

Review on Crystallization Strategies for Polymer Single Crystals

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Abstract: Polymer physics has evolved significantly over the past century, transitioning from the early recognition of the chain structure of polymers to a mature field integrating principles from statistical mechanics, thermodynamics, and condensed matter physics. As an important part of polymer physics, polymer single crystals are crucial for understanding molecular structures and behaviors, enhancing material properties, and enabling precise functionalization. They offer insights into polymer crystallization kinetics, serve as templates for nanofabrication, and have applications in electronics, sensors, and biomedical fields. However, due to the complexity of molecular chain movement, the formation of polymer single crystals is still very difficult. Over the decades, numerous researchers have dedicated themselves to unraveling the mysteries of polymer single crystals, yielding substantial findings. This paper focus on the historical evolution and advancements in polymer single crystal research, aiming to offer valuable insights and assistance to fellow researchers in this field.

Keywords: polymer single crystal; crystallization strategy; functionalized application



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1. Introduction

In 1920, Hermann Staudinger proposed for the first time that polymers are linear structures consisting of monomers connected by covalent bonds, thus founding modern polymer science [1,2]. In the course of one hundred years of development, polymer materials have gradually become an indispensable part of our daily lives. Scientists have gradually deepened their research on polymer chemistry and polymer physics, especially on polymer crystallization.

A polymer single crystal is defined as a highly ordered arrangement of polymer chains in a three-dimensional lattice structure, wherein all the molecules are aligned in a specific orientation with respect to each other. Unlike polymer polycrystals, which consist of multiple crystal domains with varying orientations, polymer single crystals exhibit uniformity and perfect geometric symmetry. It was first thought that it was difficult for polymer chains similar to random line clusters to be ordered, and that there was a very high thermodynamic energy barrier for the untangling and movement of molecular chains. However, experimental results showed that under appropriate crystallization conditions, polymer chains will spontaneously form geometrically symmetric structures similar to small molecule crystals. The structure of the crystal reflects the stacking of the lattice, and the close arrangement of the molecular chains also leads to excellent mechanical or optoelectronic properties. The study of polymer single crystals has promoted the development of polymer crystallization theory, greatly deepened the understanding of polymer chain behavior, and made important contributions in many aspects:

I. Polymer chain folding. Polymers have a long chain structure, and the conformation inside their crystals was unknown. In 1957, Keller, Till, and Fischer independently cultured single crystals of polyethylene almost simultaneously [3–5]. They used a dilute solution of polyethylene, cooled down at an extremely slow rate, and allowed the solvent to evaporate slowly, eventually obtaining single crystals of polyethylene. Experimental observations

revealed that the thickness of the resulting single crystals was much lower than the length of the polymer chains, while single-crystal electron diffraction showed that the molecular chains were oriented along the thickness direction, based on which, a unique folding phenomenon of the polymer chains was proposed. The conformation of a polymer chain should follow two principles: one is the principle of lowest energy, and the other is the principle of shortest repetition period. In a folded chain model, the molecular chain of the regular arrangement of the bundle is the basic structural unit of polymer crystallization. The regular crystalline chain bundles are elongated and have a large surface energy, and will spontaneously fold into a band structure. In order to further reduce the surface energy, the crystalline chain bundles should fold and grow into regular single-layer lamellae on the surface of the formed nuclei. In the folded chain model, the crystal will be divided into several sectors, and the sectorization effect is a unique feature of polymer single crystals. The observation of single crystals was also indispensable for the subsequent proposals such as Flory's plugboard model and Keller's regular folding model [4,6].

II. Lamellar thickening. The state of polymer crystals with the lowest free energy is an elongated chain, and the lamellar structure has a non-stationary conformation (Figure 1). Annealing can lead to further evolution of the single-crystal structure, and lamellar thickening occurs. Stack et al. were the first to observe a gradual broadening of the thickness distribution of polyethylene lamellar crystals during annealing in 1982 [7]. Strobl and Fischer pointed out that lamellar thickening exists during annealing due to the fact that the melting point of the folded-chain lamellar crystals is well below the thermodynamic equilibrium melting point of the infinite-sized crystals [8]. Interestingly, the surface of polymer crystals in the lowest state of free energy is that of straight chains. Interestingly, when the annealing temperature is high enough, holes form on the surface of the lamellar crystals. Roe et al. proposed that the holes are due to melt recrystallization occurring at local defects in the lamellar crystals, and that the localized thickening causes the lamellar crystals to shrink laterally [9]. Reiter attributed this to the fact that the thickness of the initial lamellar crystals is not uniform, and that localized troughs, corresponding to melting points that are lower than the annealing temperature, melt to form the holes during the heat treatment process (Figure 1c) [10]. The Hu group observed differences in the thickness distribution of single-layer lamellar crystals through molecular simulations, confirming that thinner regions of lamellar crystals preferentially melt to form holes during the high-temperature annealing process [11].

III. Crystal surface growth. Polymer single crystals usually show anisotropy, which means that the growth of crystals along a certain crystallographic direction is faster than the other directions, and thus the nucleation barriers for polymer crystallization on different crystal planes are different. Flory first pointed out that the boundary between the crystal region and the liquid region of polymers is different from the small molecule system in that it is not very sharp [12]. The growth of crystal surface plays a crucial role in the mechanical behavior of crystalline polymers. It provides essential insights into phenomena like polymer material deformation, physical aging, shear yielding, and silver grain formation.

IV. Determination of the size of the critical nucleus. Single crystals are essential for the study of critical nucleation size. Nucleation is the key to controlling the crystallization rate. Determining the size of the critical nucleus is key to understanding the nucleation mechanism and is a great challenge. Jun Xu's group proposed a method to calculate the size of the critical secondary nucleus formed at the lateral growth front of folded polymer chain lamellae crystals. It was found that the critical secondary nuclei consisted of 15–27 units, corresponding to 5–8 chain columns, when butylene succinic acid copolymers were isothermally crystallized from quiescent melts in the temperature range of 70–95 °C (Figure 1d) [13]. On this basis, they used α -crystalline polylactic acid (PLA) as a research object, in the temperature range of 120–140 °C, and gave an upper limit of 4.1–5.4 for the average number of chain columns contained in the secondary critical nucleus, which originated from 1.5–1.9 molecular chains. In agreement with the previous results, the secondary critical nucleus contains multiple chain columns, which are not suitable to be

explained by the Lauritzen–Hoffman theory of secondary nucleation [14]. Recently, Jun Xu's group extended the method to the crystal system of polylactic acid cubic complexes containing two components consisting of levo- and dextro-PLA. The numbers of both types of units in the critical secondary nuclei were obtained [15]. These results provide rich information on the ordering process during melt crystallization of crystalline polymers, which is useful for understanding the crystallization mechanism.

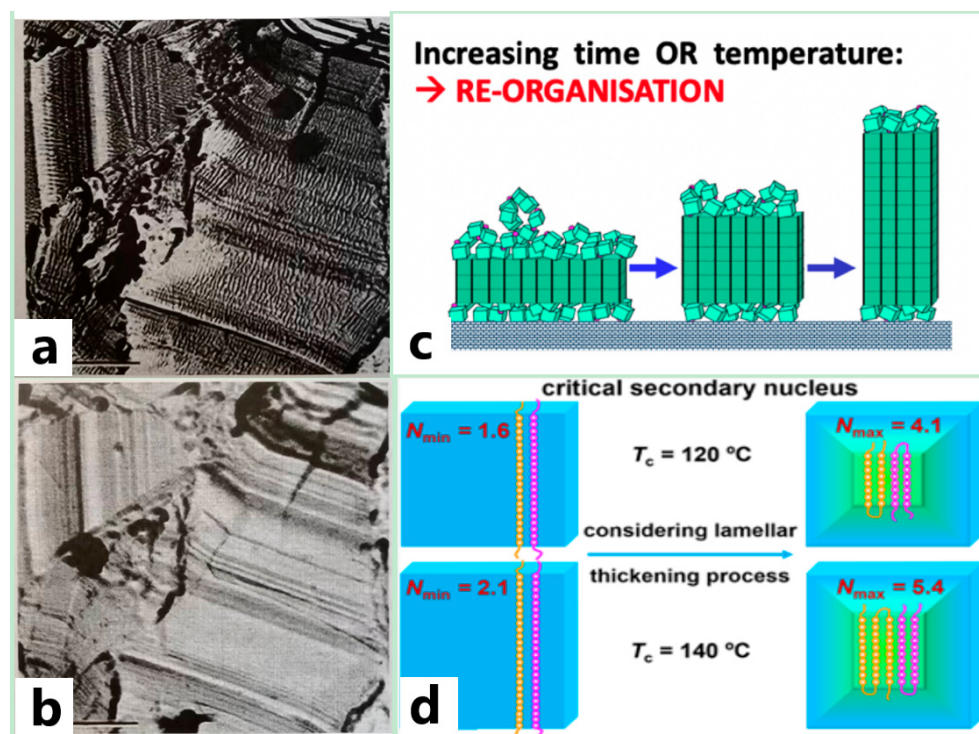


Figure 1. (a) Electron microscope photographs before the growth of folded chain crystals. (b) Electron microscope images of folded chain crystal growth. (c) Schematic presentation of lamellar thickening. (d) At crystallization temperatures ranging from 120 to 140 °C, a critical secondary nucleus of a PLLA α -form crystal contains around 4.1 to 5.4 L-lactide units [14]. Copyright © 2009, Springer Nature Limited, Copyright © 2020, American Chemical Society.

The key to preparing high-quality single crystals is to ensure that they crystallize under low supercooling and a low concentration. Single crystals of polymers can usually only be obtained under special conditions, and are generally produced by slow crystallization in very dilute solutions (0.01% to 0.1%). Within the single crystal, the molecular chains are arranged in a highly regular three-dimensional order, with the chains oriented perpendicular to the surface of the lamellar single crystal. When the degree of supercooling or the concentration of the solution is slightly higher, the growth of polymer crystals is no longer limited to lateral growth, but can form multiple crystals containing a number of overlapping crystals of equal thickness. Helical dislocations in these crystals provide a step that can be grown continuously without restriction, culminating in the formation of helical-stepped multilayer crystals.

In this review, we summarize the crystallization strategies of polymer single crystals, ranging from traditional melt crystallization and solution crystallization to novel strategies such as self-seeding, epitaxial crystallization, controlled evaporation, vapor diffusion, meniscus-guided coating, and topological polymerization. Then, the functionalized applications of polymer single crystals are also discussed, including single crystal substrate modification, single crystal fluorescence, and conductive polymer single crystals.

2. Traditional Crystallization Strategies

2.1. Solution Crystallization

Solution crystallization is an important strategy for the cultivation of polymer single crystals [16,17]. By introducing solvent molecules, it is possible to disrupt the van der Waals forces between the polymer chains, thus allowing the molecular chains to gain motility to participate in the crystallization process. Single-crystal structures are generated by repeated folding of polymers in very dilute solutions [4,18]. They can be directly observed under the electron microscope as lamellar crystals with regular geometrical shapes, which are usually around 10 nm in thickness and can range in size from a few micrometers to a dozen or more micrometers or even larger [3,5,19,20]. In dilute solution environments, polymer chains are not affected by the neighboring chains, making it easier for them to grow into regular single-crystal structures [21]. Unlike melt crystallization, which is driven by supercooling, crystallization in the solution state is driven by supersaturation. At the same time, the nucleation conditions for crystallization in solution are also affected by phase separation, and by setting up the solution system for molecular simulation, it can be seen that the nucleation rate will be accelerated after phase separation, and crystallization will occur at higher temperatures [22]. Throughout the process of solution crystallization, the growth rate decreases with time as the space for the crystals to grow in solution gradually decreases [23]. The growth rate of the crystals is also affected by phase separation.

Keller obtained solution-crystallized polymer single crystals in 1957 and 1958 [24]. In 1964, Holland obtained isotropic morphologies of isotactic poly(1-butene) (iPB-1) from a 0.01% solution of iPB-1 in pentyl. The crystal transformation between the different morphologies was observed at room temperature. For the first time, it was found that the type of single crystal depended not only on the temperature of the solution at the time of crystallization, but also on the initial temperature of the solution prior to cooling down for crystallization [25]. In 1970, Patel investigated the growth of single crystals from solution. Isothermal crystallization of polymers in solution was carried out on a substrate by evaporating the solvent in a gas of the same solvent. Single crystals of PE (shown in Figure 2b), polypropylene (PP), iPB-1, polyacrylonitrile (PAN), and cellulose triacetate (TCA) were obtained. By varying the solution temperature and concentration of these polymers, they found that different growth stages show different growth characteristics [26].

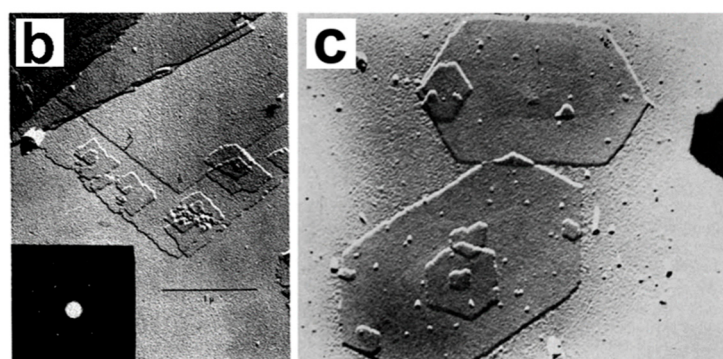


Figure 2. (b) Type III single lamella and corresponding electron diffraction pattern of single-layer iPB-1. (c) Single crystal of PE grown from 0.5% solution in xylene at 100 °C. Magnification: 15,000× [26]. Copyright © 1970 managed by AIP Publishing, Copyright © 1970 John Wiley & Sons, Inc.

In 1984, Booy et al. prepared single crystals of straight-chain starch with a low degree of polymerization from dilute aqueous solutions and aqueous ethanol mixtures. Three different crystal types were produced depending on the ethanol concentration. The results showed that although water and ethanol were classified as poor solvents or even precipitants of straight-chain starch, small changes in their relative concentrations must cause changes in the conformation of straight-chain starch molecules in solution [27]. In 1994, Haisan Bu was the first to obtain single-chain monocrystals in solution and observed the

morphology and crystal structure of isotactic polystyrene (PS) single-molecule monocrystals [28]. In 1997, Renyuan Qian et al. used transmission electron microscopy to observe single-chained single crystals of dulcimer deposited by jetting particles from a very dilute chloroform solution onto a carbon film, which was contacted on the lower side with ethanol-soaked filter paper. It was shown that the polymer nematic clusters in the spray droplets contracted significantly upon contact with non-solvent ethanol, demonstrating that ethanol promoted the crystallization of the sprayed single-chain particles [29]. In 2004, Zhu et al. investigated the effect of phase morphology on the crystallization kinetics of polystyrene-block-poly(ethylene oxide) (PS-*b*-PEO) diblock copolymers with a PEO volume fraction of 37 vol% in different nano-limited spaces. Various phase morphologies such as double helical icosahedral (DG), hexagonal cylindrical (Hex), and lamellar (Lam) morphologies were obtained. The crystal morphologies were characterized by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The crystallization kinetics of the nanoconfined geometries were investigated by differential scanning calorimetry (DSC) using Avrami analysis. The results showed that the Lam phase had the fastest crystallization kinetics and the thermodynamic stability of the PEO crystals was higher than that of the DG and Hex phases [30]. In 2013, Zhaohui Su et al. investigated the crystallization behavior of poly(2-vinylpyridine)-block-poly(ϵ -caprolactone) (P₂VP-*b*-PCL) diblock copolymers in the presence of selective solvents. As shown in Figure 3a,b, the addition of water to a solution of P₂VP-*b*-PCL in *N,N*-dimethylformamide generated elongated truncated rhombic single crystals of uniform size and shape in large quantities. The results suggest that the adjacent re-entrant folding mode plays a major role in crystallization from solution [31].

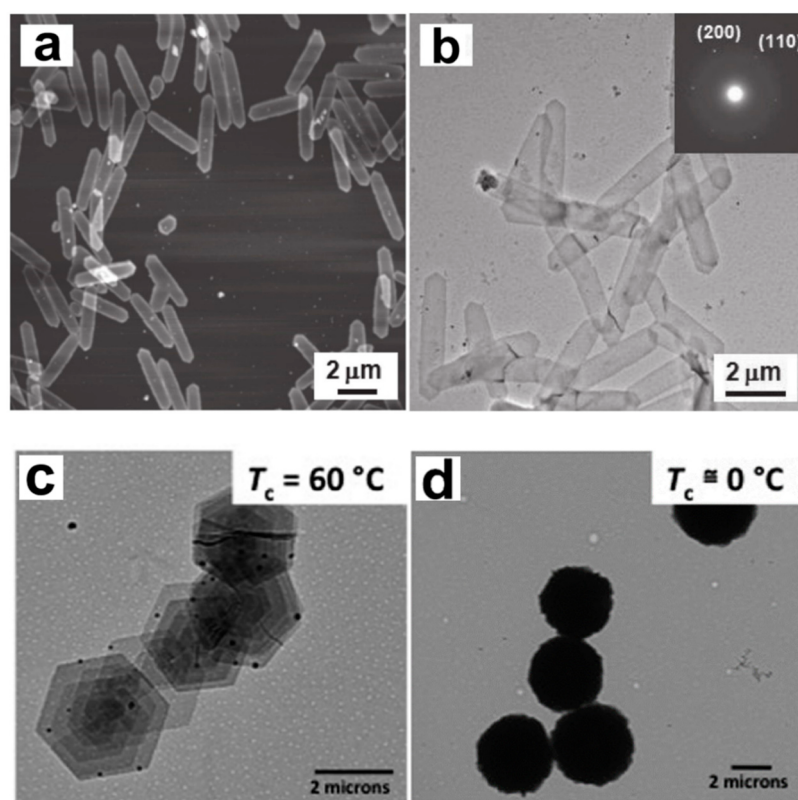


Figure 3. (a) AFM height image and (b) TEM bright field micrograph of P₂VP₁₉₉-*b*-PCL₃₁₀ single crystals formed in DMF/water mixture at 20 °C. The inset shows the corresponding selected area electron diffraction pattern. TEM images of iPB-1 hexagonal and round single crystals crystallized at (c) $T_c = 60\text{ }^{\circ}\text{C}$ and (d) $T_c = 0\text{ }^{\circ}\text{C}$ [31,32]. Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Copyright © 2014, American Chemical Society.

In 2014, Miyoshi used ^{13}C - ^{13}C double-quantum (DQ) NMR to determine the chain-folding structure of ^{13}C -CH₃-labeled iPB-1 in solution-grown crystals mixed with unlabeled iPB-1 over a wide range of crystallization temperatures (T_c). The results indicate that both high and low T_c lead to the formation of clusters of single molecules through neighboring re-entrant structures. As shown in Figure 3c,d, the change in crystal pattern from hexagonal at $T_c = 60^\circ\text{C}$ to circular at $T_c = 0^\circ\text{C}$ can be explained by the kinetic-driven attachment of single-molecule clusters on the growth front of crystal [32]. They found that the crystallization process of iPB-1 can be divided into two steps: (i) cluster formation by self-folding at the pre-crystallization stage and (ii) deposition of nanoclusters as building blocks at the growth front of the single crystals [33]. In 2018, Miyoshi systematically investigated the folded structure and crystallization behavior of ^{13}C -CH₃-labeled poly(L-lactic acid) (PLLA). It was concluded that PLLA chains with different molecular weights initially adopt the same nanoclusters by folding (stage i), and that the kinetically controlled process of nanocluster aggregation leads to different morphological features (stage ii) [34].

2.2. Melt Crystallization

Crystallization requires the sufficient mobility of polymer chains. When the temperature is above the glass transition temperature of the polymer and at the same time, below the equilibrium melting point, polymer chains gain thermal energy in the environment above the van der Waals forces, and thus crystal nucleation and growth occur. Early on, it was thought that only spherulites could grow in the melt until some examples of polymer single crystals growing in the melt were found [35,36]. When the temperature conditions are suitable, polymer single crystal structures can be obtained under melt conditions. Observations of melt-crystallized polymers confirm their support for the adjacent reentry model [37–41]. Striped micellar crystal nuclei are formed in the melt during the early stages of crystallization, followed by the formation of folded-chain crystals [42–44].

In 1963, Symons studied the melt crystallization of polytetrafluoroethylene (PTFE). Single crystals with thicknesses of about 150–900 Å and molecular chains perpendicular to the substrate were observed, suggesting that melt crystallization of PTFE occurs by a chain-folding mechanism [45]. In 1972, Kovacs and Gonthier used an ultrathin film melt crystallization method to obtain single crystals of poly(ethylene oxide) (PEO). The effects of crystallization temperature and molecular weight on the morphology of single crystals were studied [46].

In 1993, Toda studied the three-dimensional shapes of melt-grown polyethylene (PE) single crystals: lenticular (planar) and truncated rhombic (chair-like). The correlations between lateral extension, the growth kinetics, and the three-dimensional shape of the lamellar crystals were investigated by further classification of single crystals with curved cross sections [47]. In 1997, Liu prepared lamellar single crystals of poly(ethylene terephthalate) (PET) at different temperatures by using the confined thin-film melt polymerization method. Based on the electron diffraction results, it was confirmed that “perfect” PET single crystals were obtained. It was found that the molecular chains tilted towards the substrate at different angles at different crystallization temperatures, and the crystal density was affected by the thermal history [48]. In 2002, Yan Shouke investigated the morphology and crystal structure of melt-crystallized ultrathin isotactic iPB-1 films. As shown in Figure 4a,b, it was observed that melt-grown iPB-1 single crystals have a hexagonal shape, while type I crystals transformed from type II display their tetragonal precursor morphology. Electron diffraction showed that the directly formed type I single crystal exhibited a non-twinned hexagonal shape instead of the twinned hexagonal shape of the converted type I single crystal [49].

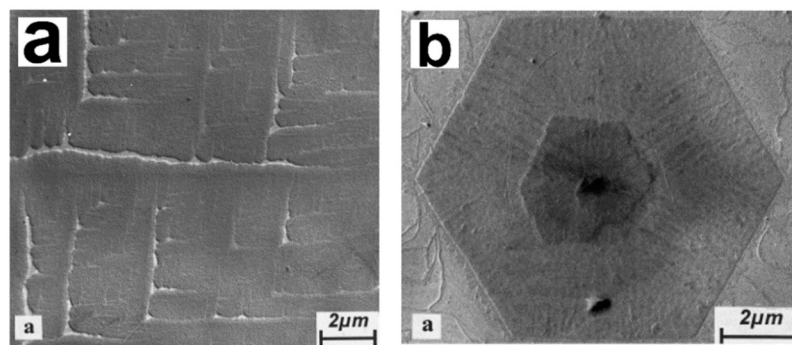


Figure 4. (a) Bright-field electron micrograph of an iPB-1 film that was heat-treated at 160 °C for 15 min and then isothermally crystallized at 95 °C for 30 min. (b) Bright-field electron micrograph of an iPB-1 film that was heat-treated at 160 °C for 15 min and then isothermally crystallized at 110 °C for 5 days. Topographic images of polyethylene single crystals of 32 K fraction grown from the melt [49]. Copyright © 2002 Wiley Periodicals, Inc.

In 2005, Toda et al. observed the three-dimensional morphology of PE single crystals grown from dilute solutions and melts using atomic force microscopy. The selection rule for the rotational orientation of the helical terraces was determined from the observation of the single crystals, confirming that the dislocations of the chair screws follow a bias chiral selection law [50]. In 2007, Rastogi et al. traced the mechanism of crystallization of the non-homogeneous melt state by solid-state NMR. It was observed that the crystallization rate of the de-entangled chain segments was faster than that of the entangled chain segments, indicating that homogeneous nucleation occurs faster than heterogeneous nucleation. The effect of the number of entanglements on crystallization was investigated and it was concluded that the time required for crystallization to occur increases as the number of entanglements per unit chain increases [51]. The following year, Gedde et al. used AFM to study the morphology and thermal stability of different sectors in melt-grown crystals of poly(ϵ -caprolactone) (PCL). The melt crystallization process of star-branched and linear PCL films was monitored in real time using thermal grade atomic force microscopy. Striated, folded surfaces were observed in star-shaped branched and linear PCL crystals, and real-time monitoring of melt crystallization proved that this structure was originally present and not caused by the collapse of tent-like crystals [52].

Solution crystallization and melt crystallization are rather convenient and controllable approaches to forming single crystals of a polymer. They provided rich samples for the early analysis of single-crystal structures and morphologies, and gave rise to a variety of theoretical models of crystallization. Single crystals obtained by melt and dilute solution crystallization are and will continue to be an effective sample for studying crystallization kinetics.

3. Novel Crystallization Strategies

3.1. Self-Seeding

The primary step in polymer crystallization is nucleation. To grow single crystals, control of the nucleation and number of nuclei is critical. In polymer solutions, solvent–polymer interactions and solubility limits are additional key parameters. When the concentration is below the solubility limit, the polymer solution is homogeneous and no crystalline structures are formed. At concentrations above the solubility limit, polymer–polymer interactions become more frequent, at which point, crystals can only be formed by overcoming the nucleation energy barrier [53–56]. At temperatures close to the melting point of the polymer, the process of crystallization becomes extremely slow and is often accompanied by competition for heterogeneous nucleation with nucleating agents, surfaces, or impurities [56–59]. If the onset of nucleation and the number density of nuclei are not controlled, the final crystal structure is usually the result of multiple nucleation steps, resulting in a complex crystal morphology [60,61].

In the crystallization strategy for single crystals, large-sized single crystals can be formed by incorporating small crystals or seeds of the polymer, which can effectively provide crystallization nucleation sites. This strategy is then called self-seeding or self-nucleation. Unlike the narrow melting peaks of small molecules [62,63], polymer crystals have a wide range of melting temperatures due to differences in lamellar thickness. The number of nuclei in the system can be effectively controlled by adjusting the experimental conditions like temperature to eliminate most of the randomly generated nuclei. This method has been extensively studied in thin films and polymer solutions. Through self-seeding, it is possible to grow almost defect-free and large polymer single crystals at low supercooling or low supersaturation.

Blundell first introduced the concept of self-seeding in 1966 during the formation of homogeneous monolayer polydimethylene crystals. He believed that the phenomenon of self-nucleation was very important for crystals, and through this phenomenon, he investigated the nature and origin of the nuclei themselves [64]. In a 1972 publication, Kovacs applied self-seeding to obtain low molecular weight PEO single crystals. The obtained self-seeding samples showed the initiation of crystal unit growth as lamellar single crystals with regular crystal faces, similar to the crystals obtained by crystallization from dilute solutions. At the same time, they found that the shape and thickness of the crystal lamellae depended on the molecular weight and crystallization temperature (T_c). They directly examined some representative crystals and gained new insights into chain folding and lamellar thickening [46].

In 1987, Blundell chose materials with low-density nuclei to obtain large-sized crystals of linear PE [65]. In 1991, Cebe adopted the “two-stage self-seeding technique” for the first time in the preparation of polyphenylene sulfide crystals. The experimental results showed that the controlled conditions in the self-seeding method mainly determine the number and nature of the nuclei, and the crystal morphology obtained by crystallization at different temperatures is different. The limitation of this experiment was that the nucleated crystals could not be observed in solution at high temperature, and the nature of the self-seeding crystals could not be investigated even after the concentration of the solution was reduced by dilution [66].

The concept of self-seeding in the preparation of metal crystals was also well documented in the 1980s, but was quite different from that in polymers. In 1998, Ivanov introduced in his research a self-seeding strategy applicable to the growth of large single crystals of materials with a low thermal conductivity from melts. This is a method of controlling the crystal composition by maintaining a “supersaturated” partial pressure of highly volatile components in the melt, and was first applied to the preparation of single crystals of Cd compounds [67].

Reiter developed the self-seeding technique and has obtained various single crystals. In 2009, he clearly stated that the self-seeding method consists of two steps: first, a crystallized sample is melted at a temperature slightly above its nominal melting point; then, the sample is cooled down to a lower temperature, at which point, the crystals start to grow. By forming the initial seeds through this two-stage growth process, his team “cloned” polymer single crystals, the number density and location of which could be predetermined by controlling the thermal history of the starting crystals [10].

In his 2011 article, Reiter pointed out that polymer crystals allow for self-seeding due to kinetically determined lamellar crystal thicknesses and corresponding melting temperature variations, i.e., a small number of thermodynamically stable residual crystals can be used as seeds from which the melt can re-grow crystals. Thus, when a crystal melts, all the residual portions are oriented and the crystals regrow from these crystal seeds. The article specifically explains the difference in the mechanism when polymers and small molecules crystallize [68]. In another article from 2018, he found that the mode of crystallization of crystals when culturing low molecular weight PEO single crystals was in the form of self-seeding. In particular, he investigated the effect of nucleation temperature (T_s) and rate of warming (V_h) on different crystallization modes. Crystallization at 49 °C resulted

in dendritic PEO crystals consisting almost entirely of twice-folded chains. Upon heating these crystals, crystal thickening was observed to be caused by a decrease in the average chain folding number [69].

In 1992, Müller proposed a new technique for the separation of molecules during crystallization, the successive self-nucleation/annealing (SSA) technique [70]. In another article, he summarized that self-seeding is a specific nucleation process triggered by seeding in a given polymer material through the induction of chain orientation in the molten or partially molten state. It provides a way to quantify the nucleation efficiency of additives such as nucleating agents and nanofillers [71].

In the same year, Peters was devoted to the synthesis of two linear high-density PEs with different molecular weight distributions, and was followed by self-seeding crystallization using other homopolymers. The crystallization strategy is based on the fact that stretching polymers allows for nucleation at temperatures above the melting point. Crystallization parameters such as crystallization temperature were essentially controlled by macroscopic strains after shearing at 142 °C for the bimodal PE [72].

Overall, the self-seeding strategy takes full advantage of the melt-limiting features of polymer crystals that distinguish them from small molecule crystals. It is an effective means of forming large-sized polymer single crystals. Self-nucleation techniques are now mature and have been applied to the study of homopolymers, random and graft copolymers, polymer blends, polymorphic polymers, and nanocomposites. We believe that the self-seeding method will have an even wider range of applications in the future, ranging from semiconductors, microelectronics, micro-purification, and surface treatments to medical systems.

3.2. Epitaxial Crystallization

Epitaxial crystallization is a commonly used method to obtain single crystals of polymers; it refers to a process in which the growth of a crystal occurs on a substrate in a manner that preserves the structural orientation and lattice arrangement of the substrate. The polymer crystallization process involves nucleation and growth, in which the nucleation process needs to cross a high energy barrier [53–56]. By providing a crystallization interface to amorphous polymers, the surface energy during nucleation can be reduced, thus promoting rapid crystal growth [73–75]. Unlike the one-dimensional point nucleation of self-seeding, epitaxial crystallization usually provides a two-dimensional surface for polymer crystal growth. By choosing a suitable crystallization interface, the effect of lattice matching can be exploited to form a variety of different crystal structures [76–79].

Epitaxial crystallization was first proposed by Baer in 1966 in an article describing the crystallization of homopolymers on alkali halide single crystals. Crystallization on the substrate can be fulfilled by two methods: isothermal immersion of the crystals (shown in Figure 5a) and solvent evaporation over the crystals (shown in Figure 5b). The results showed that the cleaved alkali halide crystals have a unique effect on the crystallization pattern of the various polymers studied. Electron diffraction patterns from the polymer crystals indicated that the chains were parallel to the NaCl surface. This phenomenon, in contrast to the usual dissolution crystallization of polymers on amorphous substrates, reveals the influence of directional interaction forces associated with the polymer chain axes on the non-homogeneous nucleation process [80].

In 1972, Baer reported an interfacial epitaxial crystallization method for PE, in which the formation of thin epitaxial layers of polyethylene on the surface of alkali halide crystals by isothermal solution crystallization was investigated. It was found that in the case of NaCl epitaxy, the growth of monoclinic forms of crystals dominated more than the usual orthorhombic forms as the thickness of deposition decreased. The concentration and degree of supercooling had a significant effect on the growth rate. He proposed a model for the long-range electrostatic forces generated on the surface of alkali halides and used it to explain the phenomenon of “limiting crystal height” at low supercooling [81].

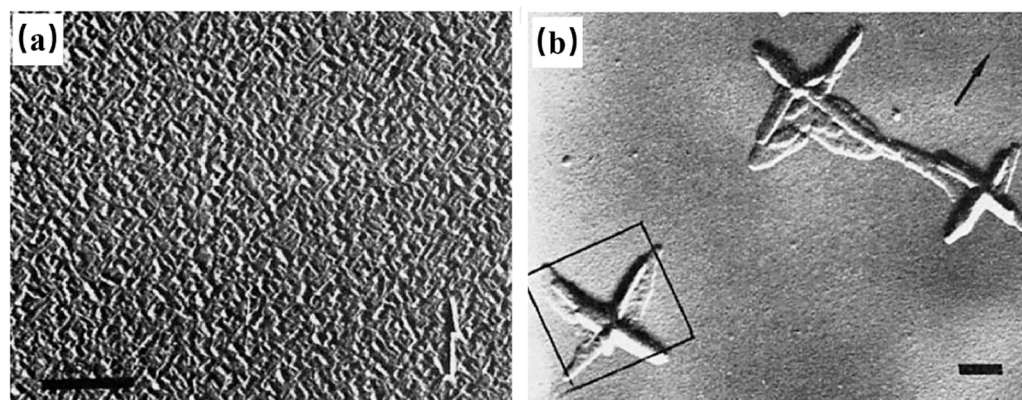


Figure 5. (a) Oriented network overgrowth of polyethylene grown on a surface of NaCl. Arrow indicates $[110]$ NaCl direction. Immersion temperature: $105\text{ }^{\circ}\text{C}$; C-Pt replica; shadow angle: 45 ° ; $0.5\text{ }\mu\text{m}$ mark. (b) Incipient polyethylene “rose” structures grown by method B on (001) NaCl surfaces. Arrow indicates $[110]$ direction of NaCl [80]. Copyright © 1966 John Wiley & Sons, Inc.

In 1981, Wittmann’s group reevaluated the mode of action of nucleating agents selected for epitaxial crystallization of PE on organic substrates. They first used conventional optical and electron microscopy techniques to dry dilute ($\sim 0.5\%$) p-xylene solutions on slides to obtain PE films several hundred angstroms thick, and then deposited thin crystals of hydrocarbons on these films. For anthracene and phthalates, such crystals were obtained directly on PE films by drying a drop of their solutions in xylene and water, respectively [82]. Another article from 1983 similarly investigated the crystallization of several types of polymers dominated by PE, using benzoic acid as a substrate. Polymer films were first formed on microscope slides by evaporation of dilute solutions ($\sim 0.5\%$) in formic acid or xylene (shown in Figure 6). The films were then melted or dissolved in the presence of benzoic acid at temperatures above the melting point of the polymer and the mixture was recrystallized by slowly moving the slide along a temperature gradient on a hot bar. The benzoic acid was then dissolved in methyl or ethanol, and the polymer film left on the glass was covered with carbon and floated in water [83].

In 1985, in a collaborative study by Wittmann and Lotz, they introduced a new technique for the surface modification of polymer crystal folds. Through condensation and crystallization, highly asymmetric modified molecules were oriented parallel to the folding direction (shown in Figure 7). These molecules formed thin layers of miniature crystals with rod-like edges that could be observed by TEM. They analyzed the decorative patterns of crystals with different surface structures, compared the decorative patterns made by PE under different conditions (from solution, from the native configuration, from mixtures of low-molecular paraffin diluents, etc.), and finally determined the applicability of the method to a variety of polymers under different conditions. This modification technique revealed the functional partitioning of polymer single crystals grown from solution, which can be used to determine the local folding orientation of polymers crystallizing under various conditions [84].

In 1990, Lotz provided a comprehensive exploration of the utilization of various organic substrates in epitaxial crystallization. The organic substrates exhibited highly anisotropic folded chain lamellae when crystallized. Organic substrates have three significant improvements over inorganic substrates: 1. better chemical compatibility with polymers; 2. asymmetric crystal structure; and 3. a wide range of characteristic cycles, which allows for a number of different crystalline phases, contacts, and surfaces to be used for a given polymer through different interface matching [85].

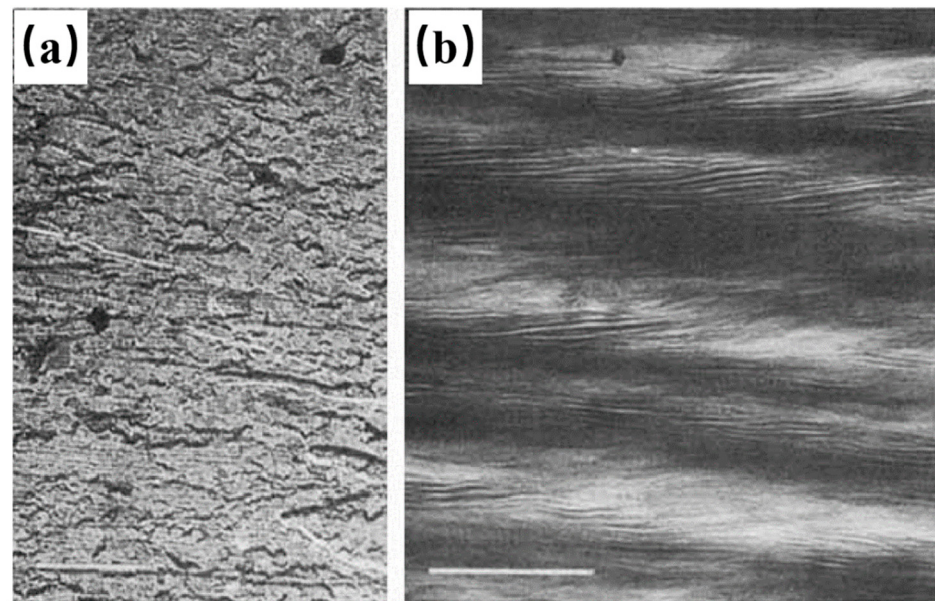


Figure 6. (a) Electron micrograph of a film of polyethylene etched with permanganic reagent, detachment-replicated, and shadowed with Pt-C; scale bar: 1 μm . (b) Electron micrograph of a similar PE films stained with chlorosulfonic acid. Lamellae are properly oriented for visualization in only part of the field. A small fraction of the lamellae are oriented at right angles to the main orientation; scale bar: 0.5 μm [84]. Copyright © 1983 John Wiley & Sons, Inc.

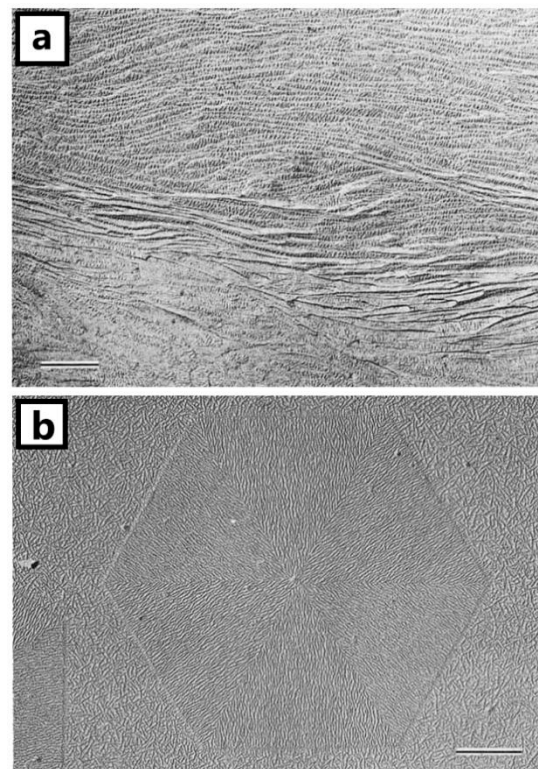


Figure 7. (a) Surface morphology of a thin film of polyethylene ($M_w \approx 20,000$) crystallized by moderate cooling to room temperature and decorated with PE vapors. (b) Single crystal of polyoxymethylene (chlorobenzene solution, $c \approx 0.1\%$, $T_c = 120^\circ\text{C}$) decorated with PE vapors. Scale bar: 1 μm [84]. Copyright © 1985 John Wiley & Sons, Inc.

In 1998, the team of Wittmann and Lotz investigated the epitaxial crystallization of isotactic polypropylene (iPP) structures. As a convenient method, interfacial epitaxial

crystallization can be used to orient the chain axes of a crystal parallel to the substrate surface [86]. In 2000, Lotz investigated interfacial attachment and crystalline polymorphism in PLA. He cast PLA films (typically in the 10–50 nm range) onto glass covers by evaporating dilute solutions in xylene or dichloromethane. A small amount of hexamethylbenzene (HMB) was deposited on the slide, which was covered by the PLA film. It was shown that two crystallizations of PLA could be produced on a single substrate by interfacial attachment [87].

In 2005, Yan Shouke's team studied the epitaxial crystallization of polybutylene adipate (PBA) on highly oriented PE films. The highly oriented PE films were obtained by the melt stretching technique. The results showed that PE has a strong nucleation ability for PBA, and the interfacial attachment of PBA occurring on PE substrates can form PBA crystals under any crystallization conditions (as shown in Figure 8). This is related to the perfect lattice match between PBA and PE crystals [88]. Further, they investigated the crystallization of the interfacial attachment of isotactic poly(methyl methacrylate) (iPMMA) on highly oriented PE. He investigated the annealing behavior of amorphous iPMMA films on highly oriented high-density PE substrates using transmission infrared spectroscopy and electron diffraction. Uniaxially oriented HDPE films were prepared by the melt stretching technique. The accelerated crystallization behavior seen in the study indicates a special interaction between PE and iPMMA, which facilitates the nucleation and crystallization of iPMMA [89].

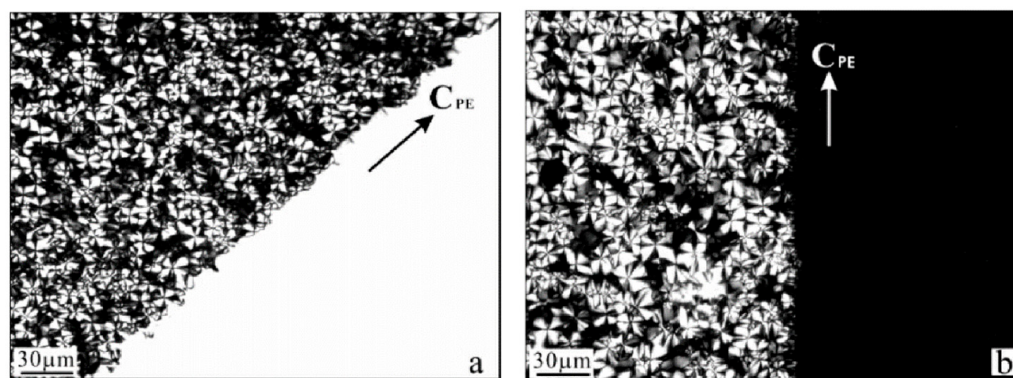


Figure 8. (a) A POM micrograph showing a boundary region of PBA crystallized from solution on a glass slide, which was partially covered with a highly oriented PE substrate. The PE substrate is located in the lower right corner of the picture. The arrow indicates its molecular chain direction. (b) A POM micrograph taken from the same area as in (a) but rotated 45° anticlockwise about the light beam [88]. Copyright © 2006, American Chemical Society.

In 2011, Yan Shouke's team investigated the epitaxial crystallization of poly(3-hexylthio phene) (P3HT) on highly oriented PE films. The results clearly showed that P3HT crystallized on the PE substrate by heterogeneous epitaxial crystallization, resulting in a parallel alignment of P3HT on the PE substrate. Infrared spectroscopy and electron diffraction analyses showed that the molecular chains of P3HT were oriented in the membrane plane and parallel to the chain direction of the PE substrate crystals, while the (100) lattice plane of P3HT was in contact with the PE substrate. The observed interfacial attachment can be explained by the existence of a lattice match between the (110) lattice plane PE inter-chain distances and the (100) lattice plane P3HT interchain distances (shown in Figure 9). This method of interfacial attachment provides an effective method for the preparation of large-area P3HT films with unique orientation structures [77].

Epitaxial crystallization is increasingly vital for the formation of polymer crystals. Researchers vary in their approaches to epitaxial attachment, particularly in their selection of interfaces and the methodology employed to determine lattice matching parameters. The innovative two-dimensional crystallization mode, manifested in the acquisition of crystals

through epitaxial attachment, offers a pioneering perspective that brings fresh insights to the exploration of novel crystallization methods.

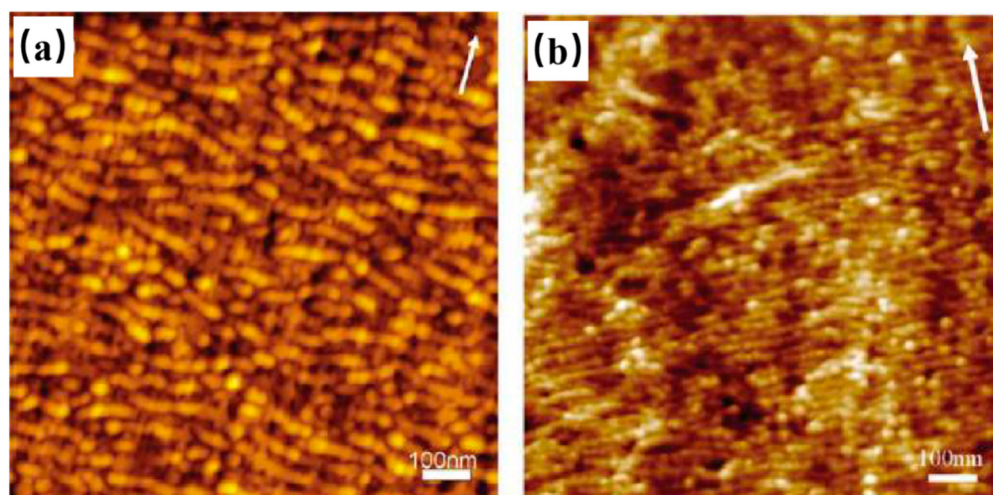


Figure 9. AFM height images of (a) an oriented PE film and (b) the morphology of P3HT grown on a PE substrate. The white arrows indicate the drawing directions of the PE films during preparation [77]. Copyright © 2011, American Chemical Society.

3.3. Controlled Evaporation

In the field of polymer physics, polymer single-crystal materials have been shown to have greatly different material properties compared to polymers in the amorphous state due to the planarization of the main chain and the close stacking of the molecular chains during the crystallization process [90–94]. Controlled evaporation of the solvent is one of the main research methods used in the study of polymer single crystals. A series of experiments were conducted by controlling the rate of solvent evaporation from thin films of dilute solutions using a device such as the one shown in Figure 10. By controlling the rate of evaporation of the solvent from the solution, dendritic crystals were able to form [95,96].

In 1964, Somorjai introduced controlled volatilization in the study of inorganic crystals, noting that prolonged exposure of vaporized crystals to external Cd or S fluxes led to a permanent reduction in the vacuum evaporation rate. The experiments demonstrated that the increased surface concentration of Cd or S diffused into the crystal body, resulting in a slower recovery of the evaporation rate [96]. In 2009, Lin utilized P3HT as a solute in a toluene solution, confined within a sphere-on-flat geometry, to create an axisymmetric capillary microfluidic structure. The controlled “stick-slip” motion of the solution contact lines, regulated by solvent evaporation, led to the formation of highly regular hierarchical structures [97]. In 2018, Yuren Li’s group prepared PLLA-b-PEG block copolymer crystals with controlled temperature quenching (e.g., Figure 11) in their work investigating the use of ultrathin-shelled block copolymer crystals for prolonged blood circulation time [98].

Controlled evaporation facilitates a gradual increase in solution concentration, promoting the formation of well-organized polymer single crystals. However, there is still a lack of simple and effective methods for real-time tracking of the crystal state within the solution, and it is believed that there will be further development in the near future.

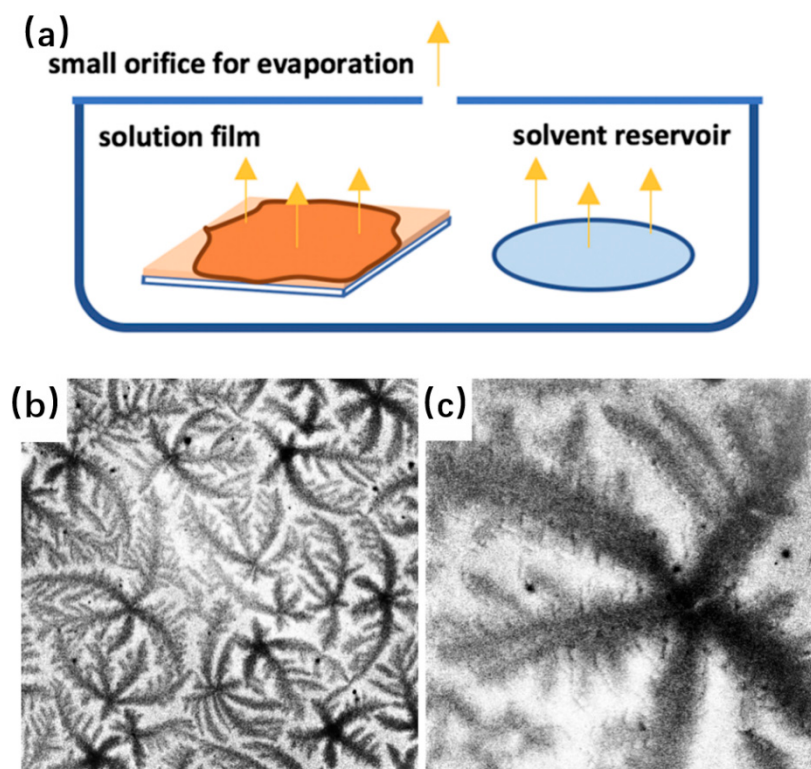


Figure 10. (a) Schematic of the experimental setup. The small orifice (varying diameter) on the cover allows for slow evaporation of the solvent from the dilute solution film. Optical micrographs (contrast enhanced) of the iPpMS film obtained by slow evaporation of toluene ($1.8 \mu\text{L}/\text{min}$) at room temperature. The size of the images: (b) $400 \mu\text{m} \times 400 \mu\text{m}$ and (c) $80 \mu\text{m} \times 80 \mu\text{m}$ [95]. Copyright © 2019, American Chemical Society.

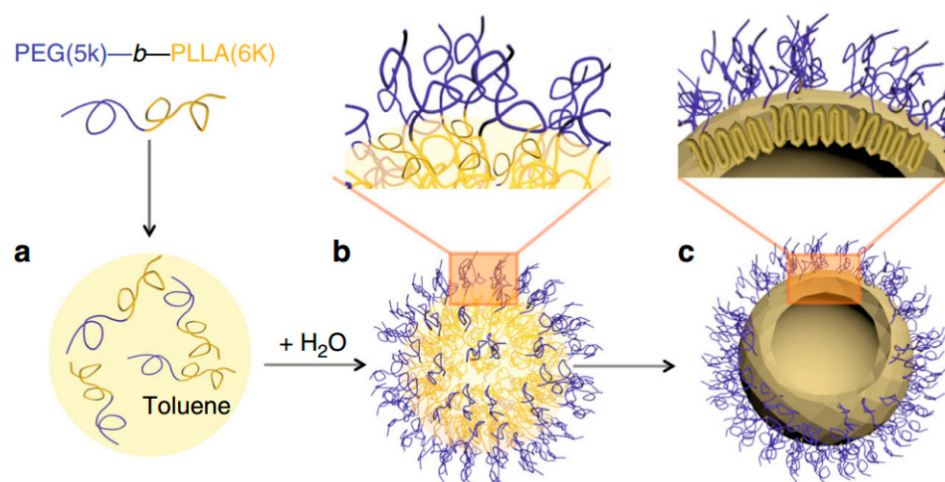


Figure 11. Fabrication of PLLA-*b*-PEG block copolymer crystalsomes. (a) Dissolution of the BCP in toluene; (b) emulsification at 95°C ; (c) quenching to 25°C for crystallization. The driving force of this assembly process is confined PLLA crystallization at the toluene/water interface, leading to a ninefold PLLA chain conformation as shown in c. This confined crystallization process also leads to a 2.5 nm thick PLLA crystal layer, covered with a precisely controlled, uniform PEG brush layer [98]. Copyright © 2018, The Author(s).

3.4. Vapor Diffusion

Although there is no difference between crystalline and amorphous polymers in terms of their chemical structures, their physical properties are extremely different [56].

In polymer crystallization, the solution method and the melt method have been widely used, but both methods have some drawbacks in different areas. For example, for the solution method, there are usually unwanted polymer films outside the crystals after solvent evaporation, while in the melt method, the crystalline polymers may thermally degrade or decompose after annealing at high temperatures [99]. Therefore, the vapor diffusion method would be an alternative strategy [100].

Vapor diffusion is a widely used technique in protein crystallization; it allows for the slow equilibration of the protein and precipitant concentrations, promoting the formation of well-ordered crystals. In this method, a concentrated protein solution is mixed with a precipitant solution, creating a vapor diffusion environment. As the two solutions mix, water evaporates from the drop, leading to a gradual increase in the concentration of both the protein and precipitant (Figure 12) [101].

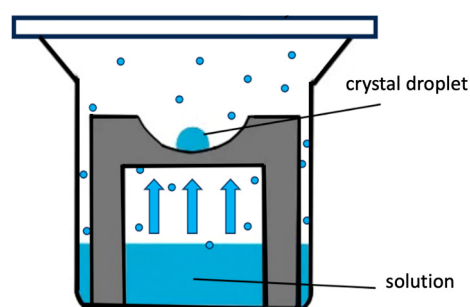


Figure 12. Schematic diagram of protein crystallization using the static drop vapor diffusion method. The solution to be crystallized is placed on a raised platform set in a vessel, and the undesirable solvent is diffused by vapor, eventually causing the polymer to form crystals.

In 1995, Mansky et al. in their study to create large-area films of diblock copolymers suggested that annealing would result in films with a cylindrical structure perpendicular to the surface. Within individual grains, the annealing retained the perpendicular cylindrical orientation extremely well, while improving the transverse order [102]. Yang, in 2007, investigated the “solvent annealing” effect of P3HT and methane–fullerene polymer solar cells [103].

Vapor diffusion was described in detail in a 2012 article by Chen. The morphology of PS and PMMA nanostructures depends on whether the swollen polymer is in a partially or fully wetted state, which is characterized by the diffusion coefficient. When the swollen polymer is in a partially wetted state, the polymer wets the nanopores by capillary action, resulting in the formation of polymer nanorods; when the swollen polymer is in a fully wetted state, the polymer forms a wetting layer in the nanopores, resulting in the formation of polymer nanotubes. The solubility parameters of the polymer and solvent were also used to predict the wetting behavior of the swollen polymer in a cylindrical geometry [99]. Based on the article published by Mansky, a more in-depth study was summarized by Sinturel in 2013. They identified the key challenges to be overcome in the future development of solvent vapor annealing as a practical and reliable technique for the crystallization of polymers [100].

Zou and Welch continued their research on the application of the vapor diffusion approach to organic materials in 2018. They demonstrated how the performance requirements could be met by a post-deposition solvent vapor annealing treatment, further confirming the value of vapor diffusion for applications in organic materials [104]. In 2022, Reiter successfully obtained large-sized single crystals of P3HT by diffusing poor solvent vapor onto a dilute solution. The degree of supersaturation of P3HT can be effectively controlled, leading to a low density of nuclei and slow growth rate [105].

3.5. Meniscus-Guided Coating

Liquid-surface drag, also known as meniscus-guided coating (MGC) [106–108], including dip coating [109–113], solution shearing blade coating, and region casting [114–118], is an important experimental method in polymer research. In this method, the substrate is typically partially immersed in the polymer solution, and as the solvent evaporates, the concentration of the polymer increases near the meniscus. This localized increase in polymer concentration promotes crystallization, leading to the formation of ordered structures.

In 2013, Yanchun Han's team found that oriented nanofibers in stripes could be obtained by oriented diffusion of P3HT flakes and the formation of one-dimensional crystals on the three-phase contact line of a liquid droplet. By controlling the crystallization liquid surface to reduce the tilt angle by means of liquid-surface dragging, it is possible to prepare stripe structures with orientation, and the distance between adjacent stripes can be controlled to between 40 and 100 μm [119].

In a 2014 article on organic semiconductor (OSC) thin films, Mannsfeld introduced MGC as a method using the linear translation of a substrate or coating tool in solution coating techniques for promoting aligned crystal growth. These techniques involve a solution meniscus forming as an air–liquid interface during solvent evaporation. As solvent removal concentrates the solution, reaching supersaturation, solute precipitation occurs, depositing a thin film [106]. MGC is a promising crystallography technique for regulating the crystallization of OSCs and their thin-film morphology. Because OSC processing is achieved through solution, there is a promising future for OSC materials in low-cost, large-area, and flexible electronic devices [120,121].

The advantages offered by MGC technology were described in an article published by Gu in 2018. Due to the inherent directionality of the coating process, the MGC technique allows for molecular alignment of the deposited OSC layers and is well suited for continuous, steady-state printing [107]. MGC technology relies on external shear forces, such as gravity in immersion coatings or mechanical motion in slot-mold coatings, to direct and control the molecular alignment in OSC films. The strength of these forces is determined by the coating speed, and therefore the coating speed has a strong influence on the morphology of the deposited salt–carbon compound films [53]. Based on the morphology of the salt-content films obtained at different coating speeds, three zones can be delineated, and the salt content of the films generated in the corresponding zones can be demonstrated experimentally [116].

In 2020, Pisula proposed the critical role of the meniscus shape for organic semiconductors that crystallize under the guidance of liquid drag. It was demonstrated that angle-dependent dip coating (ADDC) can precisely control the meniscus shape, yielding aligned crystalline thin films with a high surface coverage. This work elucidated how the interplay between film formation rate and evaporation rate influences the anisotropy and regularity of the crystalline domain size and shape [121].

In conclusion, meniscus-guided coating offers precise control over crucial material properties, including domain size, crystallinity, and film morphology. Through the manipulation of solution drag and factors like its speed, this method allows for the production of polymer crystalline films with enhanced properties, making them more suitable for practical applications.

3.6. Topological Polymerization

Topological polymerization represents a solid-phase reaction orchestrated by the arrangement of single crystals. Through the confinement of monomer molecules within the crystal lattice, this method grants precise control over the elasticity, filling, and crystallinity of the resulting polymer. By leveraging the structural template provided by the crystal lattice, researchers can engineer polymers with custom-tailored properties, ensuring that the desired structure and characteristics are achieved. Ordered packing confers attractive properties to topochemically synthesized polymers. Topochemical polymerization methods are diverse, ranging from polymerization via $[2 + 2]$, $[4 + 4]$, $[4 + 2]$, and $[3 + 2]$

cycloadditions, to the existence of polymerizations of diynes, triynes, dienes, trienes, and quinodimethanes, each of which requires control of the appropriate conditions for them to take place, such as heat, light, or pressure. Each class of reaction requires a unique packing arrangement of the corresponding monomer for the reaction to proceed smoothly and form the polymer [122].

In 2021, Li's group constructed polymer single crystals using a topological polymerization approach. They synthesized sub-millimeter-sized two-dimensional scale polymer single crystals (T-2DP) by the photochemical [2 + 2] cycloaddition method through single-crystal-to-single-crystal transformation, and achieved a successful transformation from monomer to polymer in the single-crystal state [123]. In 2022, Mircea Dincă et al. relied on topological polymerization methods to prepare the first 3D polymers with a permanent porosity by using C-C bonds to MTBA (methane tetraalkyl tetrakis(benzene-4,1-diyl)tetrakis(anthracene-9-carboxylate)). This suggests that topochemical polymerization is an effective method for generating stable, crystalline, and porous 3D organic frameworks [124]. In the same year, Kuntrapakam Hema's group tuned the regioselectivity of topological chemical polymerization by co-crystallizing with an inert aliquot. The regioselective chemistry of topological chemical reactions relies on the filling and biasing of crystals. This technique demonstrated the power of crystal engineering for regioselective chemistry [125].

In 2023, J. Fraser Stoddart proposed UV-induced topochemical polymerization using precisely designed monomers to generate a large number of [2 + 2] cycloaddition reactions in a photo-induced manner, resulting in polymeric single crystals with high crystallinity and excellent solubility. This study demonstrated the ability of researchers to synthesize soluble polymeric single crystals in a controlled manner and fully characterize them [126].

The method of topological polymerization has a high yield, high selectivity, and specificity, which can obtain specializing functional materials.

4. Polymer Single-Crystal Functionalization Applications

4.1. Single-Crystal Template Modification

The typical structures of polymer crystals include spherulites [127–130], dendritic crystals [131–133], extended-chain crystals [134–137], fibrous crystals [138–140], and lamellar crystals [141–144]. Among them, polymer single crystals are lamellar crystals with regular geometrical shapes, usually formed by folding molecular chains back and forth [145]. For now, there are limited studies using single crystals as a functional template [146].

The advantage of polymer single crystals is that when the end-functionalized polymers form monolithic folded-sheet single crystals, the chain ends are excluded from the crystal surface and can be coupled to various nanoparticles (NPs) to form nanosandwich structures. After the coupling reaction and dissolution of the polymer single crystals, free Janus nanoparticles (with a non-centrosymmetric structure and single nuclei surrounded by a separated coronal structure) can be obtained, providing a unique approach to the preparation of asymmetric nanoparticles [147]. When polymer single crystals are used as substrates, the method is referred to as the “polymer single crystal templating” (PSCryT) method [147–163]. PSCryT uses surface chemical coupling similar to that of self-assembled monolayers (SAMs), and the advantage of using polymer single crystals for nanoparticle assembly is that the SAMs are usually confined to solid substrates [164–167], whereas PSC is solution-independent. Yuren Li's group proposed the PSCryT method and has been working on this unique application of polymer single crystal for years.

In 2006, Yuren Li's group first reported the application of polymer layered single crystals as a solid substrate to create a graphically functional (thiol) surface and immobilize gold nanoparticles (AuNPs) [148]. Two years later, they applied a self-seeding method to prepare terminated thiol-poly(ethylene oxide) (HS-PEO) single crystals, which also enabled the asymmetric functionalization of AuNPs. As shown in Figure 13, AuNPs were immobilized using HS-PEO as a substrate, a method called “solid-state grafting” [149]. In the same year, it was reported that AuNPs were immobilized using HS-PEO as a substrate

by combining the “solid-state grafting” and “grafting” methods. In the same year, it was reported that Janus AuNPs were functionalized with two different types of polymer chains on the other side of the AuNPs using HS-PEO as a substrate by combining the “solid-state grafting” and “grafting” methods [147]. The application of polymer single crystals as a substrate is advantageous because they have higher fluxes than self-assembled monomolecular membranes. The dissolution of the single crystals also leads to NPs with well-defined polymer patches (functional groups). This method will be able to serve as a general method for the synthesis of polymer-functionalized Janus NPs and is expected to lead to the controlled assembly of NPs and tunable optical and electronic properties.

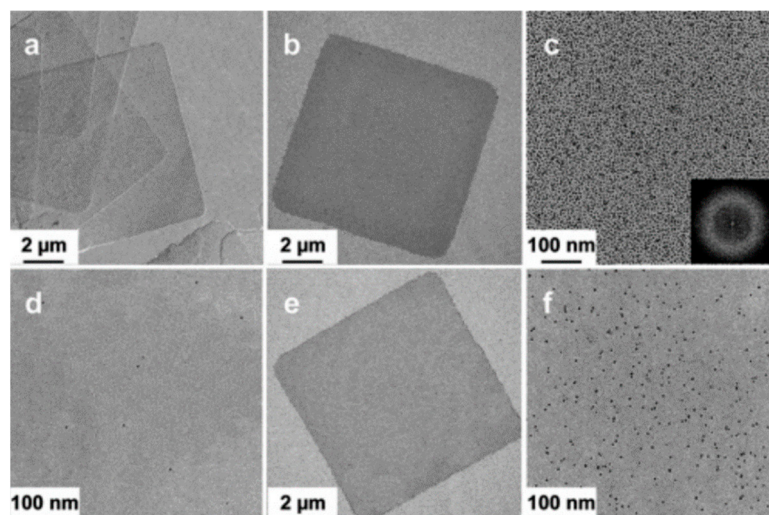


Figure 13. TEM micrographs of (a) HS-PEO(2K) single crystals and (b,c) 5 nm AuNP-covered HS-PEO(2K) single crystals. The inset shows the FFT pattern. (d) HO-PEO(2K) single crystals after incubation with 5 nm AuNPs. (e,f) AuNP-covered HS-PEO(48.5K) single crystals [149]. Copyright © 2008, American Chemical Society.

A new method for the large-scale production of NP sheets with programmable patterns was investigated by Yuren Li’s group in 2009. In the preparation of HS-PEO single crystals, nanoparticles were assembled in situ during the polymer crystallization process (as illustrated in Figure 14). This approach enables precise control over the three main features of the nanoparticle pattern on the single crystals: the NP spacing, the width and length of frames/chains, and the distance between frames/chains [150].

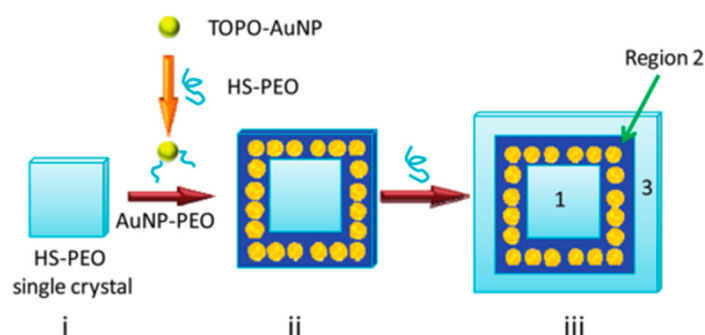


Figure 14. (i) A HS-PEO lamellar single crystal, which has already formed prior to the addition of gold colloid. The PEO chains are parallel to the lamellar normal and the thiol groups are on the crystal surface. As gold colloid is added to the HS-PEO solution, AuNP-PEO conjugates are formed via the place exchange reaction. The AuNP-PEO conjugates crystallize around the already formed single crystals, generating AuNP frames (ii) After these conjugates are exhausted, PEO continues to crystallize around the AuNP frames, forming a blank margin (iii) The numbers 1, 2, and 3 in part iii denote the three distinct regions of the pattern [150]. Copyright © 2009, American Chemical Society.

In 2010, Yuren Li's group and others demonstrated that polymer single crystals can be used as a versatile substrate for immobilizing NPs. By using PEO and PE-b-PEO as a single-crystal substrate, gold, magnetic, and semiconducting nanoparticles were immobilized on the surface of the polymer single crystal. The subsequent single-crystal dissolution generated different types of Janus nanoparticles and nanoparticle clusters of different polymers [152]. In the same year, Wang et al. faced the challenge of synthesizing Janus nanoparticles (JNPs) with diameters of less than 20 nm by using atom transfer radical polymerization to grow polymer brushes on polymer single crystal-immobilized gold nanoparticles (AuNPs) with diameters of 6 and 15 nm. By combining both the "grafting-to" and "grafting-from" approaches of polymer-functionalized Janus AuNPs, PEO-SH single crystals with HS groups on the surface were synthesized and then AuNPs were immobilized on top of them. The polymer brushes were grown on the AuNPs by applying an initiator on the top surface of the immobilized AuNPs [151].

In 2011, Yuren Li's group utilized the polymer single-crystal template approach to provide a new method for the synthesis of functional Janus nanoparticles. Polymer single crystals of bifunctional polymers were used as templates to which NPs were attached via covalent bonding with the thiol groups exposed on the surface of the single crystals. Covalent bonding was used to attach to this template, while asymmetric modifications and end-group functionalization were introduced to the NP surface [161]. The group introduced a facile method to synthesize amphiphilic Janus silica nanoparticles (SiNPs) with a two-compartment polymer in 2012 [154]. Single crystals of poly(ϵ -caprolactone) with alkoxy silane terminations (PCL-SiOR) were prepared using a self-seeding method, and silica nanoparticles were immobilized on the surface of the single crystals. The Janus particles of this method showed lower thermal transition temperatures and much narrower transition ranges [154].

In order to develop a low-cost and high-yield template for the synthesis of heterogeneous nanoparticles, Zhang Hui et al. from Yuren Li's group reported a new polymer single-crystal substrate method for directional self-assembly of heterogeneous nanoparticles. Polymer single crystals consisting of hydroxyl-terminated polycaprolactone (PCL-OH) with hydroxyl groups on the surface were formed using the self-seeding method. This approach is generally applicable to different nanoparticle systems as long as there are specific interactions between the first adsorbed nanoparticle and the single crystal as well as between the first and second adsorbed nanoparticles [153].

In the following two years, Yuren Li's group used the polymer single crystal substrate approach for the self-assembly of nano-motors [155,156]. This approach opens up great opportunities for miniaturization and mass production of future nano-motors as well as for other applications including sensors and directed transport. In 2014, Yuren Li's group provided a method to synthesize "dumbbell" nanoparticle dimers through one-step coupling of nanoparticles and quasi-two-dimensional polymer single crystals [157]. In subsequent work, the group reported a shape-controlled freestanding sheet composed of nanoparticles generated using the PSCryT method. Using the self-assembly technique, nanoparticle assemblies were obtained with nanoparticles and polymer single crystals as the basic building blocks [158].

In 2016, Tian Zhou et al. from Yuren Li's group combined the advantages of the traditional "grafting-to" and "grafting-from" methods of synthesizing polymer brushes to achieve the synthesis of polymer brushes with controlled structures and high grafting densities on planar surfaces [162]. For a given molar mass, the chain-folded structure can be precisely controlled by varying the crystallization temperature, which can ultimately be used to tune the grafting density of subsequent polymer brushes [162]. In 2017, Shan Mei et al. from Yuren Li's group used single-crystal templates to provide a directed assembly method to precisely assemble NPs into well-defined, independent frameworks [159]. The PEO single crystals were used as a template to direct the crystallization of the block copolymer (BCP) poly(ethylene oxide)-b-poly(4-vinylpyridine), which directs the AuNPs to

form AuNP frameworks. The reported method may become a new approach to synthesize precisely assembled, free-standing cyclic NP chains and nanocycles.

In the following year, Yuren Li's group proposed a bottom-up method called "polymer single crystal assisted grafting method (PSCAGT)" to synthesize gradient polymer brushes with pre-designed and precisely controlled grafting density gradients and patterns, as shown in Figure 15 [160]. By varying the incorporation rate of PEO₁₁₄-OH, polymer brushes were successfully synthesized with pyramidal and smooth gradient structures with pyramidal micropatterns [160]. In 2020, Yuren Li's group reported a new method for synthesizing diblock copolymer brushes. The resulting diblock copolymer brushes showed a relatively high grafting density and also retained the original single-crystal morphology with high fidelity, providing a unique method for patterning polymer brushes [163].

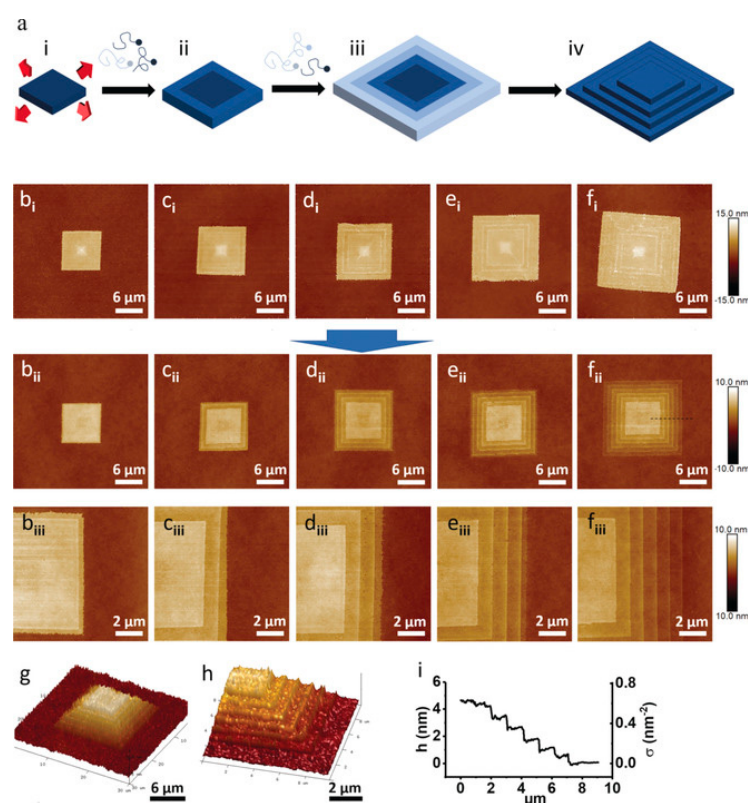


Figure 15. Terraced gradient PEO polymer brush. (a) Synthesis procedure. (**b_i–f_i**) PEO single crystal with 1–5 concentric bands; (**b_{ii}–f_{ii}**) PEO brushes with 1–5 concentric bands. (**b_{iii}–f_{iii}**) are enlarged images of (**b_{ii}–f_{ii}**). (**g,h**) Three-dimensional images of the terraced gradient PEO brush with five bands. (**i**) Height profile and the corresponding σ , measured from dash line area in **f_{ii}** [160]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

The initial application of the polymer single-crystal template approach involved immobilizing nanoparticles to achieve patterning and asymmetric functionalization. Subsequently, the approach demonstrated capabilities in growing polymer brushes, modifying Janus NPs, and synthesizing small-sized Janus NPs on a substrate surface. Over time, it evolved into a cost-effective, high-yield template for heterogeneous nanoparticle synthesis and directed assembly of nanoparticles, facilitating diverse functionalities.

4.2. Photoresponsive Polymer Single Crystals

In 2000, Heeger [168–170], MacDiarmid [171–173], and Shirakawa [174–176] were awarded the Nobel Prize in Chemistry for the discovery and development of conductive polymers. It is common knowledge that plastics do not conduct electricity, so they can be used as insulating materials for wire cladding, socket switches, and so on. However,

the discovery of electrically conductive polymers in the mid-1970s changed the long-held notion that polymers could only be insulators and led to the development of polymer materials with photo- and electro-activity.

In the past decades, conjugated polymers have been widely studied due to their excellent optoelectronic properties [177–181]. Compared with inorganic semiconductors, conjugated polymers have the advantages of being lightweight, corrosion resistant, environmentally stable, and cost effective [182–186]. Conductive polymers have become an alternative material for photovoltaic devices, e.g., conductive polymers have been successfully used in solar cells [187–193], light emitting diodes [194,195], chemical sensors [196], thin-film transistors [197–200], and field-effect transistors [201–203]. Compared with amorphous polymers, crystalline polymers with planarized main chains and close stacking of neighboring chains can greatly enhance the photovoltaic performance [204]. Single crystals normally show a better photovoltaic performance because of the perfect ordering of their molecular chains, the absence of grain boundaries, and good interfacial contacts [205–214].

In order to optimize the electrical properties, Kim et al. developed P3HT structures with strong π - π interactions in the same direction [207]. A solvent-assisted crystallization method was developed by Ma et al. for the growth of high-quality regionally regular poly(3-butylthiophene) (rr-P3BT) single crystals. As shown in Figure 16, needle-like rr-P3BT layered single crystals up to millimeters in length were successfully cultured using the solvent-free crystallization method. In the single crystals, the molecules were aligned perpendicular to the lamellae in an extended chain conformation [208].

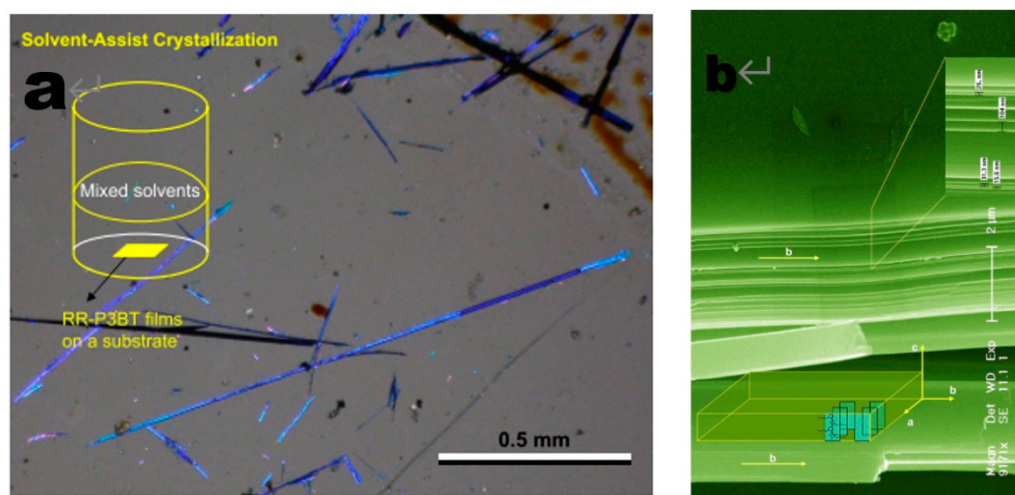


Figure 16. (a) Scanning electron micrograph of a typical P3BT single crystal from solvent-assist crystallization. (b) The lamellar thickness varying between 15.6 nm and 104 nm can be identified from enlarged inset picture in upper right corner. Schematic diagrams of molecular packing in the lamellar crystals, molecular chain direction, and growth direction are also included in the inset [208]. Copyright © 2006 Elsevier Ltd. All rights reserved.

Jeon proposed a method to control the morphology and size of conducting polymer nanostructures for their ordered growth. Using organic single crystals of monopotassium salt of 4-sulfobenzoic acid (KSBA) as a soluble template, KSBA precipitated as individual micro-sized crystals in an aqueous medium with a hexagonal plate-like shape. It was shown that the organic crystal surface-induced polymerization of the conductive polymer was able to replicate the shape of the organic monocrystal when the organic monocrystal was present in the polymerization medium. This method can be widely used in the fabrication of sensors, templates, catalyst carriers, and carbon material substitutes [206].

Xiao proposed another method to prepare poly(3-octylthiophene) (P3OT) needle-like single crystals by tetrahydrofuran steam annealing. This work demonstrated that the crystallization conditions can modulate the molecular orientation and help to further in-

investigate the structure–property relationship of conducting polymers [212]. Xiao prepared P3HT and P3OT by tetrahydrofuran steam annealing and controlling the solvent evaporation, respectively (e.g., Figure 17). When the films were annealed for 42 h, the P3HT single crystals were predominantly needle-like crystals with lengths of 20–60 μm and diameters of 1–2.2 μm [213]. The mobility of the P3HT single crystals was $1.57 \times 10^{-3} \text{ cm}^2/\text{Vs}$ in the field effect transistor, where the current was parallel to the length axis of the single crystals. The mobility of P3OT single crystals was $0.62 \text{ cm}^2/\text{Vs}$. The shorter length of the alkyl side chains of P3HT compared to P3OT results in a higher mobility. This suggests that the alkyl side chains act as a barrier to carrier migration between poly(3-alkylthiophene) (P3AT)-like polymers [213].

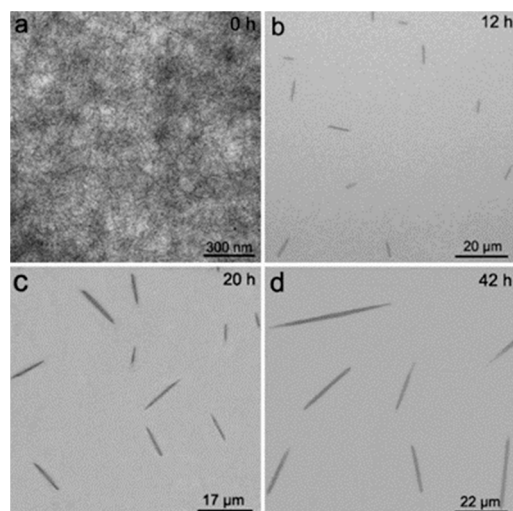


Figure 17. Time-dependent morphology of the P3HT crystals with different annealing times of 0 (a), 12 (b), 20 (c), and 42 h (d) [213]. Copyright © 2010, American Chemical Society.

Rahimi et al. used tetrahydrofuran as a solvent to prepare P3HT solutions at concentrations ranging from 0.1 mg/mL to 10 mg/mL, which were heated to 82 $^{\circ}\text{C}$ to completely dissolve the polymer. These solutions were then filtered using 0.45 μm PTFE filters and the temperature of the solutions was controlled with an accuracy of 0.1 $^{\circ}\text{C}$ using a silicone oil bath thermostat. To obtain films from solutions containing single crystals, they had the substrates preheated to T_c , spin-cast 200 μL of the solutions onto wafers, and then dried them in a vacuum oven for 1 h at room temperature, ultimately yielding P3HT macromonomers [214].

Nuraje prepared single crystals of poly(aniline) (PANI) by using the interfacial polymerization method. The resulting crystalline polymers showed conductivity switching times on the order of milliseconds between the insulating and conducting states [209]. Su prepared for the first time single-crystal poly(3,4-ethylenedioxythiophene) (PEDOT) nano-needles that exhibited fast conductance switching using interfacial polymerization. By investigating the electronic conduction behavior of the single crystals, they found field-induced conductance switching within a response time of milliseconds [211].

Zenoozi used P3HT homopolymers and block copolymers to prepare single crystals and nanofibers in a range of solvents such as toluene, xylene, and anisole. It was found that when single crystals and nanofibers are developed from good solvents, the crystal structure becomes more ordered, yielding higher current densities [204]. Cho et al. developed single-crystal PEDOT nanowires with ultra-high electrical conductivity using liquid-bridge-mediated nanotransfer printing and gas-phase polymerization. The PEDOT nanowires had a tightly packed single-crystal structure with orthorhombic lattice units. Its electrical conductivity averaged 7619 S/cm and reached up to 8797 S/cm [205].

Wu et al. proposed a self-seeding method carried out in situ in solution to obtain highly ordered single crystals of P3HT. Precise control of the degree of supersaturation in

space and time was achieved by forming a concentration gradient of poor solvents by vapor diffusion in the solution system. Eventually, the long needle-like crystals were formed after drastically reducing the nucleation density while maintaining a limited growth rate. The spectroscopic results showed (as shown in Figure 18) that the obtained single crystals are capable of absorbing long wavelength light, which is promising for applications in the energy field [55].

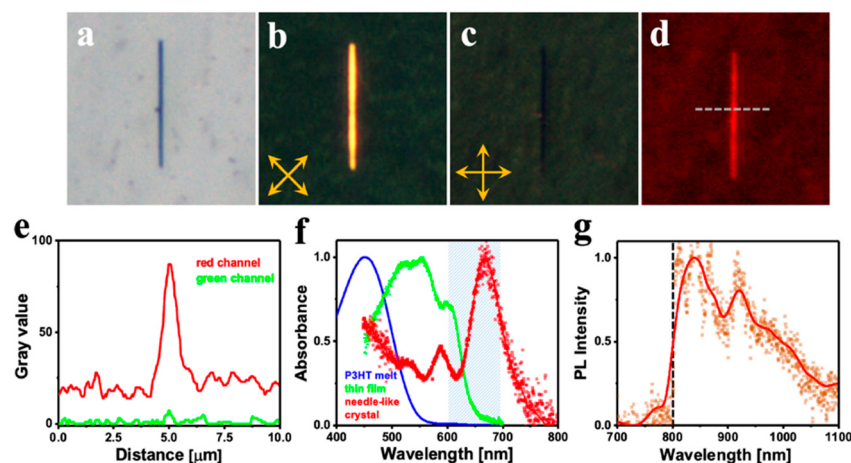


Figure 18. Optical micrographs of a P3HT crystal ($t_{\text{heating}} = 10$ min, $t_{\text{growth}} = 4$ h). Image sizes are $25\ \mu\text{m} \times 25\ \mu\text{m}$. (a) Bright field. (b) Under crossed polarizers, the long axis of the crystal is at an angle of 45° to both the polarizer and the analyzer. (c) Under crossed polarizers, the long axis of the crystal is at an angle of 0° to the polarizer. (d) Photoluminescence image showing a red emission color (HBO lamp, excitation at 450–500 nm, emission > 500 nm, recorded by a CCD color camera). (e) Intensity profiles of the R and G channels for the cross section indicated by the dashed line in (d). (f) Normalized absorption spectra of P3HT melt at 280°C (blue), drop-casted thin film at room temperature (green), and a needle-like crystal (red) similar to the one shown in (a–d). (g) Photoluminescence spectrum of a needle-like crystal (excitation at 600–700 nm, marked as the shaded area in (f)) collected after a long pass filter (marked as a dashed line in (g)) [55]. Copyright © 2020, American Chemical Society.

5. Conclusions and Outlook

In this paper, we reviewed the history and progress of polymer single-crystal research, and discuss in detail the crystallization strategies and functionalization applications of polymer single crystals. The formation of polymer single crystals requires precise control of the crystallization driving force, thus ensuring a smaller number of nuclei with a slow growth rate. By adopting different single-crystal crystallization strategies, the ordered arrangement of polymer chains can be achieved, thus improving their various properties. More importantly, the formation process of polymer single crystals reveals the universal law of microscopic motion of soft matter, which greatly enriches the connotation of polymer physics and deepens our understanding of material motion at the molecular level. We believe that polymer single crystals have rich theoretical significance and broad application prospects, and will flourish in the historical stage of “the second hundred years of polymer science”.

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