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Introduction to Polymer Crystallization

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1.1 Introduction

Long-chain molecule polymeric materials have benefited from the use of crystallization as a fundamental thermodynamic phase transition in condensed matter physics of pure substances. Keller made the electron microscope findings on polyethylene (PE) single crystals grown in diluted solutions in 1957, following the synthesis of high-density PE with the development of Ziegler–Natta catalysts, thus developed the chain-folding model [1]. Since then, the discovery of diverse polymer crystal morphologies has been aided by the chain-folding concept. Nowadays, semi-crystalline polymers, such as polyolefins, polyesters, and polyamides, account for more than two thirds of all synthetic polymer products produced worldwide due to their numerous uses in our everyday lives. The degree of crystallinity, which normally ranges between 10% and 80%, describes the proportion of organized polymer molecules [2]. Only small-molecule materials, which are often brittle materials, can attain the greater value of crystallinity.

Hu asserts that the chemical structures of repeating units of polymer can be categorized using two distinct contributions to the perseverance of melting points: intramolecular interactions of collinear connection energy of bonds on the chain for

Polymer Crystallization: Methods, Characterization, and Applications, First Edition.
Edited by Jyotishkumar Parameswaranpillai, Jenny Jacob, Senthilkumar Krishnasamy, Aswathy Jayakumar, and Nishar Hameed.

thermodynamic adaptability and intermolecular interactions of local bond–bond interactions for the parallel-packing of two neighboring bonds in the conventional lattice models for parallel-packing order [3]. As a result, the melting temperatures of polymers with repeating units that favor greater stiffness or more dense/stronger packing are typically higher. Techniques used to evaluate the crystallinity of polymers include density measurement, X-ray diffraction (XRD), infrared spectroscopy, differential scanning calorimetry (DSC), and nuclear magnetic resonance (NMR) [4, 5].

Referring to Zhang et al., the mechanical and optical performance of crystalline polymers like PE and polyethylene terephthalate (PET) corresponds with molding parameters that are strongly influenced by their crystallinity [6]. Crystalline polymers undergo stress at freezing and retain stress from crystallization, according to Kato et al. [7]. Due to the lack of appropriate methods for quantitatively evaluating these transitions, the micro-mechanical forces during polymer crystallization remain a highly discussed topic. Up until now, the forms of proof have been theoretical, indirect experimental, or empirical discussions [7]. There are several experimental methodologies and approaches to estimate the amplitude of micro-mechanical forces during polymer crystallization to limit and avoid material failure owing to these forces. This includes non-destructive test [8], destructive test [9], and computer simulation [10]. Between these, non-destructive techniques have been employed to examine the physical relaxation of components during heating and determine their initial stress state, such as holographic interferometry and synchrotron XRD research. Despite the benefits of these techniques being non-destructive, neither a qualitative computation nor a stress visualization can be completed instantly.

Approximately 30–60% of the substance was comprised of polymer crystals, which ranged in size from a few nanometers to several, randomly oriented in space. Because crystalline polymers could withstand loads and act in diverse directions like reinforced rubber, as well as because macromolecules were often much longer than the crystal dimensions. The fundamental understanding that crystals might function as cross-linkers similar to those in cross-linked rubbers [11]. The tensile, microhardness, and compression behavior patterns of semi-crystalline polymers (Figure 1.1b) have been significantly influenced by micro-mechanical forces throughout polymer crystallization through tie chain portions, which appear to be molecular connections between individual crystallites from the perspective of the molecular topology of the amorphous phase (Figure 1.1a). Additionally, tie chain polymer crystallization improves fracture toughness and slow crack propagation resistance [12, 13].

Most molecular-level descriptions of the semi-crystalline phase are based on topological properties, including the theories of tie chain segments, loop segments, tails, and the alternating of crystalline and amorphous domains [14]. Olsson et al. claim that interface Monte Carlo moves are utilized to relocate sites and change chain connections on the atoms and chains in the amorphous domain to produce new loops, tails, and bridges. The resulting samples' crystalline components are still faultless, that is, devoid of twins or dislocations. According to reports, these faults weaken the critical shear stress and weaken slide processes. As a result, the models under consideration are idealizations of a true semi-crystalline PE material, and

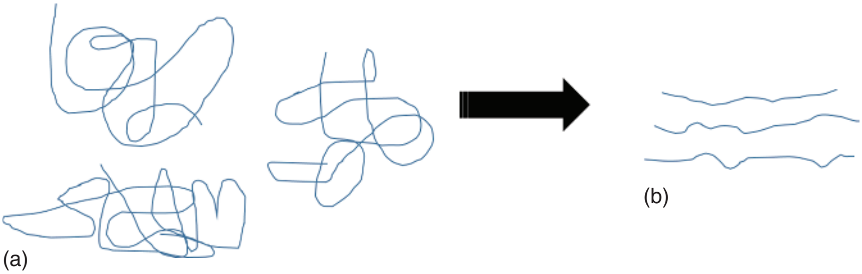

Figure 1.1 The arrangement of polymer molecular chains (a) in amorphous and (b) in semi-crystalline polymers state.

the anticipated resistance to crystal yielding is anticipated to be larger than what has actually been empirically observed [15].

1.2 Degree of Crystallinity

The degree of crystallinity determines how ordered a solid is structurally; the more crystalline a polymer is, the more regularly its chains are aligned, and the arrangement of atoms or molecules is repeatable and consistent. The degree of crystallization of polymer materials has a big impact on their characteristics. In terms of performance, a molded part is stiffer, stronger, but also more brittle the more crystallization there is. Hardness, density, transparency, and diffusion are all significantly influenced by the degree of crystallinity. Chemical composition and thermal history, such as cooling conditions during manufacturing fabrication process and post-thermal treatment, have an impact on the degree of crystallization. However, the characteristics are also influenced by the size of the structural units or the molecular orientation in addition to the degree of crystallinity [16, 17]. In general, a higher degree of crystallinity is typically the result of variables that make polymers more regular and organized because fewer short branches allow molecules to pack more tightly together. Syndiotactic and isotactic polymers have a higher degree of stereoregularity than atactic polymers, but the polymers are also more organized and have regular copolymer structures [18]. Based on the study by Yao et al., it was discovered that a rise in crystallinity directly correlated with an improvement in mechanical characteristics by examining the effects of various crystallization parameters, such as crystal shape ratio and crystallinity [19]. The PET crystal structure ratios did not, however, substantially enhance the mechanical characteristics. Furthermore, at a higher isothermal temperature, considerably higher than the T_g, the crystallinity of PET foam will be strongly increased. Slow crystallization can be used to explain the increase in crystalline content at higher temperatures, which promotes regular chain folding and subsequently reduces topological disorder at the surface of the crystallites. According to Jonas et al., the relationship between the service temperature and crystallinity is strong within the experimental range of 10–150 °C. When the operating temperature is close to or higher than T_g, migration causes isothermal-induced crystal perfection, and

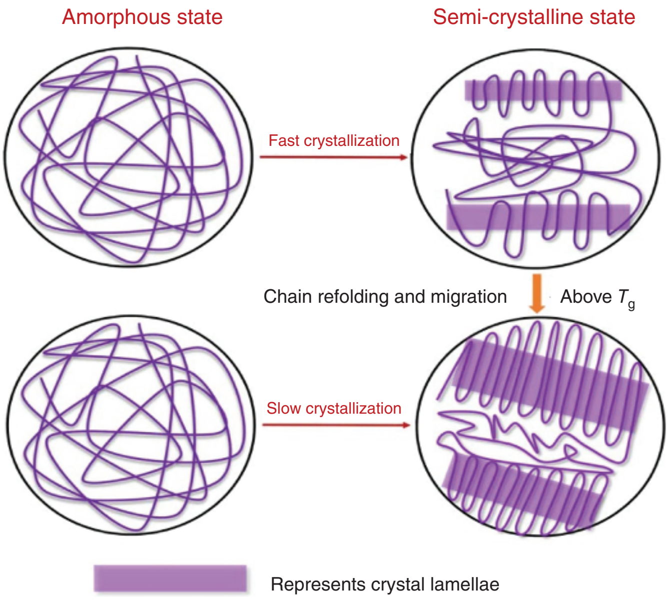

Figure 1.2 The schematic diagram of the mechanism of crystallization enhancement formation from the amorphous state to crystalline in isothermal treatment above T_g. Source: Adapted from Yao et al. [19].

rejection of the structural faults at the crystal's surface causes a rise in the crystalline phase content [20]. The mechanism of crystallization enhanced development from the amorphous state to the crystalline state in isothermal treatment above T_g is schematically depicted in Figure 1.2. The delayed crystallization promotes better crystal lamella development and chain refolding, as seen in Figure 1.2.

1.3 Thermodynamics on the Crystallization of Polymers Characteristics

The partial alignment of the molecular chains in polymer materials can cause crystallization. Amorphous and crystalline domains coexist in these thin lamellar formations, which are created on the scale of nanometers when molecular chains change from a high-entropy random coil state to a reduced-entropy partially folded (semi-crystalline) state [1]. The majority of the solid-state attributes created by polymer materials were impacted by crystallization. Although there is a significant thermo-mechanical dependence in polymer crystallization, one of the major difficulties is controlling the semi-crystalline state precisely. In order to manage the crystalline behavior of the polymers for practical applications, processing factors such as (i) the crystallization temperature [21], (ii) cooling rate [22], and (iii) the application of high shear strain [23] are varied.

Generally, as the crystallization temperature rises, so does the thickness of the crystalline lamellae. Slower cooling rates lead to greater crystallinity, and applying shear stress or shear strain speeds up the nucleation and crystallization of polymer structures [24, 25]. Additionally, the presence of shear stress or shear strain will lead to shish-kebab morphologies of the crystalline polymer and provide rise to varied crystalline morphologies [26]. Crystalline polymers typically exhibit spherulitic structure [27] and fiber formation [28, 29] in the absence of shear. It is true that the crystallization of polymers results in non-equilibrium states. While there is a sizable disparity between melting temperatures (T_m) and crystallization temperatures, there is no thermodynamic phase cohabitation for semi-crystalline polymers (T_c).

From condensed matter physics perspective, the close packing of molecules necessary to create the crystalline lattice order is typically caused by intermolecular interactions. Polyolefins, such as isotactic polypropylene (PP), organize their internal rotations to generate helices in their crystalline states, notably zigzag 2/1 helices for PE and also twisting 3/1 helices, by minimizing their local intramolecular interaction potentials [30]. Consequently, the rigid-rod helices highlight the anisotropic characteristics of intermolecular interactions: the local intermolecular interactions between two rods differ significantly depending on whether they are packed parallel or crossing each other. This leads us to the macromolecular component of the thermodynamic forces that drive polymer crystallization, which is illustrated by the interactions between local chains of macromolecules parallelly packed together [31]. For instance, the stereo-optical sequence regularity of polymers with strong intermolecular interactions like polyvinyl chloride (PVC) and polyacrylonitrile (PAN) may be compromised during crystallization [32]. According to a different theory of protein folding, the lengthy hydrogen-bonding interactions further along the chain are what cause extreme β-folding for the crystalline sequence, whereas the short-range hydrogen-bonding interactions along the chain correspond to intermolecular interactions in polyamide crystals.

Conclusively, the most essential factor in the parallel packing of polymers during their crystalline phase is chain connectedness. Therefore, even though the melting enthalpy and intermolecular interactions of polyolefins may be influenced by intramolecular interactions, considerations from anisotropic intermolecular interactions favor parallel packing as the thermodynamic driving forces for polymer crystallization in accordance with the nature of condensed matter physics [3].

1.4 Polymer Crystallization Mechanism

1.4.1 Strain-Induced Crystallization of Polymer

The development of a highly oriented crystalline phase has a favorable effect on the material's mechanical behavior in many of these applications. The development of extended crystals in the direction of extension during fiber spinning significantly boosts the fiber's strength. The melt is exposed to bi-axial extension during the film-blowing process, and the films have crystals orientated on the plane, giving them the appropriate mechanical characteristics. The invention of a special blow molding procedure that guarantees that the polymer is bi-axially oriented has made it possible to use polyester bottles to accommodate carbonated beverages. Injection molding, for example, the production of a highly oriented outer layer might result in readily cleaved articles. Orientation can also have a negative effect on the mechanical behavior of articles [33].

According to Nitta, a melt-crystallized polymer displays an alternating two-phase structure made up of layers of amorphous material and crystalline lamellae that resemble plates (Figure 1.3a). Folded chain crystallites made up of partially stretched conformations emerge when a polymer molecule's contour length is noticeably greater than the typical lamellar thickness of the order of 10 nm and the chain axes within the lamellae are generally normal to the face of the lamellae [34]. The oriented skin is the layer that is closest to the wall. It is preceded by a partially oriented fine-grained layer with isotropic structural morphology in stress-free areas close to the die's center [35]. Solid-state drawing is typically done during the production of polymer films utilizing a high-speed drawing technique under flowing melt conditions. The manner in which polymer molecules crystallize in the drawing solid and flowing melt determines the structure and characteristics of these polymeric products (Figure 1.3b).

At high temperatures, polymers above their melting point are modeled as viscoelastic liquids. The solid phase can be either amorphous or semi-crystalline depending on the molecular composition and cooling rate. While polymers with regular structures can crystallize because the chains are too regular to allow for regular packing, those with irregular structures cannot. The rate of crystallization is typically zero at the T_m and T_g states and achieves its highest at a temperature in between these two when polymers typically crystallize. The glass transition temperature is the point below which the polymer molecules cease to be mobile and turn "frozen" or also called vitrified. As a result of their high rates of crystallization at temperatures below the melting point and the inability to cool polymers like PE quickly enough to temperatures below the glass transition temperature without significant crystallization occurring, polymers like PE have always been

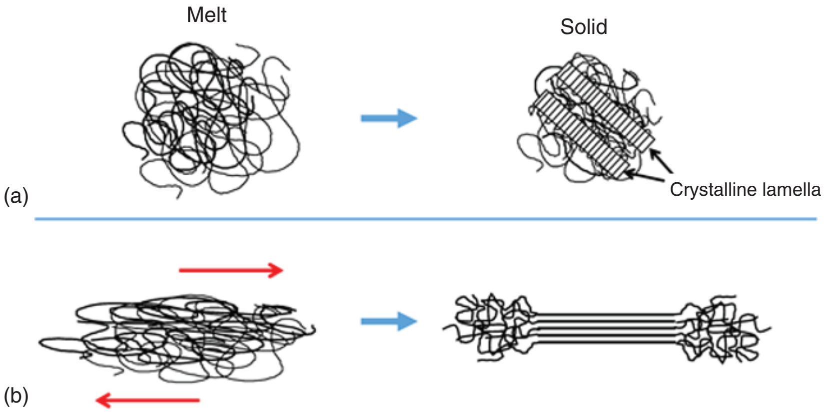

Figure 1.3 Schematic illustrations of crystallization (a) from an equilibrium melt and (b) in the drawing solid and flowing melt.

semi-crystalline in solid form. The melt must be chilled gradually for significant crystallization in polymers like PET, which crystallize slowly. These polymers retain an amorphous state if they are cooled below their glass transition temperature. Crystallization is triggered by the deformation when amorphous PET is subsequently distorted at temperatures barely above the glass transition temperature. The majority of PET products are produced by deforming at these temperatures because the amount and orientation of the crystalline phase can be regulated, allowing for precise control of the final solid's mechanical properties.

1.4.2 Crystallization of Polymer from Solution

Depending on the degree of dilution, polymer crystallization can occur from a solution or by evaporating solvent. In diluted solutions, the molecular chains have no interaction with one another and exist as isolated polymer coils in the solution. Solvent evaporation causes the concentration of the solvent to rise, which encourages molecular chain interaction and the potential for crystallization, such as when a melt crystallizes [36]. The highest level of polymer crystallinity might be achieved through crystallization from the solution. For instance, when crystallizing from a diluted solution, extremely linear PE can produce single crystals resembling platelets with a thickness of 10–20 nm. Using a solvent that dissolves individual monomers but not the final polymer, precipitation is a distinct procedure. After a certain level of polymerization, the semi-crystalline, polymerized product precipitates out of the solution.

According to Huang et al., the kinetics of crystallization from solvent evaporation as well as thermodynamics determine the crystal structure and morphology of polymers. To better comprehend the crystallization process and resulting final structure of polymers, several kinetic parameters were applied to a model system [37]. The migration of polymer chains to the crystal growth front and the rate of crystal development, which may be altered in solution crystallization by modifying the rate of solvent evaporation, are two opposing processes that influence the formation of crystal structure and morphology. By altering the kinetic process, Huang and his colleagues have investigated the crystalline form and structure of poly(L-lactide) (PLLA) in a PLLA–chloroform mixture. The findings led to the identification of the three stages of the PLLA crystallization process: solvent adsorption, surface gel formation, and crystallization. The tiny chloroform molecules that were continually adsorbed into the PLLA samples ignited the solvent adsorption. As shown in Figure 1.4a, the formation of surface gels and even local PLLA–chloroform solutions was caused by the adsorption of chloroform onto the PLLA film's surface, diffusion of the PLLA segments, and hydrodynamic flow. Because the amount of solvent adsorbed into each layer of PLLA decreased along the direction perpendicular to the substrate, which is coupled to the amount of solvent adsorbed as well as the migration of PLLA segments, a concentration gradient of PLLA chains was also produced. PLLA then crystallized as a result of its concentration fluctuation, which was connected to a shifting concentration gradient and nonlinear solvent evaporation kinetics. As a result of solvent evaporation at that point, PLLA crystal lamellae began to form around the nuclei from the PLLA–chloroform system (Figure 1.4b).

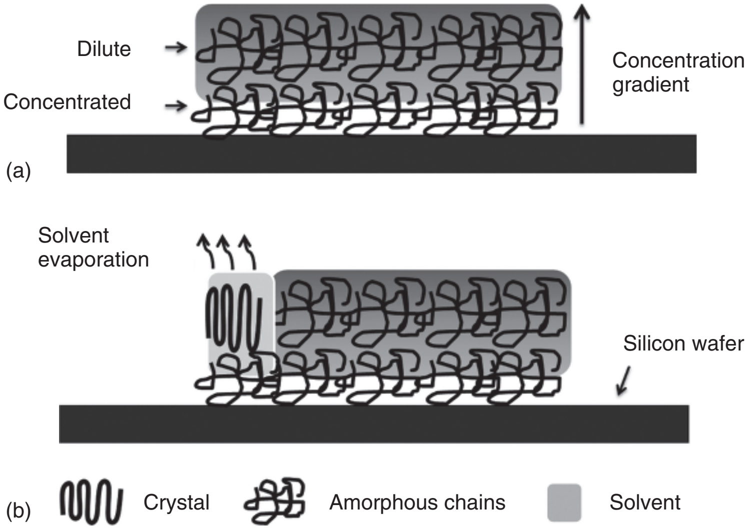

Figure 1.4 Diagrammatic representation of PLLA crystallization caused by solvent evaporation and PLLA concentration gradient. In (a), solvent is adsorbed onto the surface of the film to create a PLLA solution with concentration gradient. In (b), solvent evaporation drives PLLA crystal nucleation and growth. Source: Reproduced from ref. [37].

1.5 Applications of Crystalline Polymer

All polymers have some degree of crystallinity. As has been previously discussed, crystallinity of polymer has a significant influence on its properties, with more crystalline polymers having chains that are more regularly aligned. By increasing the degree of crystallinity, the density and hardness of the material are increased. This is due to the fact that more intermolecular bonds are formed when it is in the crystalline phase. Therefore, the polymer gets stronger and its deformation can result in the higher strength owing to oriented chains [38]. Besides, highly crystalline polymers are stiff, less susceptible to solvent penetration, have high melting points, are barriers to moisture and gases, and are resistant to oil and grease [39]. For instance, PP, PE, nylon, syndiotactic polystyrene, and Kevlar. Even though crystallinity makes a polymer strong, it also lessens its resistance to impact.

Conversely, amorphous polymers are softer, have lower melting points, and are more permeable to solvents. Some highly amorphous polymers include polycarbonate, poly(methyl methacrylate), polyisoprene, and polybutadiene. While semi-crystalline polymers, on the other hand, have both crystalline and amorphous areas. Most plastics benefit from semi-crystallinity because it combines the flexibility of amorphous polymers with the strength of crystalline polymers, making this form of polymer both strong and flexible. Semi-crystalline polymers have a limited heat tolerance before softening and bending. Yet, semi-crystalline plastics

Table 1.1 Difference in general properties of highly crystalline, semi-crystalline, and amorphous polymers [40, 42].

	Type of polymer		
Properties	**Highly crystalline**	**Semi-crystalline**	**Amorphous**
Hardness	Hard	Hard	Soft
Melting point	High and sharp melting point	High and sharp melting point	No distinct melting point and softens over a broad range of temperature
Mechanical	High strength	High strength	Low strength
	High fatigue and wear resistance	Good fatigue and wear resistance	Poor fatigue and wear resistance
Clarity	Opaque to visible light	Translucent	Tend to be translucent or transparent
Resistance to chemical	High	High	Low
Gas permeability	Low	Low	High
Arrangement of molecules	Regular and uniformly packed molecules	Regular and uniformly packed molecules	Random
Ideal application	Ideal for long exposure and high strength applications such as in structural applications	Ideal for applications that need high strength and low friction and have an environment that experiences any repeated cyclic loading and chemical contact	Ideal for applications that require high dimensional accuracy and stability with a transparent, overall good appearance, low to zero mechanical abuse, and chemical contact

have a propensity to quickly shift from a solid state to a low-viscosity liquid once the melting point is achieved [40].

In the industrial sector, crystallization kinetics are a crucial factor to take into account while designing a polymer for a certain application because it will affect the final polymer product [41]. For instance, flexibility at low to ambient temperatures is required for many applications of polymers and polymer coatings. Amorphous polymers are the best option in this situation since they have some resistance to elasticity and impact. In contrast, a polymer with more crystallinity may be favored when hardness and rigidity are needed. The difference between highly crystalline, semi-crystalline, and amorphous polymers as well as their ideal applications are highlighted in Table 1.1.

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