## **Supporting Information**

## Elucidation of the Chain-Folding Structure of a Semi-Crystalline Polymer in Single Crystals by Solid-State NMR

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Materials. <sup>13</sup>C CH<sub>3</sub>-labeled butene-1 and butene-1 were purchased from CDN Isotopes, Ltd., and Matheson, Ltd., respectively. Strum Chemicals provided the rac-Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub> catalyst. Toluene was distilled from sodium and benzophenone under a nitrogen atmosphere. iPB1 was synthesized using rac-Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub> and methylaluminoxane (MAO, [Al]=10 wt% in toluene) as a cocatalyst (commercial product from Aldrich). During polymerization, 20 µmol of catalyst in 1 ml of distilled toluene was dispersed in the solution. A Varian INOVA 400 NMR was used to determine the tacticity of pure iPB1 in 1,1,2,2-tetrachloroethane-d<sub>2</sub> at 120 °C. In the <sup>13</sup>C NMR spectrum, the side-chain CH<sub>2</sub> signal was used to determine the tacticity: mmmm = 96.6 and 96.0% for <sup>13</sup>C-labeled and non-labeled *i*PB1, respectively. The molecular weights of <sup>13</sup>C-labeled and non-labeled *i*PB1 were determined to be 37,002 and 36,153 g/mol, respectively, by PolymerChar GPC-IR at 140°C in 1,2,4-trichlorobenzene. The <sup>13</sup>Clabeled *i*PB1 was blended with non-labeled *i*PB1 in various compositions and dissolved in a *n*-butanol and amyl acetate mixed solvent with a weight ratio of 9:1, respectively, and amyl acetate solvent at 90 °C. Hexagonal single crystals were prepared in the former at 60 °C for 1 and 24 h. To avoid stacking of numerous single crystals, the formers were used for TEM and AFM experiments. Rounded crystals were prepared by rapidly pouring the latter into the excess and same solvent controlled at ~ 0 °C. <sup>13</sup>C direct polarization (DP) MAS NMR spectra revealed that the crystallinity of the *i*PB1 single crystals was 73 and 70% at 60 and ~ 0 °C, respectively (Fig. S5). Based on the heights of the single crystals, the crystal thickness and amorphous loop length were determined to be 4.7 and 0.9 nm, respectively.

SS-NMR experiments. SS-NMR experiments were performed on a BRUKER AVANCE III 300 equipped with 4

mm double resonance MAS probe. The carrier frequencies for <sup>1</sup>H and <sup>13</sup>C were 300.1 and 75.5 MHz, respectively. The sample volume was limited to 12 µl to maintain rf pulse homogeneity. The PostC7<sup>1</sup> sequence was used for exciting <sup>13</sup>C-<sup>13</sup>C DQ signals at a MAS frequency of 5102 Hz at ambient temperature. A PostC7 pulse with a field strength of 35.7 kHz was used to excite <sup>13</sup>C-<sup>13</sup>C DQ signals. High-power two-pulse phase modulation and continuous wave decoupling with a field strength of 104 kHz were used during the acquisition and recoupling periods, respectively. A <sup>1</sup>H spin-locking filter with a field strength of 62.5 kHz for 10 ms was used to suppress the amorphous contribution to the SQ and DQ signals. The cross polarization time and recycle delay were 1 ms and 2 s, respectively. Chemical shift was referenced to the CH signal of the external reference adamantane at 29.46 ppm. Numerical spin dynamics simulation was performed using SPINEVOLUTION.<sup>2</sup>

AFM and TEM experiments. An Icon<sup>®</sup> atomic force microscope (Bruker Nano) operating in tapping mode under ambient conditions was used to observe the morphology and measure the size of single crystals with a typical scan size of 50  $\mu$ m, a scan rate of 1 Hz, an operating frequency between 250 and 350 kHz, and a resolution of 512. A JEM-100CX II transmission electron microscope with an accelerating voltage of 120 kV was used to examine crystal morphology on the nanometer scale.



Figure S1. AFM image (up) and thickness (bottom) of isolated *i*PB1 Form I single crystal. The height of the hexagonal single crystal crystallized at  $T_c = 60$  °C for 1h is ca. 6.5 nm.



**Figure S2.** Schematic illustration of chain-folding structures and definition of chain-folding fraction,  $F = (\sum_{i=1}^{l} (n_i + 1) / N)$  using multiple cluster number, *l*, chain-folding number, *n*<sub>i</sub> in each cluster, and all stem number of *N* per a chain.



**Figure S3.** Calculated DQ sub build-up curves of different spin topologies. Individual build-up curves  $(q_{m_j})$  of (A) 2(pink), (B) 3(yellow), (C) 4(red), (D) 5(blue), (E) 6(green), and (F) 7(sky blue) spin systems of <sup>13</sup>C 35% labeled CH<sub>3</sub> *i*PB1 in different spin topologies being shown as black curves. (G) Each colored lines represent the summations of different spin topology weighed by  $w_{m_j}$  in *m* spin system ( $\Sigma w_{m_j} q_{m_j}$ ) and (H) DQ curves of individual *m* spin systems weighting by  $P_m$ (( $\Sigma w_{m_j} q_{m_j}$ )  $P_m$ ).



**Figure S4.** DQ NMR of *i*PB1 at  $T_c = 60$  °C and CFII models with superfolding. (A) sn = 1 with F = 85% (blue) and (B) sn = 2 with F = 80% (green).



**Figure S5.** <sup>13</sup>C DPMAS NMR spectrum of the CH<sub>3</sub> region of *i*PB1 measured at 60 °C. Using Lorentzian functions, best-fit peak to the crystalline and amorphous peaks determines crystallinity to be (A) 73% at  $T_c = 60$  °C and (B) 70% at  $T_c = \sim 0$  °C.

## References

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- (2) Veshtort, M.; Griffin, R. G. J. Magn. Reson. 2006, 178, 248-282.