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**Understanding Melt-Memory of Commercial Polyolefins**[1]

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Self-nucleation (SN) or controlling self-generated seeds in a polymer melt is an avenue to increase the rate of solidification of semicrystalline polymers of commercial relevance. Self-nuclei are remains in the melt of the segmental self-assembly to form polymer crystallites providing a path to enhance primary crystal nucleation. SN has been extensively studied in homopolymers such as iPP. Recently, a strong memory effect of crystallization has been observed in melts of random ethylene copolymers well above the equilibrium melting temperature. The melt memory is associated with clusters or seeds that remain in the melt from the copolymer's sequence length partitioning. Cooling from progressively lower self-seeded melt temperatures, ethylene copolymers with a broad inter-chain comonomer composition (1 – 15 mol%) display first the expected accelerated crystallization, followed by a decrease in the rate in a range of melt temperatures where narrow copolymers show a continuous acceleration of the rate. This unusual inversion of the crystallization rate was postulated to arise from the onset of liquid-liquid phase separation (LLPS) between comonomer-rich and comonomer-poor components of the broad copolymer. The UCST type phase diagram of these commercial copolymers has been documented via SANS using a blend of components, some deuterated, to reproduce the broad distribution. Furthermore, the components that contribute to LLPS have been identified by the crystallization behavior of molar mass fractions. The influence of long chain branching on the topology of copolymer melts has been analyzed using model 3-arm stars hydrogenated polybutadienes. The effect of melt viscosity on strength of melt memory is also evident when SN data of random ethylene copolymers are compared with those of propylene-ethylene copolymers. The strong dependence of melt viscosity on melt memory, and a critical threshold crystallinity level to observe the effect of melt memory on crystallization rate, support the kinetic nature of the SN phenomenon.

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