Effect of length of 1-alkene on melt memory of crystallization above the equilibrium melting temperature of random ethylene copolymers.

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Model random ethylene copolymers with ethyl branches are known to exhibit strong melt memory of crystallization even above their equilibrium melting temperatures. Seeds remain in the melt at high temperatures lowering the change in free energy barrier for nucleation, and hence increasing the crystallization rate. The seeds are molten ethylene sequences from the initial crystallites that remain in close proximity due to restrictions to diffuse and reach the initial copolymer random melt topology. We found that erasing memory of the prior sequence selection in ethylene 1-butene copolymers requires temperatures ~ 25 degrees above the equilibrium melting (1, 2). The ethylene 1-butene data are contrasted in the present work with data of 1-alkene ethylene copolymers with longer branches. The effect of branch length in melt diffusion is correlated with the range of melt temperatures where seeds survive and, hence, with the strength of melt memory. Narrowly distributed, metallocene catalyzed, ethylene copolymers with 1-butene, 1-hexene, 1-octene or 1-decene comonomer are analyzed in a range of comonomer content from 0.6 to 12.6 mol%, and Mw ~ 10^5 g/mol. Independently of branch length, the critical temperature of the melt to reach a homogeneous copolymer melt state ($T_{critical}$) shows a bell-shape with increasing comonomer content. $T_{critical}$ reaches its maximum at ~1.5 mol% and reaches the equilibrium melting at 0 and ~4.5 mol% branches. Moreover, the nominal $T_{critical}$, and strength of melt memory defined as ($T_{critical}$ - T_m^o), decrease up to 20 °C with increasing branch length. We attribute the decrease in strength of melt memory with increasing branch length to less restricted topological ties, loops and knots in the inter-lamellar region of the semicrystalline structure, which are aided by faster melt diffusion of copolymers with longer branches. Data on ethylene 1-octene copolymers with a small content of long chain branches support that the limit of branch length to decrease strength of melt memory is reached at the critical entanglement length (~1,300 g/mol).

References:

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