Electronic Supporting Information:

Hyperbranched Polyesters by Polycondensation

of Fatty Acid-based AB_n-type Monomers

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Figure SI 1. Stacked ¹H NMR spectra of (1) M2HS, (2) M2HB, (3) M2HU and (4) M3HS in

DMSO-d₆



Figure SI 2. Stacked FT-IR spectra of HBPEs prepared by polycondensation of (1) M2HS, (2)

M2HB, (3) M2HU and (4) M3HS



Figure SI 3. MALDI-TOF MS analysis of M3HS-based HBPE (Matrix trans-3-idoleacrylic acid)

Same nomenclature was used



Figure SI 4. (1) 1 H- 1 H COSY and (2) 1 H- 13 C HSQC of a M2HS-based HBPE in CDCl₃



Figure SI 5. ¹H NMR spectrum of a HBPE prepared by polycondensation of M2HB in CDCl₃

(P10)

Considering the unequal reactivity of the primary and secondary alcohols of M2HU, HBPEs derived from this AB2-type monomer are not described on the basis of three, but four different subunits as followed. These polyesters were preferably characterized in DMSO-d₆, due to a strong overlapping of the signals in CDCl₃. With the help of 2D NMR techniques, ¹H NMR spectrum of P12 was partly elucidated as can be seen in Figure SI 6(1).



Protons H_d , H_e and H_g characteristic of the subunits L1, L2 and D, respectively, were identified at 3.85, 4.72 and 4.93 ppm. For the purpose of subsequently assessing the molar ratio in linear unit L2, a few drops of water were added in the NMR tube in order to 'switch off' the signals assigned to the hydroxyl functions. Accordingly, as can be seen in Figure SI 6 (2), all peaks attributed to $-OH_1$, $-OH_2$, $-OH_3$ and $-OH_4$ were no longer observed. Therefore, based on the respective integration of protons H_d (L1), H_e (L2) and H_g (D), the degree of branching of P12 was found to be equal to 0.25. This result tended to indicate the formation a rather linear structure, in agreement with the higher reactivity of primary alcohols upon secondary ones.



Figure SI 6. Stacked ¹H NMR spectra of a HBPE prepared by polycondensation of M2HU in (1) DMSO-d₆ and in (2) DMSO-d₆ & a few drops of water

Entry	Monomer	Catalyst	M _n ^a (g.mol ⁻¹)	Ъ	DB _{Fréchet} b	DB _{Frey} ^b
P1	M2HS	Zn(OAc) ₂	3 500	2.71	0.18	0.07
P3		TBD	4 100	2.46	0.43	0.35
P5		TBD	7 600	>12	0.44	0.41
P6		NaOMe	6 100	3.08	0.32	0.29
P7	- M2HB	Zn(OAc) ₂	3 000	1.93	0.29	0.09
P8		Zn(OAc) ₂	5 600	>11	0.26	0.18
Р9		TBD	5 600	3.05	0.39	0.33
P10		NaOMe	9 200	3.27	0.30	0.30

Table SI 1. Catalyst dependence of DB values ($DB_{Fréchet}$ and DB_{Frey}) for M2HS and M2HB-based

HBPEs

(a) SEC in THF - calibration PS standards. (b) ^{1}H NMR spectroscopy



Figure SI 7. ¹H NMR spectrum of a HBPE derived from M3HS in CDCl₃ and schematic representation of terminal, linear, semi-dendritic and dendritic units





polycondensation of M2HS



Figure SI 8. Stacked ¹H NMR spectra of (1) methyl 12-hydroxystearate and (2) its related linear polyester (LPE) in CDCl₃



Figure SI 10. DSC thermograms at 10°C.min⁻¹ for HBPEs derived from (1) M2HS and M3HS,

(3) M2HB and (4) M2HU, and a linear reference LPE (2)



Figure SI 11. WAXS patterns at 5, 25 and 80°C of a HBPE prepared from M2HB

The semi-crystalline character of M2HB-based HBPEs was further investigated by wideangle X rays diffraction measurements (WAXS), carried out as a function of the temperature at 5, 25 and 80°C. Figure SI 11 depicts the different WAXS patterns obtained. Results clearly confirm the semi-crystalline properties of the HBPEs. Apart from the apparent large amorphous halo, two diffraction peaks can be distinguished. Their position as well as their intensity depend on the temperature of analysis. At 80°C, *i.e.* well above the melting point, these two diffraction peaks disappeared leading to a broad amorphous halo, due to the lost of crystallinity at that temperature.



Figure SI 12. Weight loss as a function of temperature for HBPEs derived from M2HS, M2HB, M2HU and M3HS, from TGA experiments at 10°C.minutes⁻¹ under nitrogen atmosphere



Figure SI 13. (1) Weight loss as a function of temperature (2) Derivative of weight loss with temperature for M2HS-based HBPEs using Zinc acetate and TBD as catalyst obtained from TGA experiments at 10°C/min under nitrogen atmosphere

HBPEs synthesized using Zn(OAc)₂ were found to display lower $T_d^{5\%}$, in between 237 and 252°C, than materials obtained with TBD (306 to 338°C). Typical decomposition profiles of M2HS-derived HBPEs prepared using both catalysts are presented in this figure. TGA derivatives of weight loss as a function of the temperature show one additional degradation step with the organometallic catalyst between 200 and 300°C. This first weight loss was assigned to the thermal zinc acetate-catalyzed depolymerization of the HBPEs knowing that all samples were characterized without further purification. This phenomenon has already been reported in the literature for poly(ethylene terephthalate) and poly(tetramethylene succinate).



Figure SI 14. DSC trace of HBPE prepared using $Zn(OAc)_2$ after an isotherm of 15 mins at $250^{\circ}C$

The depolymerization phenomenon was investigated by DSC analyses. After an isotherm of 15 minutes at 250°C, the thermogram of HBPEs prepared using zinc acetate displayed an exothermic peak upon cooling at 10°C.min⁻¹ and one endothermic peak upon heating. Since the HBPEs were amorphous, the crystallization observed may be due to the presence of either linear segments or monomer residues within the sample. It is important to notice that this was not observed for HBPEs prepared with TBD.