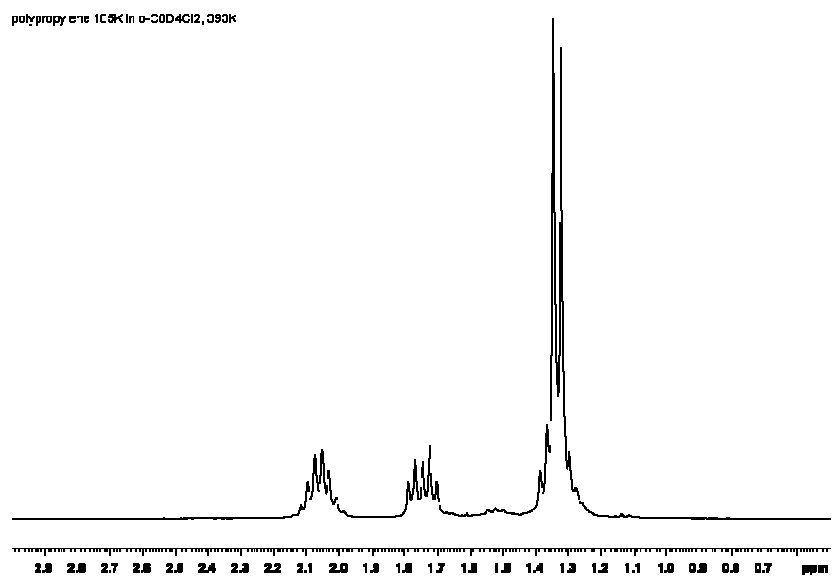


## Supporting Information

From heterogeneous to homogeneous nucleation of isotactic poly(propylene) confined to nanoporous alumina

Hatice Duran,<sup>†</sup> Martin Steinhart,<sup>||</sup> Hans-Jürgen Butt<sup>†</sup> and George Floudas<sup>\*,‡,§</sup>

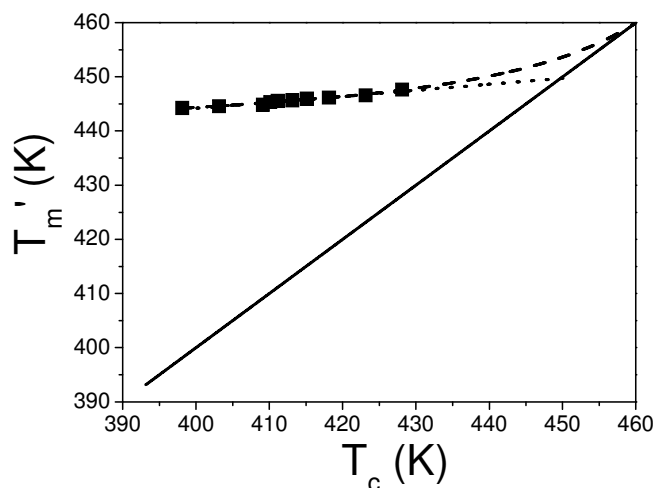
### A. Polymer tacticity



**Figure S1.** <sup>13</sup>C NMR spectra of the iPP used, recorded from *o*-C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> solutions at 393 K. The PP is highly isotactic (*mmmm* content ~99%).

**B. Polarizing Optical Microscopy (POM).** A thin film ( $\sim 30\ \mu\text{m}$ ) of the sample was placed between glasses and introduced into a Linkam THMS 600 hotplate under an Axioskop 40 FL optical microscope. Two polarizers with crossed polarization axes were placed in the light path in order to detect birefringence coming from the sample. The growth of spherulites in real time was followed under isothermal conditions at different crystallization temperatures ( $T_c$ ) in the range 393 – 428 K by capturing images with a CCD camera. The linear growth rates were thus determined. Subsequently, the corresponding apparent melting temperatures ( $T_m'$ ) were determined from the complete loss of birefringence.

**C. Equilibrium melting temperature and bulk iPP crystallization kinetics.**



**Figure S2.** Plot of the apparent melting temperature ( $T_m'$ ) versus the crystallization temperature ( $T_c$ ). The solid line has slope unity, and the equilibrium melting point ( $T_m^0$ ) is obtained in two ways: linear extrapolation following the Hoffman-Weeks equation [2] (dotted line), and a nonlinear

extrapolation using the so-called MX approach of Marand *et al.* [3] (dashed line). In the second approach, the temperature sets can be rewritten as

$$M = \gamma \left( \frac{\sigma_e^l}{\sigma_e} \right) (X + a) \quad (1)$$

where  $M = T_m^0 / (T_m^0 - T_m')$ ,  $X = T_m^0 / (T_m^0 - T_c)$ ,  $\gamma$  is the thickening coefficient,  $\sigma_e^l$  and  $\sigma_e$  refer to the fold surface free energies, and  $a = \Delta H_f C_2 / 2 \sigma_e^l$ . Herein we have followed the extensive analysis for polypropylene from ref[4], and  $\gamma$  and  $\sigma_e^l / \sigma_e$  are taken equal to unity, resulting in a fitting value of  $a = 19.8$ . The obtained equilibrium melting temperature is  $T_m^0 = 449$  K and  $T_m^0 = 461$  K, from the linear and nonlinear approach, respectively.

According to the theory of Lauritzen and Hoffman, the heterogeneous nucleation and growth of nuclei proceeds with an overall linear growth rate,  $G$  (in cm/s), that can be represented by an equation of the form

$$G = G_0 \exp \left( \frac{-E_D}{kT} \right) \exp \left( \frac{-\Delta G^*}{kT} \right) \quad (2)$$

where  $G_0$  is the growth rate constant,  $E_D$  is the activation energy for transport of crystallization units across the crystal-liquid interphase, and  $\Delta G^*$  is the free energy required to form a nucleus of critical size on the face of a crystal. Around the glass temperature, the transport term becomes strongly temperature dependent and is better described by the Vogel-Fulcher-Tammann (VFT) equation as

$$G = \frac{z}{N^\nu} \exp \left( \frac{-E}{R(T_c - T_\infty)} \right) \exp \left( \frac{-K_g}{T_c \Delta T f} \right) \quad (3)$$

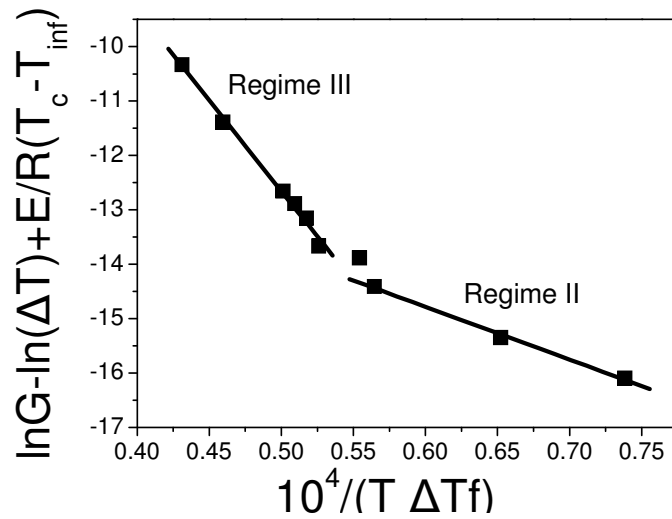
where  $\Delta G^* / kT = K_g / T \Delta T$ ,  $z$  is a parameter containing mobility terms,  $N$  is the degree of polymerization, the exponent  $\nu$  depends on the growth regime,  $T_c$  is the crystallization temperature,  $T_\infty$  is the ideal glass transition temperature,  $\Delta T$  is the supercooling ( $= T_m^0 - T_c$ ),  $f$  is a temperature

correction factor for the heat of fusion  $(= 2T_c / (T_m^0 + T_c))$ , and  $K_g$  is the nucleation rate constant, given by

$$K_g = \frac{nb_0\sigma\sigma_e T_m^0}{\Delta H_f k} \quad (4)$$

In eq. 4  $b_0$  is the width of the chain,  $\sigma$  is the lateral surface free energy,  $\sigma_e$  is the fold surface free energy,  $\Delta H_f$  is the heat of fusion, and  $k$  is the Boltzmann constant. According to the theory the variable  $n$  depends on the crystallization regime being equal to 4 for regimes I (high  $T$ ) and III (low  $T$ ) and equal to 2 in regime II (intermediate  $T$ ).

Following from equation 3, the  $\ln G - \ln \Delta T + E/R(T_c - T_\infty)$  vs  $(T_c \Delta T f)^{-1}$  representation, can be used to extract the nucleation rate constant from the slope. In the calculation we have used the  $E$  and  $T_\infty$  values obtained from the dynamic investigation (DS) as  $E=1440$  cal/mol and  $T_\infty=211$  K. There is a change from regime III to regime II crystallization. Using  $T_m^0=461$  K (Figure S3), the resulting  $K_g$  is 333600 and 97100 K<sup>2</sup> and  $\sigma\sigma_e$  is 797 and 463 erg<sup>2</sup>/cm<sup>4</sup>, and  $\sigma_e=66$  and 36 erg/cm<sup>2</sup> for the regimes III and II, respectively.



**Figure S3.** Growth rates for spherulitic growth as a function of reduced temperature plotted using  $T_m^0=461$  K.

#### **D. References**

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- (2) Hoffman, J. D.; Weeks, J. J. *J. Res. Natl. Bur. Stand.* **1962**, *A66*, 13.
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