Electronic Supplementary Information (ESI)

Melt Memory in Propene-Pentene Isotactic Copolymers: The Case of Defects Hosted in the Crystals.

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Experimental part

Sample of propylene-pentene copolymers (iPPC5) have been prepared with the C_2-symmetric metallocene catalyst dimethylsilyl(2,2′ -dimethyl-4,4′ -diphenylindenyl)$ZrCl_2$ shown in Chart 1, activated with methylalumoxane (MAO). This catalyst is highly isospecific and produces highly isotactic homopolymer sample and random iPPC5 copolymers containing negligible amount of stereodefects and very small amount (about 0.2 mol %) of regiodefects due to the presence of secondary 2,1-erythro propene units.

The copolymerizations were run at 25 °C in a 250 mL Pyrex reactor, agitated with magnetic stirrer, containing a toluene solution (100 mL) of the catalyst, MAO and liquid pentene.[S1] The Al/Zr molar ratio was maintained at about 1000. Propene was bubbled through the liquid phase at pressure of 2 bar and the polymerization was stopped when the propene pressure decreases at 1.8 bar. Under such conditions, total monomer conversions were lower than 10%, ensuring a nearly constant feeding ratio. The copolymers were coagulated with excess methanol acidified with enough HCl (*aq*, *conc.*) to prevent the precipitation of alumina from MAO hydrolysis, filtered, washed with further methanol and vacuum dried. Typical yields were 2-3 g.

The compositions of the samples were determined by ^{13}C NMR. In particular, the pentene concentration was determined by analysis of the resonances of CH_2 and CH carbon atoms.[S2] The NMR analysis also showed that all the copolymers present a random distribution of comonomers ($r_1 \times r_2 \approx 1$).

The average molecular masses were obtained by Gel Permeation Chromatography (GPC). All samples show narrow distribution of molecular masses with $M_w/M_n \approx 2$, typical of single-center metallocene catalysts.

A Mettler DSC-3+ apparatus (Mettler Toledo Instruments Inc., Switzerland) was used to characterize the standard thermal properties and the self-nucleation behavior of all samples. All the experiments were conducted at a rate of 10 °C/min in a nitrogen atmosphere. The procedure used for the self-nucleation experiments involved the following steps:[S3] a) The sample is heated up to a high temperature T_{max} (usually 30 - 40 °C above the melting temperature) to melt and erase any previous thermal history and all crystalline memory of the material, and is kept at T_{max} for 5 minutes. Since at T_{max} only temperature-resistant heterogeneous nuclei remain, upon subsequent cooling, the polymer will always crystallises at the same crystallization temperature T_c. b) The sample is cooled from T_{max} down to T_{min} (25 °C for the samples iPPC5-1, iPPC5-2, iPPC5-3, iPPC5-4, iPPC5-5 and -10 °C for the sample iPPC5-6) at cooling rate of 10 °C/min and crystallizes at the same temperature observed in the DSC standard measurements during cooling. This step creates a standard crystalline state. c) The sample is heated at heating rate of 10 °C/min up to a self-seeding temperature T_s, lower than T_{max}, and kept at T_s for a time t_s = 5 min. d) The sample is cooled from T_s to T_{min} at cooling rate of 10 °C/min, allowing crystallization at a temperature T_c during cooling. If the polymer has been self-nucleated at T_s, the measured crystallization temperature T_c is higher than the crystallization temperatures measured in the standard cooling run (step b). If T_s is high enough and no self-nuclei or self-seeds are left, the crystallization temperature is similar to the standard T_c. When T_s is low, the sample does not completely melt, and annealing occurs. e) The sample is heated again from T_{min} to T_{max} to melt the crystallised sample and is kept at T_{max} for 5 min to erase the thermal history, as in step a. The steps b-e are cyclically repeated for different decreasing values of the self-seeding temperature T_s that was varied with steps of 2 °C, and its range of variation was refined for each sample in order to determine the boundaries between the self-nucleation Domains proposed by Fillon et al.[S3] Starting form high values of the self-nucleation temperature T_s and decreasing T_s, the melt temperature at which the memory effect on crystallization is detected first (boundary between Domain I and Domain II). Then for further decrease of T_s the transition from Domain II into Domain III is determined at the T_s temperature at which the unmolten crystals are annealed at T_s and the annealing peak appears in the DSC melting curves upon heating in the step e.[S3-S5]

X-ray powder diffraction profiles were obtained with Ni filtered Cu Kα radiation by using an Empyrean diffractometer by Malvern Panalytical operating in the reflection geometry with continuous scans of the 2θ angle and scanning rate of 0.02 degree/s.

Samples of iPPC5 copolymer crystallised from different melt temperature T_s in the step d of the self-nucleation experiments described above were examined by WAXS. After the step d and cooling from T_s to room temperature, the samples were removed from the DSC pan and examined by WAXS. The results of these experiments are reported in the Figure 8 of the text.

The fraction of γ form, f_γ, with respect to the α form, that crystallize from the melt was evaluated from the intensity of the $(117)_\gamma$ reflection at 2θ = 20.1° of the γ form in the diffraction profiles of the samples crystallized from different seeding temperatures, with respect to that of the $(130)_\alpha$ reflection at 2θ = 18.6° of the α form, as the ratio: $f_\gamma = I(117)_\gamma/[I(117)_\gamma + I(130)_\alpha]$.

Results

WAXS profiles of samples crystallised by cooling from the melt at cooling rate of 10 °C as in the DSC scans of Figure 1B are shown in Figure S1. This corresponds to the standard crystalline state created by cooling from sufficiently high temperature at the same cooling rate of 10 °C/min.

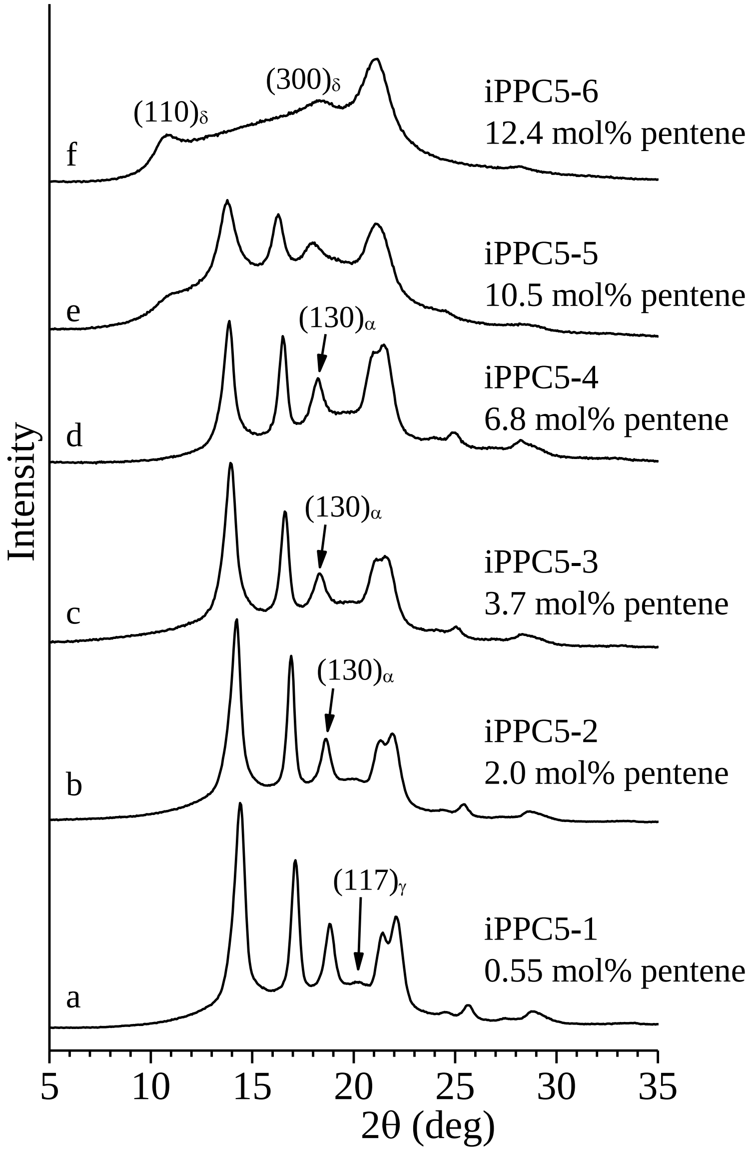

Figure S1. X-ray diffraction profiles of samples of iPPC5 copolymers samples crystallised by cooling from the melt at cooling rate of 10 °C, as in the DSC scans of Figure 1B. The $(130)_\alpha$ and $(117)_\gamma$ reflections of α and γ forms at 2θ = 18.6 and 20.1°, respectively, and the $(110)_\delta$ and $(300)_\delta$ reflections of the trigonal δ form at 2θ = 10−11° and 18−19°, respectively, are indicated.

Self-Nucleation Experiments.

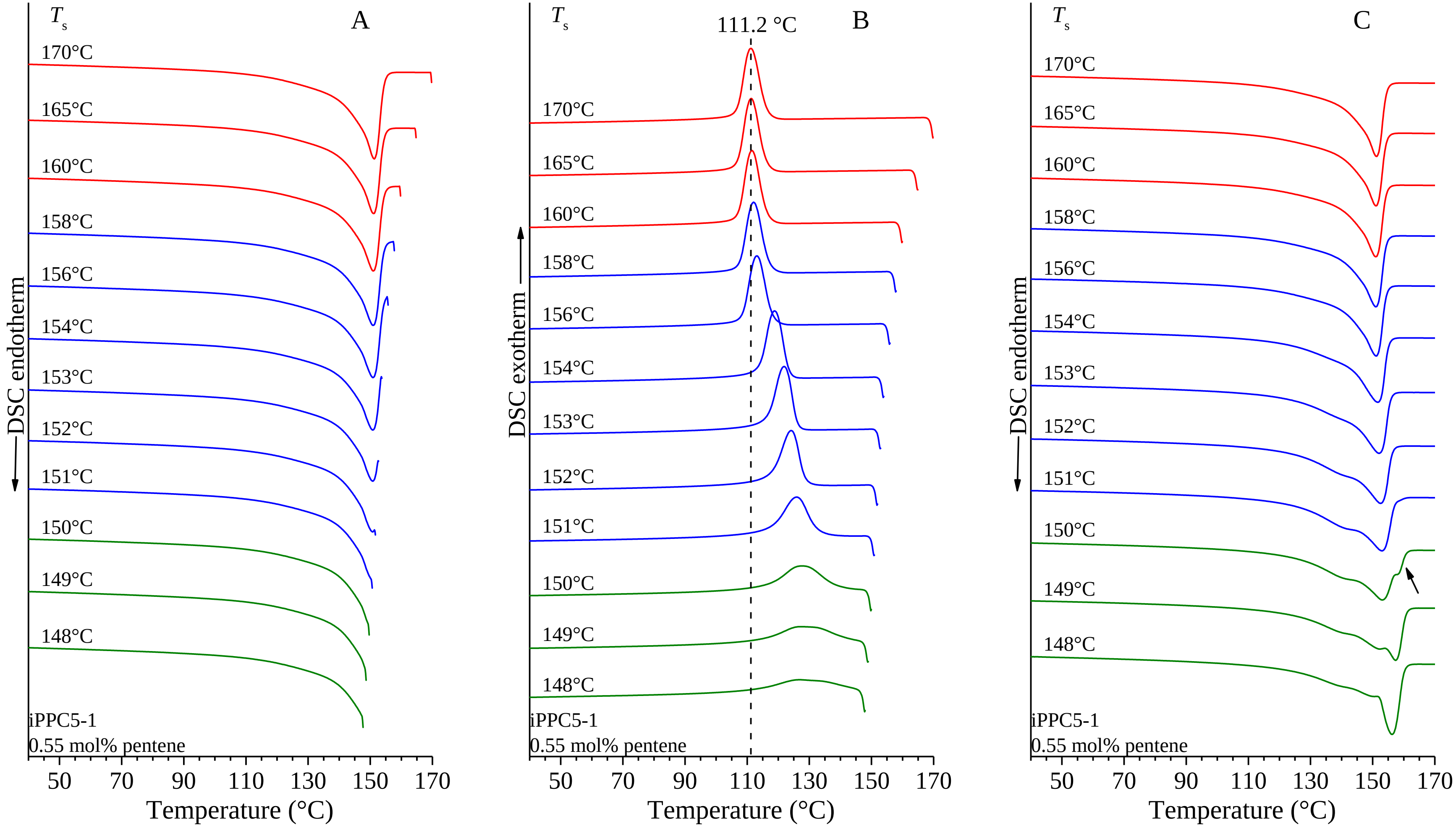

Figure S2. DSC traces recorded in the SNA experiments for the sample iPPC5-1 with 0.55 mol% of pentene, during the heating from T_{min} to different self-seeding temperatures T_s (A), successive cooling after 5 min at T_s down to 25 °C (B), subsequent heating to melt the self-nucleated crystallised or annealed samples (C). All scans are acquired at 10 °C/min. Diverse colours denote the diverse Domains I (red), II (blue) and III (green). The arrow in C denotes the annealing peak.

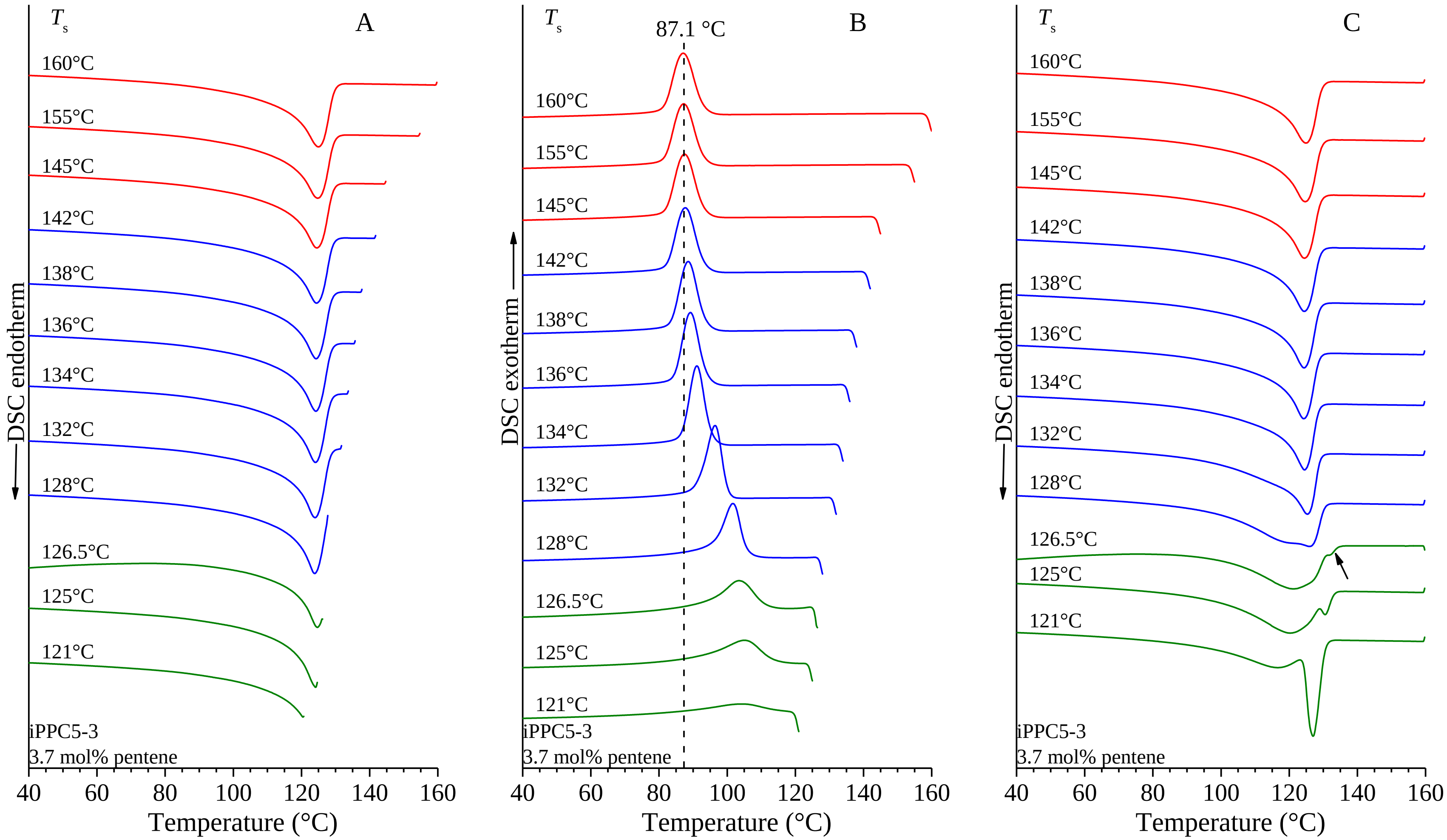

Figure S3. DSC traces recorded in the SNA experiments for the sample iPPC5-3 with 3.7 mol% of pentene, during the heating from T_{min} to different self-seeding temperatures T_s (A), successive cooling after 5 min at T_s down to 25 °C (B), subsequent heating to melt the self-nucleated crystallised or annealed samples (C). All scans are acquired at 10 °C/min. Diverse colours denote the diverse Domains I (red), II (blue) and III (green). The arrow in C denotes the annealing peak.

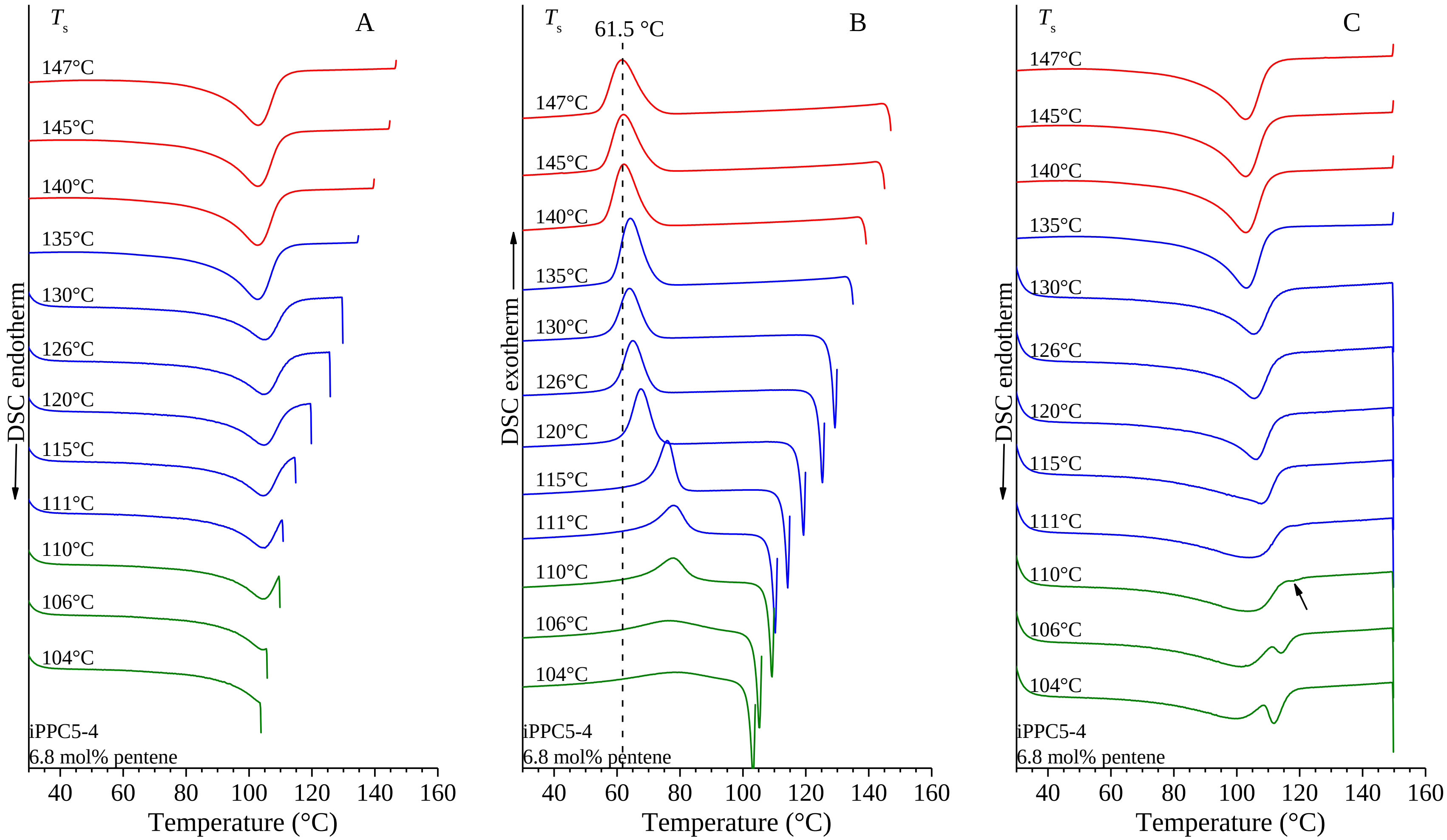

Figure S4. DSC traces recorded in the SNA experiments for the sample iPPC5-4 with 6.8 mol% of pentene, during the heating from $T_{\min}$ to different self-seeding temperatures T_s (A), successive cooling after 5 min at T_s down to 25 °C (B), subsequent heating to melt the self-nucleated crystallised or annealed samples (C). All scans are acquired at 10 °C/min. Diverse colours denote the diverse Domains I (red), II (blue) and III (green). The arrow in C denotes the annealing peak.

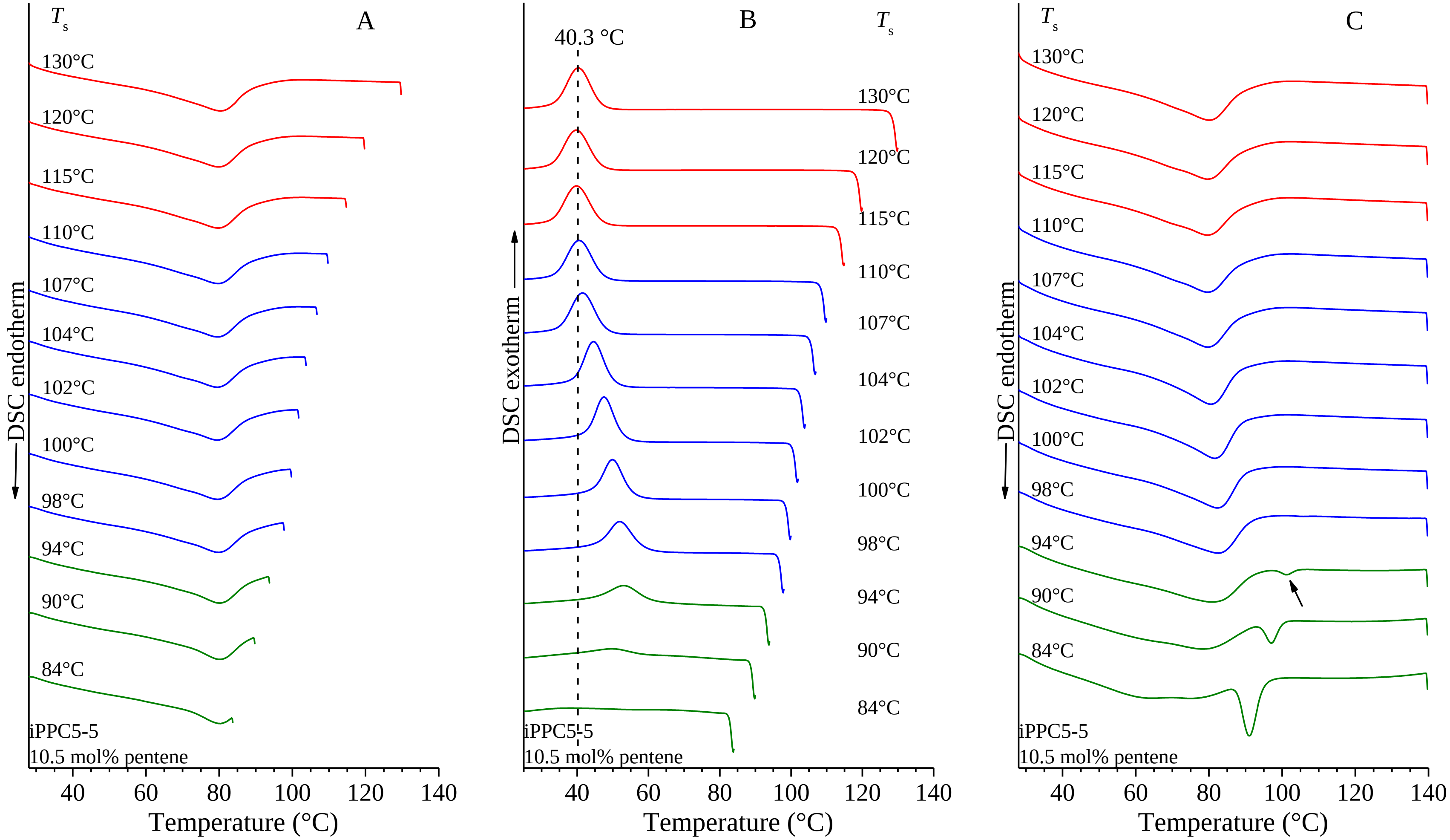

Figure S5. DSC traces recorded in the SNA experiments for the sample iPPC5-5 with 10.5 mol% of pentene, during the heating from T_{min} to different self-seeding temperatures T_s (A), successive cooling after 5 min at T_s down to 25 °C (B), subsequent heating to melt the self-nucleated crystallised or annealed samples (C). All scans are acquired at 10 °C/min. Diverse colours denote the diverse Domains I (red), II (blue) and III (green). The arrow in C denotes the annealing peak.

References

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S2) Y. V. Kissin, A. J. Brandolini, ^{13}C NMR spectra of propylene/1-hexene copolymers. *Macromolecules* 1991, **24**, 2632.

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