Structure and Properties of Tactic Hydrogenated Polynorbornenes

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— Tacticity is one of the most important structural parameters for determining the physical properties of a polymer. A high degree of stereoregularity typically promotes crystallization, with different tacticities giving rise to differences in crystal structure, melting point, and degree of crystallinity. In polynorbornene (PN) made by ring-opening metathesis polymerization (ROMP), tacticity is determined by the relative configuration of the nonplanar cyclopentylene rings enchained in the backbone. Traditional ROMP initiators yield atactic polymers (aPN); however, recent advances in catalyst design have produced both isotactic and syndiotactic PN. Newly reported cis,isotactic- and cis,syndiotactic-PNs were catalytically hydrogenated (abbreviated ihPN and shPN, respectively) without altering the tacticity. The thermal and structural characteristics of ihPN and shPN were studied by differential scanning calorimetry (DSC) and wide-angle x-ray scattering (WAXS) and compared to that of ahPN. Remarkably, all three polymers are semicrystalline, each with a distinct crystal structure. ihPN has a nominal melting point of 165 °C, more than 20 °C above that of ahPN. WAXS patterns of melt-drawn fibers of ihPN show few strong reflections indicative of either a highly symmetric unit cell or poor long-range order. ihPN fibers also exhibit a crystal-crystal transition near 130 °C, which is not fully reversible on subsequent cooling. On the other hand, shPN has a nominal melting point some 15 °C below that of ahPN, and shPN fibers show no evidence of polymorphism.