

Supporting Information

Branched polyethylene mimicry by metathesis copolymerization of fatty acid-based α,ω -dienes.

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Materials and Instrumentation

Methyl 10-undecenoate (>98.0%) was supplied by TCI Europe. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), Grubbs 1st generation metathesis catalyst, ethyl vinyl ether (99%), titanium isopropoxide (99.9%), 1,12-dodecanediol (99%), lithium hydroxide (98%), lithium aluminium hydride (95%), palladium (10%) on charcoal were obtained from Sigma-Aldrich. 12-hydroxy stearic acid (99%) was purchased from Nu-Chek Prep (US).

All NMR experiments were performed at 298 K on a Bruker Avance I NMR spectrometer operating at 400MHz and equipped with a Bruker multinuclear z-gradient direct probe head capable of producing gradients in the z direction with strength 53.5 G.cm⁻¹. Size exclusion chromatography (SEC) analyses were performed in THF (40°C) on a PL-GPC 50 plus Integrated GPC from Polymer laboratories-Varian with a series of four columns from TOSOH (TSKgel TOSOH: HXL-L (guard column 6,0mm ID x 4,0cm L); G4000HXL (7,8mm ID x 30,0cm L); G3000HXL (7,8mm ID x 30,0cm L) and G2000HXL (7,8mm ID x 30,0cm L)). The elution of the filtered samples was monitored using simultaneous refractive index and UV detection. The elution times were converted to molar mass using a calibration curve based on low dispersity (M_w/M_n) polystyrene (PS) standards. Differential scanning calorimetry (DSC) thermograms were measured using a DSC Q100 apparatus from TA instruments. Polymer samples were first heated from -100°C to 130 °C, subsequently cooled from 130°C to -100°C and then the melting points were calculated from a second heating run. All runs were performed at a rate of 10 °C.min⁻¹. Modulated DSC analyses were done from -100°C to

100°C after the sample was kept at 100°C for 3 minutes to erase the thermal history of the polymer. The analysis was performed at a rate of 3°C.min⁻¹ with a modulation amplitude of 0.64 °C and a modulation period of 60 s. Thermogravimetric analyses (TGA) were performed on TGA-Q50 system from TA instruments at a heating rate of 10 °C.min⁻¹ under nitrogen atmosphere from RT to 700°C. X-ray diffraction patterns at wide angles (WAXS) were obtained with a microfocus rotating anode X-ray source giving radiation of 1.5418 Å (Rigaku MicroMax-007 HF) combined with performant multi-layers optics and a 3-pinholes collimation that provide an intense X-ray intensity on the sample. The sample, mounted on X-Y stage, was held in a Lindemann capillary and placed in an oven providing a temperature control of 0.1 K. A 2-dimensionnal detector (Image plate from Mar Research) was collecting the scattered radiations. Calibration of the sample-detector distance was performed using silver behenate as a reference.

Synthesis of monomers

Linear α,ω -diene monomer (L). Compound (L) was prepared using methyl 10-undecenoate (15 g, 75.6 mmol) as two molar equivalents and 1,12-dodecanediol (7.65g, 37.8 mmol), representing one equivalent in terms of reactive functions. The reaction was catalyzed by Triazabicyclodecene (TBD) using a 5% mol ratio regarding 10-methylundecenoate. The mixture was flushed with nitrogen at 120°C for 6 h. Then, for the last 2 h, the nitrogen flux was substituted for vacuum. The reaction was eventually stopped and the compound was isolated by (recrystallization at 50°C in dichloromethane) and then on silica-gel column eluted with a mixture of cyclohexane/ethyl acetate (80/20). The process resulted in the isolation of compound (L) as a white solid in 61% yield (12.4 g).

Branched α,ω -diene monomer (B). The 12-hydroxy stearyl alcohol first had to be reduced from its carboxylic acid version, the 12-hydroxy stearic acid. This reaction was carried out using 10 g (33 mmol) of 12-hydroxy stearic acid and 3 molar equivalents of LiAlH₄ (3.79 g,

100 mmol) catalyst. The 12-hydroxy stearic acid was first dissolved in 100 mL of dry THF, and LiAlH_4 was slowly dissolved in 300 mL. The reaction flask with LiAlH_4 was put in an ice bath and the dissolved 12-hydroxy stearic acid was slowly added. The mixture was stirred for 16 h under nitrogen, then the ice bath was removed and the mixture was refluxed at 70°C for 6 h. Distilled water was added to deactivate the remaining hydride followed by 400 mL of 1N HCl. The synthesized compound could not be isolated using a silica-gel column, whatever the solvents or the proportions involved. The 12-hydroxystearic acid was separated from the 12-hydroxystearyl alcohol using Lithium hydroxide in THF. 12-hydroxystearic acid precipitated by forming a complex with the lithium ion whilst on carboxylate form. The 12-hydroxystearyl alcohol is still soluble in THF and can be isolated by simple filtration. Then, compound (**B**) was synthesized by transesterification using 10-methylundecenoate (6.39 g, 32.2 mmol) as 2.5 molar equivalents and 12-hydroxystearyl alcohol (4.37 g, 12.9 mmol) as one molar equivalent. The same conditions were used for the reaction than for compound (**L**) except the catalyst which was substituted by 0.2mol% of titanium isopropoxide. Compound (**B**) was isolated using silica-gel column eluted with a mixture of n-heptane/ethyl acetate (95/5). The process resulted in the isolation of compound (**B**) as a viscous liquid with a 99% purity determined by gas chromatography.

Polymerization reactions

The copolymers were synthesised by ADMET polymerization using monomers (**B**) and (**L**) in various amounts. Each reaction was catalyzed using first generation Grubbs metathesis catalyst at 1mol%. The reaction was carried out at 85°C for 8h, and vacuum was constantly applied to remove the ethylene formed during the polymerization. The reaction medium was then solubilized in THF and deactivated using ethylvinyl ether. $^1\text{H-NMR}$ and SEC (in THF) analyses of the resulting polymers showed almost quantitative conversion of the monomers as evidenced by the absence of corresponding peaks (terminal olefins in $^1\text{H-NMR}$) and traces (in SEC). Each polymer was then precipitated in methanol and dried to remove solvent traces.

Hydrogenation of the polyesters

Unsaturation in between polymer units were hydrogenated by solubilizing each polymer in toluene with a 15 mL ratio for 500 mg of polymer. The Palladium on charcoal catalyst was added with a 50 mg ratio for 500 mg of polymer. The reaction was carried out under 50 bar H_2 at 80°C for 20h. The resulting solution was filtered on Celite to isolate the saturated polymer after removal of the solvent under reduced pressure.

Additional tables and figures

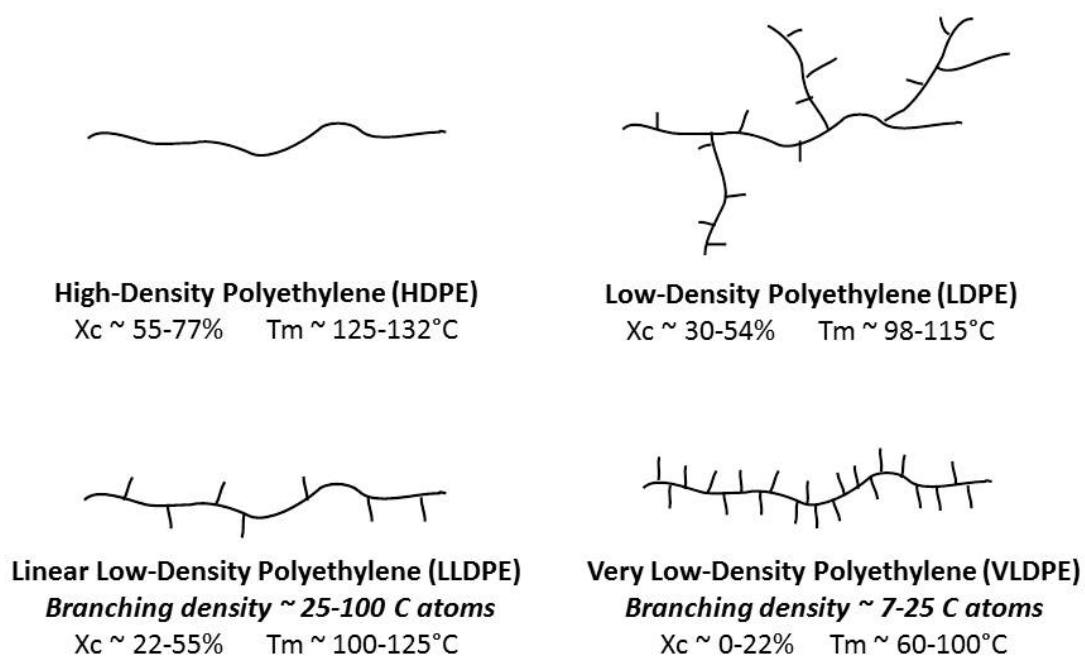


Figure S1- Schematic representation of polyethylene classes and corresponding properties

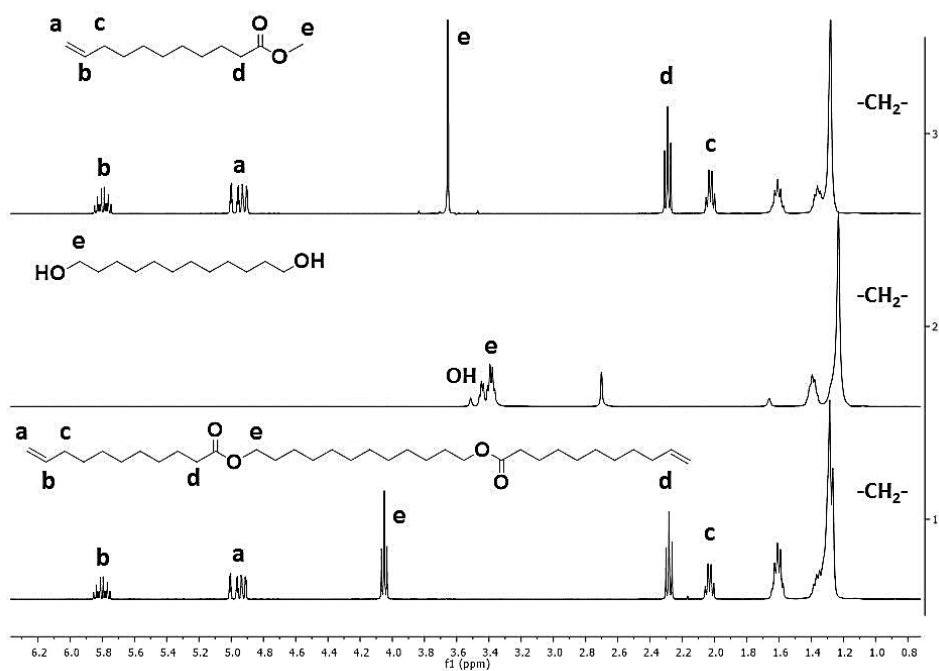


Figure S2- ¹H-NMR stacked spectra of methyl 10-undecenoate (CDCl₃), 1,12-dodecanediol (DMSO-d₆) and linear α,ω-diene (CDCl₃).

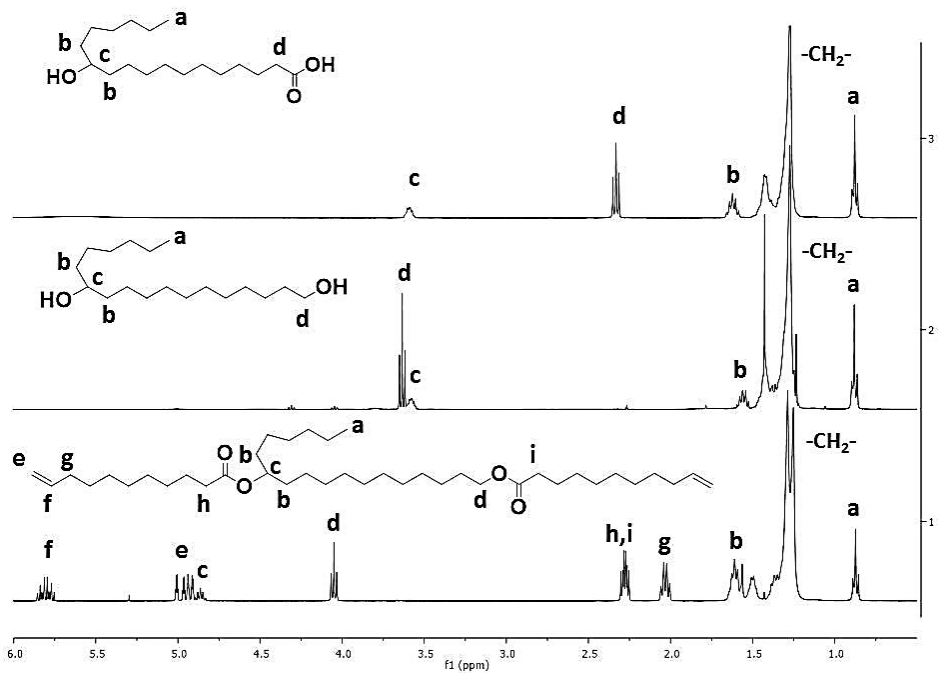


Figure S3- ¹H-NMR stacked spectra of 12-hydroxystearic acid, 12-hydroxystearyl alcohol and branched α,ω-diene in CDCl₃.

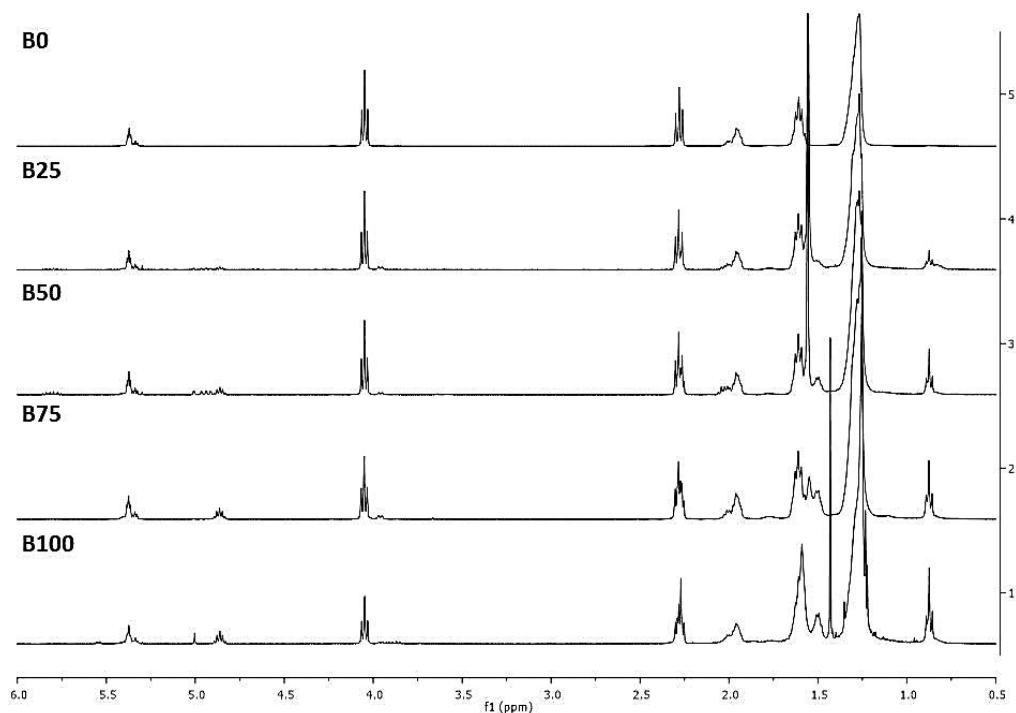


Figure S4- ¹H-NMR stacked spectra of the unsaturated polyesters in CDCl₃.

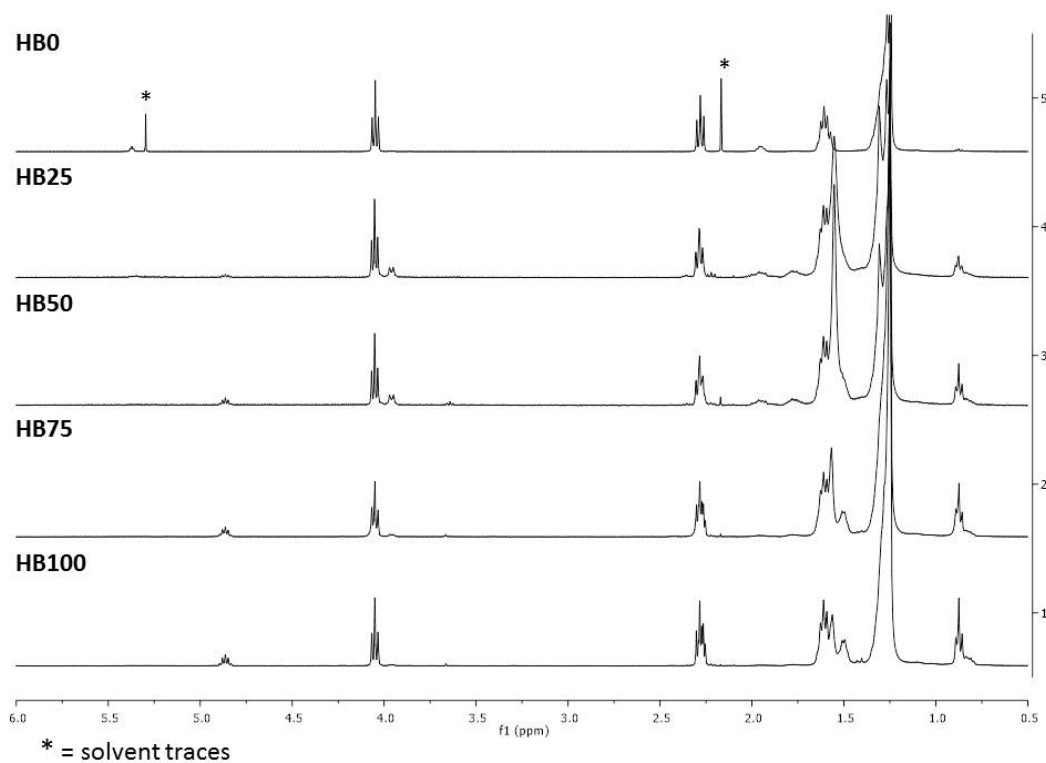


Figure S5- ¹H-NMR stacked spectra of the hydrogenated polyesters in CDCl₃.

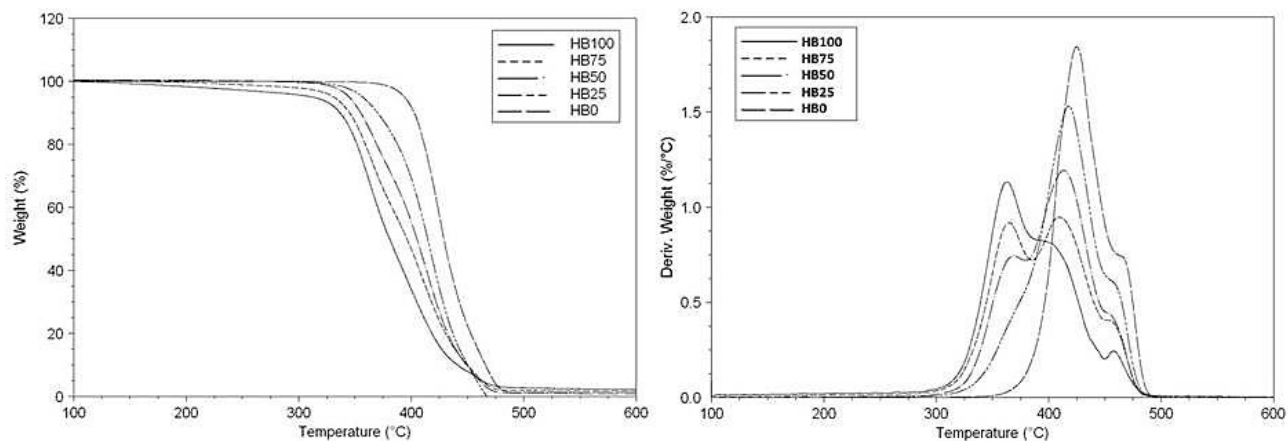


Figure S6- TGA curves and derivative curves of the saturated polyesters. $10^{\circ}\text{C}\cdot\text{min}^{-1}$.

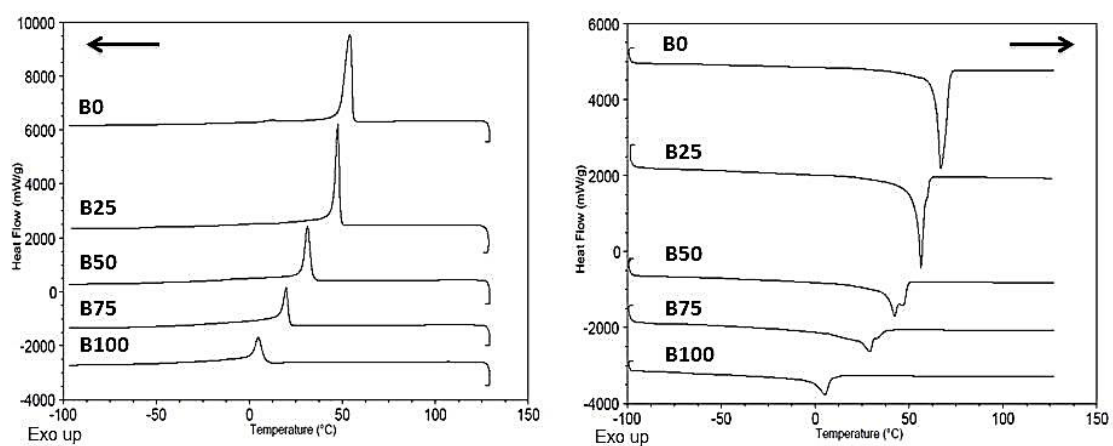


Figure S7- DSC cooling and heating curves of the unsaturated polyesters. $10^{\circ}\text{C}\cdot\text{min}^{-1}$.

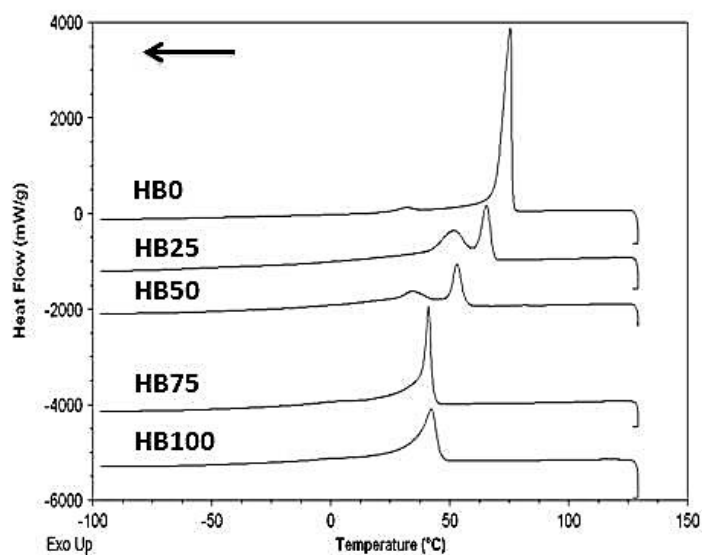


Figure S8- DSC cooling curves of the hydrogenated polyesters. $10^{\circ}\text{C}\cdot\text{min}^{-1}$.

Table S1- Crystallization parameters of the unsaturated and the hydrogenated copolyesters.

Entry	mol% (B)[d] ^a	T _c (°C) ^b	ΔH _c (J.g ⁻¹) ^b
B0	0	54.0	103.3
HB0	0	75.4	133.3
B25	22[136]	47.6	88.4
HB25	22[136]	51.3 – 65.5	92.6
B50	47[68]	31.2	62.3
HB50	47[68]	34.1 – 53.2	65.3
B75	74[45]	19.7	40.1
HB75	74[45]	41.0	62.9
B100	100[34]	4.9	32.1
HB100	100[34]	42.2	60.3

(a)¹H-NMR- [d] is the branching density (number of atoms of the main chain between two branching points) (b) DSC-10°C.min⁻¹

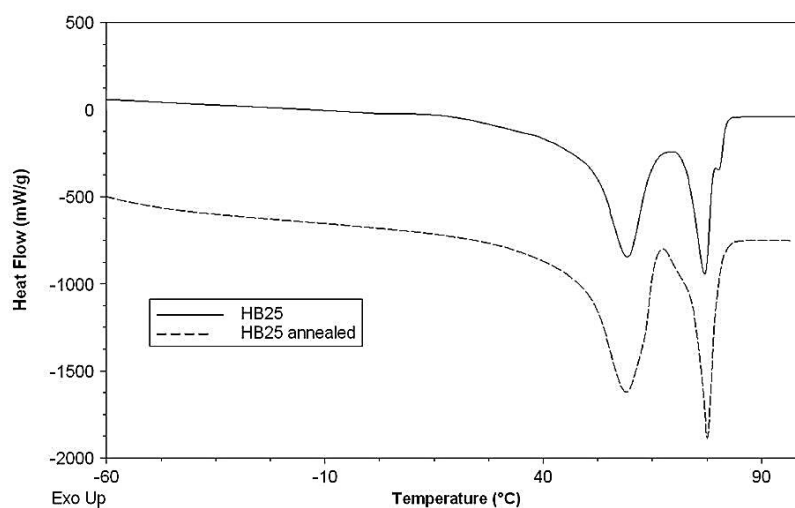


Figure S9- DSC heating scan traces of HB25 before and after annealing at 65°C during 15 minutes. 10°C.min⁻¹.

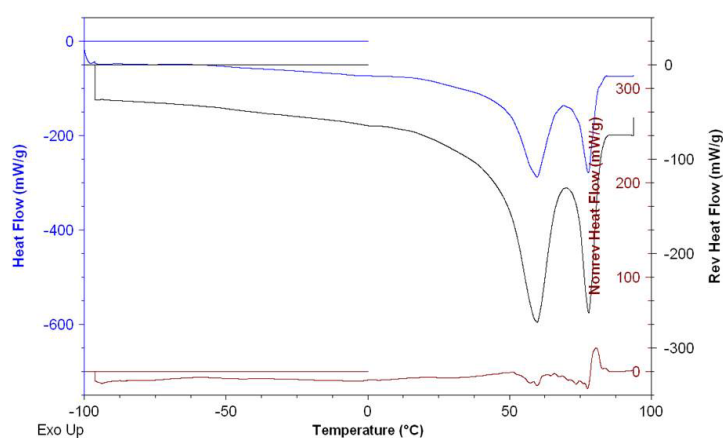


Figure S10- Modulated DSC heating scan traces of HB25. 3°C.min⁻¹.

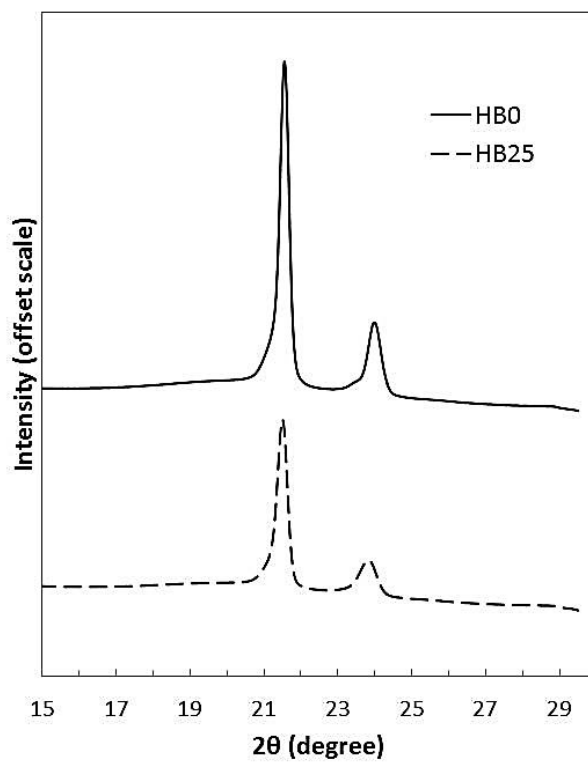


Figure S11- WAXD patterns of HB0 and HB25 obtained at 25°C.

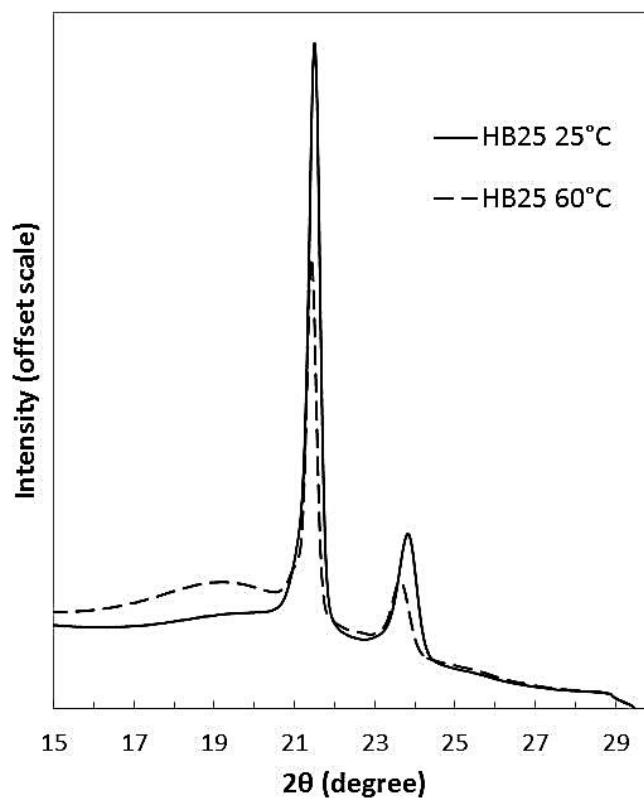


Figure S12- WAXD patterns of HB25 obtained at 25°C and 60°C.

Table S2- Scattering angle values and apparent crystallite sizes for HDPE, HB0 and HB25 at different temperatures.

	T(°C)	2θ (110) (°)	2θ (200) (°)	apparent crystallite size^a (nm)
HDPE	25	21.7	24.0	-
HB0	25	21.6	24.0	28.8
HB25	25	21.5	23.8	27.1
HB25	60	21.4	23.7	28.8

(a) Calculated using Scherrer equation¹ on the (110) reflection peak

1. P. Scherrer, *Göttinger Nachrichten Math. Phys.*, 1918, **2**, 98-100.