Melt Topology of Ethylene Copolymers above the Equilibrium Melting Temperature.

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Metallocene-made linear low density polyethylenes and commercial ethylene 1-alkene copolymers display a strong memory effect of their crystallization path even at temperatures above the equilibrium melting point. On cooling from different melt temperatures above equilibrium, the crystallization temperature (Tc) shifts to higher values, while for the homopolymer Tc remains unchanged. We correlate this phenomenon with remains in the melt of the copolymer's crystallizable sequence partitioning. Albeit molten, long crystallizable sequences remain in the copolymer's melt at a close proximity, lowering the change in free energy barrier for nucleation. The residual sequence segregation in the melt is attributed to a topology of loops, links and ties that generate in the intercrystalline regions after sufficiently large crystallinity content evolves. This topology restricts the copolymer crystalline sequences to diffuse upon melting and to reach the initial random melt topology, and hence affects a subsequent crystallization (1, 2). The effect on melt memory of copolymer molar mass, and comonomer content and distribution has been analyzed by DSC, x-ray, AFM and optical microscopy.

References:

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