The rise of semicrystalline polymers and why are they still interesting

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Abstract

Scientific research on semicrystalline polymers started before the concept of macromolecules was proposed by Staudinger. Extensive studies have been devoted by generations of scientists to establishing this profoundly complex and impactful field. In this perspective, the establishment of the polymer crystallization field will be briefly reviewed. Discussions on several interesting new developments that emerged in the past two decades will then be presented, followed by the author's view on future outlooks. In addition to the conventional studies on theory, structure, morphology, and phase transformation of semicrystalline polymers, it is believed that newly emerged fields such as biomedical engineering, energy and sustainability, additive manufacturing, and nanoscience provide both new challenges and opportunities for future polymer crystallization research.

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Polymer crystallization has been a vibrant research field and it still is

A century ago, Staudinger set the cornerstone of a new research field of Polymer Science and Engineering.[1] The concept of a linear long-chain molecule fundamentally changed our understanding of how matter behaves. The last century witnessed tremendous development of this field.[2] The exciting scientific findings and deep fundamental understanding of the subject led to profound economic impacts on our daily lives. From year 1950 to 2015, the global annual production of resins and fibers increased from 2 million tons (MT) to 380 MT, with a 7800 MT of total production.[3] We have been living in a plastic era for many decades. Throughout the evolution of polymer science, crystallization behavior of polymers has been a central piece of the field. Polymer crystallization-related study started before the concept of macromolecules was born, dating back to early 19th century when Gough examined the elasticity of a thong of Caoutchouc in 1806, and Page on natural rubber in 1847, although obviously, they were not aware that stretch-induced polymer crystallization accounted for the observed elasticity change.[4] During the early days of polymer research, it was Mark's X-ray crystallography work that confirmed Staudinger's long-chain macromolecule hypothesis, and the "two Hermans" are often considered as the founding fathers of polymer science.[5, 6]

While the basic symmetries of polymer crystals are of no difference from their small molecular counterparts, polymer's long-chain nature does bring arguably the most interesting feature to its crystallization behavior: the intricate amorphous domains in a crystalline material. The degree of crystallinity, together with the hierarchical morphology of the intertwining crystalline and amorphous domains, accounts for some most fabulous properties of semicrystalline polymers.[7] For example, the moduli of typical crystalline and amorphous phases of polymers such as polyethylene (PE) are three orders of magnitude different at ambient temperature as the crystal melting temperature is much higher than the glass transition temperature of the polymer. The dramatic modulus contrast, the fineness of crystalline and amorphous domains, the tight connection among them through tie chains, and the crystallographic slipping-associated plastic deformation of polymer crystals collectively account for the superb toughness of semicrystalline polymers, which is one of the major reasons for their broad applications as commodity materials.[7, 8] When oriented, ultra-high modulus polymer fibers can be obtained which have been widely used.[9] On the other hand, crystalline and amorphous domains show dramatic differences in gas/ion permeability.[10] The tortuous pathway imposed by the crystalline morphology provides an interesting opportunity for designing polymer membranes for controlled gas, ion, or electron conduction.[10-12] While all these aspects are interesting, the field of polymer crystallization has enjoyed nearly a century of thorough investigation and questions recently have been raised concerning if we have already explored the most exciting problems? Is polymer crystallization still an interesting field of study that is worth pursuing? Following is a simple publication chart obtained from Web of Science indicating the publication trend since 1991 using the keyword “polymer crystallization” or “semicrystalline polymers” (**Figure 1**). The number of publications steadily increases during the past few decades, and last year saw the highest annual publication of over 2,000. Note that many research works using semicrystalline polymers are not included in this data since the foci of the studies were not on crystallization.

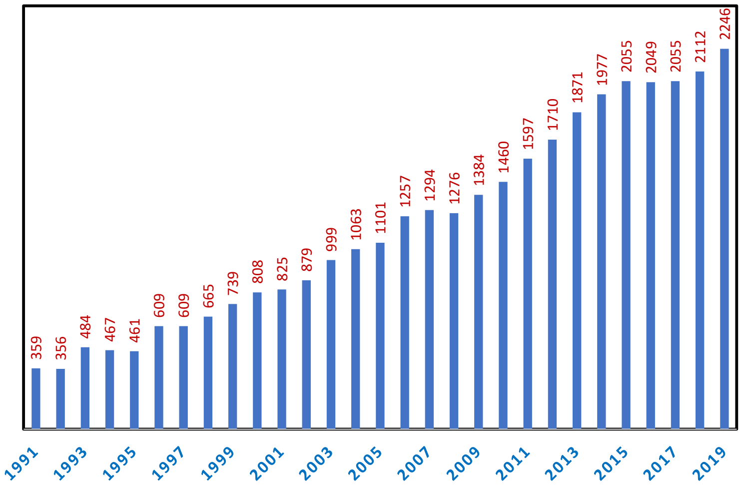

Figure 1. Number of publications in the field of polymer crystallization from 1991 to 2019. Data from Web of Science using the keywords “semicrystalline polymers” or “polymer crystallization”.

It is therefore safe to say that the field still attracts tremendous attention in our scientific community. These publications are also related to multiple research fields, ranging from classic polymer science, physics, chemistry, materials science, to biology, electrochemistry, food science, biophysics, and environmental sciences. Polymeric materials play an increasingly more important role in the newly developed fields such as additive manufacturing, energy, and sustainability, *etc.*. On the occasion of celebrating the 100th year of Polymer Science, the past development and future research directions in the field of polymer crystallization will be discussed in this perspective.

In addition to a few classical texts on polymer crystallization,[13-25] a handful of informative books and reviews have been published recently on different perspectives in the field of polymer crystals and crystallization.[26-40] For example, Cheng and Keller discussed the role of metastability in polymer crystallization and phase transformation.[26, 41] Geil summarized some "overlooked problems" in polymer crystallization.[29] Lotz, Miyoshi, and Cheng discussed their "personal journeys" on the study of the structure, morphology, and phase transformation of semicrystalline polymers.[30] Polymer crystallization theory and recent development were reviewed by Muthukumar, Xu, and Li.[31-33] Reiter *et al.* discussed a few intriguing points in crystal phase evolution.[34] Crist and Schutz summarized the history and development of polymer spherulites.[35] Hu recently reviewed polymer chain folding.[36] A few monographs are available including De Rosa's thorough summary on polymer crystal structure,[37] and collections of recent developments in the field.[28, 42, 43] This perspective will not reiterate what has been comprehensively discussed. Instead, a brief review of the history will be presented, followed by a concise summary of the recent progress during the past two decades or so and the author's view on future outlooks. It is nearly impossible to cover all the outstanding work that appeared in the past decades in this perspective. Only some selected examples will be discussed, and the author apologizes for any unintentional omissions.

The rise of polymer crystallization

The evolution of the field of polymer crystals and crystallization is a massive scientific development, contributed by many pioneers whose work led to a classical hierarchical view of semicrystalline polymers. Polymer chains adopt a helical conformation and pack into a desired unit cell, whose size is much smaller than the polymer chain itself. When applying translational symmetry to the unit cell and form a single crystal, the long-chain typically folds back and forth with a finite thickness of a few tens of nanometers leading to lamellar crystals; growth along the lamellar normal is generally prohibited due to the lack of crystallographic registration of atoms in the fold surface. The formation of thin lamellar crystals is arguably the most important factor that differentiates polymer crystallization theories from their small molecular counterparts. In a bulk system, these lamellae are formed in bundles, growth of which is a dynamic process between crystal growth and the diffusion of amorphous feeding materials, which eventually produces the extensively studied spherulites.[13, 14] The folded lamellae are considered in a metastable state, and the kinetically controlled selection process for a preferred lamellar thickness is a signature of polymer crystallization. The entire formation process of polymer crystals can be viewed as a constant competition/selection among various metastable states.[26, 41]

Decades of study and intensive debates led to the above framework. It was not obvious at the beginning of the study to relate highly entangled chains with regularly faceted, long-range ordered crystals. Furthermore, shortly after X-ray was demonstrated by Laue and Bragg to be able to determine atomic packing in small molecular crystals, this technique was applied to polymers when the materials were available. It was clear that polymers did generate X-ray diffraction peaks and the polymer diffraction peaks are broad, suggesting a correlation length of a few tens of nanometers. This, combined with the large chain size, led to the first intuitive model proposed in 1930, the fringed micelle model, which views that in polymer crystals, the entangled chains in small *local* domains adopt regular packing where nearby chain segments are parallel to each other.[44] The crystalline order is restricted to small regions with only portions of chains being part of the lattice. This view dominated the field for over twenty years during which an extensive body of work was done with the focus on using X-ray diffraction to study the crystalline structures of polymers.[45] Some of influential publications during this period include crystal structure determination of cellulose,[5] natural rubber,[6] PE,[46] and polyamide 6,6 (Nylon 6,6)[47], *etc.*.

The fringed micelle model was seemingly appropriate for polymers with low crystallinity. With newly synthesized linear and stereoregular polymers that offer high crystallinity that routinely exceeds 80%, it became increasingly difficult to justify the model.[21]

Another crystalline texture that was observed using polarized light microscopy (PLM) was polymer spherulites.[48] The familiar spherical symmetry and the banded texture associated with some of the polymer spherulites were similar to small molar mass organic crystals,[49] and were difficult to explain using the fringed micelle model.[21, 50] The landscape of polymer crystallization research took a dramatic turn in the year 1957, where Keller,[51] Till,[52] and Fischer[53] independently reported the growth of PE single crystals from solution (although a transmission electron microscopy, TEM, image of a polymer single crystal was published two years earlier[54]). TEM experiments clearly showed features of "normal" crystals, such as regular facets, can be found in polymer single crystals as well. These crystals also yield sharp single crystal electron diffraction (ED) patterns with clear symmetries and sharp diffraction spots. As Bassett mentioned in his tribute to Keller, while the three research groups might all observed ED patterns from PE crystals, it was Keller who, encouraged by C. Frank, published the inference.[55] In his paper, Keller pointed out that "*The most striking feature is the orientation of the molecules. It is found by selected area electron diffraction that the c axis (the direction of the molecular chains) is perpendicular to the surface of the crystal, the a and b axes being respectively along the long and short diagonals of the lozenge…*" and "*The above findings lead to the inescapable conclusion that the long chain molecules must bend back on themselves forming a folded configuration.*" Keller also pointed out that the folding concept was "*first suggested by Storks as early as 1938*". In his discussion on the unstretched gutta-percha,[56] Storks mentioned that "*Unstretched films of gutta-percha are found to be composed of relatively large crystallites which are precisely oriented with their fiber axis directions normal to the film surface. It is presumed that the macromolecules are folded back and forth upon themselves in such a way that adjacent sections remain parallel.*" [56] **Figures 2a,b** show a representative TEM micrograph of solution grown PE single crystals and the corresponding ED pattern. See **Figure 3** for Storks ED results.

Unfortunately, Storks' paper received little attention at that time as the fringed micelle model dominated the field and perhaps also because TEM was not available to the general research community. After 1957, the new and exciting chain folding concept immediately stimulated world-wide interests and polymer crystallization entered a "golden" era when numerous polymer single crystals were grown during this period, which was summarized in the book by Geil published in 1963,[13] and in a review by Khoury in 1976.[19] The idea of chain folding and how the folding is executed (*e.g.* adjacent reentry vs. switchboard) in polymer crystals were intensively debated in the following two decades, some of the discussions were recorded in the 1979 Faraday discussion.[57] Different technical methods were used to obtain as much information of chain folding as possible, including spectroscopy,[58, 59] gel permeation chromatography (GPC),[60] Neutron scattering,[61] *etc.*. Two types of decoration techniques were developed.[61, 62] In the early study, metal particle decoration was used to directly view fold surface features as well as the fine topographic change on the crystal surface.[61] Polymer physical vapor deposition was developed by Wittmann and Lotz to illustrate folding directions and sectorization of polymer lamellar single crystals (**Figure 2c**).[62] This method unambiguously demonstrated the folding nature of polymer single crystals, with exceptional details. The chain folding idea was also extensively studied in low and high molar mass polymers. The so-called integral and non-integral folding was discovered and extensively investigated in PE and poly(ethylene oxide) (PEO) oligomers.[41, 63, 64]

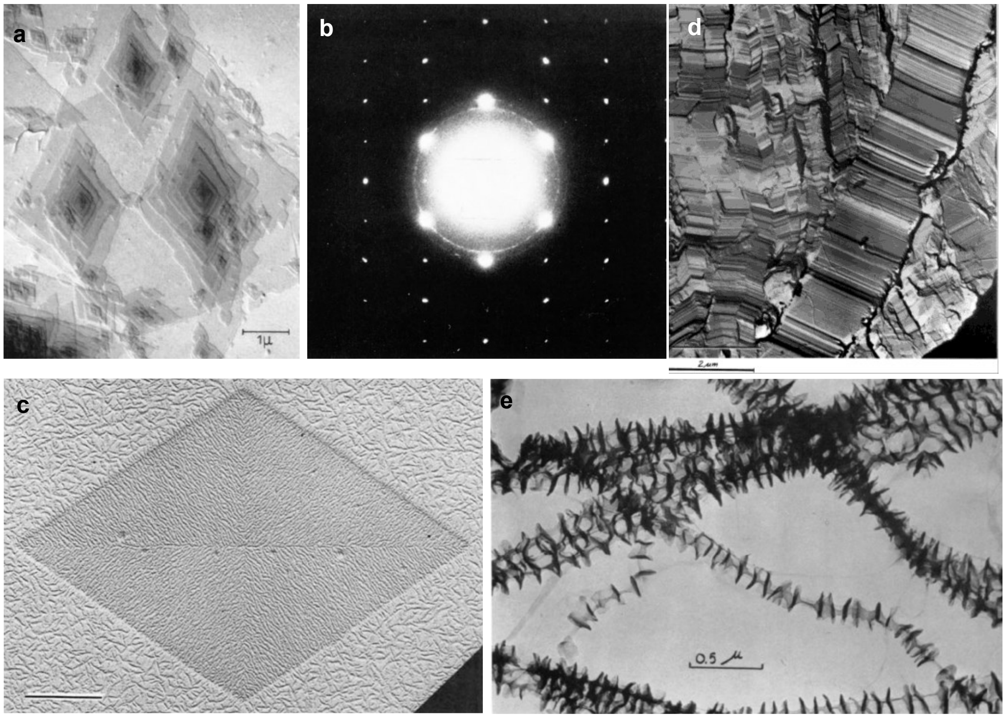

Figure 2. Profound morphology of PE crystals viewed using TEM. (a) TEM micrograph of PE crystals grown from solution and (b) its ED pattern with the corresponding orientation;[21] (c) A decorated PE single crystal. Scale bar: 1 μm [62] (d) Extended chain lamellae of PE, grown

isothermally at 4.8 kb pressure, and 220 °C from the melt for 20 hrs.[65] (e) Shish-kebab PE crystals produced by stirring in a 5% solution of PE in xylene at 102 °C.[66]

While the chain folding concept is clear in today's polymer crystallization community, some aspects of it, including the fold structure, folding direction, tilting of chains with respect to the fold surface, the fold formation process , and the unfolding process, the role of chain ends, *etc.*, remain one of the most interesting and challenging questions in polymer crystallization.[14, 19, 31, 67-70] As polymers are polydisperse with drastically different rigidity and crystallizability, answers to these questions are typically dependent on the nature of the chain itself. Crystallization methods, *e.g.* solution, melt, or vapor-assisted, can also affect the folding behavior. In general, fringed micelle and adjacent chain folded crystals can be considered as the two extremes of the continuous spectrum of the polymer crystalline morphology. In high crystalline polymer with flexible chains, which are the best model system to study crystallization, the chain folding model is the dominant mechanism.

Although folded chain crystals (FCCs) are the dominant morphology in polymer crystals, there are indeed exceptions: extended chain crystals (ECCs) are a perfect example. Obtained either under high pressure (**Figure 2d**),[65, 71-73] or external flow (**Figure 2e**),[66] ECCs came along as a surprise and highlighted the complexity and maneuverability of the polymer crystalline morphology. **Figure 2** shows TEM micrographs of folded polymer lamellar crystals, extended chain crystals, and shish kebab crystals where both can be observed. The shish-kebab structure is a signature of flow-induced crystallization and is still one of the most widely studied topics in polymer crystallization,[74, 75] mainly because such morphology is closely associated with polymer processing as well as the end properties of the material.

Shortly after the proposal of the chain folding idea, kinetics of crystal nucleation was investigated. It was shown that while in polymer bulk, heterogeneous nucleation is the dominant route, homogeneous nucleation can be achieved in polymer droplet with limited volume.[76-78] To explain the formation of folded crystal of long chain polymers, Hoffman *et al.* proposed arguably the most influential and debated crystallization model: the Hoffman-Lauritzen (HL) theory. As a kinetic theory, HL model presents a simple yet effective approach to understanding the physical picture of polymer crystallization. [20, 79, 80] Assuming that crystallization starts from a stem with a sufficient length that can survive thermal fluctuation, growth takes place by first depositing part of a polymer chain onto the atomically smooth surface (growth front) and the rest of the chain will be reeled into the vicinity of the first stem and spread on the surface to form a new layer. Repeating such a process leads to the general growth of the crystal. The idea also hints at the adjacent reentry folding as opposed to the switchboard folding model. The HL theory is successful in providing general guidelines on crystallization kinetics and morphological observations. Lamellar thickness, nucleation rate, and regime phenomena were analytically described and experimentally confirmed.[20] However, the model is oversimplified given the complexity of converting an entangled network to faceted crystals and it has been continuously under scrutiny from different perspectives, typically initiated by the experimental observation that cannot be explained by the model.[57] Hoffman later updated the theory to explain new experimental findings while the major secondary nucleation assumption and nucleation followed by reeling in polymer chains for growth stay as its fundamental hypotheses.[20, 81] The theory was also intentionally kept simple yet accurate enough to explain general experimental data.[20]

Over the years, numerous suggestions have been proposed to improve the original HL model, and there were also new theories that took drastically different approaches. For example, to address the molecular weight-dependent crystallization, Wunderlich proposed a molecular nucleation mechanism which is different from crystal nucleation.[82] According to Wunderlich, molecular nucleation is referred to the process that establishes the first part of a macromolecule in the crystalline phase, while crystal nucleation is concerned with the start of a new crystal or a new crystal layer and is considered irrespective of the noncrystallized portions of the polymer chain.[82] Therefore, the parameter of molecular weight is accounted for in molecular nucleation. The molecular nucleation conception, later discussed in Hu’s work on intra-molecular nucleation,[59] explains tie chain and molecular weight-dependent crystallization kinetics and fractionation during crystallization. While the HL model focuses on enthalpy barriers of crystallization, Sadler and Gilmer proposed a drastically different crystallization framework based on the entropy barrier of nucleation.[83] They argued that, contrary to the HL theory, the nucleation barrier is completely entropic and upon crystallization, if one segment adopts a wrong configuration, the subsequent deposition of stems will be blocked, crystallization can only be resumed after the wrong conformation is removed. More recently, a few new theories were proposed and will be discussed in the following section.

The chain folding concept and HL theory are often viewed as the two major developments in polymer crystallization. In the last century, a tremendous amount of achievements has been accomplished with regards to the crystalline structure, morphology, and the crystallization process, and a fascinating polymer crystallization field has been established. Some interesting examples are:

Crystalline structure. Determining crystalline structure has always been the central study throughout the development of polymer crystallization. It played a critical role in confirming the macromolecular concept by Mark.[5, 6] Before the chain folding concept was proposed/accepted, X-ray fiber diffraction was extensively used to determine the crystalline structure of polymers. Some of the early X-ray fiber patterns from Mark, Bunn, Fuller, Natta and Corradini, Tadokoro, *etc.*, are of excellent quality, and numerous classical polymer crystals structures were determined during this period. Because of the intrinsic high defect contents and the facile alignment of a polymer chain, typical procedures of solving a polymer X-ray pattern can be different from their small molecular counterparts and have been documented in a few excellent texts.[23, 37] Fibers are typically used for X-ray structure determination, while other methods such as mechanical shear and directional solidification experiments have been designed to introduce biased growth or break spherical symmetry to extract morphological and growth information from the polymer crystals.[84, 85] **Figures 3a,b** show the fiber pattern of polyamide 6,6 and the corresponding unit cell by Bunn and Garner reported in 1947.[47] **Figures 3c,d** show poly(vinylidene fluoride) (PVDF) spherulite morphology achieved using directional solidification and the corresponding X-ray diffraction pattern.[86]

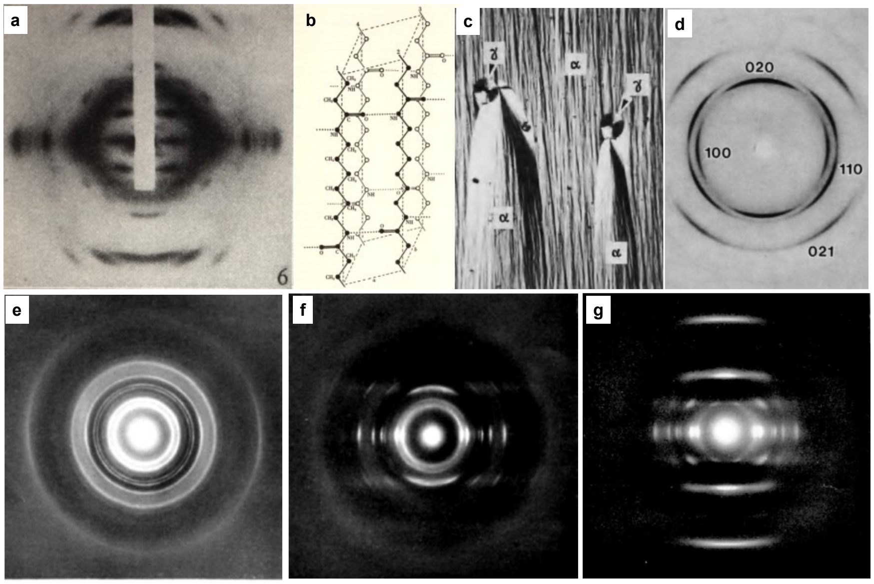

Figure 3. Polymer structural analysis using X-ray (a-d) and ED (e,f). (a-b) show the X-ray fiber pattern of polyamide 6,6 (a) and the proposed unit cell (b) by Bunn and Garner in 1947.[47] (c) Polarized light microscopy image of PVDF spherulite treated by directional solidification at 3 μm min^{-1}, and the corresponding X-ray diffraction pattern of the α-PVDF spherulite, in the correct orientation to the field.[86] (e-g) depict Storks' work on gutta-percha in 1938, showing ED patterns from (e) an unstretched sample at normal incidence, (f) an unstretched sample at 45° incidence, and (g) a stretched sample.[56]

While X-ray offers a global view of crystalline structure, ED provides local molecular information on samples such as polymer single crystals. ED was applied to study polymer crystal structures in the 1930s. Early work from Storks investigated stretched and unstretched polymer samples, showed clear chain orientation due to mechanical stretching, and reached the conclusion of chain folding for unstretched samples, highlighting the power of this technique.[56] **Figures 3e, f** show the ED patterns of unstretched (c,d) and stretched gutta-percha (e) by Storks. This method was then applied to nearly all the polymer single crystal samples obtained and led to the discovery of some major new findings in semicrystalline polymers, such as chain folding,[51] polymorphisms of isotactic polypropylene,[87] PVDF,[86] epitaxy growth of polymer crystals,[88, 89] conjugated polymers,[90-92] and many others. Compared with X-ray diffraction, the ability to approach the single crystal level length scale with sub-nanometer real-space resolution along direct viewing the crystal reciprocal space in TEM is extremely attractive, although all the polymer samples suffer from the issue of beam damage. Even with a limited beam life, some more advanced TEM work can be carried out including dark-field imaging.[93, 94] The lateral spreading extend which was assumed in the HL theory was directly observed.[94] In another example, carefully designed dark-field imaging also led to the discovery of a double-twisted chain packing scheme in a twisted polymer single crystal.[95]

Polymer spherulites. Polymer spherulites have been in the central stage of polymer crystallization investigation since they were first observed using PLM (**Figures 4a,b**).[48] The spherical symmetry and the intriguing banded pattern observed in some simplest polymers such as PE attracted intense interest to understand their origin and their effect on related macroscopic properties. Spherulites were seen in small molecules before polymer science was born.[96] The spherulitic feature of the crystals in polymers, however, was immediately realized to be at odds with the then-popular fringed micelle model. Early work started by Bunn, Price, with significant contributions from Keller, Keith and Padden, Price, Bassett, etc.[13, 14, 22, 48, 97, 98] A beautiful experiment designed by Keith and Padden revealed tie chains between lamellae and spherulites (**Figure 4c**). The topic was recently reviewed by Crist and Schutz.[35] While it is generally agreed that the continuous non-crystallographic branching of lamellar crystals leads to the spherical growth and symmetry of the morphology, some unique features, such as the origin of the banding morphology, were intensively debated.[99] The leading explanations are the continuous isochiral defects model and unbalanced lamellar stress, among others. [35] Experimental results have shown that the unbalanced lamellar stress model proposed by Keith and Padden captures the general and important aspects of the microscopic origin of lamellar banding.[100] The unbalanced lamellar surface stress in the simplest PE system was elegantly demonstrated using thin-film crystallization, where "half lamellae" were created due to surface confinement (**Figures 4d-g**).[101] These half lamellae were found to be bending towards a specific direction, which was associated with the hypothesized surface unbalanced force associated with chain tilting in the lamellae. The model was then applied to numerous systems and has been demonstrated as a reliable and powerful tool to explain the origins of some complex semicrystalline morphology.[100, 102, 103]

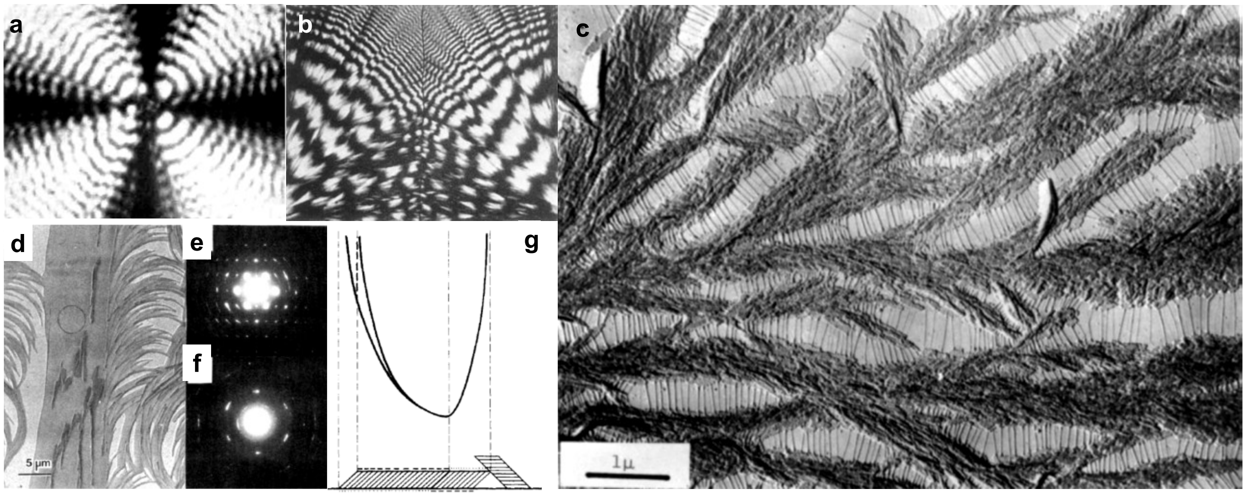

Figure 4. PE spherulite model after Keith and Padden. (a) PLM micrograph of a PE spherulite showing the banded structure. X 675 [97](b) Two spherulites in a PE film nucleated at a temperature close to the melting point and steadily cooled during growth. X 275[104] (c) Tie chains in PE spherulites grown at 95°C in a low molecular weight PE fraction. [105] (d) TEM micrograph of flat-on and edge-on lamellae of PE. (e-f) show ED patterns from the area shown circled in (d). The patterns in (e) and (f) show c* and a* projections of reciprocal space, obtained with the crystal rotated by 45° counterclockwise and clockwise about its upward-facing long axis, respectively. (g) Schematic drawing of a typical lamella illustrating direction of chain tilt and associated asymmetries of lateral growth. [101]

Recent development in polymer crystallization

The major discoveries in semicrystalline polymers were achieved before the 1990s, with numerous brilliant scientists laying the foundation of a fantastic research field. In the following three decades or so, the field continued to progress in many new directions. There has been continuous pursuit towards a better understanding of some classical topics such as new models,[106, 107] crystal structure and morphology,[28] flow-induced polymer crystallization, [74, 75] phase transformation and metastability in liquid crystalline polymers,[26] memory effect in polymer crystallization,[108-111] thin film crystallization,[112-114] etc. Besides, a few quite interesting new developments are detailed as follows.

New models and simulation. A few interesting experimental observations and theoretic interpretations started in the late 1990s. There were scattering experiments that showed that small X-ray angle scattering (SAXS) signals appear before the corresponding wide-angle X-ray diffraction (WAXD) ones, leading to the proposal of spinodal decomposition-assisted crystallization mechanism,[115, 116] which was questioned from both experimental observation and modeling perspectives. This, along with the reports on hexagonal to orthorhombic phase transition in PE when crystallizing at elevated temperatures,[74, 117] the temperature-dependent SAXS data on syndiotactic polypropylene (sPP), and a few other polymer systems showing the departure of undercooling-determined lamellar thickness,[118] led to the proposal of a multi-stage crystallization model by Strobl in 2000 (**Figure 5**).[106, 119] The multi-stage model claims that polymer crystallization is conducted via a mesophase at the crystal growth front: upon crystallization, polymer melt first organizes into highly mobile mesophase that attaches to the growth front via an epitaxy type of manner, thicken to the desired lamellar thickness, and organize to the crystalline phase. With an introduction of a new mesophase as the intermediate stage for crystallization, the model is a drastic departure from HL, moving away from the single chain reeling into a growth front hypothesis of the latter. The new model was at the center of discussion in the polymer crystallization community in the past two decades, with questions on how to reconcile the model with detailed precise helical packing, the thermodynamic nature of the "mesophase", and the introduction of the T_{mc}^{∞}.[120-122] More recently, Muthukumar proposed yet another view on the crystallization process, emphasizing the role of chain entropy in the crystallization process.[31, 107] An "inner layer" and "outer layer" were introduced with distinct chain dynamics and diffusion coefficients (**Figure 5c**). Accordingly, a free energy landscape with a globally stable state and many long-lived metastable states was proposed. A temperature-dependent equilibrium thickness was also predicted, and the equilibrium melting temperature was viewed no longer corresponding to that of extended chain dimensions. A different growth rate expression was also proposed with the contribution of the diffusion coefficients inside and outside the growth zone. While experimentally challenging, it would be interesting to quantitatively compare the new entropy model with experimental data. Molecular simulation has shown various types of new insights and will continue playing an important role to better understand the process and validate new models.[67, 123-125]

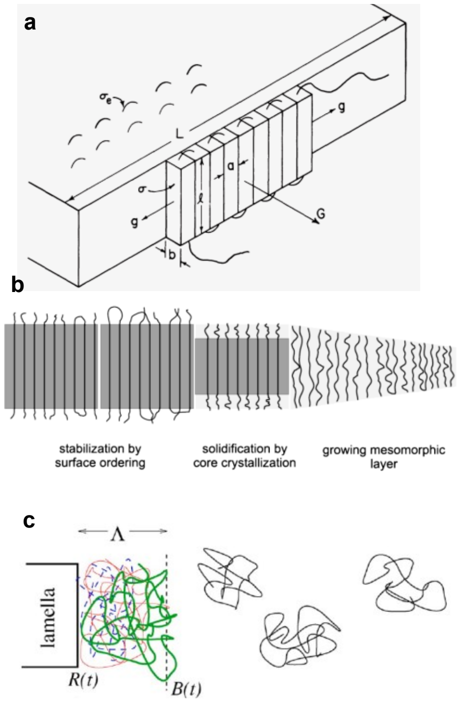

Figure 5. Schematic drawing of (a) HL model, (b) multi-stage model, and (c) continuum model.

Confinement crystallization. Another rapidly growing research field is confinement crystallization, partially due to the emergence of nanoscience and nanomaterials.[126] Confined crystallization is generally defined as the crystallization process under certain types of geometrical confinement at a small length scale that is comparable to the chain and/or lamellar dimension. **Figure 6** shows various confinement systems and the nature of the confinement based on the dimension (1D, 2D, 3D) and the confinement degree, where hard and soft confinement refer to the liquid (low moduli) and solid (high moduli) nature of the confining medium, respectively. Polymer droplets,[127] block copolymers (BCP),[128-130] anodic aluminum oxide (AAO),[131] nanofibers,[132] emulsion droplets,[133, 134] and liquid/liquid interface have been used as nanoconfined systems.[126, 135] Classical thin film crystallization can be viewed as one type of confined crystallization.[112-114] In general, the nanosized environment alters nearly all aspects of crystallization, from nucleation to growth. Since polymer crystallization itself is a kinetic process, nano environment significantly affects different stages of crystallization, leading to an even more complex crystallization behavior. Earlier thin film crystallization from Keith *et al.* demonstrated the asymmetric habit of PE lamellae.[101]

Prod'homme showed the chirality effect on the lamellar twisting/bending.[113] More recent work from Reiter showed dendritic single crystal formation, highlighting the thin film confinement effect on single crystal morphology.[136] Studies have also been conducted on a more dynamic water surface. Morphology, chain folding, as well as the crystallization kinetics are altered at liquid/air and liquid/liquid interface.[135, 137] BCP confinement and the interplay between BCP microphase separation and polymer crystallization has been an interesting and rich field for the past decades.[128, 129] The competition between the two phase transformations leads to the observations of confined, templated, and break-out modes of the crystal growth. Confinement-induced crystalline structure and morphology change was also investigated in polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO).[130] Another active research field which has a strong confined crystallization flavor is in semicrystalline nanocomposites. Nanoparticles, 0D, 1D, or 2D, have been blended with semicrystalline polymers, and depending on the particle surface chemistry, dimension, and loading, these particles can affect polymer crystallization through altering nucleation and/or hindering polymer diffusion.[138]

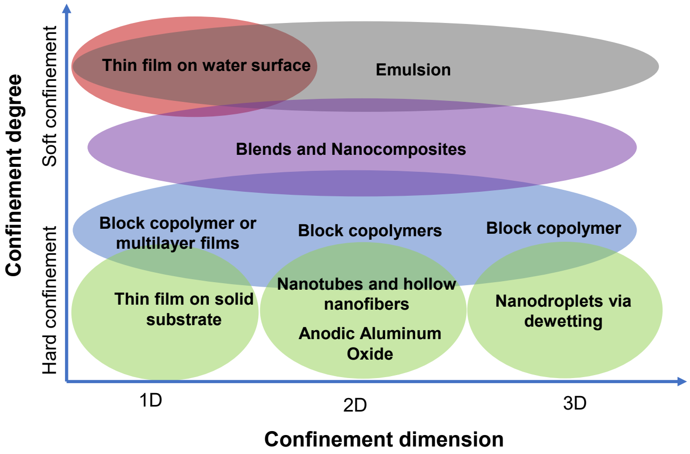

Figure 6. Overview of confined crystallization systems.

Crystallization and self-assembly. Self-assembly of polymeric materials is one of the more widely investigated research fields. In a multicomponent system such as BCP, while crystallization is confined by the local environment, it also affects BCP phase structures, as previously discussed. When crystallization dominates the phase behavior, the resultant structure can be viewed as crystallization driven self-assembly, which is particularly evident in solution systems.[139] The crystalline polymer-dominated morphology in solution was investigated by Lotz *et al.* on PS-*b*-PEO.[140] Square-shaped single crystals were obtained with the PS blocks excluded onto the two lamellar surfaces. This approach was used by Chen *et al.* to investigate polymer brush behaviors in the early 2000s as the amorphous polymers on the 2D lamellar surface are model polymer brush systems with well-defined tethering points and grafting densities.[141] Recent studies on poly(ferrocene dimethylsiloxane) (PFMS)- and PLLA-based copolymers demonstrated a plethora of controllable crystalline morphologies. [142-144] Elegant morphology control was achieved using the early developed self-seeding method.[145] Another example in the thin film system was reported by De Rosa *etc.*, where directional solidification and thin film epitaxy were combined in one system, and controlled crystallization dictated the morphology formation, leading to relatively large scale vertically aligned cylinder BCP films.[146]

Fast scanning calorimetry. One intrinsic feature of polymerization is its lamellar thickness-associated metastability. Because of the constant annealing process upon heating, it is always challenging to measure the true melting point of a polymer crystal obtained in a pre-determined crystallization condition, which cast doubts on the early experimental data used to interpret polymer crystallization and melting behaviors. The recently developed chip calorimeter enabled fast heating and cooling.[147, 148] At a heating/cooling rate approaching 10^6 K s^{-1}, it covers all processing-relevant rates and allows for by-passing the annealing process during scanning for all semicrystalline polymers – the starting amorphous or mesomorphic phase can be quenched for detailed analysis. Fast scanning calorimetry can be applied to non-isothermal, isothermal crystallization, nucleation agent-induced fast crystallization, homogenous nucleation, and melting kinetics.[148] A broad range of polymers has already been studied.[148] With the capability of accessing a completely new time scale, it is anticipated that many new insights can be achieved regarding classical crystallization theories.

Hybrid and functional polymer crystals. Another recent direction emerged is exploring how to use the well-defined 2D polymer single crystals as functional nanomaterials. For example, by introducing end-functional groups, polymer single crystals become functional nanoplates which, depends on the end groups, can be used to immobilize nanoparticles or as templates for polymer brush synthesis (**Figure 7**).[149-151] The nanoparticle-decorated crystals enable a plethora of new properties. For example, directed assemblies of nanoparticles can be achieved.[152-154] Iron oxide/platinum nanoparticle-decorated polycaprolactone (PCL) single crystals were used as a recyclable catalyst system as well as nanomotors that can autonomously “swim” in a suitable medium such as hydrogen peroxide.[153, 155] Multi-functional nanomotors that catch/release cargos and further self-decompose were also demonstrated.[156] Gold nanoparticle-decorated single crystals showed excellent surface-enhanced Raman behaviors.[153, 157] Polymer single crystals were also used as the templates for Janus nanoparticle synthesis.[158] As the nanoparticles are immobilized onto the single crystal surface, part of the particle surface is chemically coupled with the polymer. Grafting polymer brushes on the exposed nanoparticle surface leads to the formation of Janus nanoparticles with two distinct surface brushes. Such Janus nanoparticles can be used as model systems to study phase behavior and self-assembly of hairy nanoparticles.[159, 160] Furthermore, we have recently demonstrated that polymer single crystals can be used as the template to synthesize polymer brushes with precisely defined tethering density and brush conformation. Loop brushes, gradient brushes, and BCP brushes have been synthesized.[150, 161, 162]

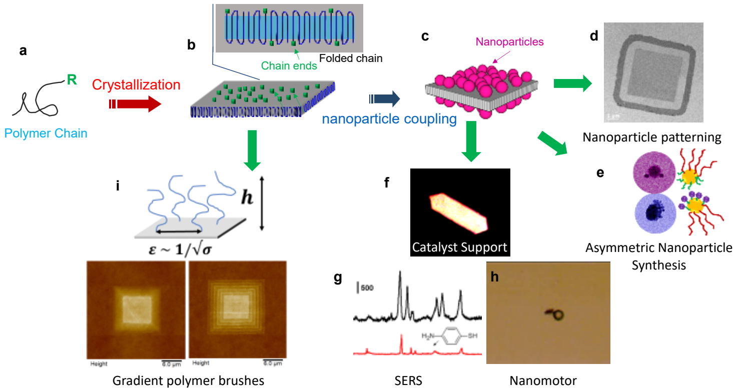

Figure 7. Functional polymer single crystals. (a) an end-functionalized polymer chain. (b) A thin, 2D polymer lamella with the end functional groups on the lamellar surface. (c) Nanoparticle-decorated 2D polymer single crystals.[153] (d) Patterned nanoparticles using programmable crystal growth.[154] (e) Asymmetrically functionalized nanoparticles (Janus nanoparticles) using (c) as the templates. (f-h) A nanoparticle-decorated PCL single crystal that can be used (f) as a catalyst support, (g) for surface Raman enhancement, and (h) as a nanomotor.[153] (i) Gradient polymer brushes with precisely controlled grafting densities and tethering points using (b) as the templates.[151]

Future research directions in polymer crystallization

It has never been a problem to find new and interesting fundamental questions in the field of polymer crystallization during the century-long investigation. With the ever-changing scientific field, one would ask what the most important and interesting questions in the field would be in the next decade or two? A short answer is that there are many intriguing problems, while personal interests can steer towards quite different directions. The more recent work discussed above perhaps indicates some near-term research directions. There will always be quests towards a deeper understanding of the complex subject. It is also of critical importance to improve the properties of semicrystalline materials. Besides, polymer crystallization must serve the interests of the polymer science community and the broader societal needs, adapting itself as new fields emerge. A few examples are briefly discussed.

Polymer crystallization mechanism. There is always a push for better and improved theories to deepen our understating of the complex polymer crystallization process. The recently developed multi-stage and continuum models are excellent examples. The field welcomes new understandings of the subject and calls for experimentalists to testify these proposed new ideas. Considering the history of the crystallization theory, the general idea was borrowed from small molecule crystallization, and the long-chain connectivity was incorporated into each theory to a certain degree with different "flavor". The nature of the growth front has been the center of many theories. As previously discussed, the multistage model introduced a mesophase layer to explain the diverging of T_m^∞ and T_c^∞, while the continuum theory introduced a boundary layer at the growth front with its own dynamics. If we turn our attention to small molecule crystallization research, the classical theory has also recently been challenged, and multiple crystallization pathways have been proposed including the conventional "monomer-by-monomer", complexes, droplets to amorphous solid, amorphous nanoparticles, poorly crystalline nanoparticles, and nanocrystals.[163] These intermediate states are certainly different from the hexagonal phases in the high pressure crystallized PE. [74, 117, 164] Nevertheless, the proposed ideas, supported by liquid phase TEM studies, clearly suggest that the crystallization process does not need to be limited to a single component intermediate state, nor need it to follow a single pathway. The complex free energy landscape could be affected by solvent, molecular characteristics such as molecular weight and dispersity, and conformation of the local segments in the growth zone, which in turn, could lead to a biased/selected crystallization pathway. To this end, *in situ* and *ex situ* investigation of the structure and dynamics of the growth zone would be both challenging and rewarding. With much improved computational power, simulation could become the central force to improve our understanding. Results from these studies will certainly shed light on some fundamental questions such as intramolecular phase separation, the nature of the growth front, the exact structure of fold surfaces, and so on.

Hierarchical defects in hierarchical polymer crystals. One signature of polymer crystals is that they are defect-rich. While defects are normally considered as the unwanted "byproduct" in the crystallization process, they could significantly affect materials properties, either providing a pathway for transport or serving as the molecular level "hot spots" for shock absorption. As the polymer crystals are deemed hierarchical, defects themselves can also be divided into lattice-level, lamella-level, and spherulite-level. Collectively, these hierarchical defects play an important role in determining the end properties of the material. Lattice-level defects, such as the classical vacancy, dislocations, *etc.*, have been investigated using XRD and ED,[14] while lamellar fold surface can be viewed as the lamella-level defects. Inter-lamellar and inter-spherulites tie chains and amorphous domains as revealed by Keith and Padden make up the spherulite-level defects. It has been shown that tie chains are critical to the mechanical properties of semicrystalline polymers.[7] The search for improved dielectric and ferroelectric polymers involved tuning the structure at all levels.[165, 166]

Defects on the lattice-level and lamella-level can significantly affect crystal morphology and properties, which has been extensively studied in conjugating polymer crystals.[12, 90, 91, 167] Recently we discussed a class of polymer crystals whose shapes are incommensurate with translational symmetry, named as shape-translational symmetry incommensurate crystals (SSICs), which include helical, helicoidal, scrolled, and spherical crystals.[168] Due to the broken translational symmetry, SSICs typically are defect-rich. While the mechanisms of helicoidal and scrolled crystals have been extensively studied, both in polymers and small molar mass organics,[96, 102] their physical properties are rather unexplored. Considering the fascinating properties discovered in nanomaterials, engineering defects on the single crystal or lamellar level in polymers could lead to exciting new properties. For example, in the recently discovered crystalsome systems, it was shown that mechanical properties such as bending modulus of the defect-rich, spherical crystalsomes are hundreds of times greater than that of polymersomes with similar sizes and shell thicknesses .[133, 169] BCP crystalsomes also showed ultra-long blood circulation time.[170] Single-crystal level shape-changing Janus plates were also achieved.[171] We anticipated that engineering defects can provide control over these exotic morphologies for application purposes.

New molecules, new opportunities. Model polymers are unique in studying polymer crystallization. For example, cyclic polymers and oligomers of PE and PEO have been used as the model system to better understand polymer folding behaviors.[63, 172] With the fast-developing polymer synthesis techniques, polymer chains with a well-defined architecture and precisely controlled chemistry are more readily available. For example, molecular bottlebrushes (mBBs) have recently attracted significant attention due to the chain architecture-associated unique properties such as tunable assembly behavior and mechanical properties. [173, 174] Crystallization of mBBs has been studied; steric crowdedness can facilitate crystal nucleation and retard its growth.[175-177] We recently showed that in a series of PEO-bearing mBBs, upon PEO sidechain crystallization, spherical hollow crystals name mBB crystalsomes (mBBCs) are formed. Translation symmetry is spontaneously broken in this unique mBBCs due to the side PEO chain overcrowding, which can be readily controlled by the sidechain grafting density.[178] In another avenue of research, a library of giant molecules has been synthesized. [179, 180] These topologically distinct molecules often have similar size of a typical linear polymer, but with reduced chain entanglement. Self-assembly and crystallization of this series of molecules have led to the observation of extremely rich structure with conventional and unconventional symmetries.[180] It is therefore rather clear that with the newly developed, precisely controlled polymers, novel structure and findings will be discovered.

Advancing properties of semicrystalline polymers. Another frontier of polymer crystallization research is advancing properties of semicrystalline polymers through better understanding their structure. The main driving force for the field of polymer crystallization has been the broad applications of semicrystalline polymers. Extensive work has been done on how to improve polymer properties by controlling processing/crystallization conditions, introducing new additives, and tuning the molecular structure of the polymers.[7, 181] Mechanical and optical properties are most extensively investigated.[7] For biomedical applications, crystalline structure and morphology significantly affect polymer's biodegradation and biocompatibility.[182, 183] Dielectric and ferroelectric properties of high polymers are also of great interest. Studies in PVDF showed that different polymorphisms have significantly different ferroelectric properties.[86, 165] Crystallization has been extensively used in shape-changing polymers.[184] The semicrystalline morphology also imposes challenges on understating transport properties of semicrystalline polymers. In most cases, the tightly packed polymer crystalline domains are impermeable to diffusants such as ions and gas molecules. The later have to migrate in a confined tortuous pathway. A previous study on multilayered films showed that PEO crystallized as single, high-aspect-ratio lamellae, which led to two orders of magnitude reduction in gas permeability (**Figures 8 a-c**).[10] In searching for high-performance solid polymer electrolytes (SPE) for lithium battery applications, PEO is typically used as the model electrolytes while its high crystallinity often negatively impact the SPE's ion conductivity, although the crystalline domains are critical for the SPE membranes to retain sufficient mechanical strength. The effect of semicrystalline structure on ion transport is often considered two-fold: the crystalline domains provide a tortuous diffusion pathway while the tethered chains can cause sluggish ion diffusion. Our recent work using aligned PSC SPEs demonstrated that tortuosity is the main effect that retard ion transport, particularly in low ion content SPEs, suggesting that semicrystalline polymers can be used for future SPE design if the crystalline morphology is controlled (**Figures 8d-i**).[11, 185] Crystallinity effect on exciton transport and photovoltaic device performance have been extensively studied in semiconducting polymer such as poly(3-hexylthiophene) based systems.[12, 186] All the examples indicate that morphology control is the key to the performance of the final material.

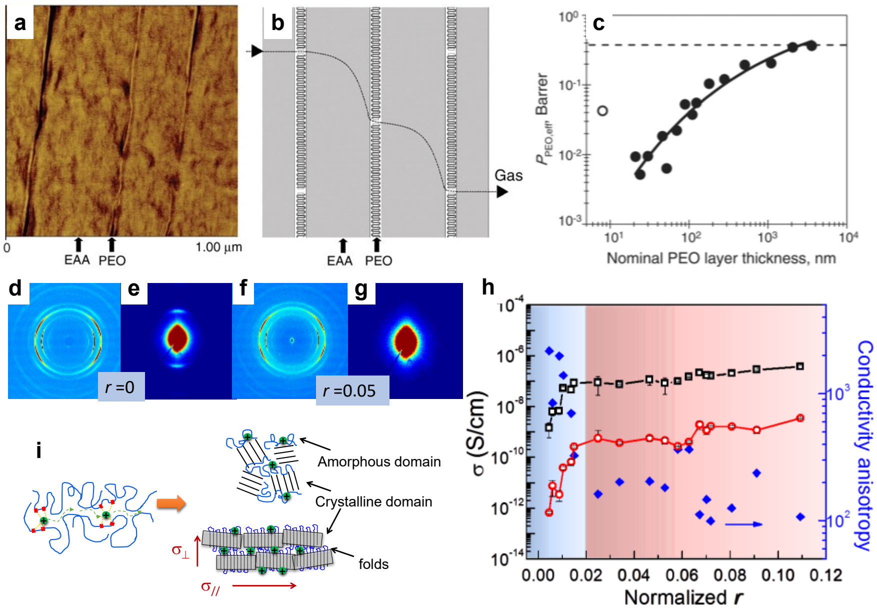

Figure. 8. Crystallization dictated transport properties. (a-c) Oxygen permeation behavior of PEO-containing multilayer films. (a) AFM images of an poly(ethylene-co-acrylic acid)/PEO film with 90/10 composition. (b) A schematic showing the gas diffusion pathway through the layered assembly. (c) Oxygen permeability of the PEO layers from films of varying composition.[10] (d-i) Anisotropic ion transport in aligned polymer single crystal SPEs. (d-e) WAXD (d, f) and SAXS (e,g) of edge-on polymer single crystal film with a normalized Li+/EO of 0 (d,e) and 0.05(f,g). (h) In-plane (black open squares) and through-plane (red open circles) ion conductivities. Fill blue diamonds are the conductivity anisotropy. Over 1,000 conductivity anisotropy can be achieved at low ion concentrations (blue shaded area).[11]

New characterization methods. The development of the polymer crystallization field has benefited from the evolution of new characterization techniques. Mark's early XRD work was critical to confirming the macromolecular hypothesis.[5, 6] TEM and ED played a key role in discovering the chain folding mechanism. *In situ* and *ex situ* synchrotron X-ray scattering has provided insightful structural information and kinetics. Numerous techniques have been used to study crystalline polymers since the early days. In addition to classical X-ray scattering, microscopy, and thermal analysis techniques including modulated differential scanning calorimetry,[187] neutron scattering and spectroscopy techniques such as NMR, FTIR have been employed. The previously discussed fast scanning calorimetry will provide important new information, which was previously unattainable, particularly in metastable states and far from equilibrium conditions. [147, 148] Atomic force microscopy (AFM) has also been used to reveal detailed features of polymer crystals. Single crystal growth can be viewed at the molecular level *in situ*.[188] Chain folding can also be directly imaged.[189, 190] Moreover, AFM-based single-molecule force spectroscopy was employed for detailed force measurements.[191] The inter-polymer chain interaction in a PEO single crystal was measured to be ~ 42 pN, providing a new means to study single crystal properties. ^{13}C–^{13}C double quantum (DQ) NMR spectroscopy combined with ^{13}C selective isotope labeling has recently been used to study the detailed fold structure in lamella crystals.[192] A great deal of information including the chain trajectory, fold chain conformation, self-folding in the early stage of crystallization was obtained. There are also numerous new techniques that are available and potentially could impact polymer crystallization study, including liquid phase TEM,[193] electron microscopy tomography,[194] etc. As these relative new techniques are more readily available and applied to polymer crystallization study, new insights in all aspects of the field are anticipated.

Polymer crystallization in emerging research fields. As new research fields emerge, polymer crystallization research must adapt and contribute. When contributing to the development of a new field, the latter can also offer a fresh perspective that could benefit polymer crystallization study. For example, advanced manufacturing and sustainability are arguably the most rapidly developing fields.[3, 195, 196] For additive manufacturing, many semicrystalline polymers such as PLLA, PCL, Nylon, etc. have been used to form complex shapes using extrusion-based additive manufacturing. There remain significant challenges to achieve high dimensional stability of the printed parts as crystallization occurs during the fabrication process, which significantly affect interlayer adhesion. This research is similar to the classical flow-induced polymer crystallization, but in a more complex setting because of the multilayer nature of the parts. On the other hand, sustainable polymer research has become one of the most important topics as our planet is facing significant plastic pollution.[3, 196] Nature polymers such as cellulose, silk, natural rubber, *etc.* were among the first materials that were investigated in the polymer crystallization community. It is worth renewing such interests from a sustainability perspective. Understanding the crystalline structure of newly developed sustainable polymers will be a long-lasting task. Recycling existing plastics, particularly semicrystalline polymers, dictates a clear understanding of the effect of semicrystalline morphology and processing conditions on plastic recycling. Recycled polymers, different from their virgin resins, show different crystalline kinetics, morphology, and properties. Research is needed to advance in this direction to make more efficient usage of recycled polymers.

Summary

In conclusion, polymer crystallization has been extensively studied for over a century. In this perspective, the history of polymer crystallization research was briefly reviewed. A few recently emerged directions during the past two decades were discussed. The survey of literatures shows that polymer crystallization is still a vibrant field, and many fundamental questions, such as crystallization mechanisms, pathways, the nature and structure of folding, defect engineering, are begging for answers. Because of its interdisciplinary nature, polymer crystallization can contribute to, and certainly will benefit from, works on newly emerged and interdisciplinary fields such as biomedical science and engineering, additive manufacturing, energy, and sustainability.

Acknowledgments

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