

Supplementary Material for the paper:

Melt-Crystallizations of α and γ Forms of Isotactic Polypropylene in Propene-Butene Copolymers

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1. ¹³C NMR spectra

The microstructures of all samples of propene-butene copolymers (iPPC4) have been studied with ¹³C NMR spectroscopy. All spectra were obtained using a Bruker DPX-400 spectrometer operating in the Fourier transform mode at 120 °C at 100.61 MHz (Bruker Company, Billerica, Massachusetts, USA). The samples were dissolved with 8% wt/v concentration in 1,1,2,2-tetrachloroethane-d₂ at 120 °C. The carbon spectra were acquired with a 90° pulse and 15 seconds of delay between pulses and CPD (WALTZ 16) to remove ¹H-¹³C coupling. About 1500-3000 transients were stored in 32K data points using a spectral window of 6000 Hz. For all copolymer samples, the peak of the propylene methine carbon atoms was used as internal reference at 28.83 ppm. The resonances were assigned according to ref. [110] of the main text references and the butene concentrations in the copolymers were evaluated from the concentrations of the constitutional diads PP, PB, BB (P = propene, B = butene). The concentrations of diads PP, PB and BB and the composition were obtained from the S_{αα} peaks using the following equations:

$$BB = 100S_{\alpha\alpha}(BB)/\Sigma S_{\alpha\alpha} \quad (S1)$$

$$PB = 100S_{\alpha\alpha}(PB)/\Sigma S_{\alpha\alpha} \quad (S2)$$

$$PP = 100S_{\alpha\alpha}(PP)/\Sigma S_{\alpha\alpha} \quad (S3)$$

$$[P] = PP+0.5PB \quad (S4)$$

$$[B] = BB+0.5PB \quad (S5)$$

The product of reactivity ratios $r_P \times r_B$ was determined from the diads according to ref. [111] of the main text references as:

$$r_P \times r_B = 4[PP] \times [BB]/[PB]^2 \quad (S6)$$

The NMR analysis showed that all the copolymers present a statistical distribution of comonomers and homogeneous intermolecular composition with $r_P \times r_B \approx 1$.

The ¹³C NMR spectra of some samples of iPPC4 copolymers showing the resonances assigned to the butene (B) are reported in Figure S1.

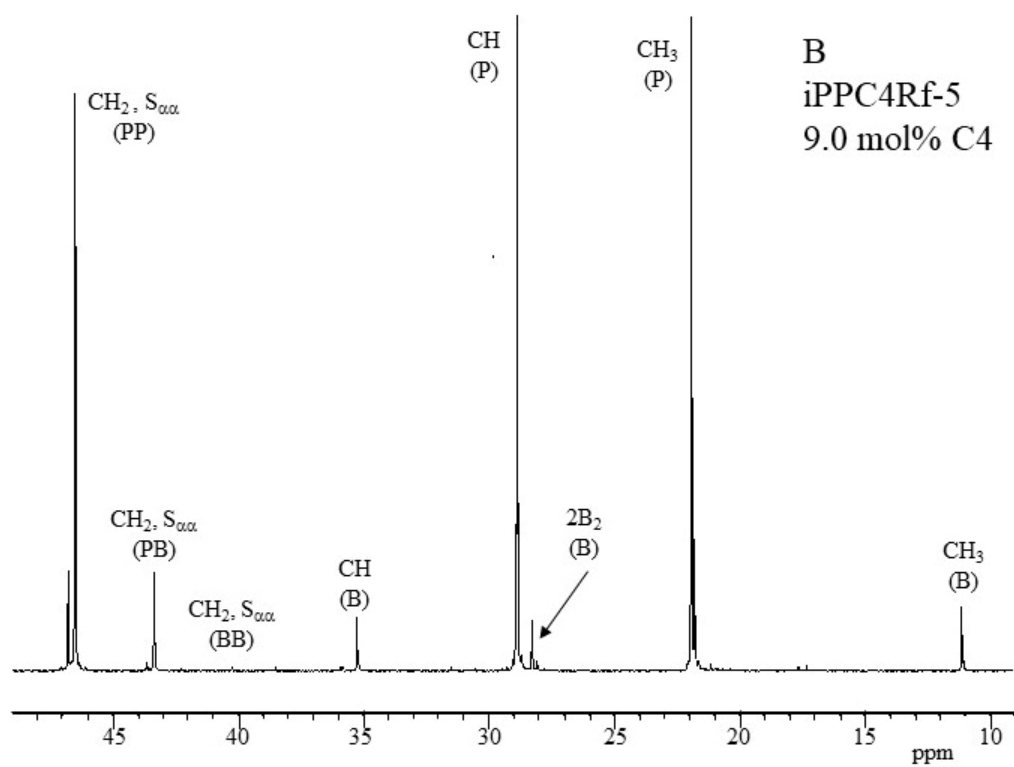
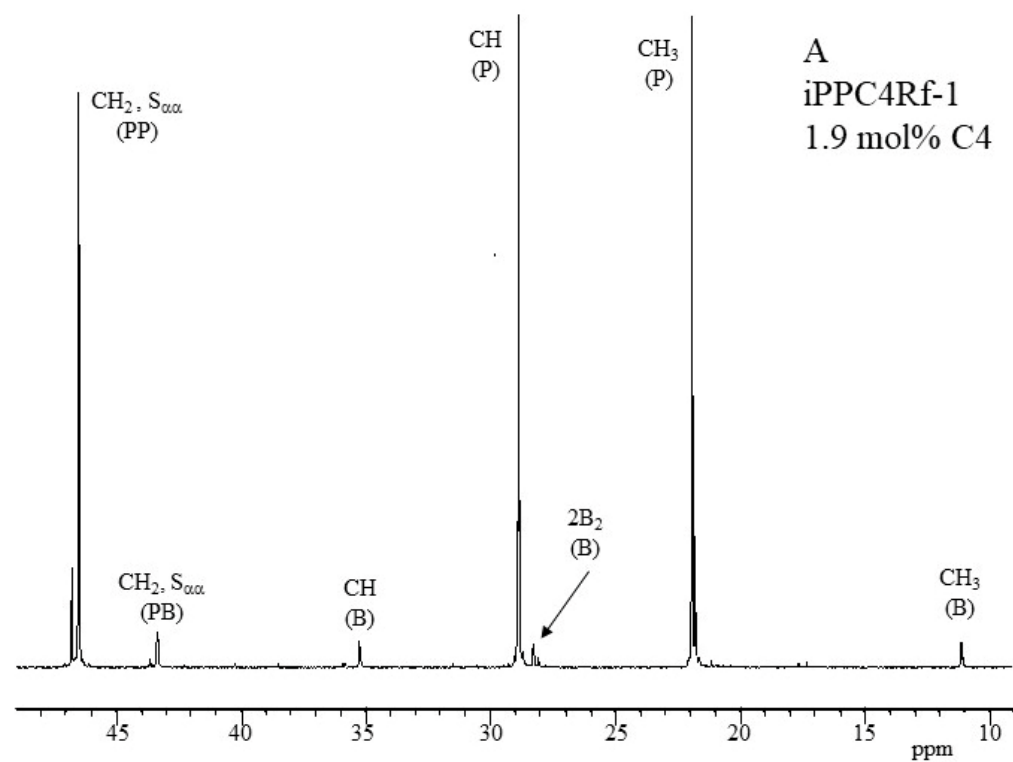


Figure S1. ¹³C NMR spectra of the iPPC4 copolymer samples iPPC4Rf-1 with 1.9 mol% of butene (A) and iPPC4Rf-5 with 9.0 mol% of butene (B). Scale is in ppm downfield of TMS.

References

110. Randall J. C. A ^{13}C NMR Determination of the Comonomer Sequence Distributions in Propylene-Butene-1 Copolymers *Macromolecules* **1978**, *11*, 592.
111. Kakugo, M.; Naito, Y.; Mizunuma, K.; Miyatake, T. Carbon-13 NMR determination of monomer sequence distribution in ethylene-propylene copolymers prepared with $\delta\text{-TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$. *Macromolecules* **1982**, *15*, 1150.