rather low i.e. the unit cell is more open. The high intensity of the new open-orthorhombic phase at these high pressures means that the new phase is formed by the crystallization of the majority of the amorphous component with the hexyl branches at the surface of the crystal, suggesting crystallization of the interphase.

The relatively high intensity of the *open-orthorhombic phase*, at these high pressures, means that this phase cannot be attributed to crystallization of the hexyl branches at the crystal surface alone – unlike in the case of branched alkanes. However, similar to the

branched alkanes the fold surface incorporating hexyl branches must be a prominent factor in forming the *open-orthorhombic phase*. In fact one envisages a major part of the orthorhombic lattice, which resorts to a less dense packing even at these high pressures, is driven by the hexyl branches. In this manner, the stresses due to crystallization of the hexyl branches residing on the fold surface lead to a further compression of the 'original' orthorhombic lattice (termed as *dense orthorhombic phase* at $d_{110} = 3.99 \text{ \AA}$) and a partial conversion of the 'original' orthorhombic phase into a monoclinic phase. On releasing pressure, multiple reflections observed in the sample crystallized at elevated pressure and temperature merge into simple 110 and 200 reflections of the orthorhombic phase, see Figure 1d. The whole process on compression or releasing pressure is fully reversible, evident from splitting of the main peak with increasing pressure, Figure 1d.

The crystallizable interphase in ethylene-octene copolymers invokes the possibility of disentangled adjacent re-entrant chains. Figure 1e shows differences in the drawing behavior of the sample crystallized from melt at elevated pressures and the same sample crystallized from melt at atmospheric pressure.

References:

1. Advances in Polymer Science 2005, **180**, 161-194;
2. Macromolecules 2002, *35*, 5861-5868;
3. Macromolecules 2005, **38**, 4744-4754.

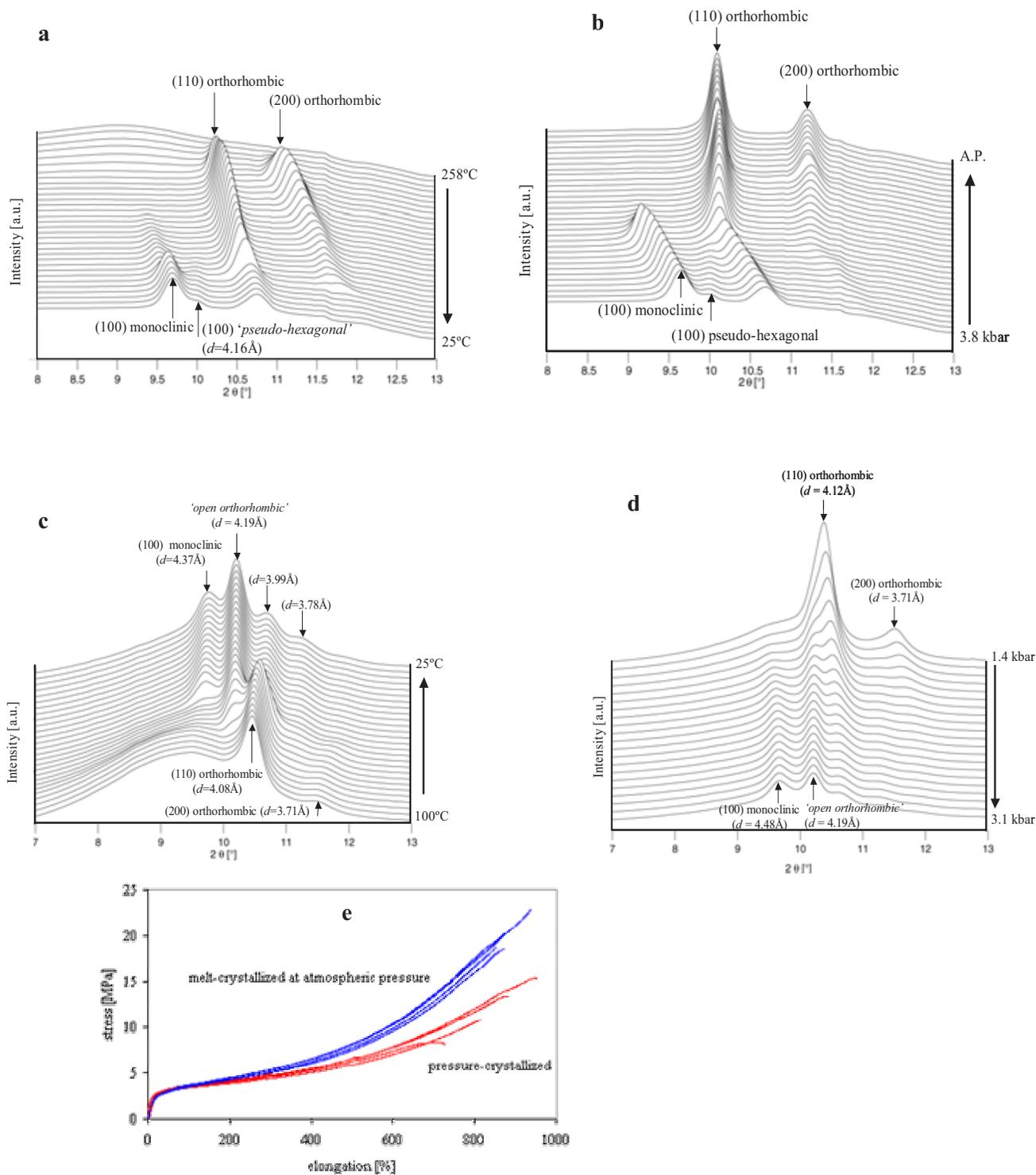


Figure 1: (a) and (c) shows crystallization of branched alkane and copolymer, respectively at 3.8 kbar from melt; (c) and (d) depicts phase changes in the pressure crystallized sample on compressing or releasing pressure; X-ray wavelength used for the experiments is 0.0744 nm (e) shows differences in strain hardening of the pressure and melt crystallized samples.