

Editorial on the Special Topic “Polymer Crystallization”

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Two thirds of polymer materials are crystalline. Their crystalline structures, characterized, e.g., by the degree of crystallinity, morphology and orientation of crystals, have a profound effect on the properties and applications of these materials. In most cases, crystallization of polymers follows the classical path of nucleation and growth, which determines the crystallization rate and the final crystalline structures. In industry, a high crystallization rate and often high degrees of crystallinity are sought to improve the production rate and heat resistance of polymer products. To accelerate the crystal nucleation of polymers, various methods have been applied. For instance, nucleating agents are added to shorten processing cycle times and to increase the optical transparency of injection-molded products. In addition, self-seeding, epitaxy and melt shearing can also enhance the crystallization rate of polymers. Besides the aforementioned methods, blending with amorphous materials or with low viscous polymers can improve the nucleation rate as well.

However, there are still many open questions in the field of nucleation in polymer crystallization:

- What are the key differences in the nucleation mechanism of polymer chains compared with the nucleation of small molecules?
- How do the mechanisms of primary and secondary nucleation differ?
- How do structures and polymer conformations in the amorphous melt affect the mechanisms and the kinetics of nucleation and crystallization of polymers?
- How is nucleation kinetics affected by constraints (nano-sized space, confinement) and the molecular weight of polymer chains?
- How does the morphology of polymer crystals (e.g., single crystals, dendrites or spherulites) depend on the competition between chain diffusion, nucleation and lamellar growth?
- How can we design novel nucleating agents, and which new methods can be developed for enhancing the nucleation rate?

Answers to these questions would be of both academic and practical importance.

The guest editors, Xu, Reiter and Alamo [1] co-wrote a review on the concepts of nucleation in polymer crystallization. Some of the remaining open questions and corresponding concepts in the field are discussed, such as crystallization from memorized or non-equilibrated polymer melts, self-induced nucleation, microscopic kinetics of different processes, metastability of polymer lamellar crystals, hierarchical order and cooperativity involved in nucleation, etc. The review was intended as a “nucleating agent” for initiating further discussions on the topic.

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At present, in addition to the review, 14 regular articles [2–15] have been published on the special topic of “polymer crystallization”. These contributions span research topics ranging from molecular mechanisms of nucleation and nucleating agents to the effect of molecular structures, chain conformations and processing parameters on the nucleation and crystallization behavior of various polymers. Systems analyzed include commodity polymers (polyethylene, polypropylene and poly(ethylene terephthalate)), biodegradable polymers (polylactide and poly(butylene succinate)), functional polymers such as poly(vinylidene fluoride), water soluble poly(ethylene oxide), natural rubber and inclusion compounds consisting of a polymer host with small guest molecules.

There are four articles focusing on the crystallization of polylactide, a prominent biobased and biodegradable thermoplastic. Zhao et al. [2] found a dependence of the crystal form of poly(L-lactide) on both temperature and molecular weight. They argued that chain entanglements would prohibit the δ to α crystal transition. At 80 °C, high and low molecular weight poly(L-lactide) formed δ and α phases, respectively. Zhong and Zhang et al. [3] observed that the spherulite morphology and crystallization rate varied with the isothermal crystallization temperature, which is attributed to the different nucleation rates at various temperatures. Via reactive blending of enantiomeric poly(L-lactide)/poly(D-lactide) mixtures with a trace amount of an epoxy-terminated small molecule modifier, Bai et al. [4] observed enhanced crystallization of the polylactide stereocomplex. The modifier led to the in situ formation of a multi-arm stereo-block copolymer which acted as a compatibilizer. We are curious as to whether the multi-arm stereo-block copolymer could work as a nucleating agent. This deserves further study.

Nucleating agents can considerably enhance the nucleation rate and the overall crystallization kinetics. Körber et al. [5] investigated the effect of different nucleating agents on the formation of stereocomplex crystals (SC) in compounded and injection molded poly(L-lactide)/poly(D-lactide) blends. Using the most effective nucleant, the level of crystallinity of SC and the heat deflection temperature increased with the mold temperature. Meng et al. [6] reported that a Zr-containing metal–organic framework is an efficient nucleating agent for poly(ethylene terephthalate). The crystallization peak temperature during cooling increased and the mechanical strength of nucleated materials improved significantly.

Intermolecular or polymer-substrate interactions also affect the nucleation of polymer chains. Dolynchuk et al. [7] reported the enhanced heterogeneous nucleation kinetics and preferred edge-on crystal orientation of poly(ethylene oxide) droplets on a graphite substrate compared to the random (isotropic) crystal orientation on an amorphous polystyrene substrate, due to the different substrate–material interactions. Ye et al. [8] revealed that the introduction of terminal 2-ureido-4[1H]-pyrimidinone (Upy) groups in poly(butylene succinate) oligomers forming strong quadruple hydrogen bonding in the melt led to depressed spherulitic growth rate. Compared to the hydroxyl-terminated oligomers, the primary nucleation rate of the Upy terminated oligomers was lowered in low molecular weight ones while it was enhanced in the high molecular weight oligomers. The latter was attributed to self-nucleation resulting from the melt-memory effect. The effect on the crystallization of ordered chain conformations and reduced chain mobility after incorporation of strong hydrogen bonding was briefly discussed.

Physical parameters during processing play important roles in the nucleation and crystallization of polymers. Liang and Wang [9] investigated the crystal structure and morphology of dried poly(vinylidene fluoride) solution droplets by varying the droplet size, solvent evaporation rate and concentration. It was revealed that the nucleation of β - or γ -phase poly(vinylidene fluoride) at the boundary of droplets was promoted by fast solvent evaporation-induced outward capillary flow. The polymorphic transition probably resulted from a gauche to trans flow-induced conformation transition. Kuehnert et al. [10] analyzed the crystallization kinetics of four grades of polypropylene (with and without nucleating agents) at different temperatures and under various pressures via PVT-

measurements and fast scanning chip calorimetry. It was observed that the pressure-dependent shift factor of the crystallization temperature was independent of the material. These crystallization kinetics data would be helpful in the tailor designing of the crystalline morphology and mechanical properties of semi-crystalline polymer materials in practical processes, such as injection molding.

Two articles focus on the crystalline structures generated in inclusion compounds containing a polymer host and small guest molecules. In poly(2,6-dimethyl-1,4-phenylene)oxide films exhibiting nanoporous-crystalline phases, Guerra et al. [11] observed that the crystalline polymer chain axes were preferentially perpendicular to the film plane in thick films while they were unoriented in thin films, which could be attributed to the dependence on film thickness of the guest sorption kinetics. Cozzolino and Rizzo et al. [12] obtained two co-crystalline forms of syndiotactic polystyrene with hexanoic acid as a guest molecule in syndiotactic polystyrene films exhibiting δ - and ϵ -nanoporous-crystalline forms. Both the δ - and ϵ -phases included hexanoic acid as isolated guest molecules, while only the latter included dimeric hexanoic acid molecules in the crystalline channels.

The application of semi-crystalline polymers as functional materials is steadily increasing. Zhao et al. [13] examined the crystalline structure in raw natural rubber coagulated with different sugars. Zhang and Weng et al. [14] utilized poly(vinyl alcohol), ethylene vinyl alcohol copolymer and clay to improve the gas barrier properties of polylactide films. Jiang et al. [15] investigated the effect of tensile deformation on the crystalline structure and the space charge in low density polyethylene/montmorillonite/silicon oxide composites. In these functional materials, the change of crystalline structures considerably affects physical properties and final performance during service.

As guest editors, we are deeply grateful to all contributors to the special topic. Their excellent work has deepened our understanding of the nucleation and crystallization of polymers. As a traditional but still highly active field, polymer crystallization will continue to attract attention of researchers. Strongly awaited progress in the field will further widen the range of applications for semi-crystalline polymers.

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