Electronic Supplementary Material (ESI) for Polymer Chemistry

SUPPORTING INFORMATION

Copolymerization of Ethylene with α-Olefins and Cyclic Olefins Catalyzed by Ti(IV) diisopropoxy Complex Bearing a Tridentate [O⁻,S,O⁻]−type Bis(phenolato) Ligand

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TABLES

Table S1. Copolymerization of ethylene with α-olefins by C_s-symmetric $Me_2C(Cp)(9\text{-Fluo})ZrCl_2$ /MAO[a]

run	4M1P (concn/M)	[4M1P]/[E][b]	time (min)	Activity[c]	4M1P[d] (%mol)	M_w[e] ×10^{-3}	M_w/M_w[e]
M1	0.15	1.4	30	0.74	17.0	95	2.5
M2	0.30	2.9	30	1.60	30.9	50	2.4

[a] Polymerization conditions: total volume, 100 mL; catalyst, 2 μmol; cocatalyst, dried-MAO; Al/Zr, 3000 (mol/mol), temperature, 45 °C; time, 30 min; ethylene pressure, 1.01 bar. [b] [Y]/[E] feed ratio (mol/mol) in liquid phase. [c]Activity in $kg_{polymer}\times mol_{Ti}^{-1}\times h^{-1}$. [d] Comonomer content in the copolymer, determined by ^{13}C NMR. [e] Molecular weight (M_w, in $g\times mol^{-1}$), and molecular weight distribution (M_w/M_n) by SEC in *ortho*-dichlorobenzene *vs* poly(styrene) standard.

Table S2. Boiling solvent fractionation of the E/PEN and E/CPE copolymers made by 1/MAO[a].

Y (type)	run	ether-soluble fraction (%)	ether-soluble fraction Y[a] (%mol)	ether-soluble fraction M_w[b] ×10^{-4}	ether-soluble fraction T_m[c] (°C)	THF-soluble fraction (%)	THF-soluble fraction Y[a] (%mol)	THF-soluble fraction M_w[b] ×10^{-4}	THF-soluble fraction T_m[c] (°C)	residue fraction (%)	residue fraction Y[a] (%mol)	residue fraction M_w[b] ×10^{-4}	residue fraction T_m[c] (°C)
PEN	2	−				49	4.9	1.00	106/102	51	2.7	3.3	118/110/106
	3	−				53	5.8	1.23	101/97	47	3.3	3.9	118/115/107
	4	65	13.3	1.1	nd	35	7.9	3.25	96/68	−			
CPE	13	−				6	nd	nd	103/97/80	94	0.6	5.5	129
	15	−				3	nd	nd	105/90	97	0.6	2.5	127

Comonomer content in the copolymer from diad distribution as Y = (YY + ½YE). [b] Molecular weight (M_w, in $g\times mol^{-1}$) by SEC in *ortho*-dichlorobenzene *vs* poly(styrene) standard. For all fractions the M_w/M_ns ranged from 1.8 to 2.5. [c] Melting temperature (T_m) by DSC second heating scan. nd, not determined.

Figure S1. DSC thermogram of the E/NB copolymers with NB mole percent: 40.6% (Table 4, run 18), 21.1 (Table 4, run 17), and 10.6% (Table 4, run 16).

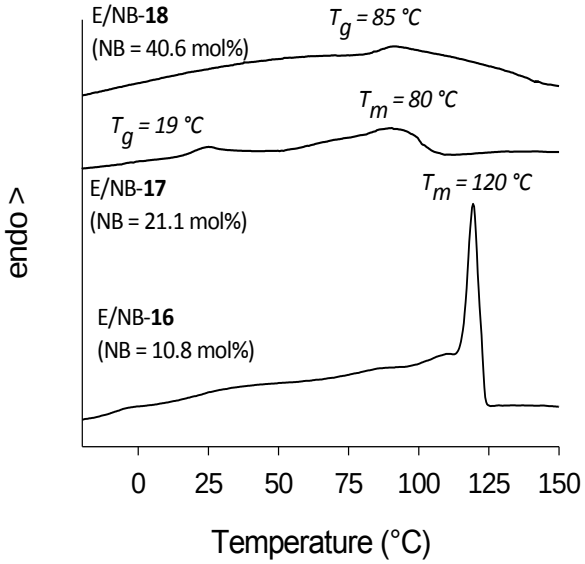


Figure S2. XRD patterns of the ether-, THF- soluble, and residue fraction of the E/HEX copolymer (Table 1, run 5).

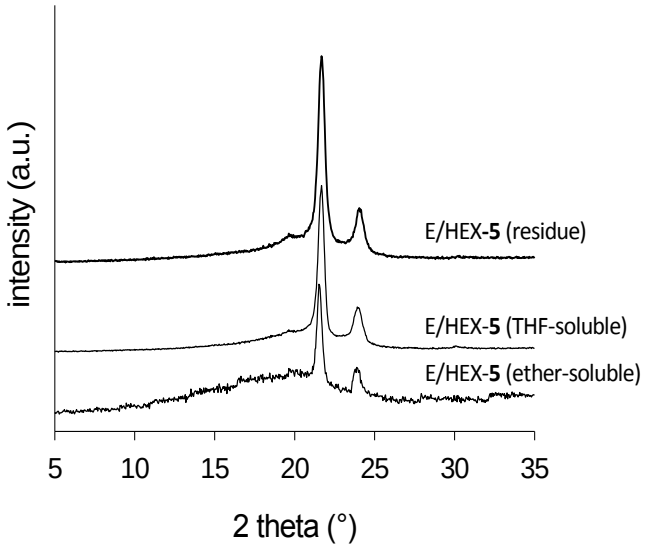
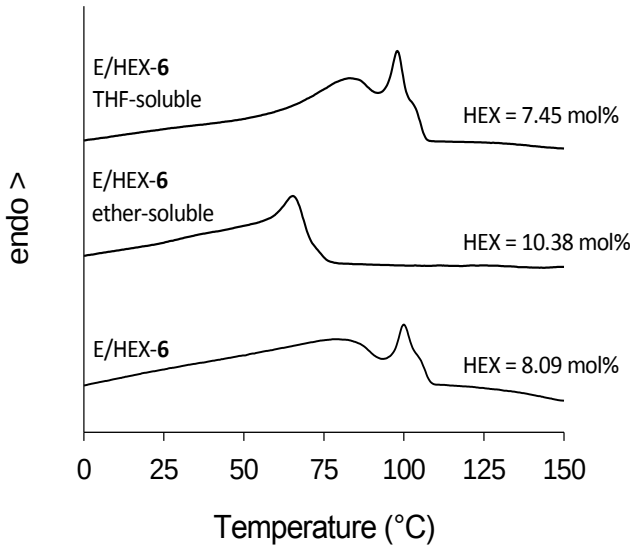
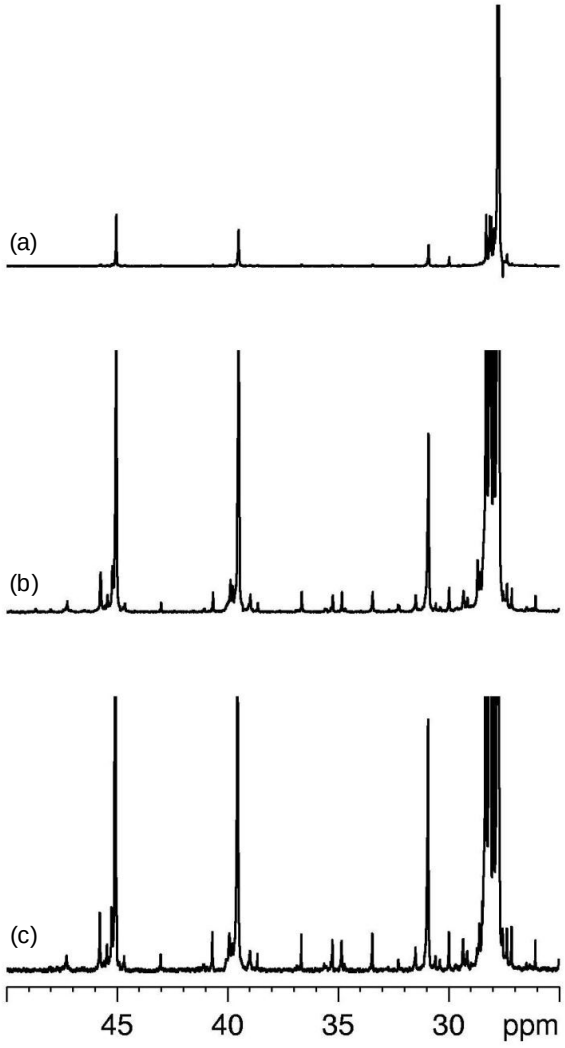


Figure S3. DSC thermogram of the E/HEX copolymer (Table 1, run 6), and the ether- and THF-soluble fraction.



In accordance to the XRD (Figure S2) and DSC characterization (Figure S3) all fractions were semicrystalline. DSC thermogram of all fractions depends on the comonomer content, the melting event of the fraction with the lower amount being shifted to a higher temperature range than the fraction with the higher content. As an example, the ether-soluble fraction of the E/HEX copolymer (run 6, HEX = 10.4 mol%) exhibited a melting transition centered at 65 °C with a heat flow of 49 $J \times g^{-1}$ (Figure S3). In contrast, a broader endothermic event spanning from 30 to 110 °C (ΔH_m= 90 $J \times g^{-1}$) with peaks at 83, 98 and 103 °C, respectively, characterized the DSC scan of the THF-soluble fraction (HEX = 7.5 mol%).

Figure S4. ^{13}C NMR spectra (in $C_2D_2Cl_4$ at 103°C) of the E/NB copolymer (Table 4, run 16) fractions: (c) the ether-soluble (NB = 17 mol%), (b) the THF-soluble fraction (NB = 14.4 mol%), and (a) and the residue (NB = 2.9 mol%).



^{13}C NMR spectra of the ether-soluble and THF-soluble fractions were very similar to that of the crude copolymer in line with a comparable NB content, whilst the spectra of the residue fraction (NB = 2.9 mol%) only showed the peak at 45.04 and 39.49 ppm ascribed to carbon C2/C3 and C1/C4 of isolated NB units.

Figure S5. DSC thermogram of the ether- (NB = 26.5 mol%) and THF- soluble (NB = 17.8 mol%) fraction of the E/NB copolymer (Table 4, run 17).