SUPPORTING INFORMATION

belonging to the paper:

Exploration of the effect of BHT in chain shuttling polymerization

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Table S1. Chain Shuttling Polymerization semi-batch experiments, at low 1-$C_8^=$ loading (10 mL unless stated otherwise).

Entry	Catalysts	Monomers	MAO	BHT	$ZnEt_2$	Yield (g)	M_n (g/mol)	PDI	T_m (°C)
				MAO only					
S1	Hf/Zr	$C_2^= + C_8^=$	1000eq	/	/	5.2	4.680	1.5	123.7
S2	Hf/Zr	$C_2^= + C_8^=$	500eq	/	/	8.6	10.100	1.9	127.2
S3	Hf/Zr	$C_2^= + C_8^=$	250eq	/	/	8.6	33.800	2.6	129.8
				MAO + BHT					
S4	Hf/Zr	$C_2^= + C_8^=$	500eq	500 eq	/	3.1	133.400	2.0	130.2
S5	Hf/Zr	$C_2^= + C_8^=$	500eq	250 eq	/	3.3	121.500	2.0	128.6
S6	Hf/Zr	$C_2^= + C_8^=$	500eq	50 eq	/	9.0	51.900	2.6	130.0
S7	Hf/Zr	$C_2^= + C_8^=$ (50mL)	500eq	250 eq	/	4.1	139.600	2.9	118.9
S8	Hf/Zr	$C_2^= + C_8^=$ (100mL)	500eq	250 eq	/	2.7	82.200	2.2	110.1
				MAO + (BHT) + DEZ					
S9	Hf/Zr	$C_2^= + C_8^=$	500eq	/	50 eq	6.8	10.100	1.7	128.0
S10	Hf/Zr	$C_2^= + C_8^=$	500eq	250 eq	50 eq	6.3	12.200	1.6	129.7

Conditions: 5 μmol each catalyst, 11 μmol DMAHBF20, unless stated otherwise, 500 mL IsoparE. 1L PREMEX reactor, 130 °C and 30 min run. 5 bars ethylene.
NB: Experimentally, it does not make a difference to add MAO/BHT together or first MAO for 1h (to scavenge) and then only BHT.

Table S2. Chain Shuttling Polymerization semi-batch experiments, use of different scavengers.

Entry	Catalysts	Monomers	Scavenger	BHT	$ZnEt_2$	Yield (g)	M_n (g/mol)	PDI	T_m (°C)
12114	Hf/Zr 3/1	$C_2^= + C_8^=$	MMAO-3A	250 eq	/	22.1	22.900	3.3	110.5
12115	Hf/Zr 3/1	$C_2^= + C_8^=$	MMAO-3A	250 eq.	10 eq.	21.3	4.700	1.7	111.8
1237	Hf/Zr	$C_2^= + C_8^=$	D 500 eq	250 eq	/	10.4	49.600	3.3	115.8
1232	Hf/Zr	$C_2^= + C_8^=$	D 500 eq	250 eq	10 eq	16.0	16.500	2.3	119.3
1246	Hf/Zr	$C_2^= + C_8^=$	D 500 eq	50 eq	10 eq	23.1	9.800	1.9	112.9 sh
1224	Hf/Zr	$C_2^= + C_8^=$	D 500 eq	/	10 eq	30.8	5.300	2.1	114.7

Conditions: 5 μmol each catalyst, unless stated otherwise, 11 μmol DMAHBF20, 500 mL IsoparE. 1L PREMEX reactor, 130 °C and 30 min run. 5 bars ethylene. 100 mL 1-octene, unless stated otherwise.

Table S3. Additional NMR data on the Cluster Index for the materials presented in Table 3.

Entry	Cat.	Ratio	BHT	$ZnEt_2$	Yield (g)	M_n[a] (g/mol)	PDI	T_m (°C)	ΔH (J/g)	Density	1-$C_8^=$ mol (wt) %	C.I.[c]
2	Zr		/	/	22.5	10.100	2.1	116.1	133.9	0.934	3.47 (12.56)	8.85
4	Hf		/	/	7.3	3.700	3.6	/	/	n.d.	27.39 (60.15)	5.60
13	Hf		250 eq	/	2.6	72.700	9.9	120.5	9.5	0.899	24.95 (57.08)	7.14
5	Hf/Zr		/	/	22.3	10.900	2.2	116.0	120.6	0.933	4.78 (16.71)	27.61
7	Hf/Zr		250 eq	/	13.5	59.600	3.3	116.4	105.3	0.934	3.26 (11.89)	43.29
17	Hf/Zr		250 eq	10 eq	17.1	15.700	2.1	119.1	124.4	0.937	2.31 (8.64)	16.67
18	Hf/Zr	5/1	250 eq	/	5.70	66.500	5.8	114.5	50.2	0.907	11.62 (34.47)	16.04

	Xylene insoluble				0.61	58.900	3.3	114.3	61.5	*n.d.*	7.21 (23.72)	20.08
	Xylene soluble				0.40	28.400	1.8	/	/	*n.d.*	36.29 (69.50)	6.40
19	Hf/Zr	3/1	250 eq	/	5.11	36.500	4.5	113.4	38.2	0.912	9.81 (30.31)	20.64
	Xylene insoluble				1.10	46.700	3.8	113.5	94.1	0.934	4.02 (14.33)	28.30
	Xylene soluble				0.43	29.800	8.9	/	/	n.d.	38.54 (71.50)	7.43
20	Hf/Zr	3/1	250 eq	10 eq	6.85	9.900	1.9	120.8	135.5	0.940	1.72 (6.56)	39.22

Conditions: polymerization conditions: 500 mL Isopar E, 100 mL 1-$C_8^=$, 500 eq MAO, TBF_{20}: 11 µmol; catalyst: 10 µmol; ethylene 5 bar, 130 °C, 30 min.

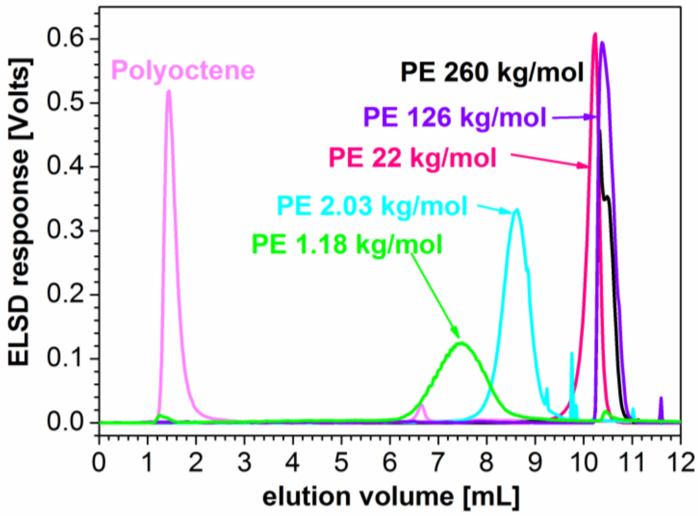

Figure S1. Overlay of HT HPLC chromatograms for standard materials used in Darmstadt (kindly provided by Dr. T. Macko).

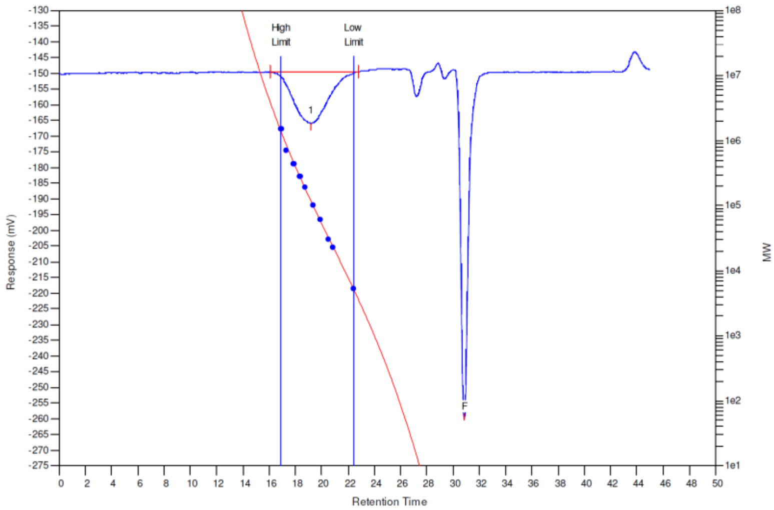

Figure S2. HT SEC plot of entry 7.

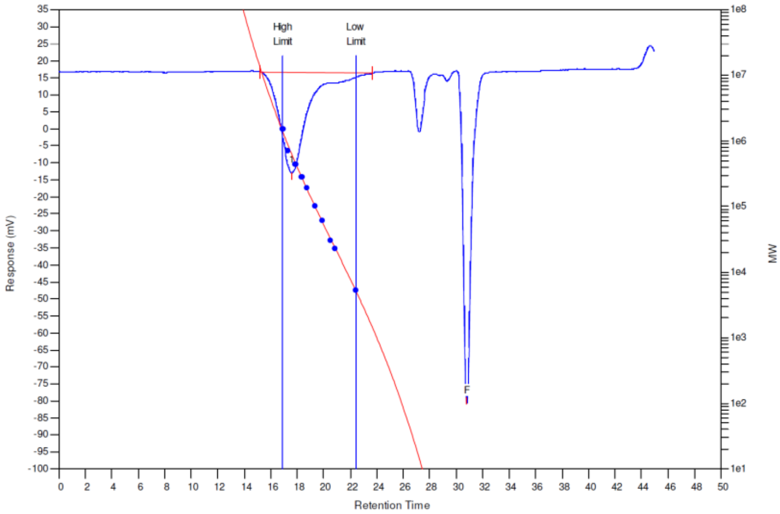

Figure S3. HT SEC plot of entry 13.

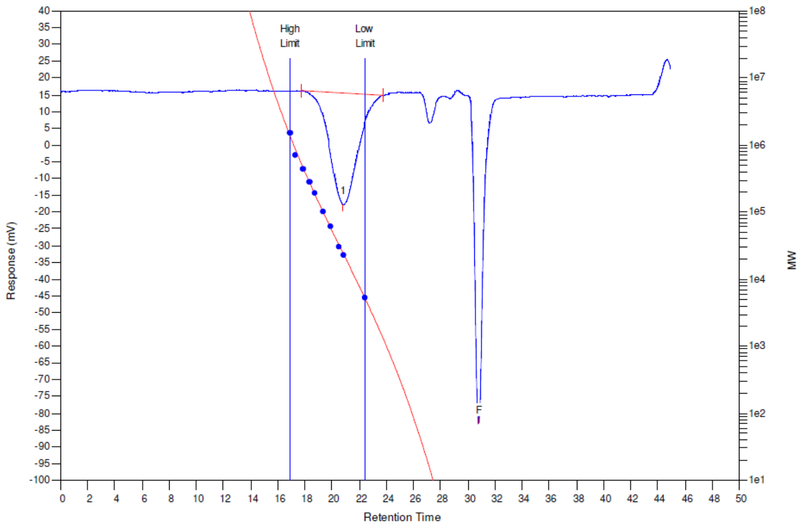

Figure S4. HT SEC plot of entry 17.

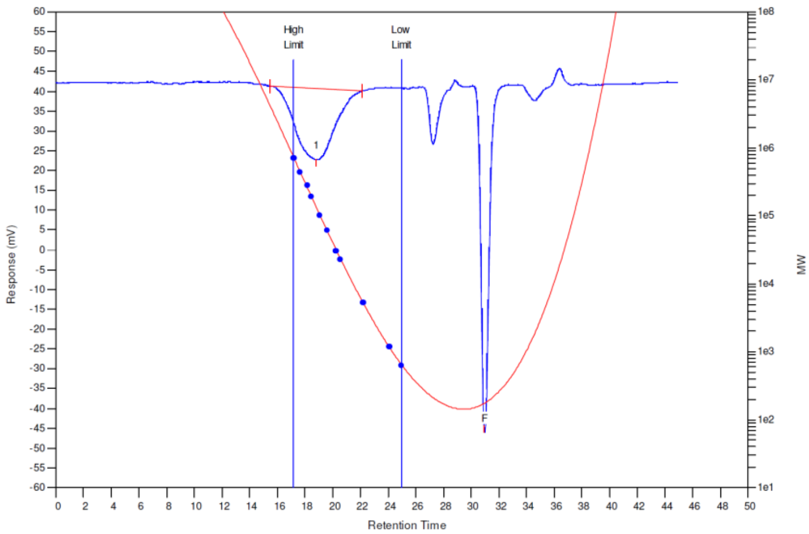

Figure S5. HT SEC plot of entry 18.

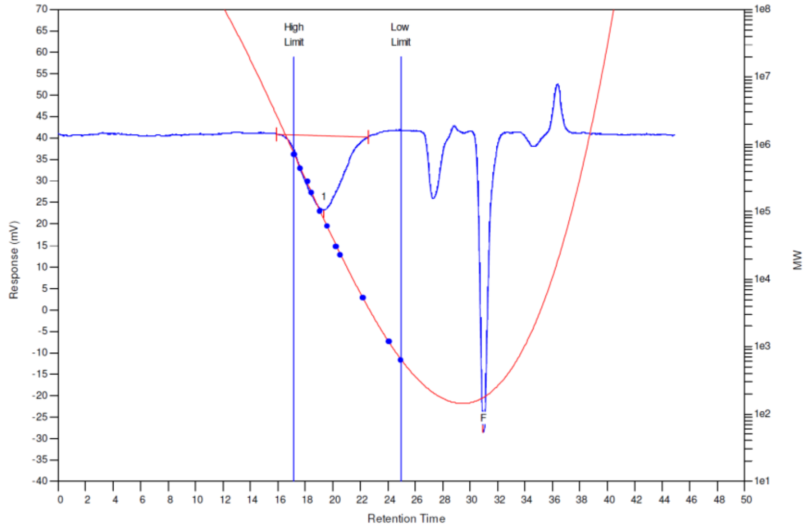

Figure S6. HT SEC plot of entry 19.

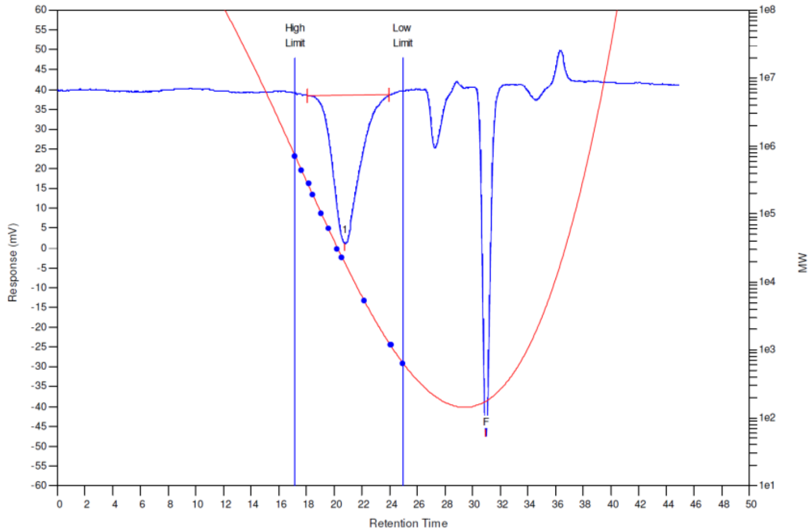

Figure S7. HT SEC plot of entry 20.

Table S4. Crystal collection and refinement data.

	4	**5**
formula	$C_{32}H_{51}AlO_2$	$C_{34}H_{56}O_2Zn_2$
FW	494.71	627.57
cryst. dim. (mm)	0.33 x 0.30 x 0.26	0.44 x 0.37 x 0.33
colour, habit	colorless, block	colorless, block
crystal system	triclinic	orthorhombic
Space group, no.[i]	P_{-1}, 2	Pbca, 61
a (Å)	10.9975(11)	17.7224(11)
b (Å)	12.3835(11)	9.6794(6)
c (Å)	13.3184(12)	19.2480(11)
α (°)	65.237(4)	90
β (°)	75.393(4)	90
γ (°)	69.574(4)	90
Z	2	4
V ($Å^3$)	1531.4(3)	3301.8(3)
ρ_{calc} (g/cm^3)	1.0729(2)	1.2625(1)
θ range (°)	2.33-28.29	3.12-28.29
λ (Å) (Mo-K_α)	0.71073	0.71073
T (K)	200(2)	200(2)

# meas. refl.	24101	58913
# unique refl.	7448	4048
# param.	316	172
weighting scheme; a,b[a]	0.1028, 0.5326	0.0420, 2.5700
$R(F)$ for $F_0 \geq 4\sigma(F_0)$[b]	0.553	0.0289
$wR(F^2)$[c]	0.1718	0.0827
GoF[d]	1.019	1.002

[a] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2F_c^2] / 3$ [b] $R(F) = \sum (||F_o| - |F_c||) / \sum |F_o|$ [c] $wR(F^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ [d] GoF = $[\sum [w(F_o^2 - F_c^2)^2] / (n-p)]^{½}$, n = # refl., p = # param. refined.

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[i] *International Tables for Crystallography; Kluwer Academic Publishers; Dordrecht, The Netherlands, 1992.*