Counit Inclusion in Hydrogenated Polynorbornene Copolymer Crystals

ADAM BURNS, MICHAEL SHOWAK, ANDREW STELLA, RICHARD REGISTER, Princeton University — Crystallization in poly(A-co-B) random copolymers, where homopolymer A is crystalline but B is not, is dictated by the degree to which crystals of A can include B units. Typically, B units are strongly excluded from the A crystals, drastically reducing the degree of crystallinity \( w_c \) and crystal thickness \( t_c \) even at modest comonomer contents. However, in some cases, B units can be incorporated into the crystals as defects, significantly diminishing the counits’ impact on \( w_c \) and \( t_c \). The extent and consequences of counit inclusion have been investigated in hydrogenated polynorbornene (hPN) with alkylnorbornene counits, synthesized by living ring-opening metathesis polymerization followed by hydrogenation. In the case of 5-hexynorbornene (HxN) counits, a steep decline in \( w_c \) and \( t_c \) with counit content is found, indicative of strong exclusion. In contrast, when the counits are 5-methylnorbornene (MeN), extensive inclusion of MeN units into the crystals is observed. hP(N-co-MeN) copolymers maintain appreciable crystallinity above 30 mol\% MeN, and the dependence of the melting point \( T_m \) on \( t_c \) tracks that of the hPN homopolymer. Four times as much MeN as HxN (molar basis) is required to produce a comparable drop in \( w_c \). Therefore, copolymerization with MeN can be used to tune \( T_m \) without drastically reducing \( w_c \). Additionally, hPN exhibits a polymorphic transition to a rotationally disordered (RD) crystal at temperature \( T_{cc} < T_m \). Incorporation of comonomers increases the disparity between \( T_m \) and \( T_{cc} \), indicating that thin crystals stabilize the RD phase.

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