Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Preparation of Polybutene-Based Thermoplastic Elastomers through the Copolymerization of 1-Butene with Higher α-Olefins

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Table S1. Results of 1-butene/higher α-olefins copolymerization[a]

Sample	Cat.	Comon. (mmol)	Act.[b]	Incorp.[c] (mol%)	M_w[d] (kDa)	M_w/M_n [d]	T_m[e] (°C)	T_c[e] (°C)
PB-$C8_1$	Cat.1	C8 (3.5)	4.5	7.6	40	1.8	–	–
PB-$C12_1$	Cat.1	C12 (3.5)	4.9	6.0	41	1.9	–	–
PB-$C16_1$	Cat.1	C16 (3.5)	5.6	6.3	44	1.6	–	–
PB-$C12_2$	Cat.2	C12 (3.5)	7.2	5.9	24	1.6	75.7	33.1
PB-$C16_2$	Cat.2	C16 (3.5)	7.1	5.5	26	1.7	74.8	34.8
PB-$C12_3$	Cat.3	C12 (3.5)	5.2	5.6	26	1.5	–	–
PB-$C16_3$	Cat.3	C16 (3.5)	6.0	5.0	35	1.6	–	–

[a] Reaction conditions: **Cat.** 5 μmol, $Ph_3CB(C_6F_5)_4$ 10 μmol, *i*Bu_3Al 0.5 mmol, V_{total} 80 mL, copolymerization for 5 min at 1-butene 1 bar and 40 °C. [b]Catalytic activity: 10^6 $g_{polymer}\cdot mol_{Cat}^{-1}\cdot h^{-1}$. [c] Comonomer incorporation (mol%) was determined via ^{13}C NMR spectra. [d] Estimated based on GPC at 150 °C in 1,2,4-trichlorobenzene versus polystyrene standard. [e] Determined using DSC during heating and cooling at 10 °C/min.

Table S2. Data of comonomers reactivity ratios [a]

Run	Cat.	Comon.[b] (mol/L)	Incorp.[c] (mol%)	X [d]	Y [e]	F [f]	G [g]
1	Cat.1	0.0497	7.74	7.65	11.9	4.92	7.00
2	Cat.1	0.0994	14.4	3.82	5.94	2.45	3.17
3	Cat.1	0.149	21.1	2.55	3.74	1.73	1.86
4	Cat.1	0.199	25.9	1.91	2.86	1.27	1.24
5	Cat.2	0.0248	3.20	15.3	30.2	7.75	14.7
6	Cat.2	0.0497	6.71	7.65	13.9	4.21	7.09
7	Cat.2	0.0994	9.57	3.82	9.45	1.54	3.41
8	Cat.2	0.199	17.7	1.91	4.64	0.78	1.49
9	Cat.3	0.0248	3.01	15.3	32.3	7.24	14.8
10	Cat.3	0.0497	6.03	7.65	15.5	3.77	7.15
11	Cat.3	0.0994	13.1	3.82	6.63	2.20	3.24
12	Cat.3	0.199	20.4	1.91	3.90	0.93	1.42
13	Cat.4	0.0497	9.21	7.65	9.87	5.90	6.87
14	Cat.4	0.0994	17.5	3.82	4.71	3.09	3.00
15	Cat.4	0.149	25.4	2.55	2.93	2.21	1.67
16	Cat.4	0.199	31.7	1.91	2.15	1.69	1.02

[a] Reaction conditions: **Cat.** 3 μmol, [Ph_3C] [$B(C_6F_5)_4$] 6 μmol, *i*Bu_3Al 0.3 mmol, reaction time 30 s, V_{total} 70 mL, 1-butene 1 bar, toluene solution, at 40 °C, initial concentration of 1-butene is 0.3823 mol/L. [b]Initial concentration of C16. [c]Comonomer incorporation (mol%) was determined using ^{13}C NMR spectra. [d]monomer feed ratio: X = [PB]/[C16] = [M1]/[M2]. [e] Content ratio of each component in the copolymer: Y = d[M1]/d[M2]. [f] $F = X^2/Y$. [g] $G = X(Y-1)/Y$.

Table S3. Calculation results of isotacticity of copolymers

Run	Catalyst	Sample	*mmmm*	*mmmr+mmmm*
1	Cat.1	PB_1	85%	96%
2	Cat.1	PB-$C8_1$	81%	92%
3	Cat.1	PB-$C12_1$	81%	95%
4	Cat.1	PB-$C16_1$	84%	92%
5	Cat.1	PB-$C20_1$	84%	93%
6	Cat.2	PB_2	96%	96%
7	Cat.2	PB-$C12_2$	94%	98%
8	Cat.2	PB-$C16_2$	95%	99%
9	Cat.2	PB-$C20_2$	95%	95%
10	Cat.4	PB_4	96%	96%
11	Cat.4	PB-$C8_4$	95%	96%
12	Cat.4	PB-$C12_4$	92%	93%
13	Cat.4	PB-$C16_4$	90%	94%
14	Cat.4	PB-$C20_4$	90%	95%

Table S4. Calculation results of isotacticity of copolymers by Cat. 3

Sample	*rmmr*	*mmrr*	*mrrr*	*rrrr*
PB_3	5.3%	6.2%	16.3%	10.2%
PB-$C12_3$	5.5%	5.0%	10.1%	4.8%
PB-$C16_3$	6.7%	4.1%	10.2%	5.9%
PB-C20	5.4%	5.9%	8.0%	8.7%

Table S5. Average elastic recovery rates of the copolymers by Cat.4

Sample	50%	100%	200%	300%	400%	500%	600%	$\bar{x}$
PB-C8(15.0)	45.4%	41.0%	41.5%	44.6%	51.3%	-	-	44.7%
PB-C12(14.1)	72.9%	60.1%	51.2%	53.2%	61.9%	65.5%	-	60.7%
PB-C16(14.5)	79.0%	67.6%	52.0%	53.6%	50.5%	61.2%	-	60.5%
PB-C20(15.5)	54.0%	52.5%	41.3%	45.6%	50.6%	52.5%	57.9%	50.6%

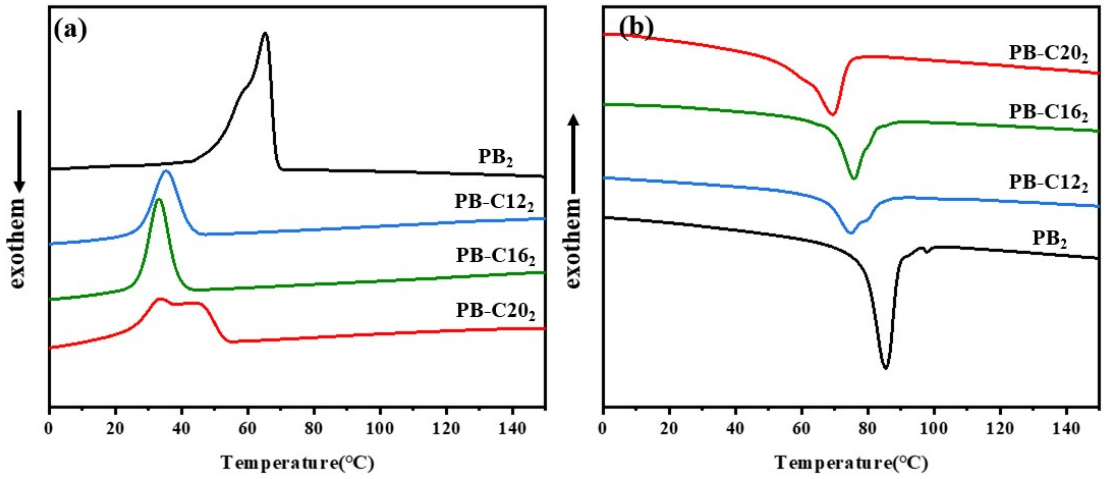

Figure S1. (a) DSC temperature cooling curves of the copolymers by Cat. 2, (b) DSC second heating curves of the copolymers by Cat. 2.

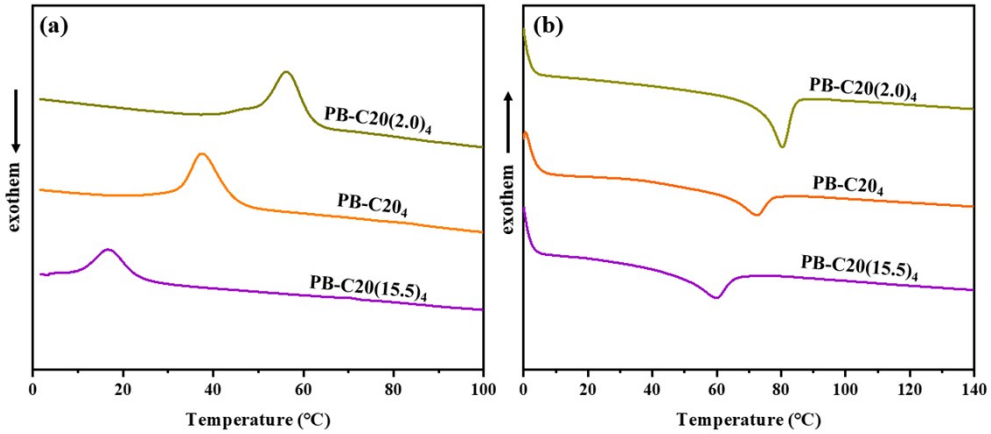

Figure S2. (a) DSC temperature cooling curves of the copolymers by Cat. 4, (b) DSC second heating curves of the copolymers by Cat. 4.

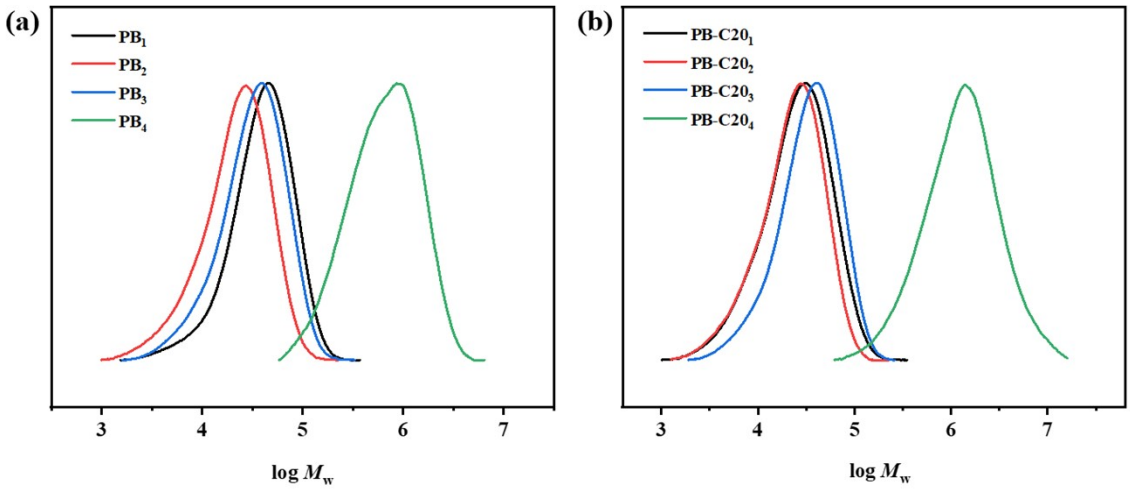

Figure S3. GPC curves of PB and the copolymers PB/C20 by different catalysts.

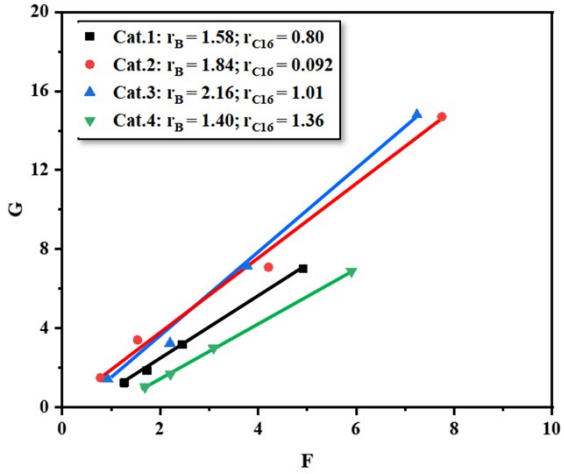

Figure S4. Fineman-Ross plots for copolymerization between 1-butene and C16 by Cat. 1-4**.**

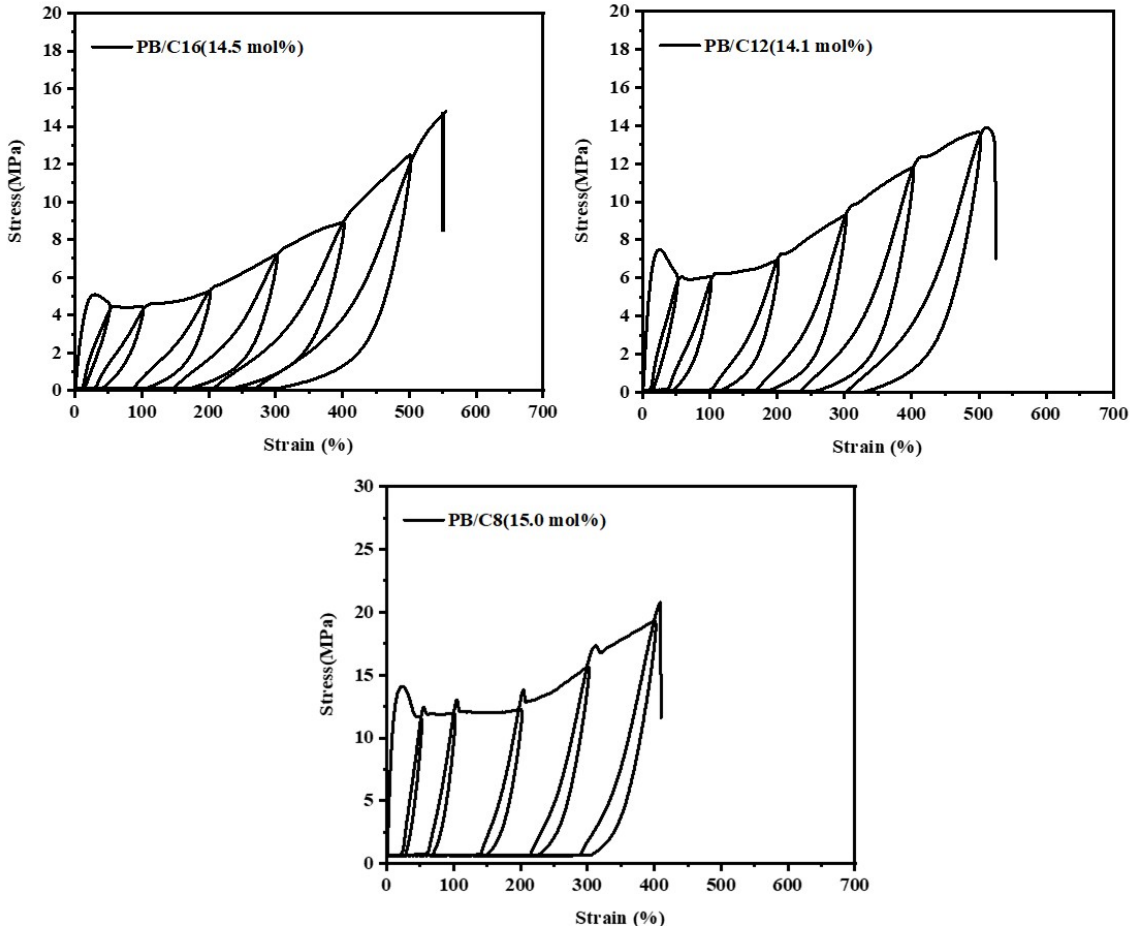

Figure S5. Cyclic tensile test curves of the copolymers by Cat.4.