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Butyl Branch Partitioning to the Crystal Surface in Polyethylenes Detected by NMR KLAUS SCHMIDT-ROHR, Brandeis University, Department of Chemistry, Waltham, MA 02453, USA, ALLISON WHITE, Iowa State University, Department of Chemistry, Ames, IA 50011, USA, KANMI MAO, DIANA SMIRNOVA, ExxonMobil Research and Engineering, 1545 Route 22 East, Annandale, NJ 08801, USA — Short-chain branches have pronounced effects on the structure and properties of semicrystalline polyethylenes. Distinct partitioning of butyl branches in high- and linear low-density polyethylenes (HDPEs and LLDPEs) synthesized with hexene comonomers has been detected by solid-state ^{13}C NMR. In mobility-selective ^{13}C NMR spectra, distinct signals of mobile amorphous and of trans-rich immobilized branches are observed, the latter with longer ^{13}C spin lattice relaxation times and limited mobility. This analysis takes advantage of double inverse filtering, which provides the signals of limited-mobility noncrystalline segments selectively. The location of the dynamically constrained branches near the crystal surface has been confirmed by ^{1}H spin diffusion measurements. The fraction of immobilized butyl branches is approximately constant at about 0.5 mol% for a series of copolymers with 0.35 – 3.3 mol% hexene. It is close to the percentage expected if one surface site is freely available for each crystalline chain stem. Lower molecular weight appears to enable better ordering of branches at the crystal surface. Further, it more strongly limits a fast-relaxing component in ^{13}C spin-lattice relaxation of the crystalline signal that can be attributed to chain diffusion. In a HDPE with 0.35 mol % hexene content, nearly all branches are at the crystal surface.

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