Electronic Supplementary Information for

Controlling Crystal Polymorphism of Isotactic Poly(1-butene) by Incorporating Long Chain Branches

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1. Experimental Section

Materials: Highly isotactic polybutene-1 was purchased from LyondellBasell Company (Grade Name: Akoalit PB 4268; MFR = 0.60 g (10min)⁻¹ (190 °C (2.16 g)⁻¹); M_w = 750 kg mol⁻¹, M_w / M_n = 5.73; density = 0.925 g cm⁻³), and used without further purification.

Irradiation and sample preparation: In a glovebox under argon atmosphere ($[O_2] < 50$ ppm), pellets of isotactic polybutene-1 were placed in glass bottles (250mL), sealed with GL45 blue screw caps, then irradiated at an ambient temperature with different doses in a ⁶⁰Co source at Shanghai Institute of Applied Physics. After irradiation, the pellets were annealed at room temperature for 14 days, allowing the trapped radicals to react completely. After annealing, the pellets were preheated on a plate vulcanization press in a 220 mm × 220 mm × 1.8 mm sheet die (1.0 mm thin film for comparison), held between two layers of PET film and stainless-steel plates (250 mm × 250 mm) at 190 °C and 0.3 MPa for 10 min, then compressed at 190 °C and 10 MPa for 5 min. After compression, the sheet was cooled to room temperature over a 5-min period. The irradiated samples were labelled as PBX (X = dose, kGy), *e.g.*, PB400 indicates a sample irradiated at 400 kGy. For mechanical testing, a rectangular plate was cut from the sheet and recompressed into 100 mm × 10 mm × 1.8 mm sheets under the same conditions.

Gel Content Analysis: Sol- gel analysis was carried out to determine the gel content of the compressed molded sheets of gamma-irradiated iPB-1 pellets. The insoluble fraction after xylene extraction was evaluated according to ASTM D2765-01. Approximately 0.3 g of the sample was wrapped in a 120-mesh stainless-steel cage and subjected to extraction for 8 h in refluxing xylene. Samples were then dried under

vacuum at 60 °C to a constant mass and weighed. Gel content was then calculated as a ratio of final weight to initial weight of the sample multiplied by one hundred.

Molecular Characterization: Molecular characterization was performed according to the procedure described in the literatures.¹⁻⁴ The absolute molecular weight ($M_{w,LS}$), root-mean-square radius of gyration $\langle R^2 \rangle^{1/2}$, and intrinsic viscosity $[\eta]_B$ of every fraction, and polydispersity index (M_w/M_n) of the branched iPB-1 were determined at 150 °C using a Polymer Labs PL-GPC 220 high temperature gel permeation chromatography (equipped with a two-angle laser light scattering detector (TALLS), viscosity detector, and differential refractive index detector with 1,2,4-trichlorobenzene (TCB) as the solvent at a flow rate of 1.0 mL min⁻¹. Data collection was performed using Viscotek TriSEC software version 3.2 and a four-channel Viscotek Data Manager DM400. The system was equipped with an on-line solvent degassing device from Polymer Laboratories. The chromatographic columns used were three PL gel 10 μ m MIXED-B LS 300 imes7.5mm X3 columns obtained from Polymer Laboratories. All the samples used for SEC analysis were purified by extraction with hot toluene to remove the polymer gel and stabilized with 0.0125 % BHT. The injection volume used was 200 mL. The calibration was done using the polystyrene standard EasiCal PS-1 (PL Ltd.). The refractive index increment, dn/dc, was calculated from the calibrated DRI detector as 0.0965 mL g^{-1} . The contraction factor of the radius of gyration for branched macromolecules, g (Zimm-Stockmayer branching parameter), and that of the intrinsic viscosity, g', were calculated by the ratio of the root-mean-square radius or the intrinsic viscosity of the branched polymer $\langle R^2 \rangle^{1/2}_B$ or $[\eta]_B$ to that, $\langle R^2 \rangle^{1/2}$ or $[\eta]_L$, of the linear polymer with the same molecular weight:

$$g = \frac{\langle R^2 \rangle^{1/2}{}_B}{\langle R^2 \rangle^{1/2}{}_L}$$
(1)

$$g' = \frac{[\eta]_B}{[\eta]_L} \tag{2}$$

The $[\eta]_{L}$ of each fraction was calculated from a Mark – Houwink plot, using the following Mark – Houwink parameters: K of 1.95×10^{-4} dL g⁻¹ and a of 0.712, calculated for the linear iPB-1 from a polystyrene calibration :

$$[\eta]_L = K \cdot M^a \tag{3}$$

For a trifunctional randomly branched polymer of approximately equal length branches, g can be related to the number of branching points m along the molecule by:

$$g = \left[\left(1 + \frac{m}{7} \right)^{0.5} + \frac{4m}{9\pi} \right]^{-0.5} \tag{4}$$

From m, the number of LCBs per 1000 monomer units λ_{LCB} can be determined for each fraction:

$$\lambda_{LCB} = \frac{m}{M} \cdot 1000 \cdot M_M \tag{5}$$

 $M_{\rm M}$ is the molecular weight of the monomer unit and M the molecular weight of the branched polymer. The segmental molecular weight $M_{\rm S}$ can be determined from the number of LCBs per chain. As each molecule containing m branching points has 2m + 1 segments, $M_{\rm S}$ follows as:

$$M_s(M) = \frac{M}{2m+1} \tag{6}$$

X-ray Powder Diffraction (XRD) Testing: X-ray diffraction patterns were obtained with CuKa ($\lambda = 0.15418$ nm) radiation. The powder profiles were obtained with autonomous Bruker D8 Advance diffractometer performing a continuous scan at the diffraction angles $2\vartheta = 5 - 40^{\circ}$ at scanning rate of $2\vartheta = 0.02^{\circ}$ (2ϑ) s⁻¹ and total scanning step of 1750. After the first recoding for forms II and III, the tested samples were aged at least 30 days allowing a complete transformation from form II into form I and recorded again for forms I and III.

The fraction of crystals of form III (f_{III}) is calculated by equation as follows:

$$f_{III} = \frac{100 \cdot \left(A_{(110)_{III}} + A_{(201)_{III}}\right)}{\left(A_{(110)_{III}} + A_{(201)_{III}} + A_{(110)_{I}} + A_{(220 + 211)_{I}}\right)}$$
(7)

where $A(110)_{III}$ and $A(201)_{III}$ are the peak area of $(110)_{III}$ and $(201)_{III}$ reflections, and $A(110)_{I}$ and $A(220+211)_{I}$ are the peak area of $(110)_{I}$ and $(211)_{I}$ reflections, respectively.

Differential Scanning Calorimetry (DSC) Characterization: DSC measurements were performed on a TA Q2000 differential scanning calorimeter, calibrated with indium, under a flowing N₂ atmosphere. The fresh compressed samples were aged at room temperature at least 20 days and cut into 8 – 10 mg pieces for testing. The melting temperatures (T_m) for the aged samples in forms I and III and the re-melted samples in forms II and III were considered as the peak temperatures of the first and second heating curves of DSC, respectively, and were recorded at a standard heating rate of 10 °C min⁻¹. The crystallization temperatures (T_c) were considered as peak temperatures of cooling curves, and were recorded at a standard cooling rate of 10 °C min⁻¹. The glass transition temperatures (T_g) of the samples were considered as the inflection point temperatures of the second heating curves previously cooled from the melt to - 80 °C at 10 °C min⁻¹. All samples were isothermal for 3 min at the end of each step.

¹³*C*-*NMR characterization*: ¹³C NMR for measured polymers were obtained at Bruker AV 400 pulsed NMR spectrometer using o-dichlorobenzene as solvent at 140° C with 10 wt% polymer solution using 5mm probe; the data collection condition were 90 pulse angle with 6.9us, inverse gated proton decoupling, 8 s pulse delay time, 0.3 s acquisition time, 25000Hz spectral width, 5000 scans.

Tensile Strain-Stress Testing: The as-crystallized and aged samples irradiated at different doses were cut into ISO 527-2 Type 5A dumb-bell-shaped specimens with length of 75 mm, width of 42 \pm 0.5 mm, and thickness of 1.8 \pm 0.1 mm. The strain-stress testing was conducted in an Instron 5940 at a testing speed of 50 mm min⁻¹ at 23 °C. The Young's modulus was calculated from the strain at stresses of 1.5 % and 7.5 %.

References

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2. Results and Discussions

⁴ J. A. Langston, R. H. Colby, T. C. M. Chung, F. Shimizu, T. Suzuki and M. Aoki, *Macromolecules*, **2007**, *40* (8), 2712-2720.



Fig. S1. SEM image of cell morphology of linear isotactic poly(1-butene) foam prepared by super critical CO₂ assisted bed foaming process.



Fig. S2. Root-mean-square radius of gyration $\langle R_g^2 \rangle^{1/2}$ vs absolute molecular weight determined by HT-GPC+TDs.



Fig. S3. DSC melting curves of the linear and branched iPB-1 sheets in forms I and III (PB0-450 and iPB700 in thickness of 1.8 mm; PB500-600 in thickness of 1 mm), aged for 20 days after as-crystallization.



Fig. S4. DSC non-isothermal crystallization curves of the remelted linear and branched iPB-1 sheets in forms III and II.



Fig. S5. XRD profiles (a) and DSC melting (b) curves for purified soluble highly branched PB400P and PB700P films, and crosslinked PB400G and PB700G films.



Fig. S6. ¹³C-NMR spectrum for pristine and irradiated iPB-1.



Fig. S7. DSC non-isothermal crystallization curves of the remelted moderately and highly branched iPB-1 samples.



Fig. S8. Stress- strain tensile properties of the linear and branched PB0-700 sheets, as-crystallized from melt in forms II and III.



Fig. S9. XRD profiles for PB400.



Fig. S10. X-ray diffraction profiles for the as-crystallized pristine and irradiated iPB-1 sheets of 1.8 mm thickness at doses of 0 - 700 kGy, prepared by compression molding of the corresponding sheets under pressure and by fast cooling the melt to room temperature at an average cooling rate of 34 °C min⁻¹.



Fig. S11. X-ray diffraction profiles for the aged pristine and irradiated iPB-1 sheets of 1.8 mm thickness at doses of 0 - 700 kGy, prepared by aging the corresponding as-crystallized samples for 30 days, made by compression molding of corresponding sheets under pressure and by fast cooling the melt to room temperature at an average cooling rate of 34 °C min⁻¹.