

Effects of Processing Conditions on Polymer Morphology

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Introduction

The morphology of a polymer can vary significantly, depending on the type of process and operating conditions at which it is crystallized. A hierarchical model for melt processed semi-crystalline polymers will be presented that begins with the basic building block of a polymer, the repeat unit, and progresses through structures of increasing size. From the repeat unit, the unit cell, helix, lamella, and the spherulite and shish kebob can be formed. In addition, tie molecules, either as loose energy absorbers or taut reinforcing units between lamellae, will be incorporated. Processing conditions, namely stress, temperature and time, will be discussed and how they affect the formation of the crystalline structure.

Explanation of Polymer Morphological Hierarchy

Understanding the effects of processing conditions on the morphology of a polymer requires the establishment of a clear hierarchy. The various sub-units of the proposed hierarchy were defined, based on their ability to be characterized through prevalent analytical techniques, and will be used to explain how primary components are used to build sub-units of structural significance during polymer crystallization. The changes in the morphology of critical sub-units, as a result of processing parameters, will then be discussed and how these variances affect the macro-structure of the polymer.

The following figure shows the primary unit of a polymer, the repeat unit, which is the basic building block for the macro-scale structure.

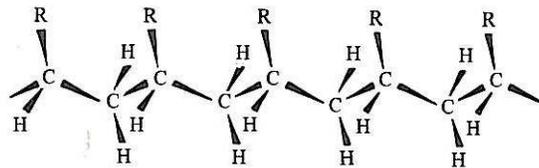


Figure 1. The primary unit, or the repeat unit, is the basic building block used to form larger scale structure, such as the unit cell, helix, lamella, spherulite, shish-kebob, and extended chain [1].

The repeat unit, the primary unit, is the basis for all hierarchical structure. During polymerization, these units are linked together through covalent bonds, and when exposed to the proper conditions, begin to crystallize. Upon crystallization, the polymer chain takes an ordered form, called the unit cell, which is regular and serves as the building block of the next largest sub-units. Figure 2 shows the schematic of the unit cell of polyethylene.

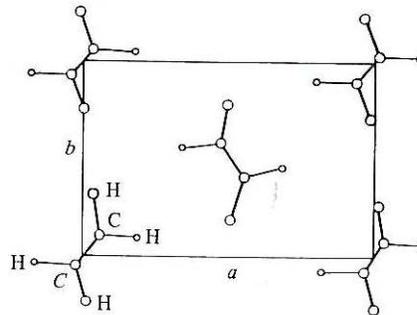


Figure 2. Schematic drawing of the unit cell for polyethylene. [1]

As the crystallization process proceeds, the polymer begins to combine the unit cells into larger, ordered structures, which include helices and lamellar sub units. The importance of the monomer unit is again seen, where side groups spouting off the backbone of the polymer greatly influence the structure at this level. Secondary effects, such as steric hindrances (van der Waal effects) or hydrogen bonding between neighboring chains (as in nylon), greatly affect the geometry of the formed crystal. For example, polypropylene, which has a methyl group extending off the backbone, forms a 3:1 helix, while polyethylene, which has hydrogen groups extending off the backbone, simply forms a planer zig-zag (a 2-dimensional helix). Figure 3 shows a schematic of a polypropylene helix and a planer zig-zag of polyethylene.

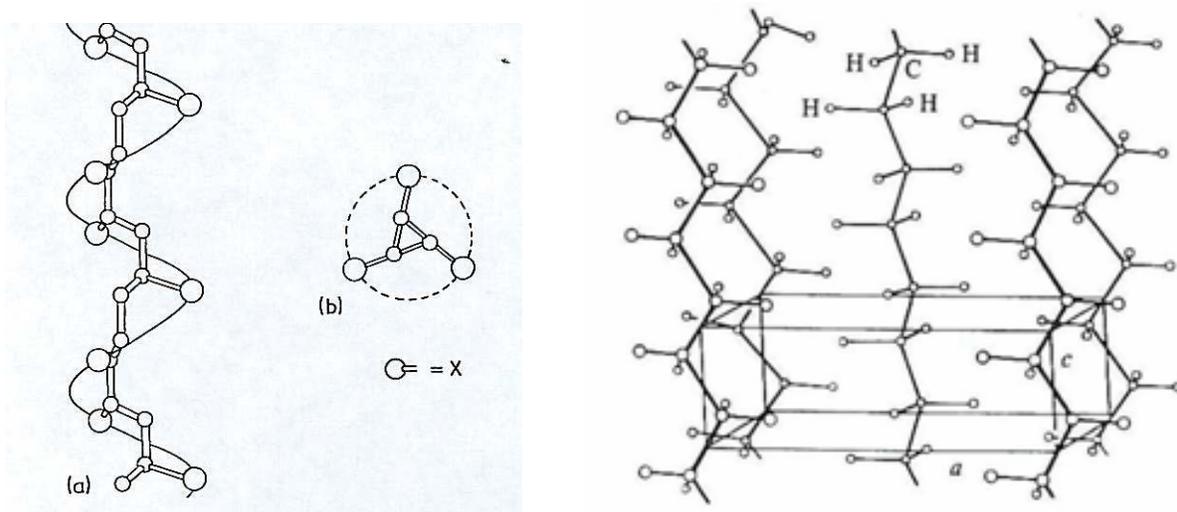


Figure 3. Schematic of a polypropylene 3:1 helix and a polyethylene planer zig-zag [2].

These smaller sub-units can be characterized through numerous analytical techniques, including quantized methods, such as IR spectroscopy, Raman scattering, and NMR, as well as refractive and diffractive techniques such as birefringence and XRD.

Helices (whether 3D or 2D) are then packed into a larger sub-unit, again highly ordered, and are known as lamellae. This subunit has an aspect ratio similar to that of a piece of paper, with the thickness much less than the lateral dimensions. The lamellae thickness is greatly influenced by the supercooling associated with the crystallization process, as we will discuss later. Figure 4 shows a schematic of a polymer lamella and parallel lamellae connected with tie molecules.

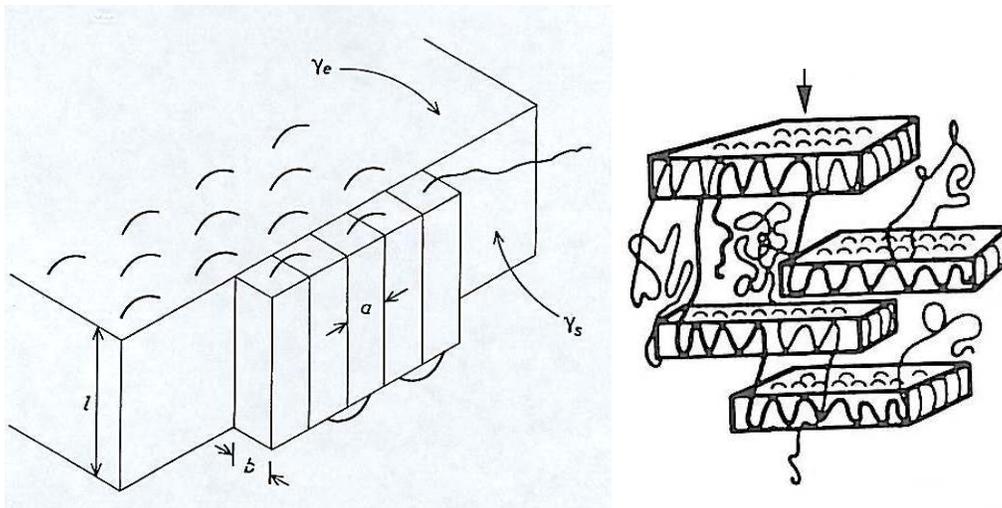


Figure 4. Schematic of a polymer lamella and lamellae connected by tie chains [2, 4].

In addition, we will begin to discuss the concept of “imperfections” at this particular size scale. The term imperfection refers to several structural entities, including the fold surface (loose or direct re-entry into the lamellae), chain ends, tie molecules, and mosaic boundaries. Figure 5 shows a schematic of the imperfections associated with polymer lamellae.

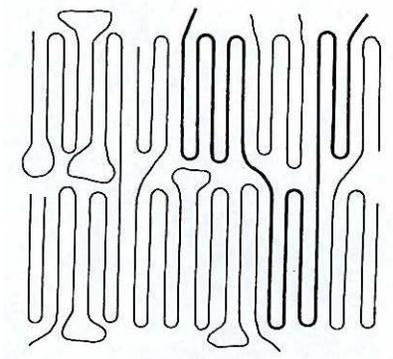


Figure 5. Imperfections associated with polymer lamellae [2].

For the purposes of this paper, tie molecules will be the key imperfection discussed, as they are critical to understanding the relationship between stacks of lamellae during orientation. SAXS is the primary analytical technique used to characterize polymer lamellae. Microscopic techniques, such as AFM and TEM are also used to compliment SAXS to visualize the stacking of lamellae.

Lamellae are used to form the next largest hierarchical structure, which is greatly influenced by the processing conditions. Later portions of this paper will focus primarily on this structural level. Depending on the processing conditions, lamellae can be organized into spherulites (formed from high or low supercooling, low stress) or a shish-kebob (formed from low supercooling, high stress). Figure 6 shows a schematics and images of a spherulite and a shish kebob structures.

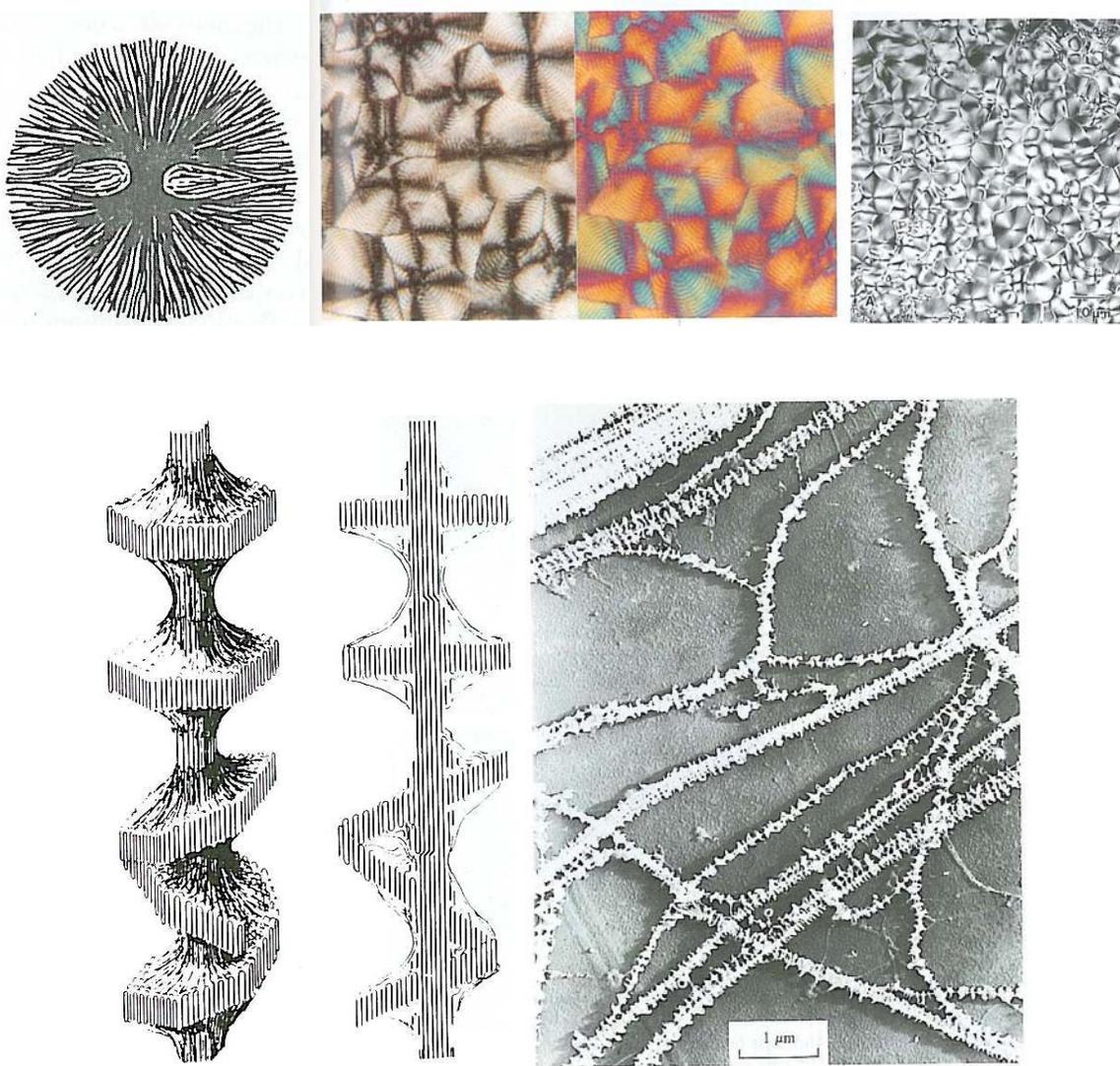


Figure 6. Schematic drawings and images of a spherulites and shish-kebobs [1, 4]. An image of a shish kebob structure crystallized in solution is used for visual clarification.

In the spherulite, the lamellae radiate from a central nucleation site and twist outward in “ribbons”, forming a spherical structure. Figure 7 shows a schematic of this twisting ribbon.

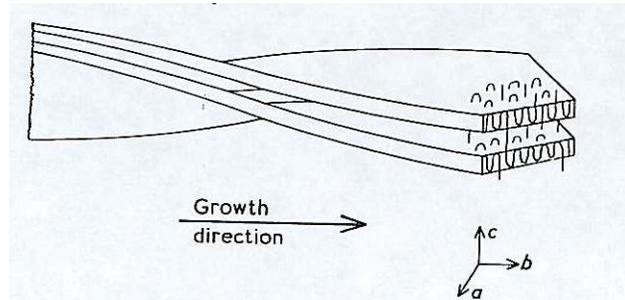


Figure 7. A schematic of a spiraling lamella in a growing spherulite [2].

In the shish-kebob, lamellae stacks (the kebobs) are joined by a central column of extended chains (the shish). For the shish-kebob, two relative types are evident, the low and high stress structures.

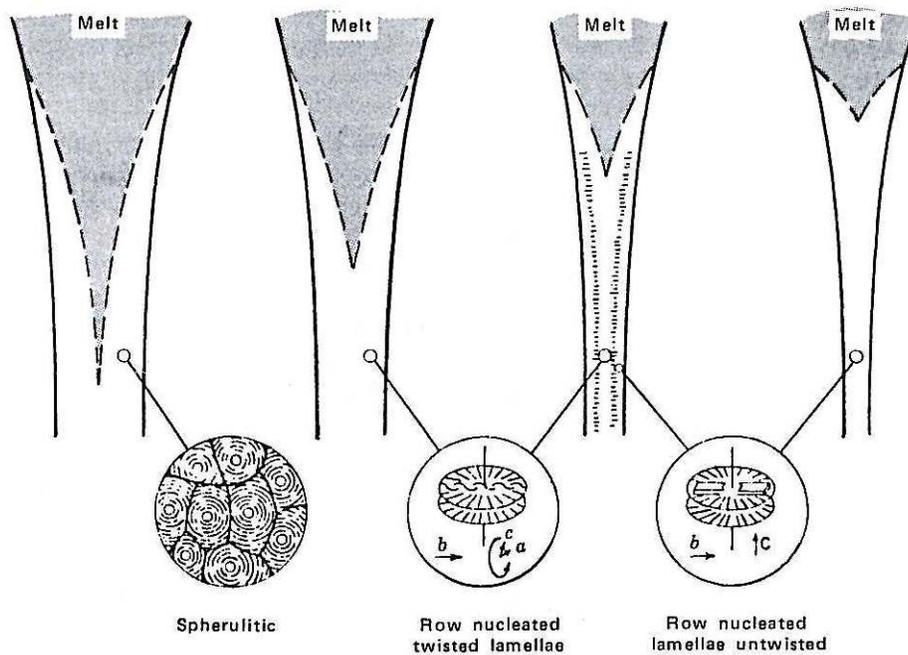


Figure 8. Low (twisted) and high (untwisted) stress shish-kebob structures. The stress applied to the melt is increasing from left to right in the figure.

In the low stress shish-kebob (which is typically still a higher stress than that forms spherulites) the lamellae have more freedom to rotate about the normal direction to the shish, resulting in a spiraling pattern along the growth direction, as seen in Figure 8.

The high stress shish kebob is unable to rotate, resulting in the alignment of the lamellar normal in the direction of the shish.

Microscopic techniques, such as AFM, TEM, SEM, and OM are the primary tools for understanding the structure of these larger entities. A common practice is to utilize the analytical techniques of the smaller sub-units, in conjunction with the microscopic techniques, in an attempt to fully understand the morphology of a polymer structure.

The extended chain is another structural unit that functions on many length scales. In the purest sense, the extended chain is an entire polymer chain completely extended in the direction of the stress. In most commercial melt polymer processes, such an entity does not exist, primarily due to viscous hindrances and limitations in processing conditions (namely time and temperature). In solution processing, such chains have been observed. In addition, the solid state polymerization of polydiacetylene has been shown to produce extended chains, primarily due to the rigidity of the backbone as a result of the high levels of unsaturation [2]. One interesting work in oriented linear polyethylene, conducted by Bassett, argues for the presence of extended chains by the evidence of a higher temperature melting peak seen in DSC data [5]. This peak, some 5 °C higher than the bulk peak, suggests a lower entropy structural unit that could be extended chains. The extended tie molecule between lamellae is also a critical component to Peterlin's model for oriented semi-crystalline polymers [3] and the structure model proposed by Gibson, Davies, and Ward [6] for similar oriented systems. In addition, Peterlin proposed a clever means for determining the volume fraction of tie molecules through XRD, SAXS, and density measurements [7]. For the purpose of this paper, the extended chain will not be elaborated upon in great detail, other than the fact that tie molecules exist between crystallites and upon orientation by high uniaxial stress, can be extended.

Effects of Stress on Morphology

The stress applied to the polymer (be it shear or extensional) greatly influences the structure of the polymer crystals. In a low stress process, such as sheeting or high stalked blown film, the polymer remains in a melted state of reduced stress for a relatively long period of time prior to crystallization. This allows for randomization of the crystallites of the polymer, relative to the machine direction (stress direction). Figure 9 shows a schematic of a sheet or cast film line and a blown film line.

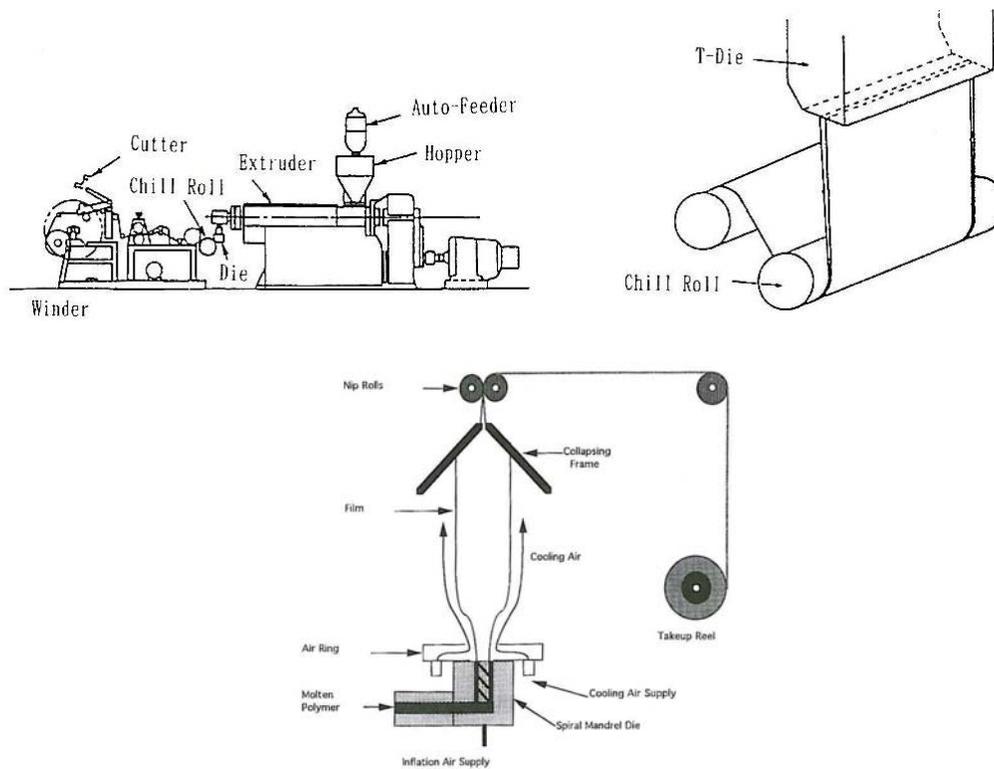


Figure 9. Schematic of a sheet or cast film line and a blown film line [8].

In contrast, a process with high stress, such as a cast film or in-the-pocket blown film imposes a large amount of uniaxial stress on the polymer melt prior to crystallization.

To further understand the significance of uniaxial stress on melt processed polymers, the processes of in-the-pocket blown film versus high stalk blown film will be compared for high molecular weight high density polyethylene. Film that is blown in-the-pocket is crystallized very quickly as it exits the die. Such a process results in drawing the film down to its final gauge, relative to the die gap, in a short period of time and limits the amount of relaxation allowed to occur in the melt. This means that whatever morphological characteristics induced by the shear stresses caused by the polymer melt passing over the land of the die and the fact that the film is being drawn down quickly during the crystallization process are retained in the film. This characteristic is typical of conditions where processing times are significantly less than the relaxation time of the polymer melt. As a result, this technique locks in the morphology of the high stress process, resulting in the high stress shish-kebob structure. In contrast, the high stalk process gives the polymer additional time to relax in the melt state prior to crystallization. This means the polymer is allowed to randomize and more importantly, be partially drawn down to its final gauge in a melt state and not during the crystallization process. As a result, the low stress shish-kebob structure is observed.

A similar discussion can be made for sheeting versus cast film, with the key difference between the two processes involving the crystallization rate and process time. Sheeting is typically much thicker than cast film (5-40 times thicker) and operates at much slower line speeds (10-100 times slower). The thicker final gauge of the sheet line results in a much lower draw down ratio, which is defined as the ratio of the die opening to the final film thickness. This induces a lower stress to the melt between the exit of the die and the chill roll, relative to a cast film line that attempts to maximize the rate of achieving this draw down ratio to produce the thinnest film possible from a large die gap. As a result, larger and more perfect spherulites are seen in the sheet relative to the smaller, less perfect spherulites that are often observed in some cast films.

In oriented films, such as MDO (machine direction oriented) or biaxially oriented (BO) film, the morphology of the tie chains is of greater significance. Prior to orientation, the tie chains are mostly flexible entities between crystallites, giving the film improved impact and tear properties (Figure 4). Upon orientation at temperatures below the melting point (noted as solid state orientation); the tie molecules become more rigid and taunt. Upon further orientation, the lamellae begin to tilt, slip, and eventually unravel to some extent, resulting in the formation of fibrils and microfibrils on numerous length scales, ranging from angstroms to microns. The following figure shows a schematic of lamellar orientation with taunt tie molecules and respective SAXS patterns, as well as images of taunt tie bridges between crystallites.

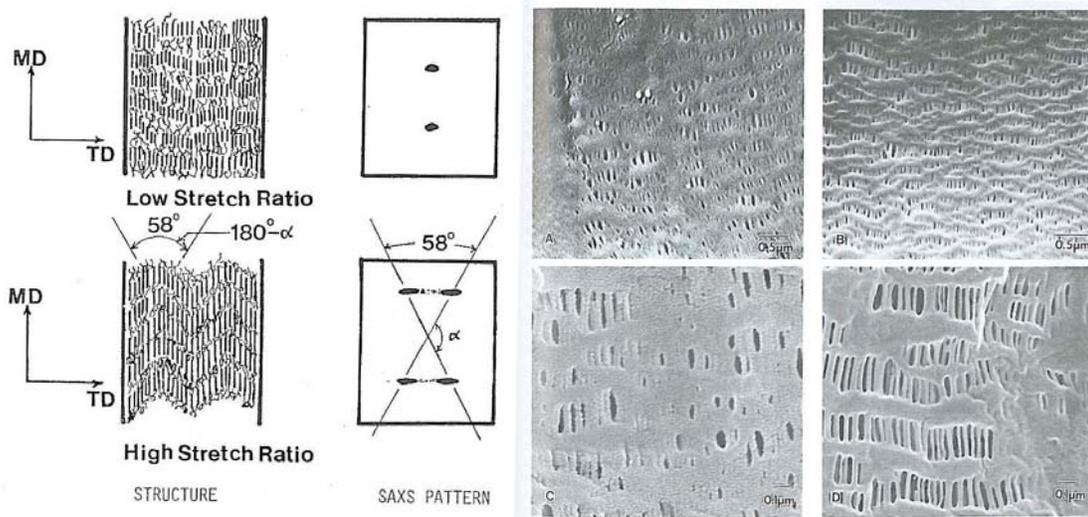


Figure 10. Schematic of lamellar orientation with taunt tie molecules and respective SAXS patterns, as well as images of taunt tie bridges between crystallites [4, 8].

Effects of Crystallization Kinetics on Morphology

The effects on the morphology from the crystallization process of the polymer are a function of both crystallization temperature and crystallization time. Larger supercooling results in thicker lamellae, as noted by the Hoffmann-Lauritzen equation [2]:

$$L = \frac{2\sigma T_m^\infty}{\Delta H_f (T_m^\infty - T_m)}$$

Where L is the lamella thickness, σ is the surface energy of the folded surface, T_m^∞ is the melt temperature of a perfect crystal, ΔH_f is the heat of fusion, and T_m is the melting temperature of the crystal.

The following plot shows the increase in lamellae thickness (L) relative to the reciprocal of the supercooling.

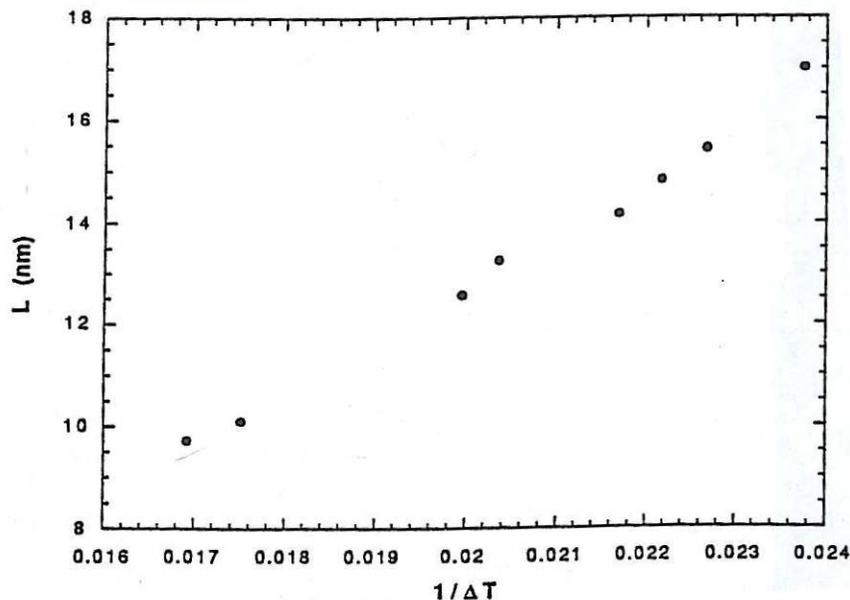


Figure 11. Change in lamellae thickness relative to the reciprocal of the supercooling [9]. Note that larger supercooling (ΔT) results in thinner lamellae.

The percent crystallinity is related to the crystallization time, and is given by the Avrami equation [9]:

$$\ln(1 - X_c) = kt^n$$

Where X_c is the volumetric crystallinity, t is the time, n is the Avrami exponent and is related to the shape and nucleation of the crystallite, and k is a scaling constant.

The following figure shows the Avrami plots for the crystallization of a polymer at various temperatures relative to time. Note that for lower temperatures, the polymer has a higher percent crystallinity at a given time in the crystallization process.

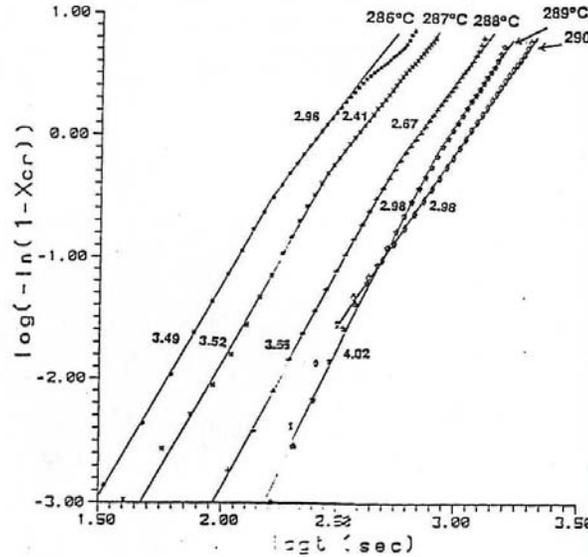


Figure 12. Avrami plot of crystallization data conducted at various crystallization temperatures relative to crystallization time [9].

In addition, the crystallization rate, G , is related to the crystallization temperature, and is given by [9]:

$$G = G_0 \exp\left(\frac{-\Delta F}{kT}\right) \exp\left(\frac{-\Delta U}{kT}\right)$$

Where G is the linear growth rate, G_0 is the pre-exponential factor, ΔF is the free energy of formation of the critical nucleus and ΔU is the activation energy of the elementary jump process.

The following figure shows a plot of crystallization growth rate relative to temperature for a polymer of varying molecular weight.

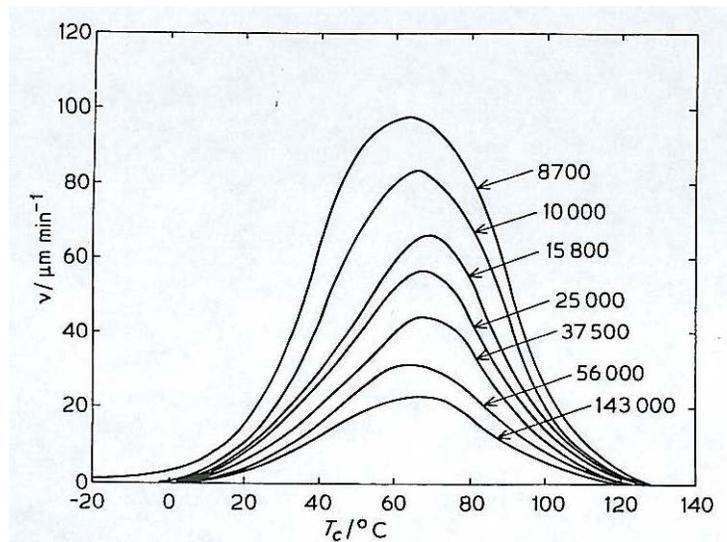


Figure 13. Plot of crystalline growth rate relative to crystallization temperature for a polymer of varying molecular weight. Note that the extremes of low and high supercooling, the growth rate is at a minimum value, while the growth rate is optimized at some intermediate temperature.

At low temperatures, the growth rate has a low value, primarily due to viscous hindrances that inhibit material from diffusing to the nucleating site and “impurities” from being expelled from the growing crystallite. Greater detail of this subject is described by Keith and Padden and outlined in Bassett [1]. The growth rate at low supercoolings (high crystallization temperature) is also relatively low, which is a result of the low thermodynamic driving force associated with forming crystallites at these elevated temperatures. The crystallization rate is maximized at an intermediate temperature, where the hindrances from both the viscosity of the melt and the thermodynamic driving force are balanced.

Polymer processes that crystallize at high supercoolings (low temperatures) produce thinner lamellae due to the large thermodynamic driving force to form crystallites. In addition, these specimens have a higher overall percent crystallinity (at a given time in the crystallization process), as shown in Figure 12, and have a low crystallization growth rate, as shown in Figure 13. These conditions provide for the formation of smaller spherulitic structures (in low stress processes) and stacks of thinner lamellae with greater amounts of defects in high stress applications. Cast film extrusion into a quenched water bath is an example of a process that would produce small spherulites while blown film extrusion at high line speeds is an example of a process that would produce thin stacks of lamellae.

In contrast, a process that involves low supercoolings and long processing times produce thick lamellae and a lower percent crystallinity at a given time in the crystallization process. The slower crystallization rate (Figure 13) provides the extended time necessary for the additional thermal energy from the higher temperature to allow the chain to conform to a higher ordered (lower energy) arrangement.

Conclusion

The hierarchical structure of a semi-crystalline polymer is a complex problem, with many levels of structure that can be characterized with various analytical techniques. To gain a full appreciation for the structure of semi-crystalline polymers, the structure at each level must be well understood. In addition, the effects of the choice of process and operating conditions must be included to better understand the means of which the various levels of structure originate.

A hierarchical model that utilized the basic unit of a polymer, the repeat unit, has been presented that explains the formation of the various levels of semi-crystalline structure. From the repeat unit, unit cells, helices, lamellae, tie molecules, spherulites and shish kebobs are formed. In addition, an explanation regarding how variations in operating conditions, namely stress, temperature and time effect the formation of the hierarchical structure.

References

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