Supporting Information for

Annealing-Induced Periodic Patterns

in Solution Grown Polymer Single Crystals

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1. Experimental Section

1.1 Synthesis of Ethylene/Ethylene-d4 Diblockcopolymer

Toluene was distilled from sodium and passed through columns of Al_2O_3 and R3-11 (BASF) before it was used as a polymerization medium. Ethylene-d4 (99 % D) was purchased from Sigma-Aldrich. Methylaluminoxane (10 wt.% MAO in toluene, AXION 1310) was kindly donated by Chemtura. MAO was evaporated to dryness in vacuum before use, to remove free $AlMe_3$. The living polymerization catalyst precursor dichloro-bis[κ^2-N,O-4-(2,6-difluorophenylimino)-1,1,1-trifluoropent-2-en-2-olato]titanium(IV) was prepared according to literature procedures.[S1]

1.1.1 Ethylene-d4 Homopolymerization

Ethylene-d4 homopolymerization was carried out in an argon purged 250 mL glass reactor (Büchi Ecoclave) equipped with a heating/cooling jacket, a mechanical stirrer and a massflow controller. Toluene (150 mL) was saturated under stirring at 25 °C with ethylene-d4 at atmospheric pressure. Subsequently, solutions of dry MAO (340 mg) and catalyst precursor (12 µmol), each in 25 mL toluene, were added to the reactor to initiate the polymerization with continuous ethylene-d4 massflow at atmospheric pressure. After 10 min the ethylene-d4 feed was closed and the polymerization was allowed to proceed for additional 10 min during which the pressure decreased to 0.6 bar. The polymerization was quenched by addition of EtOH and the reaction mixture was poured into MeOH/conc. HCl. The polymer was filtered off, washed with MeOH and dried at 50 °C in vacuum.

### 1.1.2 Ethylene/Ethylene-d4 Diblockcopolymer Synthesis

Diblockcopolymer synthesis was carried out in an argon purged 500 mL glass reactor with a bottom valve (Büchi Ecoclave) equipped with a heating/cooling jacket, a mechanical stirrer and a massflow controller. Toluene (250 mL) was saturated under stirring at 25 °C with ethylene at atmospheric pressure. Subsequently, solutions of dry MAO (610 mg) and catalyst

precursor (1 μmol), each in 25 mL toluene, were added to the reactor to initiate the polymerization with continuous ethylene massflow at atmospheric pressure. After 3 h the ethylene was removed by repeatedly evacuating and purging the reactor with argon. The second block was grown by reducing the pressure in the reactor to 0.7 bar followed by saturating the polymerization mixture with ethylene-d4 at atmospheric pressure. After 1 h the ethylene-d4 feed was stopped and the polymerization was allowed to proceed for additional 5 h during which the pressure decreased to 0.9 bar. The polymerization was quenched by addition of EtOH and the reaction mixture was poured into MeOH/conc. HCl. The polymer was filtered off, washed with MeOH and dried at 50 °C in vacuum.
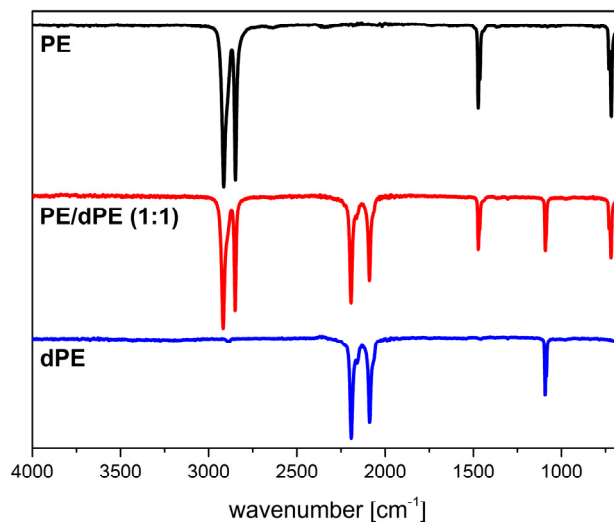
1.2 Materials Characterization

1.2.1 Nuclear magnetic resonance spectroscopy

NMR spectra of polymers were recorded on a Varian Unity INOVA 400 MHz spectrometer at 130 °C in $C_2D_2Cl_4$ with 1 mg mL^{-1} Cr(acac)$_3$.
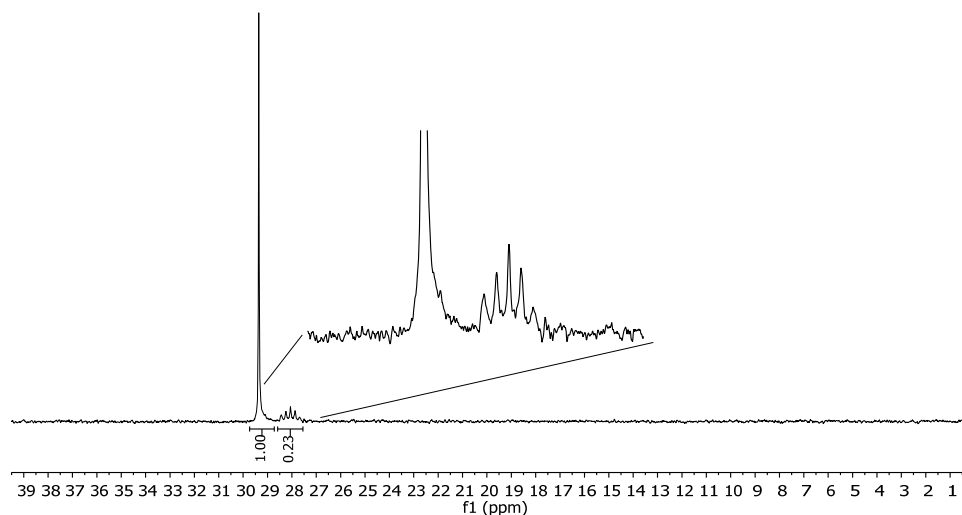
Figure S1. $^{13}C\{^1H\}$ NMR spectrum ($C_2D_2Cl_4$, 101 MHz, 130 °C) of poly(ethylene-*b*-ethylene-d4). The integral of the CD_2 signal is too low, due to slow relaxation.

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Figure S2. IR spectra of polyethylene (PE), deuterated polyethylene (dPE) and an equimolar mixture of both (PE/dPE). The CH_2 stretching vibrations (3000-2750 cm^{-1}) are by a factor of 1.15 more intensive than the CD_2 vibrations (2350-2000 cm^{-1}).

Infrared (IR) spectra were recorded on PerkinElmer Spectrum 100 FTIR spectrometer (PerkinElmer, Norwalk, CT, USA) with an ATR unit. The ethylene-d4 content of the block copolymer was determined by integration of the CH_2 (3000-2750 cm^{-1}) and CD_2 (2300-2000 cm^{-1}) stretching vibrations in the IR spectrum. Integrals were corrected according to an IR spectrum of an equimolar mixture of PE and dPE.
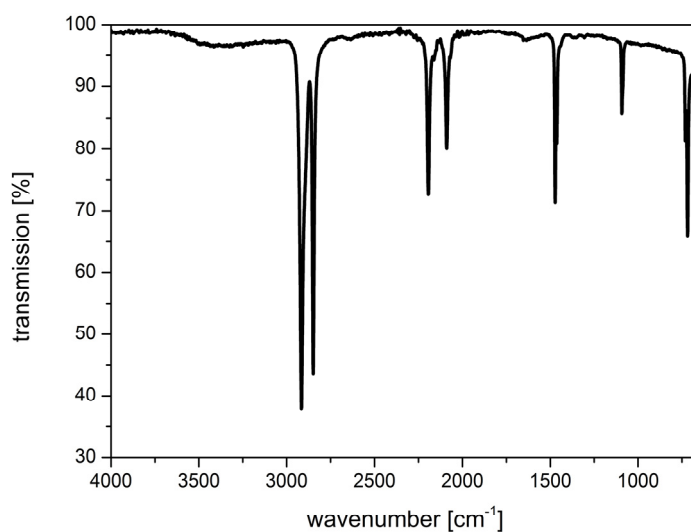
Figure S3. IR spectrum of poly(ethylene-*b*-ethylene-d4).

1.2.3 Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed on a Netzsch Phoenix 204 F1 (Netzsch, Germany) at a heating/cooling rate of 10 K min^{-1}. Polymer crystallinities were calculated based on a melt enthalpy of 293 J g^{-1} for 100% crystalline polyethylene.
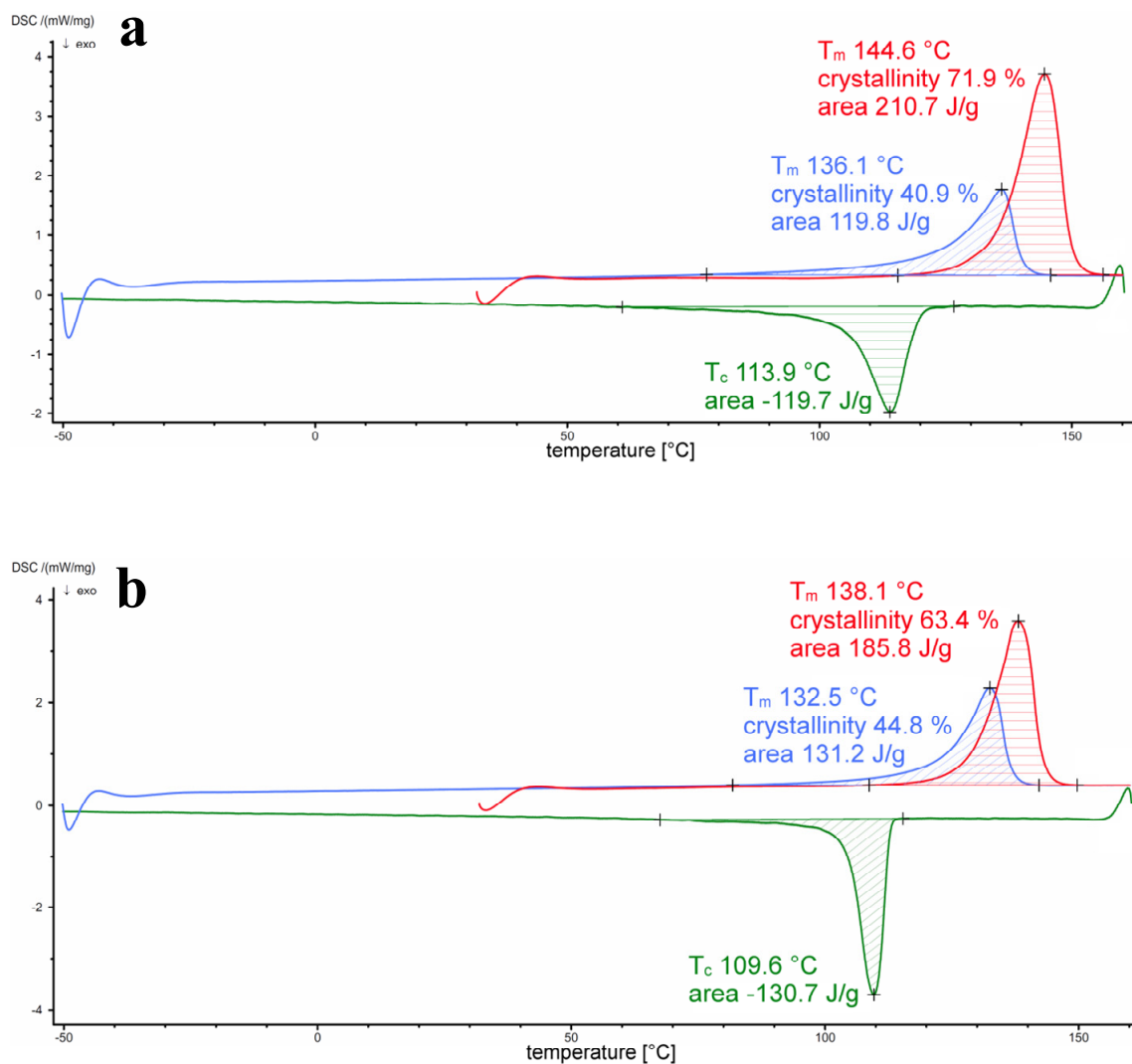
Figure S4. DSC traces (10 K min^{-1}) of (a) poly(ethylene-*b*-ethylene-d4) and (b) deuterated polyethylene.

1.2.4 Gel permeation chromatography

Gel permeation chromatography (GPC) was carried out in 1,2,4-trichlorobenzene at 160 °C at a flow rate of 1 mL min^{-1} on a Polymer Laboratories PL-GPC 220 instrument equipped with three PLgel Olexis columns with differential refractive index, viscosity and light scattering (15° and 90°) detectors. Molecular weights were calculated by the triple detection method of the Cirrus GPC multi detector software.
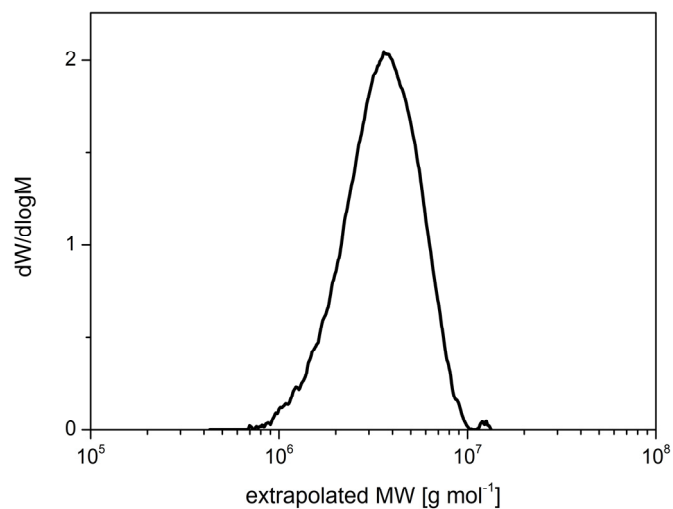
Figure S5. GPC molecular weight distribution of poly(ethylene-*b*-ethylene-d4).

2. Supplementary results, confirming the observations presented in the main text
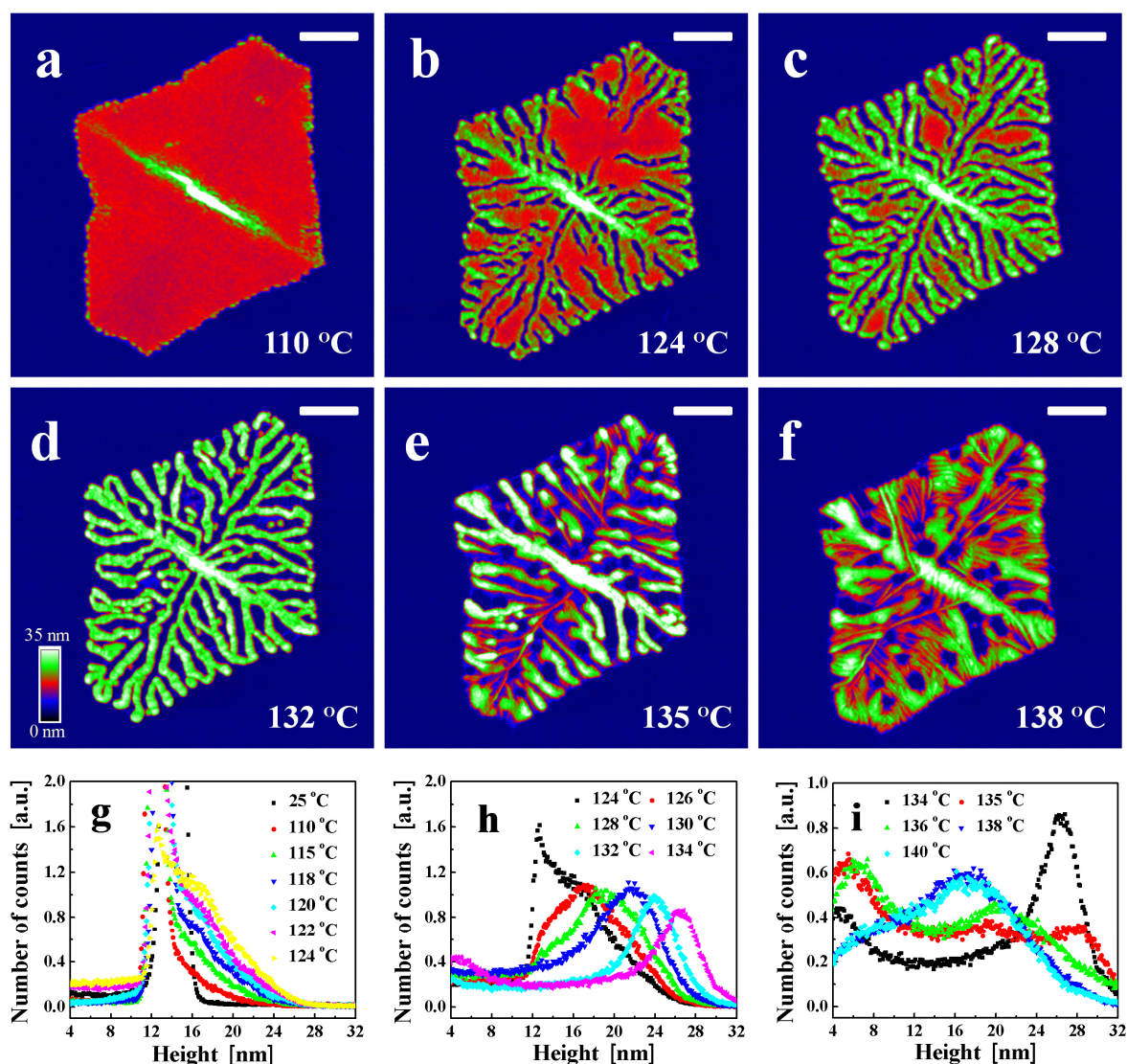
2.1 Ex-situ annealing

Upon cooling, all molten polymers re-attached to the remaining branches, making them visible again in the AFM topography images. A series of high resolution AFM high images of **PE1** single crystals were taken at room temperature after annealing at various T_a (see Figure S6). When annealing at temperatures lower than 126 °C, the morphological evolution of the annealing-induced branched pattern was obviously very similar to what has been demonstrated in the in-situ AFM images (Figure 2 of main text). Crack-like structures could be seen both in the central region and at the crystal edges after annealing at 122 °C. As shown in the AFM height image (Figure S6), when cracks touched each other, they formed a branched pattern. Transport of polymers over short distance is responsible for the changes in lamellar thickness within such single crystals occurring upon annealing.

However, upon quenching the sample to room temperature, re-crystallisation of polymers in the "partially molten state" contributes to the reorganization and thus to the morphological changes. This became particularly visible for annealing temperatures above 128 °C. It can be observed that re-crystallisation of the molten polymers is guided by the crystalline branched pattern.

Self-seeding[S2] of polymers, a memory effect of crystal structures, strongly depends on the annealing temperature. Accordingly, at high annealing temperatures only few parts of the branched structure can survive and play a role as nuclei in the present study. As shown in Figure S6e, an annealing temperature of 135 °C was enough to destroy most of the "memory" of the branched structures. With a further increase of annealing temperature

(T_a>136 °C), the peak representing the thickened part of the crystal decreased in height and shifted to about 17 nm (See Figure S6i). This phenomenon can be attributed to a complete loss of memory of crystalline polymer conformation. Consequently, random homogeneous nucleation induced crystallisation.

Figure S6: Re-crystallisation of branched morphology. A PE1 single crystal obtained by isothermal growth [(T_c, t_c) = (82 °C, 20 min)]. Height images were taken **ex-situ** at room temperature after annealing at various temperatures, increasing stepwise from 25 °C to 138 °C for a constant annealing time t_a of 20 min at each step. The size of the scale bar is 500 nm. The evolution of the thickness and thickness distribution within the crystal is shown in histogram plots for the images taken after annealing steps at various T_a: (g) 25-124 °C, (h) 124 -134 °C, (i) 134 -140 °C.

2.2 In-situ annealing

During the annealing process of the single crystal, the evolution of the thickness and the thickness distribution within the crystal is shown in histogram plots of Figure S7, allowing also to characterize the melting behavior of such lamellar crystals in a quantitative way. Three stages could be identified:

(1) At early stages, mainly observable at low temperatures ($T_a \leq 122$ °C), the lamellar thickness did not change much. However, elongated-crater-shaped valleys developed within the crystal, starting at the edges. This suggests higher chain mobility at the edges which facilitated reorganization of thermodynamically meta-stable states towards more stable states.

(2) After prolonged annealing or after short annealing at higher temperatures $T_a > 122$°C, a stage of significant partial melting and reorganization followed (Figure S7b). This was accompanied by the appearance of regions of increased lamellar thickness (17.5 nm at T_a of 124 °C, increasing to 22 nm at 128 °C). In parallel, especially for annealing at temperatures above 126 °C, the peak area of regions with the initial lamellar thickness (14 nm) decreased rapidly.

(3) At annealing temperatures above 130 °C, the lamellar thickness started to vary over a wide range. This broadening was related to the simultaneous melting of large parts of the crystal and a thickening of the remaining parts, i.e. the branches, which were reinforced (stabilized) by annealing.
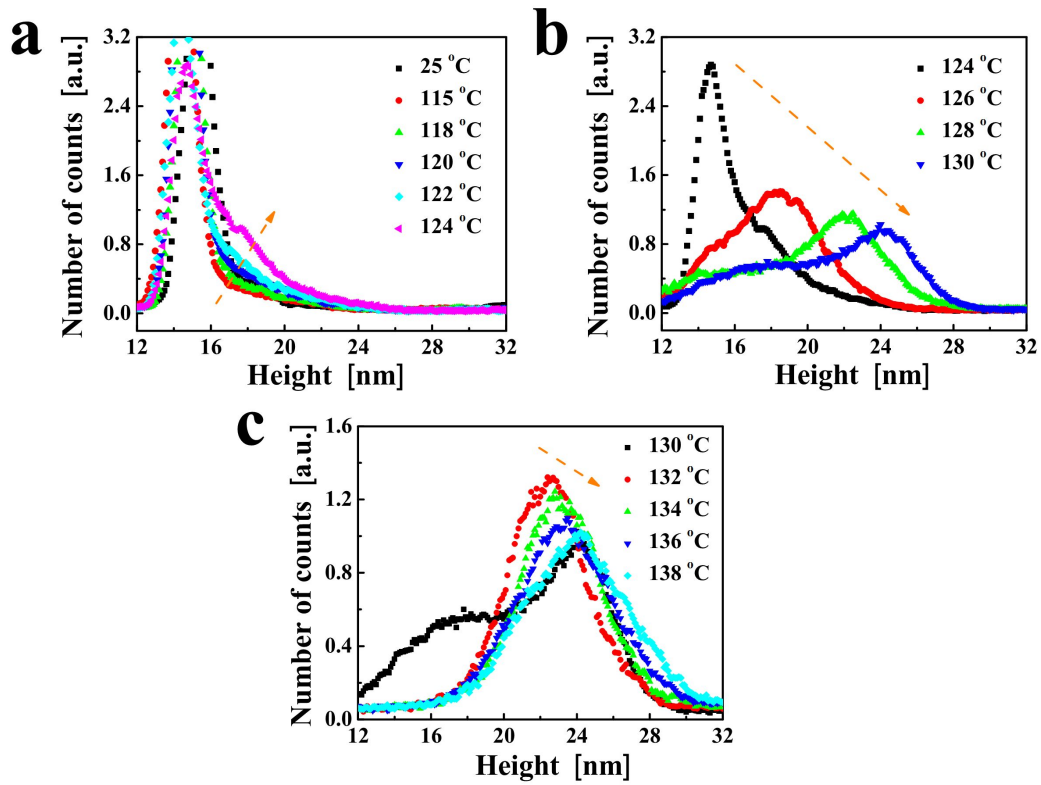
Figure S7. Height histograms obtained from AFM height images for the sample shown in Figure 2 of the main text. A **PE1** single crystal was annealed in-situ at T_a ranging from (a) 25-124 °C, (b) 124 -130 °C, (c) 130 -138 °C.

References

S1. Yu, S.-M., Mecking, S. Extremely Narrow-Dispersed High Molecular Weight Polyethylene from Living Polymerization at Elevated Temperatures with o-F Substituted Ti Enolatoimines. *J. Am. Chem. Soc.* **130**, 13204-13205 (2008).

S2. Xu, J., Ma, Y., Hu, W., Rehahn, M., Reiter, G. Cloning polymer single crystals through self-seeding. *Nature Mater.* **8**, 348-353 (2009).