

Electronic Supplementary Information (ESI)

Structure and Morphology of Isotactic Polypropylene-Polyethylene Block Copolymers Prepared with Living and Stereoselective Catalyst.

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Experimental part

¹³C NMR spectra were recorded on Varian INOVA 500 MHz at 135 °C. A 90° pulse width and 25 second relaxation delay with proton decoupling were used to obtain quantitative spectra processed with MestReNova software using residual solvent peak as a reference (1,1,2,2-tetrachloroethane-*d*₂ at 73.8 ppm).

X-ray powder diffraction profiles (WAXS) were obtained with Ni-filtered CuK α radiation ($\lambda = 0.15418$ nm) with a powder diffractometer (Empyrean by Marvel Panalytical). Simultaneous time and temperature resolved wide angle X-ray diffraction (WAXS) and small angle X-ray scattering (SAXS) experiments were performed with synchrotron radiation at the Dutch-Belgian beam line BM26-Dubble of European Synchrotron Radiation Facility (ESRF) (Grenoble, France). A modified Linkam hot stage that allows the transmission of X-rays through Kapton windows has been employed to heat and cool the samples at controlled scanning rates during recording the WAXS and SAXS profiles. An acquisition time of 6 s and a delay time of 6 or 0 s were used. The wavelength of incident X-rays was $\lambda = 0.10402$ nm and the sample to detector distance was 0.27 m for WAXS and

4.58 nm for SAXS measurements. The covered range for the scattering vector $q = 4\pi \sin\theta / \lambda$ was $q = 6 - 30 \text{ nm}^{-1}$ for WAXS experiments and $q = 0.06 - 2.0 \text{ nm}^{-1}$ for SAXS experiments, where 2θ is the scattering angle.

Calorimetric measurements (DSC-822 by Mettler Toledo) were performed under flowing N_2 at heating and cooling rates of $10 \text{ }^\circ\text{C}/\text{min}$. Optical microphotographs in polarized light were taken using a Zeiss Axioscop 40 microscope provided with a Mettler FP82 hot stage. Thin films (10-100 μm thick) sandwiched between glass cover slips are melted at $\approx 200 \text{ }^\circ\text{C}$ and cooled to room temperature at 10 and $5 \text{ }^\circ\text{C}/\text{min}$.

^{13}C NMR analysis

The ^{13}C NMR spectrum of the iPP homopolymer sample prepared with the catalyst based on the pyridylamidohafnium complex (Scheme 1) and in the same experimental conditions used for the preparation of the BCPs, is reported in Figure S1. The complete assignment of resonances to different carbon atoms belonging to different stereosequences and constitutional sequences is also reported. From the intensities of resonances in the region of the methyl carbon atoms the stereoregularity of the sample has been calculated. The concentration of the fully isotactic pentad *mmmm* is 91% with the presence of defects of stereoregularity represented by *rr* triads. Statistical analysis of the methyl region revealed a 2:2:1 ratio of the intensities of resonances corresponding to the pentads *mmmr*, *mmrr*, and *mrrm*. This indicates that an enantiomorphic site-controlled mechanism of isotactic monomer enchainment was operative. Moreover, the presence of 2% of defects regioregularity represented by secondary 2,1 propene units has been detected.

This analysis indicates that the homopolymer sample is characterized by not high isotacticity produced by the pyridylamidohafnium catalyst that introduces *rr* defects of stereoregularity and 2,1 secondary units regiodefects. The low isotacticity explains the low melting temperature of $135 \text{ }^\circ\text{C}$ the iPP homopolymer sample.

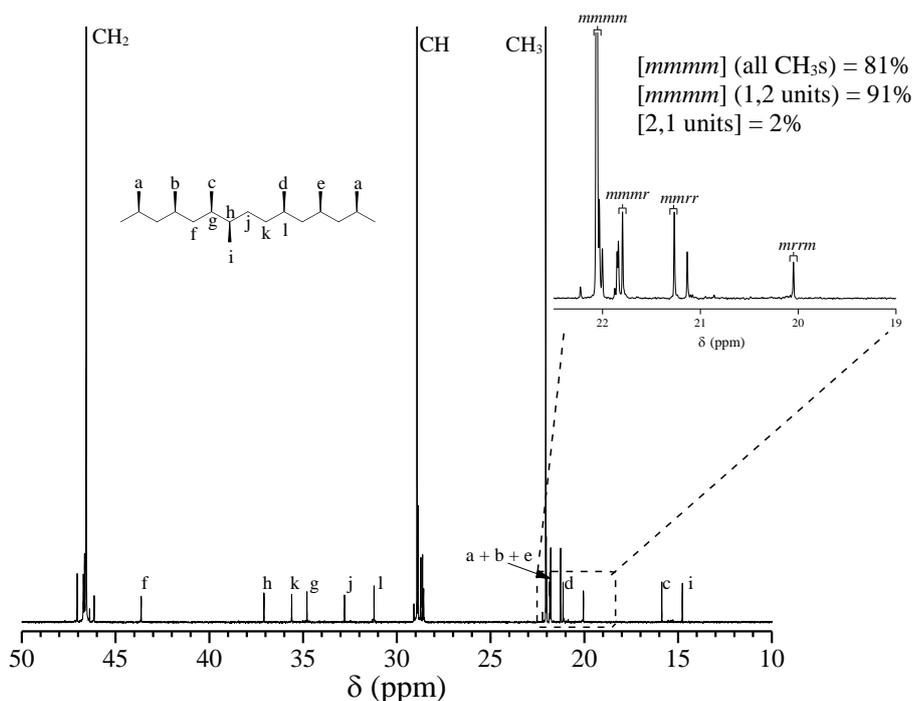
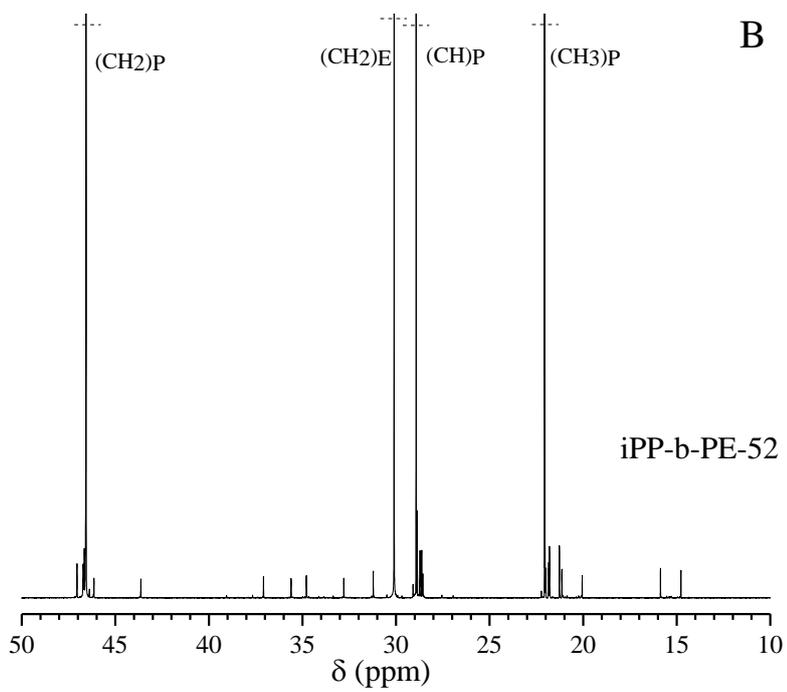
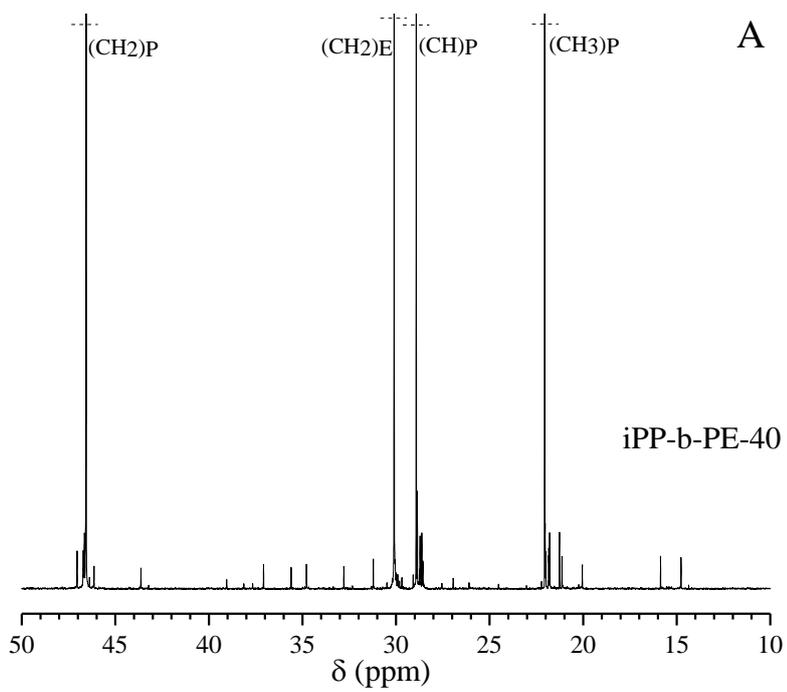
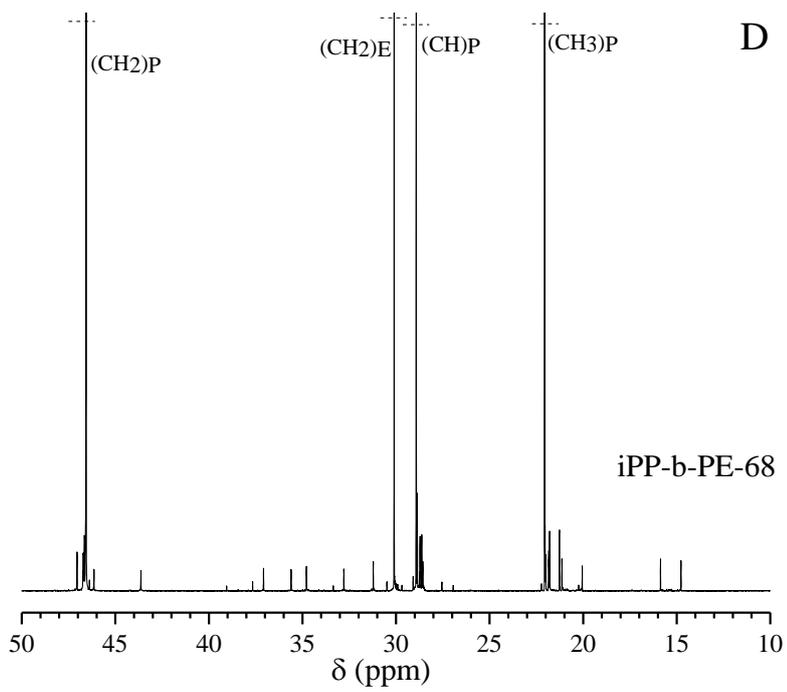
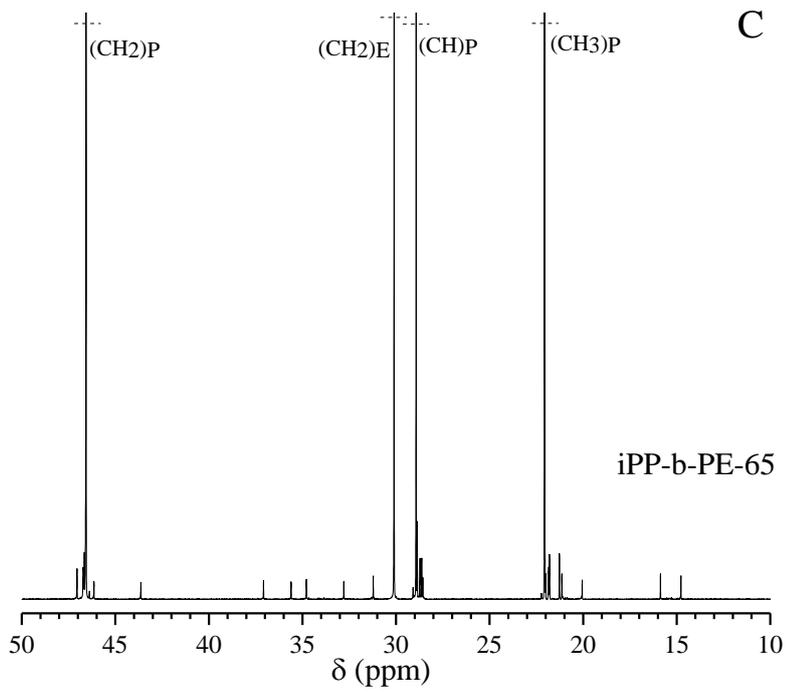


Figure S1. ^{13}C NMR spectrum of the iPP homopolymer sample.

The ^{13}C NMR spectra of the samples of iPP-*b*-PE block copolymers are shown in Figure S2. The molar fraction of the iPP block has been determined from the integrated intensities of the iPP methylene (CH_2)_P and PE methylene (CH_2)_E resonances. From the analysis of the resonances in the region of the methyl carbon atoms, a degree of isotacticity of the iPP blocks of the BCPs samples similar to that of the iPP homopolymer with $[\text{mmmm}] = 91\%$ has been evaluated. Moreover, the concentration of defects of regioregularity in the iPP blocks is also similar to that of the homopolymer (2% of 2,1 secondary propene units). The low isotacticity explains the low melting temperature of the iPP blocks of the BCP samples. The complete resonance assignment of the ^{13}C NMR spectra of Figure S1 and S2 allows excluding heterogeneity of both iPP and PE blocks since resonances associated with random ethylene-propylene sequences have not been detected. For examples, resonances due to constitutional sequences like PEPEPE at a chemical shift of 37.86 ppm and/or EPPPEPP at a chemical shift of 37.79 ppm are absent.





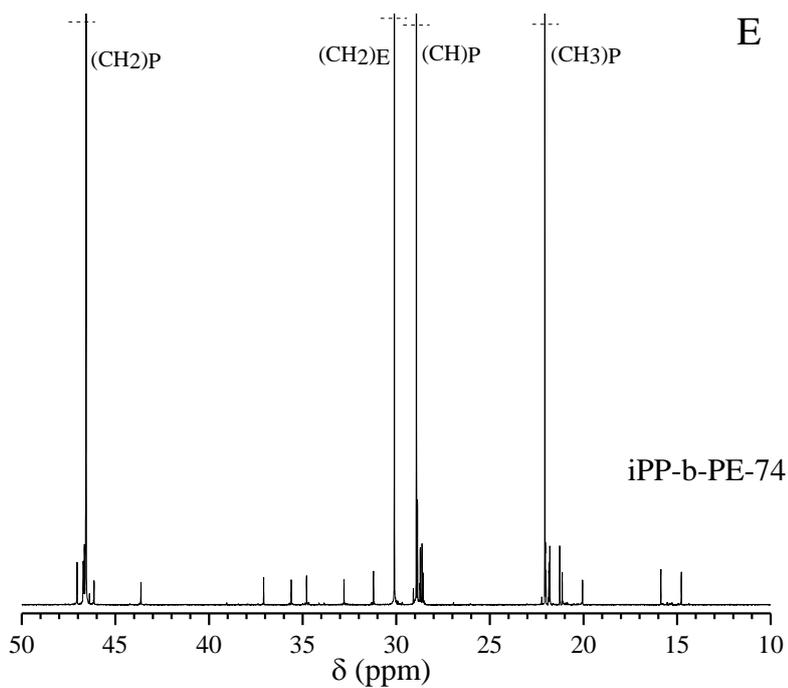


Figure S2. ^{13}C NMR spectra of *iPP-b-PE* block copolymers.

Additional DSC data

The DSC curves of samples of *iPP-b-PE* of *iPP* and *PE* homopolymers recorded at scanning rate of $2\text{ }^\circ\text{C}/\text{min}$ during first heating of the as-prepared samples, cooling from the melt to $25\text{ }^\circ\text{C}$ and successive heating of the melt-crystallized samples are reported in Figure S3.

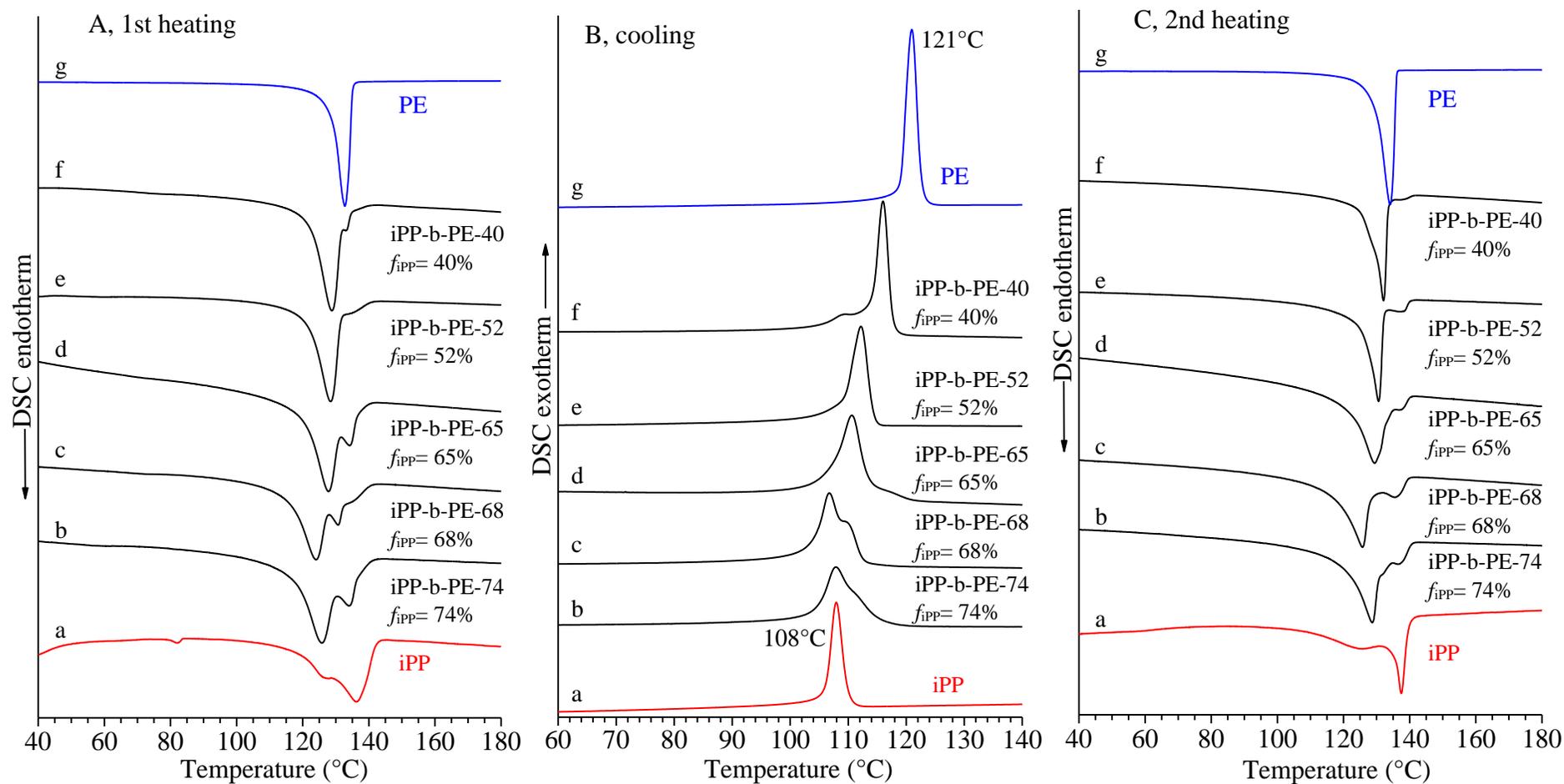


Figure S3. DSC thermograms recorded at 2 °C/min during first heating of as-prepared samples (A), cooling from the melt (B) and successive second heating of melt crystallized specimens (C) of samples of iPP (a) and PE (g) homopolymers and iPP-*b*-PE copolymers (b-f). The volume fractions of the iPP block (f_{iPP}) are indicated.