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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 alkyl-norbornene counits, synthesized by living ring-opening metathesis polymerization followed by hydrogenation. In the case of 5-hexylnorbornene (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.

Adam Burns
Princeton University

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