SUPPORTING INFORMATION
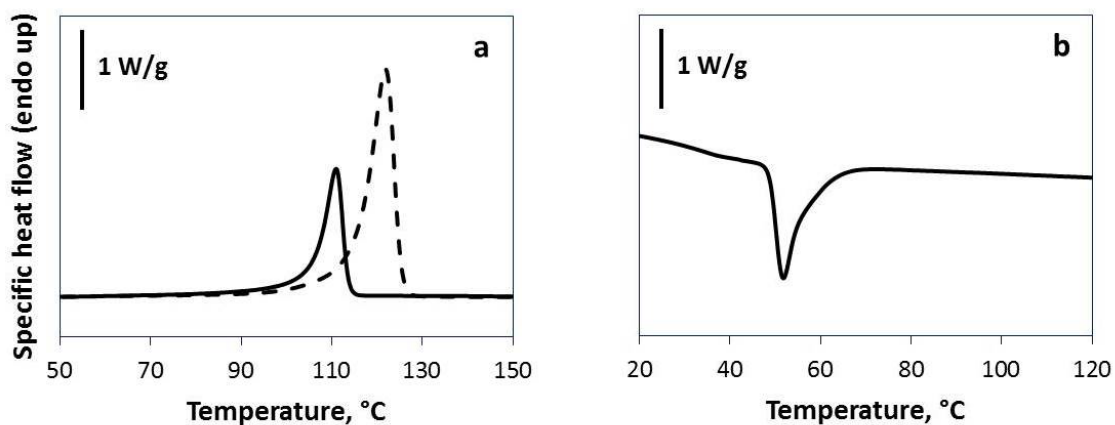
Study of the morphology and polymorphism of self-nucleated trigonal isotactic poly(1-butene) by synchrotron IR microspectroscopy

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1. **DSC characterization of isotactic poly(1-butene) sample**

Figure S.1. *DSC curves during heating/cooling of the investigated isotactic poly(1-butene) sample at 10 °C/min. (a) Melting curves of Form II (as crystallized) and Form I (fully aged) : solid and dashed lines, respectively; (b) Crystallization curve of Form II.*

2. Phase transformation experiments
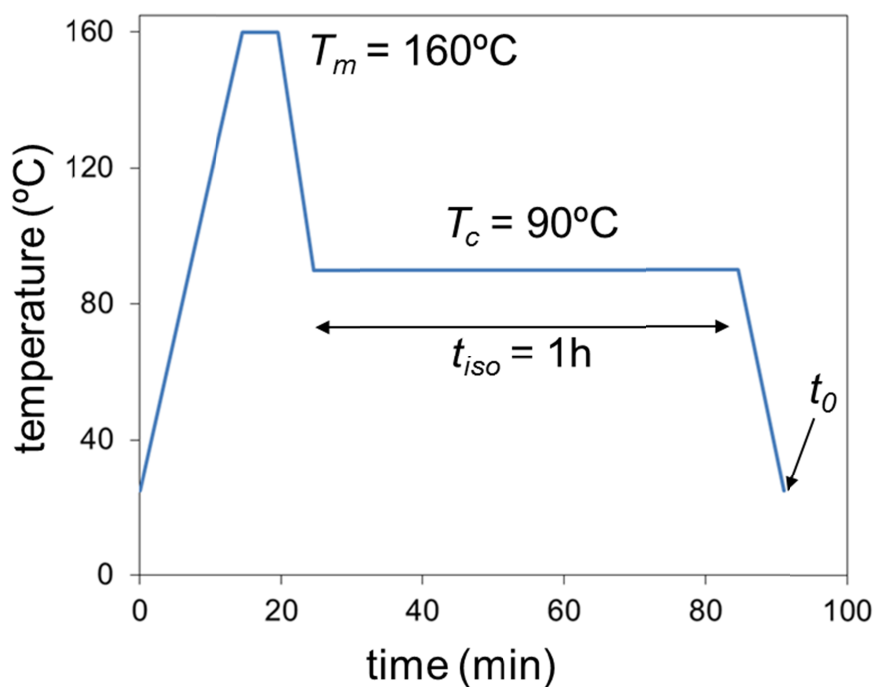
Figure S.2. *Thermal cycle corresponding to the phase transformation experiments of i-PBu in Figure 5.*

3. Hierarchical Cluster Analysis (HCA)

Cytospec software was used to perform HCA on the spectral maps[1]. Four stages were employed:

1) A second derivative was performed on the spectra recorded at each data point in order to remove long-range trends or anomalies in the spectra (such as sloping backgrounds, interference fringes, etc.).

2) Vector Normalization was performed. Here the average absorbance value was calculated for each spectrum over the spectral range $800 - 1350$ cm^{-1}, where all the spectral features were confirmed to be below the Beer limit. Each average value was then subtracted for each

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[1] See Cytospec Manual for operative details (available at www.cytospec.com)

spectrum, converting all average value in zero. Subsequently the spectra were scaled so that the sum squared deviation over the selected wavenumber range becomes unity:

$$\sum_k (x_k)^2 = 1$$

3) A Distance or Dissimilarity Matrix was calculated. This contains information on the similarity between the spectra in the dataset, and is a prerequisite for cluster analysis. The D-values correspond to the distance between two spectra j and k, d_{jk}, and were calculated using the following criterion:

$$d_{jk} = (1 - r_{jk}) \cdot 1000$$

where r_{jk} corresponds to a normalized Pearson's product moment correlation coefficient given by:

$$r_{jk} = \left[\left(\sum_{i=1}^{n} x_{ji} \cdot x_{ki} \right) - n \cdot \bar{x}_j \cdot \bar{x}_k \right] \Big/ \sqrt{\left(\sum_{i=1}^{n} x_{ji}^2 - n \cdot \bar{x}_j^2 \right) \cdot \left(\sum_{i=1}^{n} x_{ki}^2 - n \cdot \bar{x}_k^2 \right)}$$

where n is the total number of absorbance values in the spectrum, and x_{ji} and x_{ki} correspond to the i-th absorbance values for spectrum j or k, respectively.

4) HCA was performed using Wards minimum variance method[2] whereby

$$d_{i,jk} = \left[\frac{1}{n_i + n_j + n_k} \right] \cdot \left[(n_j + n_i)d_{ji} + (n_k + n_i)d_{ki} - n_i d_{jk} \right]$$

In this algorithm, the two most similar spectra are combined to form an object or "cluster" and the spectral distances between all other objects and this new object are recalculated. Then the process searches once more for the two most similar spectra or cluster, the new distance values are calculated and the process continues iteratively until a single cluster is generated.

A particularly useful tool is the possibility to extract average spectra from the generated clusters (see, for instance **Figure S.3**).

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[2] J.H. Ward: Hierarchical Grouping to Optimize an Objective Function. *Journal Amer. Stat. Ass.* 58 (1963), 236–244.
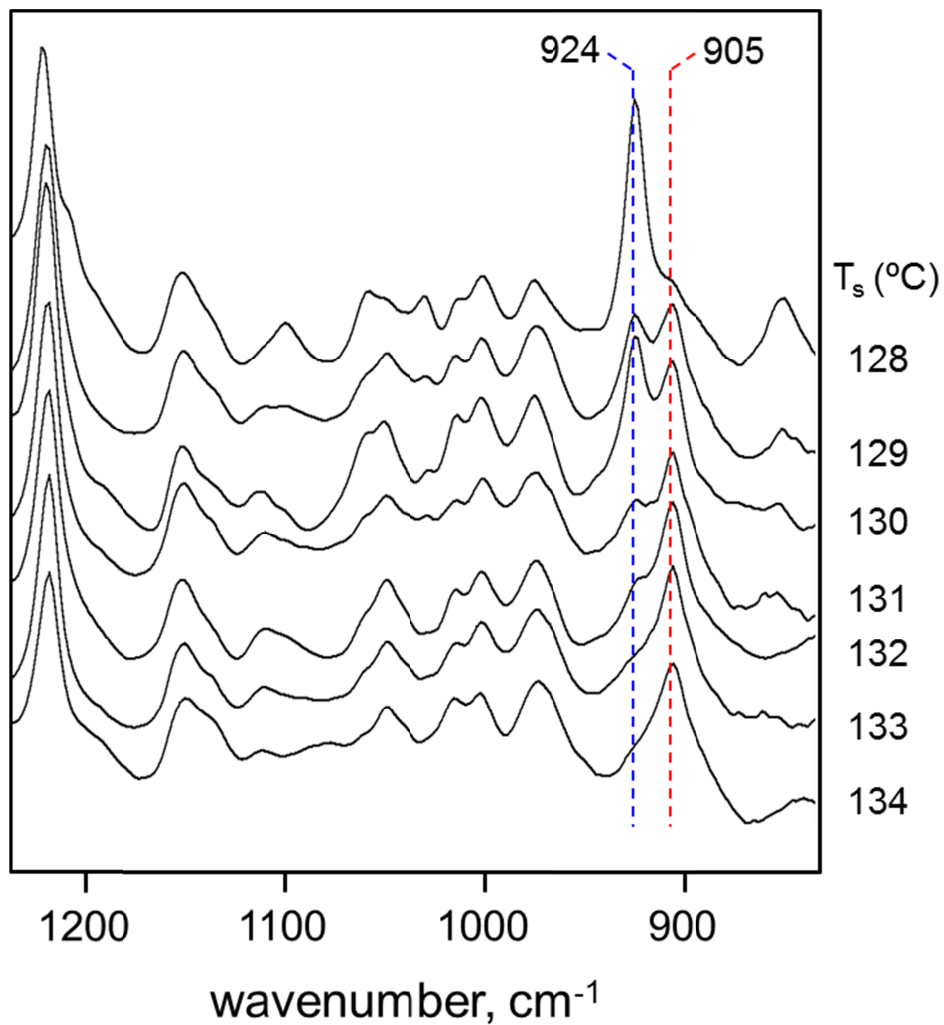
Figure S.3. *HCA average spectra obtained from the inner regions of crystalline morphologies (clusters defined in HCA analysis) as a function of seeding temperature, showing the two most characteristic bands traditionally employed for identification of Form I and Form II in i-PBu.*