

Abstract Submitted
for the MAR15 Meeting of
The American Physical Society

Effect of Crystallinity on Melt Memory of Random Ethylene Copolymers XUEJIAN CHEN, AL MAMUN, ALAMO G. RUFINA, FAMU-FSU College of Engineering, Department of Chemical and Biomedical Engineering, Tallahassee, Fl 23310 — A strong melt memory effect of crystallization has been observed in random ethylene copolymers even above the equilibrium melting temperature. Melt memory is associated with seeds that increase the crystallization rate of copolymers in a range of comonomer content between 0.5 and 4.5 mol%. The seeds are taken as molten ethylene sequences that remain in close proximity and are unable to diffuse fast to the randomized melt state. Fast diffusion is restricted by topological chain constraints (loops, knots, and other entanglements) that build in the intercrystalline region during crystallization. The molten nature of the self-seeds is supported by a linear variation of T_2^H with T_{melt} in NMR experiments in a range from 180 °C to 100 °C, covering both the homogeneous and heterogeneous melt regions. The effect of topological constraints on melt memory, or on number of seeds that remain in the melt, was analyzed studying copolymers with different levels of crystallinity. There is a threshold level of crystallinity, which depends on type and concentration of comonomer, below which copolymers do not display strong melt memory. Increasing 1-hexene content from 0.5 to 3.5 mol%, the crystallinity threshold decreases from 39 to 4%, while decreasing branch length from hexyl to ethyl, the threshold crystallinity decreases from 18% to 5% in agreement with stronger melt memory in copolymers with increasing comonomer content and with shorter branches.

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Date submitted: 13 Nov 2014

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