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Melt structure and self-nucleation of ethylene copolymers[1]

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A strong memory effect of crystallization has been observed in melts of random ethylene copolymers well above the equilibrium melting temperature. These studies have been carried out by DSC, x-ray, TEM and optical microscopy on a large number of model, narrow, and broad copolymers with different comonomer types and contents. Melt memory is correlated with self-seeds that increase the crystallization rate of ethylene copolymers. The seeds are associated with molten ethylene sequences from the initial crystals that remain in close proximity and lower the nucleation barrier. Diffusion of all sequences to a randomized melt state is a slow process, restricted by topological chain constraints (loops, knots, and other entanglements) that build in the intercrystalline region during crystallization. Self-seeds dissolve above a critical melt temperature that demarcates homogeneity of the copolymer melt. There is a critical threshold level of crystallinity to observe the effect of melt memory on crystallization rate, thus supporting the correlation between melt memory and the change in melt structure during copolymer crystallization. Unlike binary blends, commercial ethylene-1-alkene copolymers with a range in inter-chain comonomer composition between 1 and about 15 mol % display an inversion of the crystallization rate in a range of melt temperatures where narrow copolymers show a continuous acceleration of the rate. With decreasing the initial melt temperature, broadly distributed copolymers show enhanced crystallization followed by a decrease of crystallization rate. The inversion demarcates the onset of liquid-liquid phase separation (LLPS) and a reduction of self-nuclei due to the strong thermodynamic drive for molecular segregation inside the binodal. The strong effect of melt memory on crystallization rate can be used to identify liquid-liquid phase separation in broadly distributed copolymers, and offers strategies to control the state of copolymer melts in ways of technological relevance for melt processing of LLDPE and other random olefin copolymers. References: B. O. Reid, et al, Macromolecules 46, 6485-6497, 2013 H. Gao, et al, Macromolecules 46, 6498-6506, 2013 A. Mamun et al, Macromolecules 47, 7958-7970, 2014 X. Chen et al, Macromol. Chem. Phys. 216, 1220−1226, 2015 M. Ren et al, Macromol. Symp. 356, 131–141, 2015