Electronic Supplementary Information

Cyclic olefin copolymers containing both linear polyethylene and poly(ethylene-*co*-norbornene) segments prepared from chain shuttling copolymerization of ethylene and norbornene

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Contents

1. **Synthesis of *rac*-[CH_2(3-*tert*-butyl-1-indenyl)$_2$]$ZrCl_2$.** To a 250 mL Schlenk tube, 3.46 g of bis(3-*tert*-butyl-1- indenyl)methane (98.9% GC, 9.6 mmol) was added in 60 mL of Et_2O. At 0 °C, 22.0 mmol of BuLi (2.5 M in hexane) was added dropwise over 6 min under stirring. The solution was then warmed to room temperature and stirred for 24 h. In another flask, 60 mL of toluene and 2.46 g of $ZrCl_4$ (10.6 mmol) were added and cooled to -20 °C, then the mixture was quickly added to the lithium salt suspension in Et_2O at -20 °C. The reaction mixture was kept at -20 and reacted for 1 h. Then it was stirred overnight at room temperature, and finally Et_2O was removed under reduced pressure. The resulting toluene suspension was filtered, and the filtrate was evaporated under reduced pressure to give 3.26 g of a red powder as crude product (yield: 65.7%). The crude product was washed with tetrahydrofuran and dried under vacuum to give (1.2 g of red violet powder) pure *meso*-Cat. **2** as the final product (yield: 24.2%).

Table S1 Fraction of representative copolymers obtained with different Et_2Zn/catalyst ratios by methyl-tetrahydrofuran

Catalyst Package	Soluble polymer		Insoluble polymer	
	g	%	g	wt%
Cat.(1+ 2)	0.17	42	0.23	58
Cat.(1+ 2)+5 Et_2Zn	0.16	40	0.24	60
Cat.(1+ 2)+10 Et_2Zn	0.12	30	0.28	70

The copolymers (corresponding to Runs 3, 4, and 5 in Table 4) were refluxed with methyl-tetrahydrofuran (MTHF) at 85±2 °C for 6 hours. The insoluble portion content gradually increased as Et_2Zn/catalyst ratio increasing.

Table S2 Summary results of cross fractionation chromatography in 1,2,4-tricholorobenzene.

Fraction	Eluted temperature(˚C)	$Et_2Zn/Zr = 10$	
		Wt.%	∑ Wt.%
1	35	34.44	34.43
2	60	5.73	40.16
3	85	21.38	61.54
4	100	38.45	100
5	115	0	100

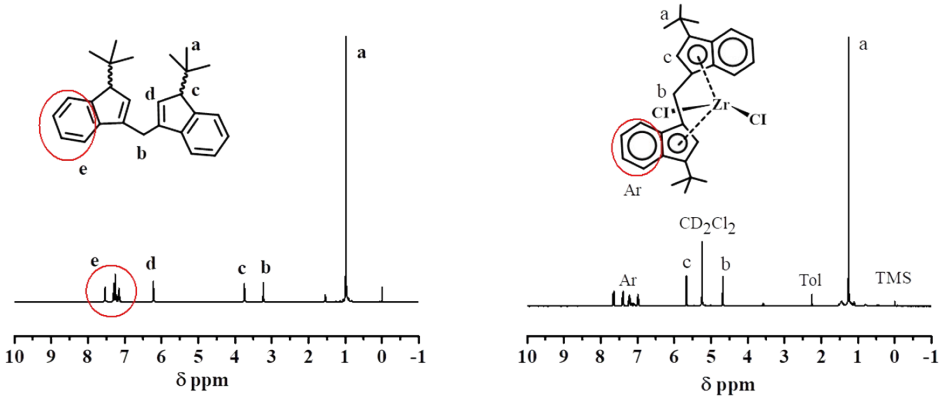


Fig. S1. The ^{1}H NMR spectra of ligand (left) and catalyst **2** (right).

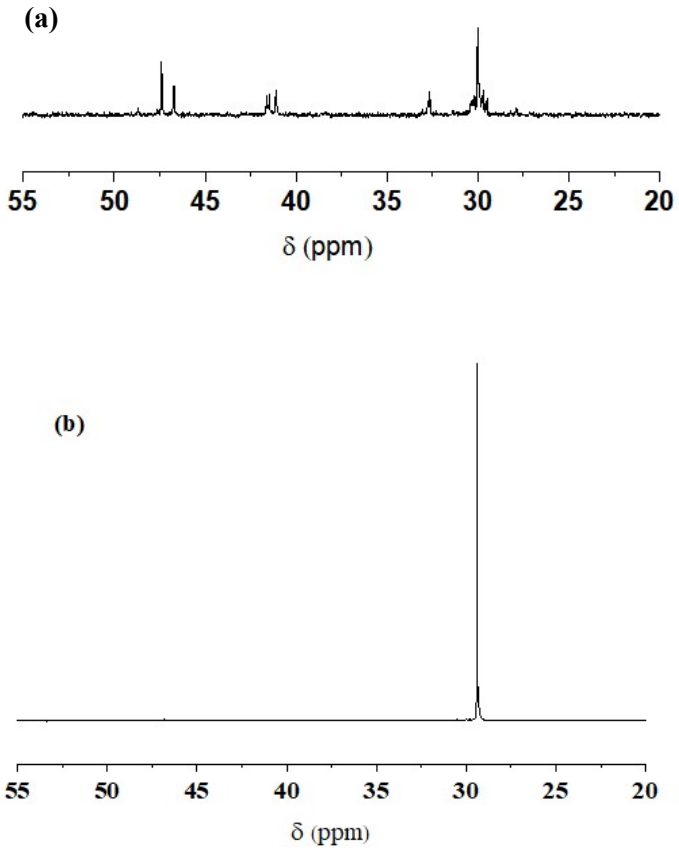
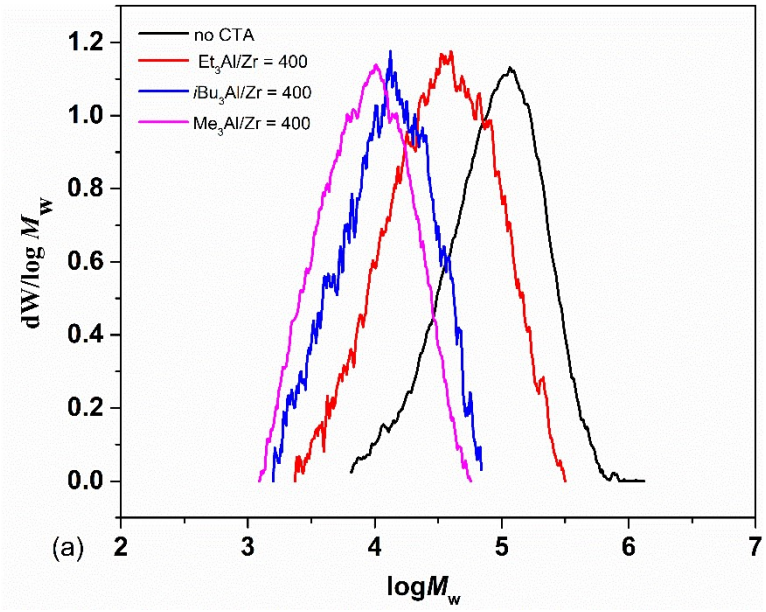


Fig. S2 (a) ^{13}C{^{1}H} NMR spectrum of poly(ethylene-*co*-norbornene) copolymer synthesized by catalyst **1** (Run 1 in Table 1, NBE incorporation = 27 mol%), and (b) ^{13}C{^{1}H} NMR spectrum of copolymer synthesized by catalyst **2** (Run 11 in Table 1, negligible NBE incorporation was found).



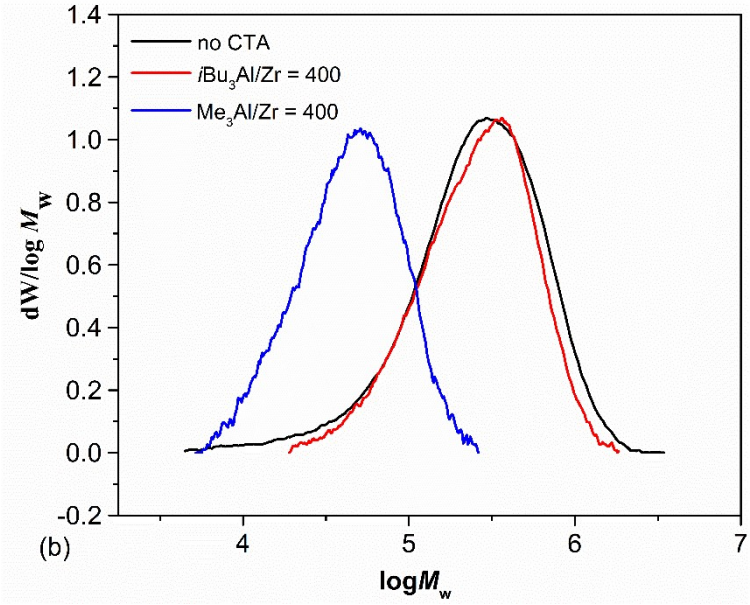
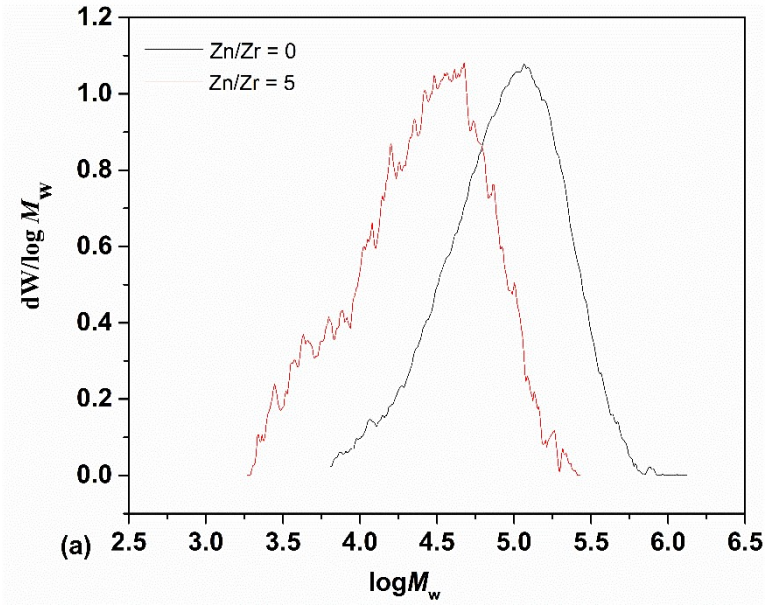


Fig. S3 Molecular weight distribution curves of copolymers synthesized from ethylene and NBE copolymerization with variable CTA synthesized by (a) Cat.1 (Runs 1, 3, 5 and 7) and (b) Cat.2 (Runs 11, 13 and 17) in Table 1.



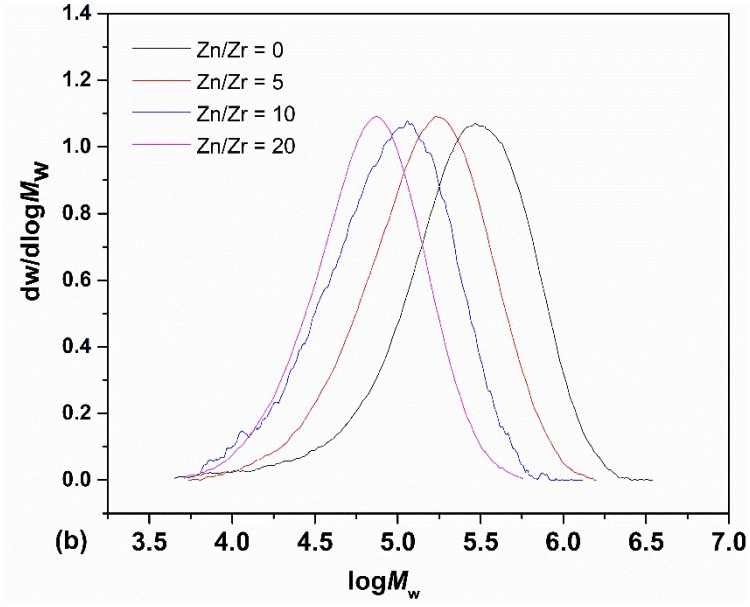


Fig. S4 Molecular weight distributions of copolymers synthesized from ethylene and NBE copolymerization with variable CTA by (a) Cat.1 (Runs 1 and 8) and (b) Cat.2 (Runs 11, 18, 19 and 20) in Table 1.

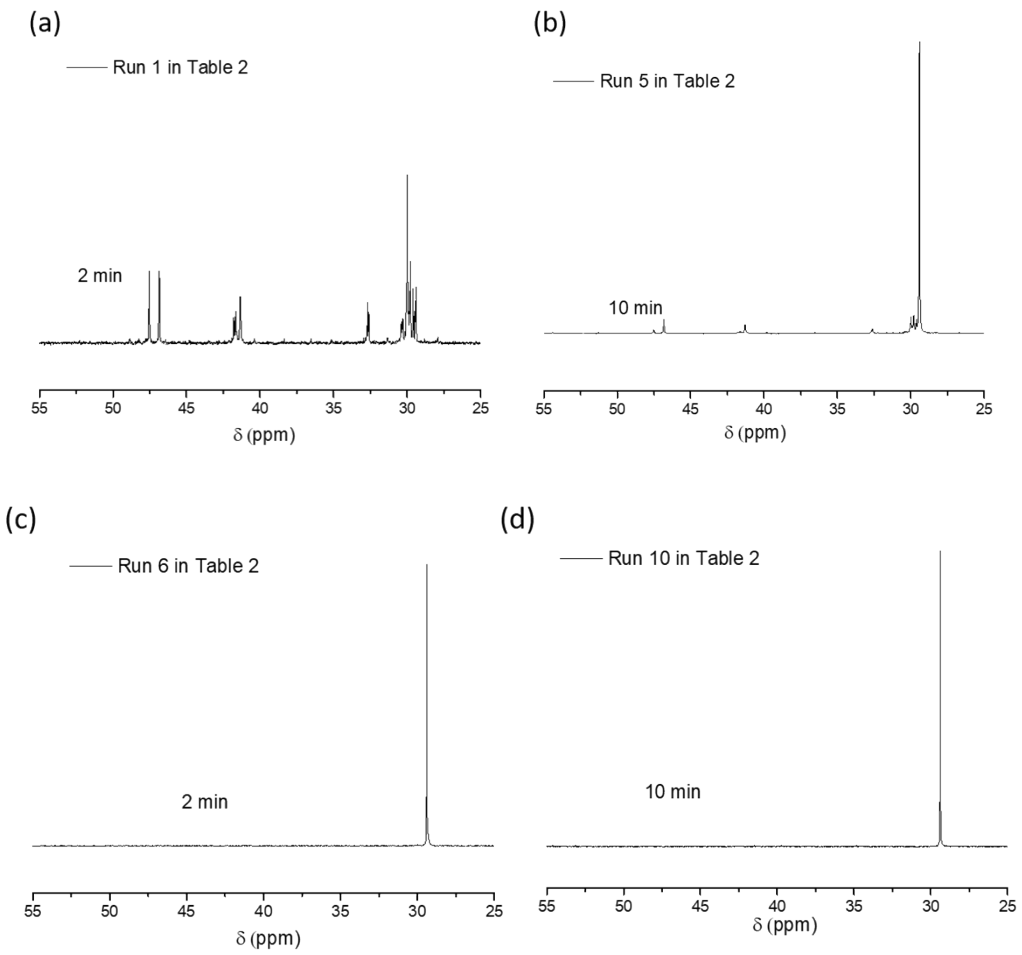


Fig. S5 $^{13}C\{^{1}H\}$ NMR spectra of poly(ethylene-*co*-norbornene) copolymer (a) Run 1, (b) Run 5, (c) Run 6 and (d) Run 10 in Table 2.

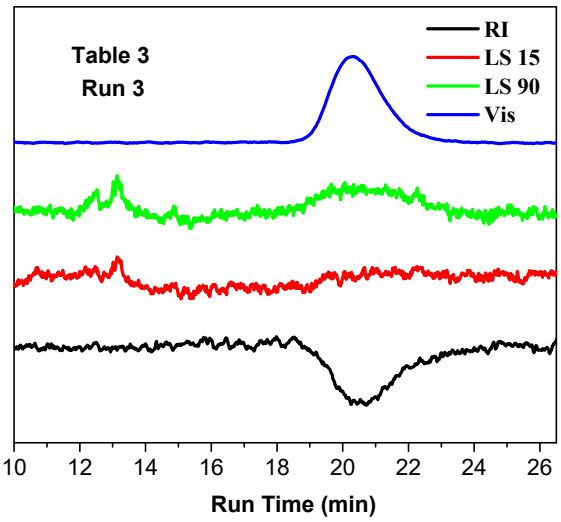


Fig. S6 GPC eluting traces of copolymer obtained by two catalysts with 10 equivalents of Et_2Zn (Run 3 in Table 3).

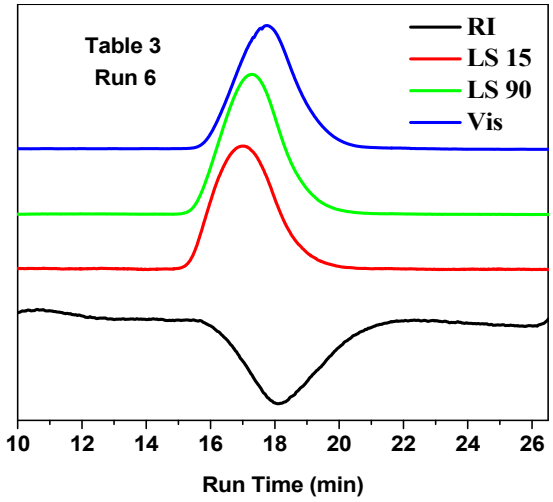


Fig. S7 GPC elute traces of copolymer obtained by two catalysts with 10 equivalents of Et_2Zn (Run 6 in Table 3)

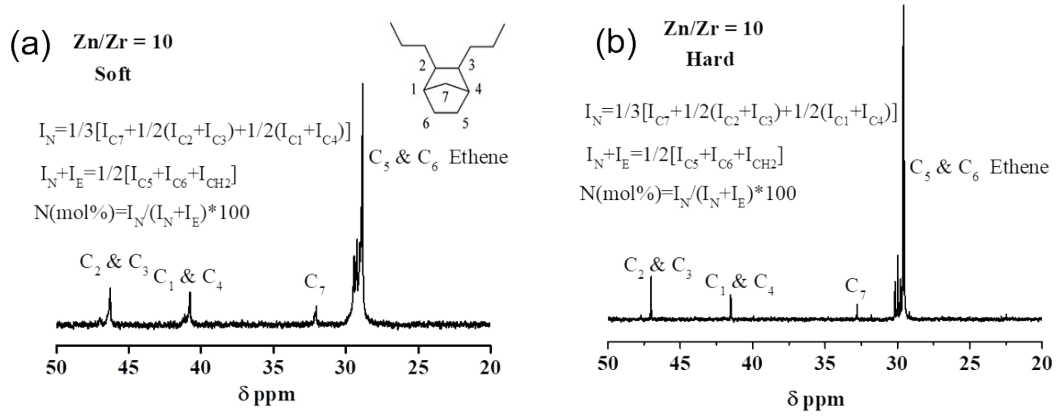


Fig. S8 $^{13}C\{^1H\}$ NMR spectra of (a) MTHF-soluble portion (0.12 g, NBE: 13 mol%) and (b) insoluble portion (0.28 g, NBE: 2.2 mol%) of poly(ethylene-*co*-norbornene) copolymer prepared by catalysts **1** and **2** in the presence of 10 equivalents of Et_2Zn (Run 5 in Table 4).

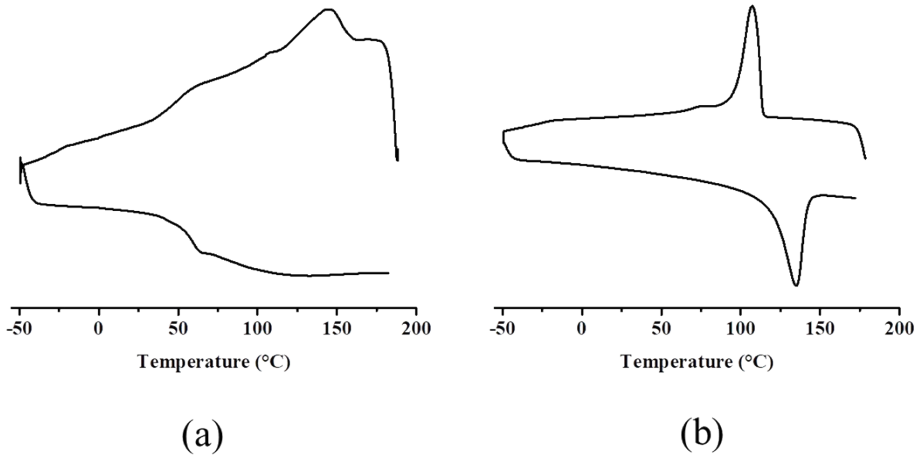


Fig. S9 DSC (cooling and the second heating) curves of poly(ethylene-*co*-norbornene) copolymers prepared by (a) catalyst **1** in absence CTA (Run 1 in Table 1) and (b) catalyst **2** in absence CTA (Run 11 in Table 1).

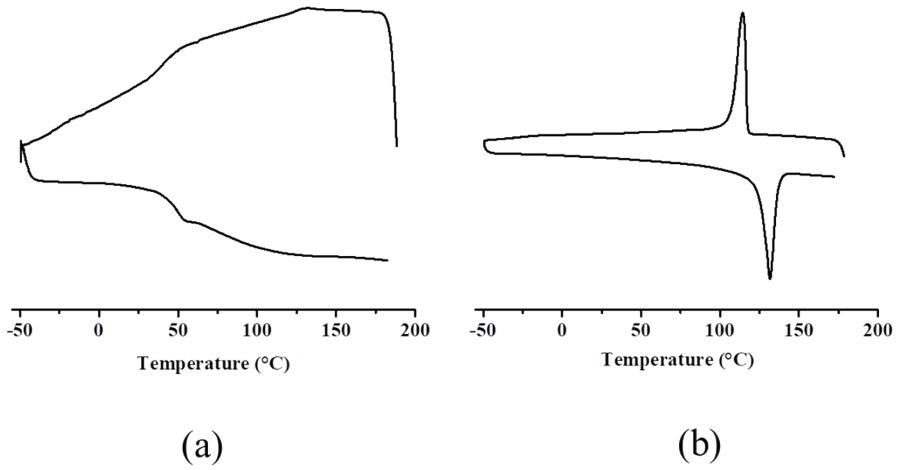


Fig. S10 DSC curves of poly(ethylene-*co*-norbornene) copolymers prepared by (a) catalyst **1** in the presence of 20 equivalents $ZnEt_2$ (Run 10 in Table 1) and (b) catalyst **2** in the presence of 20 equivalents $ZnEt_2$ (Run 20 in Table 1).

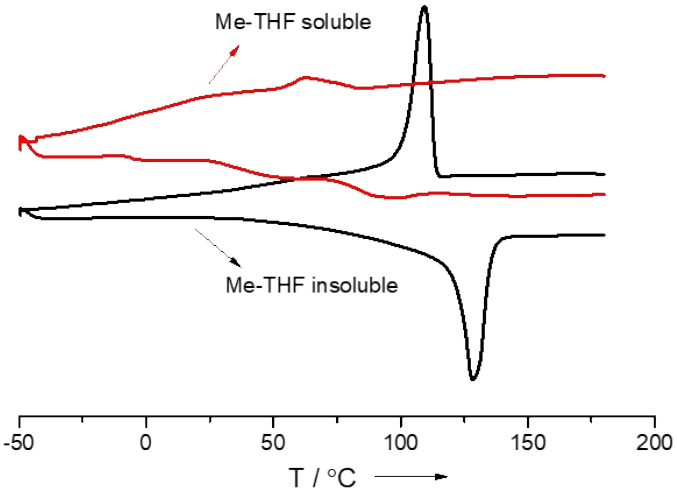


Fig. S11 DSC curves of the MTHF-soluble (red) and insoluble portion (black) of the poly(ethylene-*co*-norbornene) copolymer prepared by catalysts **1** and **2** in the presence of 10 equivalents of $ZnEt_2$.

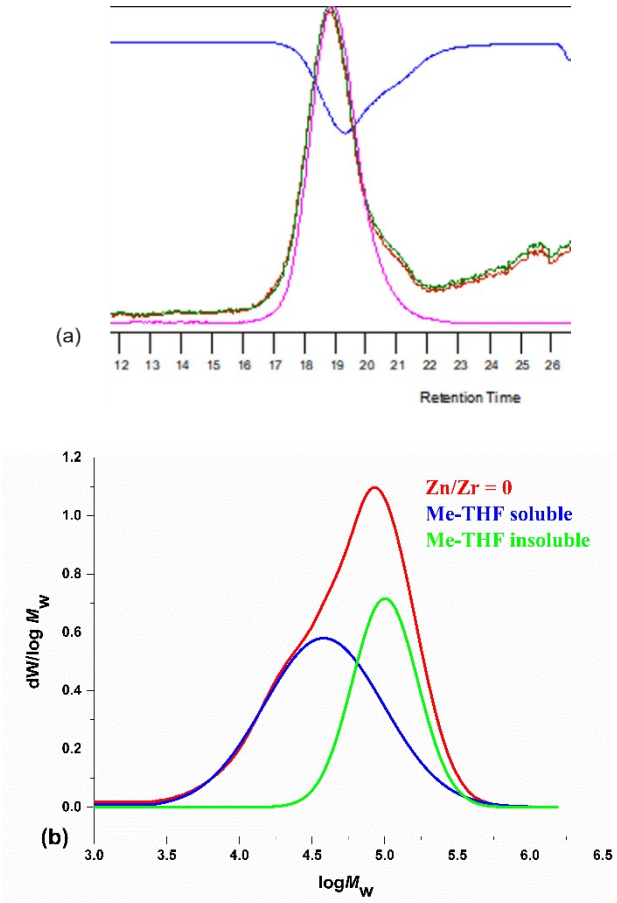


Fig. S12 (a) GPC eluting traces of copolymer (Run 3 in Table 4) and (b) its molecular weight distributions by peak fitting.

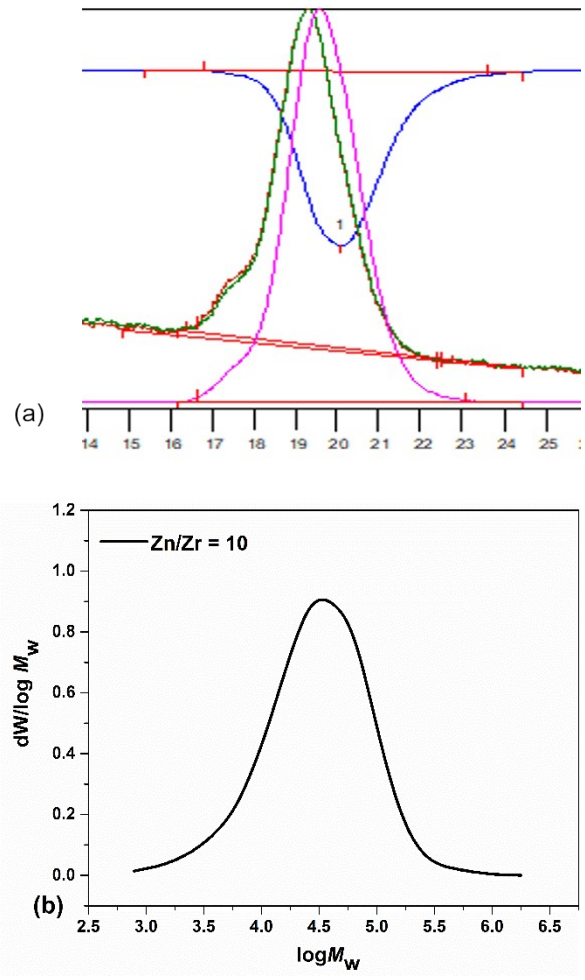


Fig. S13 (a) GPC eluting traces of copolymer (Run 5 in Table 4 and (b) its molecular weight distribution curve.

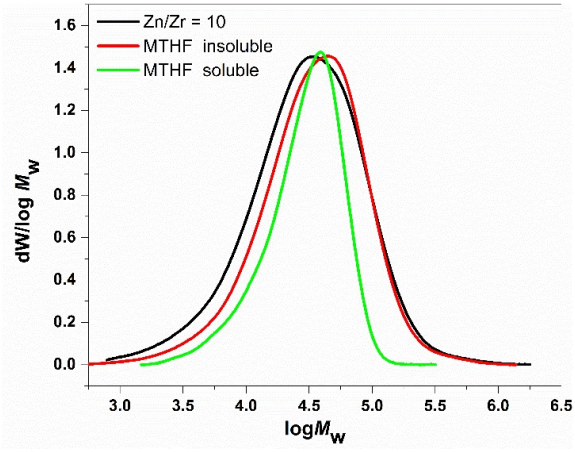


Fig. S14 Molecular weight distribution curves of polymers before (black curve, Run 5 in Table 4) and after MTHF fraction (red curve: MTFH insoluble; green curve: MTFH soluble portion).

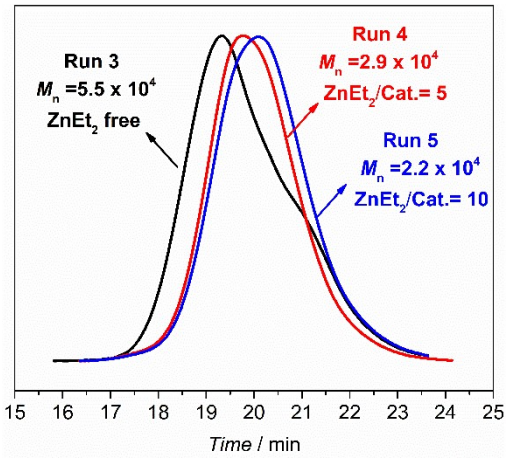


Fig. S15 Molecular weight distribution curves of polymers prepared without (black curve, Run 3 in Table 4) and with 5 (red curve, Run 4 in Table 4), 10 equivalents of Et_2Zn (blue curve, Run 5 in Table 4).

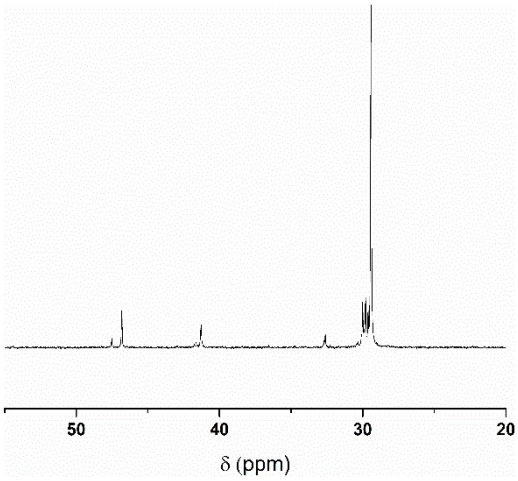


Fig. S16 $^{13}C\{^1H\}$ NMR spectrum of copolymer obtained by Cat. 1 (Run 1 in Table 4).

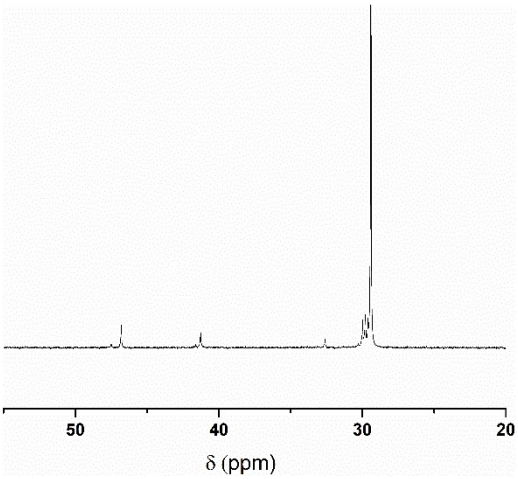


Fig. S17 $^{13}C\{^1H\}$ NMR spectrum of copolymer prepared by two catalysts without Et_2Zn (Run 3 in Table 4).

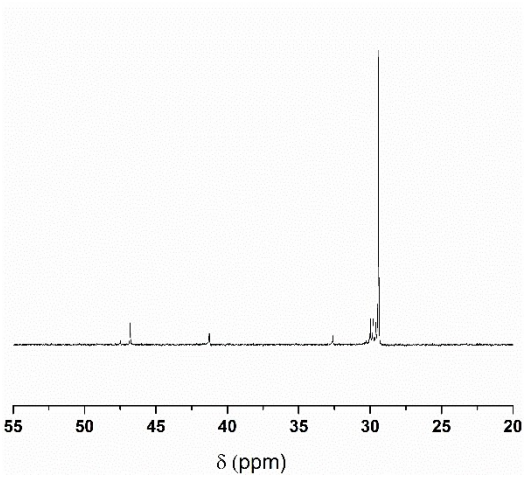


Fig. S18 $^{13}C\{^{1}H\}$ NMR spectrum of polyethylene/poly(ethylene-*co*-norbornene) multiblock copolymer prepared by two catalysts with 5 equivalents of Et_2Zn (Run 4 in Table 4).

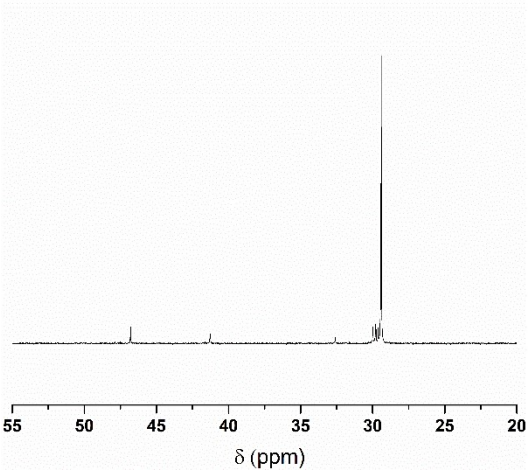


Fig. S19 $^{13}C\{^{1}H\}$ NMR spectrum of polyethylene/poly(ethylene-*co*-norbornene) multiblock copolymer prepared by two catalysts with 10 equivalents of Et_2Zn (Run 5 in Table 4)

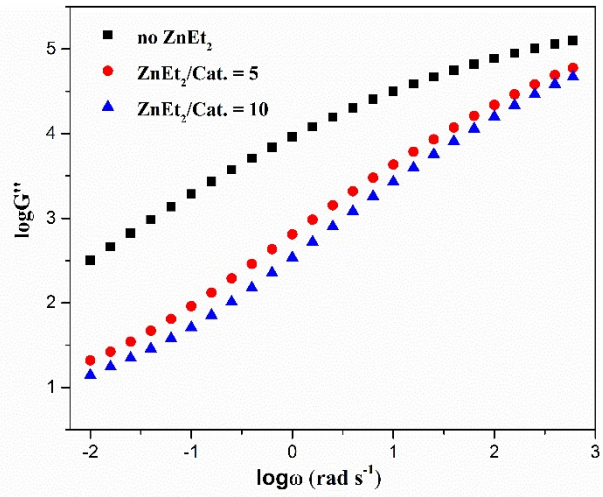


Fig. S20 Loss modulus of copolymers obtained with variable $ZnEt_2$/ catalyst ratio (Runs 3-5 in Table 4) at 170 °C.

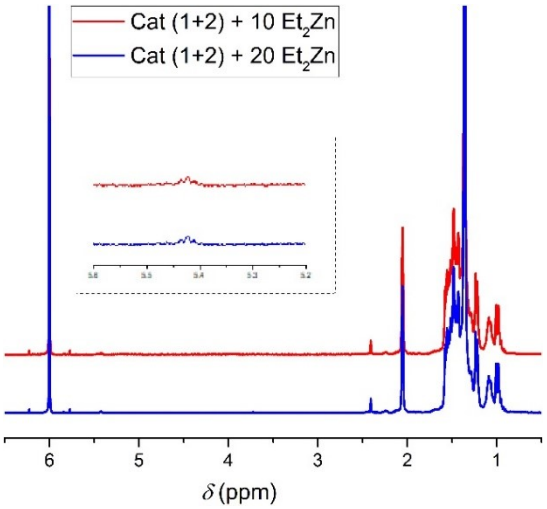


Fig. S21 ^{1}H NMR spectra and expansions (between 4.4 and 5.7 ppm) of copolymer under high reaction temperature (Run 4-5 Table 4).

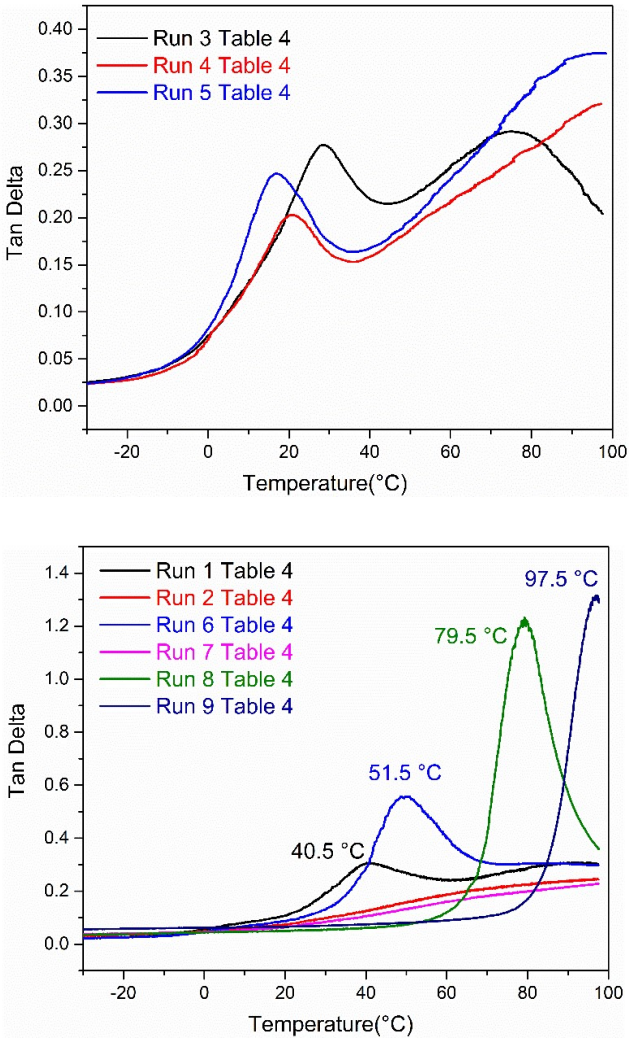
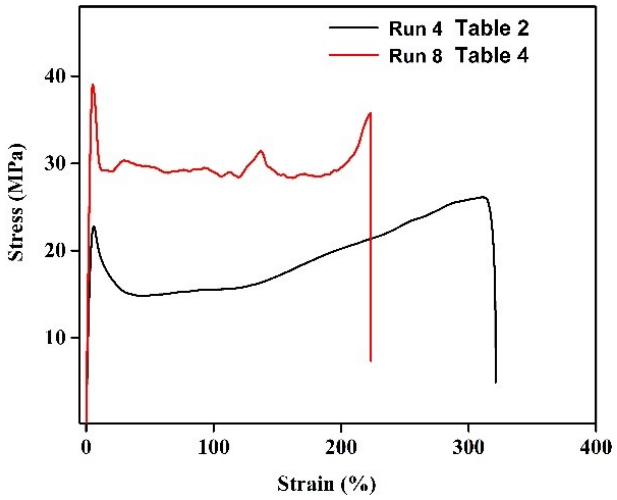


Fig. S22 DMA of copolymers obtained with variable $ZnEt_2$/catalyst ratio (Table 4).



Sample	σ [a] (Mpa)	E [b] (Mpa)	ε[c] (%)
Run 4 Table 2	26.0±1.6	7.2±0.41	313±17
Run 8 Table 4	39.2±2.1	11.0±0.53	222±15

[a]Tensile strength. [b] Young's modulus. [c] Strain at break.

Fig. S23 Tensile properties of copolymers obtained with Cat.1 or (Cat.1+Cat.2)\ $ZnEt_2$ (Run 4 Table 2 and Run 8 Table 4).