

Ordered Organization of Long Chain Polymers: Advances and Challenges

Due to the long chain character and entanglement feature, polymer chains were initially believed incapable of organizing into ordered structures. However, X-ray studies in the 1920s demonstrated unequivocally the existence of ordered structures of celluloses and their derivatives, which has thus opened a new field of polymer physics. Henceforth, the order structure of long chain polymers and its organization manner have been paid much attention. The unremitting efforts of the scientists made in the past 100 years lead to great progress in the understanding of the ordered organization process of polymers in many aspects.

The first milestone achievement in this field is the unveiling of chain fold characteristic of polymers in ordered structure in 1957 through structural analysis of the polyethylene single crystals, which generates the smallest basic blocks, *i.e.*, lamellar single crystal, for building high-level superstructures. Further developments have thereafter been achieved in the formation of versatile structures and related folding mechanisms and kinetics, such as intra- and inter-molecular folding behaviors under varied conditions. While *in situ* following the organization process of polymers has been realized only on a micron scale till the 1980s, the development of nanotechnology, such as atomic force microscopy, enables an *in situ* study on the nanometer or even molecular scale. For example, the real space visualization of the onset structure ordering, in other words the nucleation step, and propagation of ordered structure (*e.g.*, lamellar crystal growth) have been achieved by the end of the 1990s. Even the handiness of helical chains in the lamella has been disclosed unequivocally. Based on the technical developments and profound studies, the understanding has been developed on more and more issues about different order structure formation. For examples, the melting and crystallization temperature dependent polymorphic selection of polymers is recently well elucidated. Also, the distinct organization manner of polymers in confined space, at nanometer scale or at interface contacting to varied substrates, with respect to the bulk ones get better understood now. Practically, the study of the ordered organization of polymers is to expand the application of polymeric materials in advance through purposeful control of unique order structure with specific functionality. This gets also a remarkable achievement. The cloning of polymer single crystals through self-seeding provides a best illustration of it.

It should be pointed out that, even though great progress has been achieved in polymer order structure, it is

still far away from a full understanding due to the much more complicated ordering process of polymers compared with small molecules. There are still many challenges that remain in this field. From the theoretical point of view, there lack still related theories with due consideration of the chain natures of polymers including chain architecture, entanglement status, molecular weight distribution, and so forth. The interplay between them and the localized ordering is the key to understanding various unique thermodynamic and kinetic features of polymeric systems. There are many transitions involved in the ordering of polymers, such as chain collapse, helix to random coil transition, *etc.*, which warrant deep investigations to fully understand the complicated ordering thermodynamics and kinetics of polymers. This is the reason why the theory about polymer crystallization remains still the top of the ten “grand challenges” in the polymer field. From the practical point of view, even though diverse techniques have been successfully developed to regulate different structures and morphologies of polymeric materials, effective ways are still lacking for a synergistic fine control of the structures at multilength scales, such as the simultaneous control of the phase structure, including domain size and orientation, as well as the crystal structures and orientation of each component in a multicomponent system. The achievement of the related facile pathways will certainly expand the application of polymeric materials in advanced technological fields. We hope this can be achieved in the near future.



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