Supporting information for

Phosphinimide-Ligated Half-Titanocene Dichloride for the Synthesis of Polynorbornenes with Controlled Molecular Weights and Widely Tunable Thermal and Mechanical Properties

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EXPERIMENTAL SECTION

Instrumentation

^{1}H NMR spectra were obtained using a Bruker Avance III HD spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C at 25 °C in $CDCl_3$ or C_6D_6. ^{13}C and DEPT135 NMR spectra were acquired using Bruker Avance III instrument equipped with a cryoprobe (900 MHz for ^{1}H, 225 MHz for ^{13}C) in 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$) at 100 °C. Chemical shifts were reported in parts per million (ppm) downfield relative to tetramethylsilane in $CDCl_3$ (0.00 ppm for ^{1}H) and the residual solvent peak of $CDCl_3$ (77.10 ppm for ^{13}C), $C_2D_2Cl_4$ (6.00 ppm for ^{1}H, 74.47 ppm for ^{13}C), and C_6D_6 (7.16 ppm for ^{1}H). Size-exclusion chromatography (SEC) was performed using a JASCO EXTREMA system equipped with an RI-4035 (JASCO) detector and two tandem HK-404L columns (Shodex). $CHCl_3$ was used as the eluent at 40 °C with a flow rate of 0.3 mL min^{-1}. The columns were calibrated using monodisperse polystyrene standards. Thermogravimetric analysis (TGA) was conducted on a DTG-60 instrument (Shimadzu) at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. The sample sheets for tensile tests and dynamic mechanical analysis (DMA) were prepared by compression molding at 200 °C under 0.78 MPa for 5 min. Rectangular-shaped specimens (10 mm gauge length, 5.0 mm width, 0.3 mm thickness) were used for DMA measurement, while dumbbell-shaped specimens (19 mm gauge length, 2.0 mm width, 0.3 mm thickness) were used for tensile tests. DMA was performed using Rheogel-E4000 (UBM) in tensile mode. The storage modulus E' and loss modulus E'' were measured at frequencies ranging from 1 Hz and 150 Hz over a temperature range from −150 °C to 220 °C at a heating rate of 3 °C/min. Tensile tests were conducted using an AGS-500NX (Shimadzu) at an elongation rate of 10 mm/min at 25 °C. Young's modulus, elongation at break (ε_B), and tensile strength (σ_B) were calculated as the average values from independent measurements (see Fig S13). X-ray diffraction (XRD) measurements were performed using a SmartLab SE X-ray diffractometer (Rigaku) with monochromatic Cu-Kα radiation. Data was collected with a step size of 0.01°, a scan speed of 2.0°/min, and a 2θ angle range of 5° to 30°. Samples were analyzed without annealing.

Materials

Ti-catalysts, **4**–**6**,[1] **7**[2], and **8**[1] were synthesized according to the previous reports. 2-norbornene (**1**) (TCI, >99%) was distilled from CaH_2 under reduced pressure and stored with molecular sieves 3Å. MAO (Tosoh Finechem, TMAO-211, toluene solution, Al: 9.1wt%), 2,6-di-*tert*-butyl-*p*-cresol (BHT) (TCI, >99%), toluene (Wako, deoxidized, oxygen 99.5%), and chlorobenzene (KANTO CHEMICAL, >99 %) were used as received.

Coumpound **8**: ^{1}H NMR (400 MHz, C_6D_6) : δ 7.75-7.66 (6H, m), 7.07-6.94 (9H, m), 6.06 (s, 4H), 2.22 (s, 3H).

Synthesis of **2** and **3**[3]

1-Octene (15.7 g, 140 mmol) and dicyclopentadiene (9.25 g, 70 mmol) were added to a stainless-steel high-pressure autoclave equipped with a magnetic stirring bar. The autoclave was sealed, and the reaction mixture was stirred at 240 °C for 4 h. After cooling to room temperature, the mixture was distilled twice under reduced pressure to yield **2**[4] (5.24 g, 29 mmol, *endo*/*exo* = 79/21) in 42% yield. The synthesis of **3** was similarly performed in 19% yield with *endo*/*exo* = 76/24. These monomers were stored with molecular sieves 3Å. The *endo*/*exo* ratios were estimated from the integral ratio of the alkenyl signals in the ^{1}H NMR spectra.[4]

Coumpound **3**: ^{1}H NMR (400 MHz, $CDCl_3$, *endo* isomer): δ 6.09 (1H, dd, *J* = 3.0 Hz, 5.8 Hz), 6.07 (*exo*) (1H, m), 6.00 (*exo*) (1H, m), 5.90 (1H, dd, *J* = 3.0 Hz, 5.8 Hz), 2.74 (2H, m), 2.49 (*exo*) (1H, m), 1.95 (1H, m), 1.82 (1H, m), 1.40–1.13 (26H, m), 1.05 (2H, m), 0.88 (3H, t, *J* = 6.9 Hz), 0.48 (1H, ddd, *J* = 2.6 Hz, 4.2 Hz,11.2Hz). ^{13}C NMR (100 MHz, $CDCl_3$, *endo* isomer): δ 137.0 (*exo*), 136.9, 136.2 (*exo*), 132.5, 49.7, 46.5 (*exo*), 45.5, 45.3 (*exo*), 42.6, 42.0 (*exo*), 38.9, 36.8 (*exo*), 35.0, 33.2 (*exo*), 32.6, 32.1, 30.1, 29.9, 29.8, 29.5, 29.1 (*exo*), 28.8, 22.8, 14.2.

Polymerization procedure (entry 5 in Table 1)

All reagents were stored and weighed in a nitrogen-filled glovebox. The catalyst and monomer solutions were transferred using a cannula, and the polymerization was performed under an argon atmosphere. To a round-bottomed flask equipped with a three-way stopcock and a magnetic stirring bar, MAO (9.1w% Al in toluene) (1.4 mL, 2.4 mmol) and BHT (0.66 g, 3.0 mmol) in chlorobenzene (1.6 mL) were added and stirred at 25 °C for 30 min. To this flask, the solutions of **1** (4.4 M in toluene) (1.0 mL, 0.41 g, 4.4 mmol) in chlorobenzene (1 mL) were added and stirred at 25 °C for an additional 1 h. To the flask, the solution of **8** (0.95 mg, 2.0 μmol) in chlorobenzene (0.4 mL) was added to initiate the polymerization, and the mixture was stirred at 25 °C for 30 min. The polymerization was quenched by adding MeOH (1 mL). The reprecipitation into a mixture of MeOH (75 mL), acetone (75 mL), and HCl aq (2M, 1 mL) afforded poly**1** (0.36 g) in 87 % yield as a white solid. The polymerizations of **2** and **3** and the copolymerization of **1** with **3** were similarly performed.

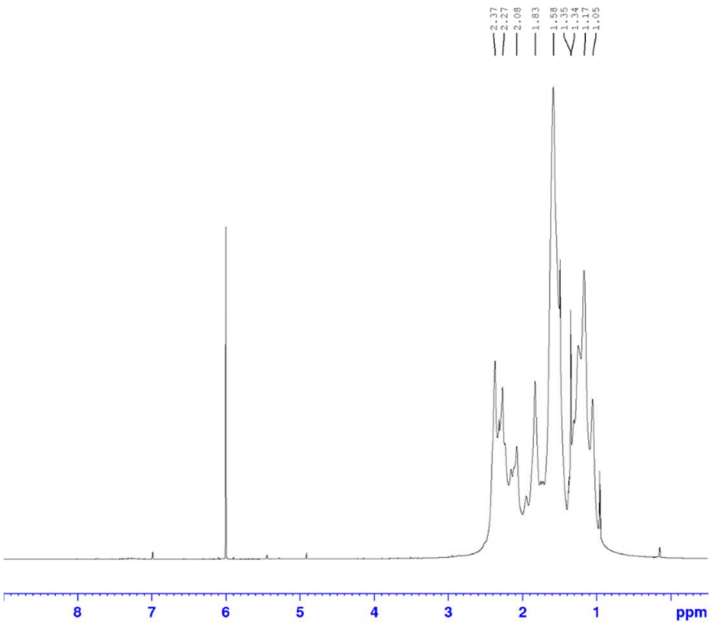

Fig S1. ^{1}H NMR spectrum of poly**1** synthesized using **8**.
($C_2D_2Cl_4$, 100 °C) (entry 5, Table 1).

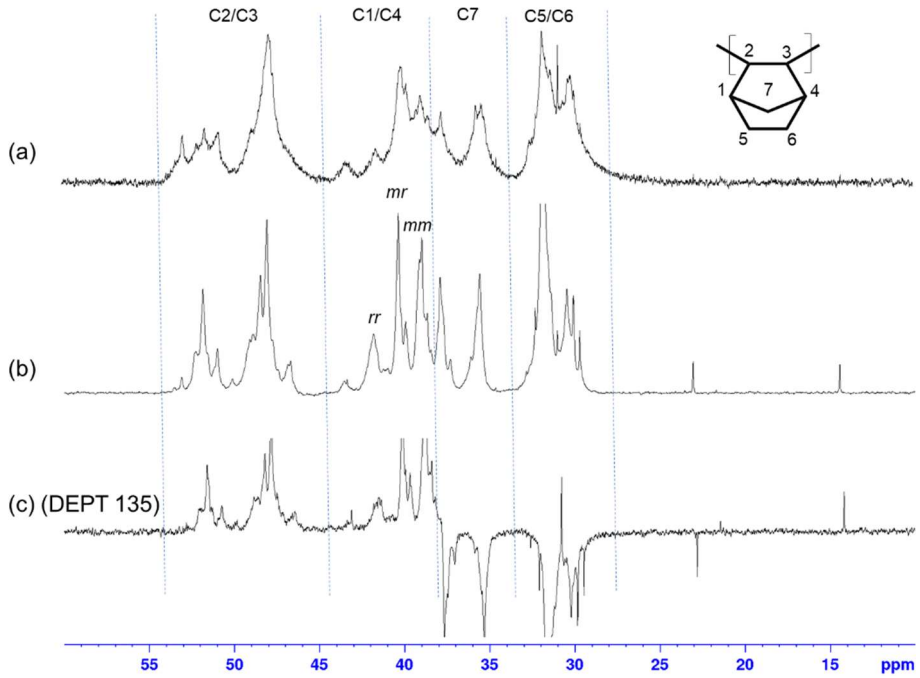

Fig S2. ^{13}C NMR and DEPT 135 NMR spectra of poly**1**.
synthesized using **8** (entry 5, Table 1) (b and c) and **9** (entry 6, Table 1) (a).

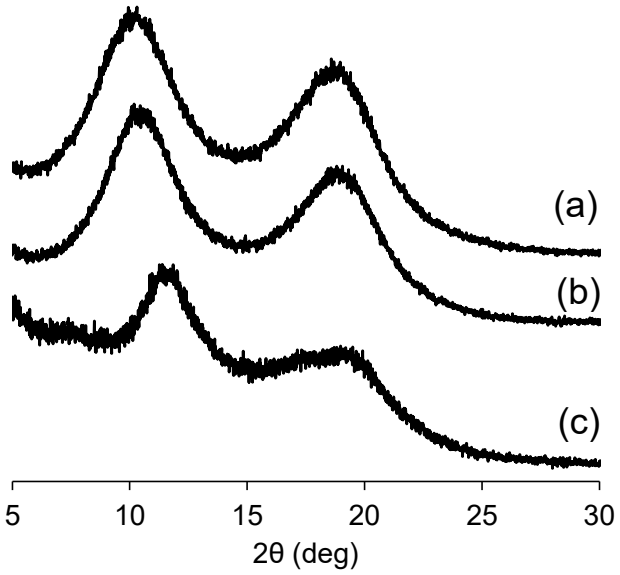

Fig S3. XRD patterns of poly**1**.
obtained using (a) **8** (entry 5 in Table 1), (b) **9** (entry 6 in Table 1)**,** and (c) **10** (entry 7 in Table 1).

Table S1. Solubility test of poly**1** in $CHCl_3$ at a high concentration[a]

entry	polymerization catalyst	poly**1**		**solubility (wt%)[b]**
		M_n (kg/mol)	$Đ^c$	**(chloroform, 30 mg/mL)**
1	**4**	67	1.8	**71**
2	**5**	28	1.6	**89**
3	**6**	27	1.6	**54**
4	**7**	34	1.5	**71**
5	**8**	132	1.5	**70**
6	**9**	59	2.2	**3**
7	**10**	-	-	**0**

[a]The entry numbers correspond to those in Table 1 of the main text. [b]Estimated from the weight percentage of the recovered poly**1** obtained by filtering the polymer solutions (30 mg/mL), which had been stirred at 25 ˚C for 2 h prior to filtration, using a PTFE filter (pore size 0.22 μm).

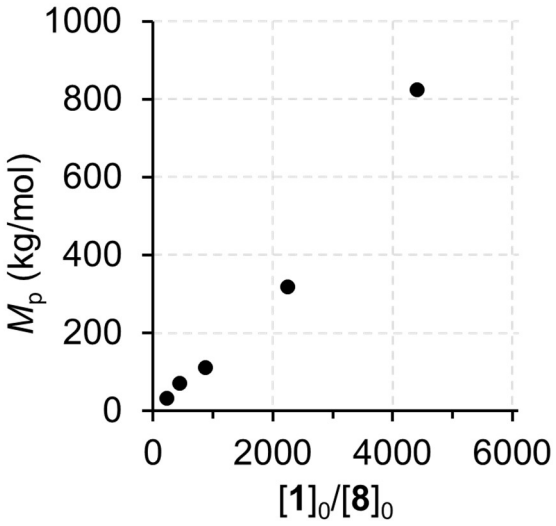

Fig S4. Plots of $[\mathbf{1}]_0/[\mathbf{8}]_0$ versus M_p (SEC peak top) values (Fig 1(A)).
The corresponding SEC curves and data are shown in Fig 1(A).

Table S2. Polymerization of **1** using various catalysts in toluene[a]

entry	cat.	yield[b]	M_n[c]	$Đ$[c]
		%	kg/mol	
1	**4**	35	30	2.4
2	**5**	74	5.8	3.7
3	**6**	65	42	2.1
4	**8**	77	61	2.0

[a]$[\mathbf{1}]_0/[\mathrm{Ti}]_0$ = 2200, **1**: 4.4 mmol, toluene: 3.0 mL, MAO (Al: 4.3 mmol, 9.1 wt%) in toluene: 1.4 mL, BHT: 3.0 mmol. The polymerizations were performed by gradually increasing the temperature from 25 °C to 90 °C over 10 min, followed by heating at 90 °C for an additional 50 min. [b]reprecipitation into MeOH/HCl/acetone. [c]SEC ($CHCl_3$ eluent) using polystyrene standards. gradually increased from 25 °C to 90 °C for 10 min.

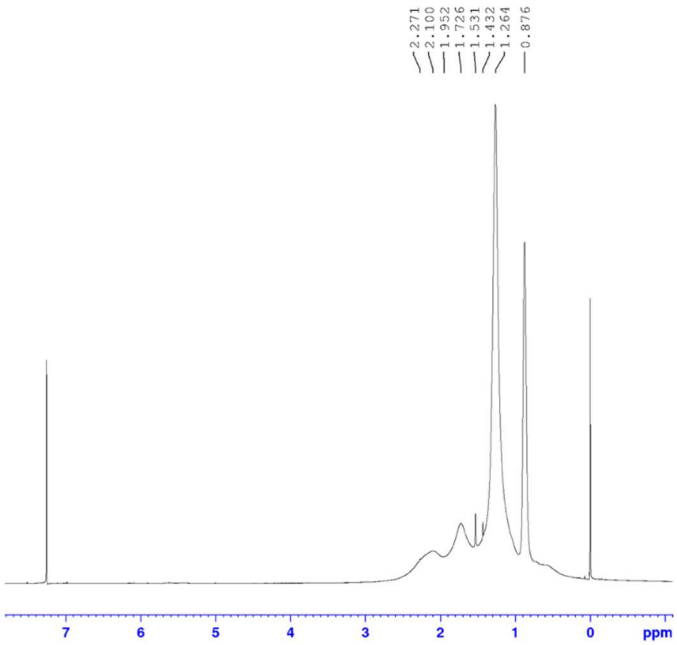

Fig S5. ^{1}H NMR of poly**2**.
(entry 12, Table 1)

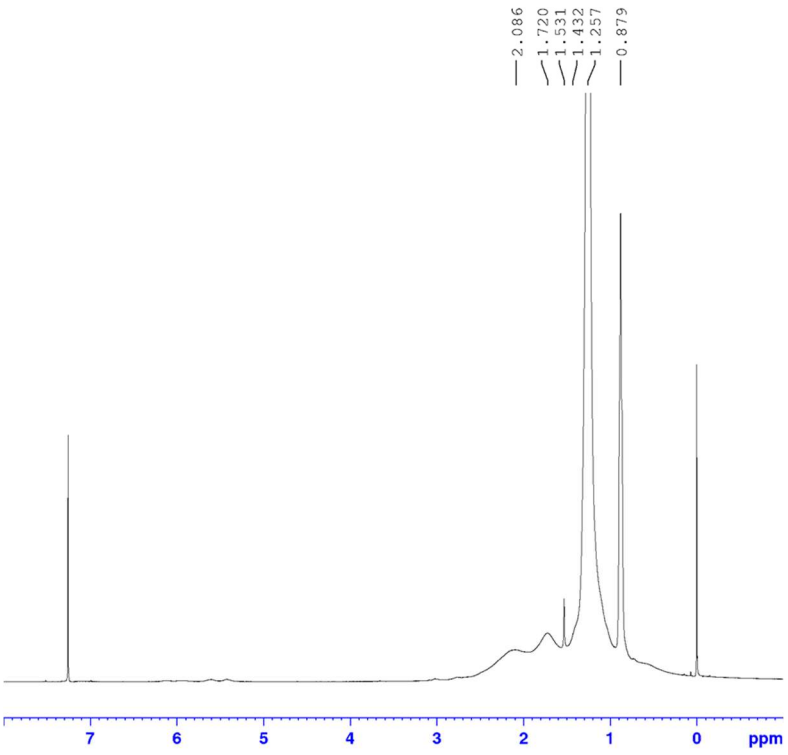

Fig S6. ^{1}H NMR of poly**3**.
(entry 16, Table 1).

Table S3. Polymerization of **2** using **8** in PhCl/toluene mixture at 25 °C for 24 h[a]

entry	**8** / μmol	$[\mathbf{2}]_0/[\mathbf{8}]_0$	yield[b] / %	M_n[c] / kg/mol	$Đ$[c]
1	10	190	60	9.3	1.7
2	5	860	80	15.2	2.1
3	2	2200	67	21.6	2.0

[a] **2**: 1.9 mmol for entry 1, 4.3 mmol for entries 2 and 3, PhCl: 4.0 mL, MAO (9.1 wt%) in toluene: 1.4 mL, BHT: 3.0 mmol. [b] reprecipitation into MeOH/HCl/acetone. [c] SEC ($CHCl_3$ eluent) using polystyrene standards.

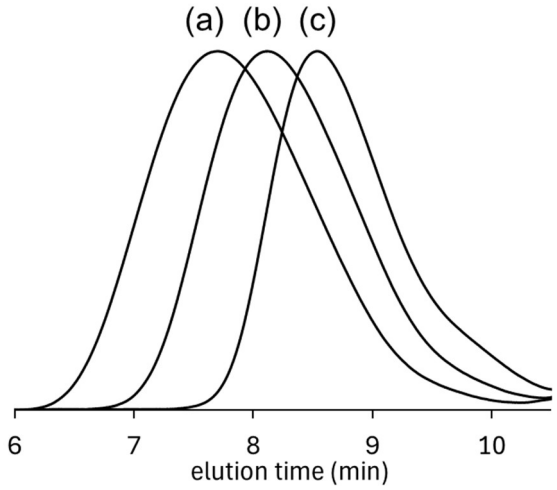

Fig S7. SEC traces of poly**2**s obtained at 0 °C.
various initial monomer-to-catalyst ratio ($[\mathbf{2}]_0/[\mathbf{8}]_0$). (a) entry 15 ($[\mathbf{2}]_0/[\mathbf{8}]_0$ = 870), (b) entry 14 ($[\mathbf{2}]_0/[\mathbf{8}]_0$ = 440), and (c) entry 13 ($[\mathbf{2}]_0/[\mathbf{8}]_0$ = 210) in Table 1.

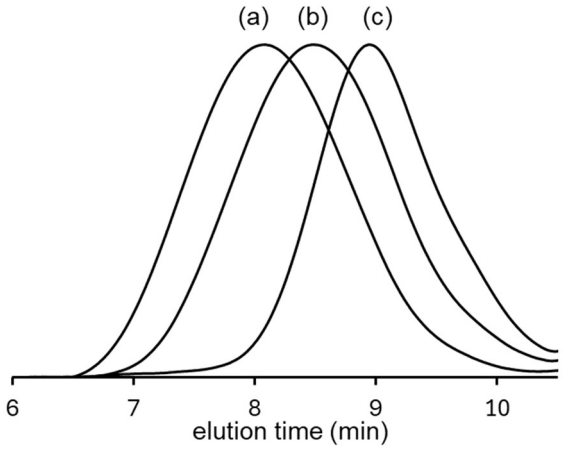

Fig S8. SEC traces of poly**2**s obtained at 25 °C.
various initial monomer-to-catalyst ratio ([**2**]$_0$/[**8**]$_0$). (a) entry 3, (b) entry 2, and (c) entry 1 in Table S2.

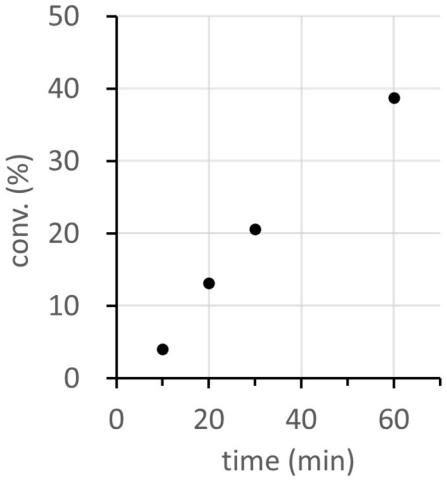

Fig S9. Time versus conversion plots for the polymerization of **2**.
The corresponding SEC curves and molecular weight data are shown in Fig 1(B).

Table S4. Copolymerization of **1** with **2** using **8** in PhCl/toluene mixture at 25 °C.[a]

entry	$[\mathbf{1}]_0/[\mathbf{2}]_0$	yield[b]	M_n[c]	$Đ$[c]	composition of **2**	T_{d10}[d]
		%	kg/mol			˚C
1	48/52	87	31	2.7	0.56	426

[a] for 24 h, total number of moles of **1** and **2**: 8.8 mmol, **8**: 10 μmol, PhCl: 4.1 mL, MAO (9.1 wt%) in toluene: 1.4 mL, BHT: 3.0 mmol. [b] reprecipitation into MeOH/HCl/acetone. [c] SEC ($CHCl_3$ eluent) using polystyrene standards. [d] 10% weight loss temperature by TG/DTA.

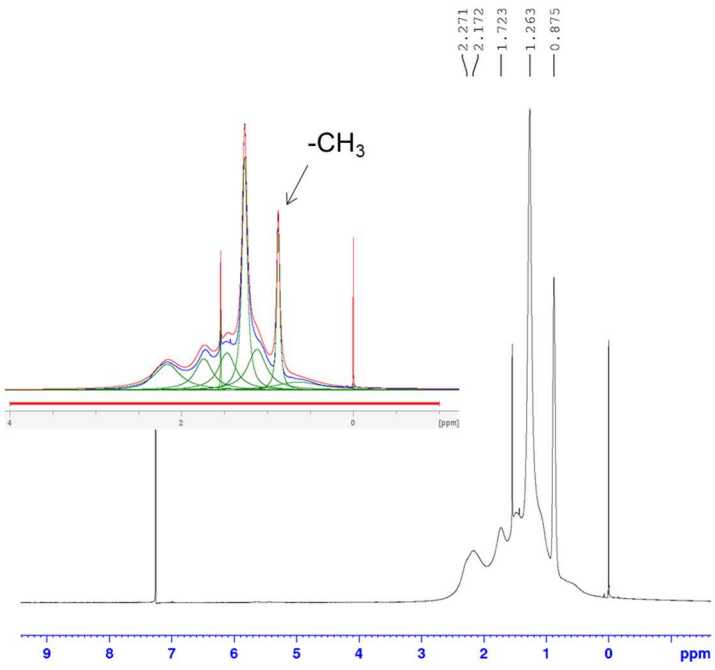

Fig S10. ^{1}H NMR spectrum of poly(**1**-*co*-**2**).
(entry 1, Table S3)
The integral ratio was estimated by deconvolution of the overlapping methyl signal.

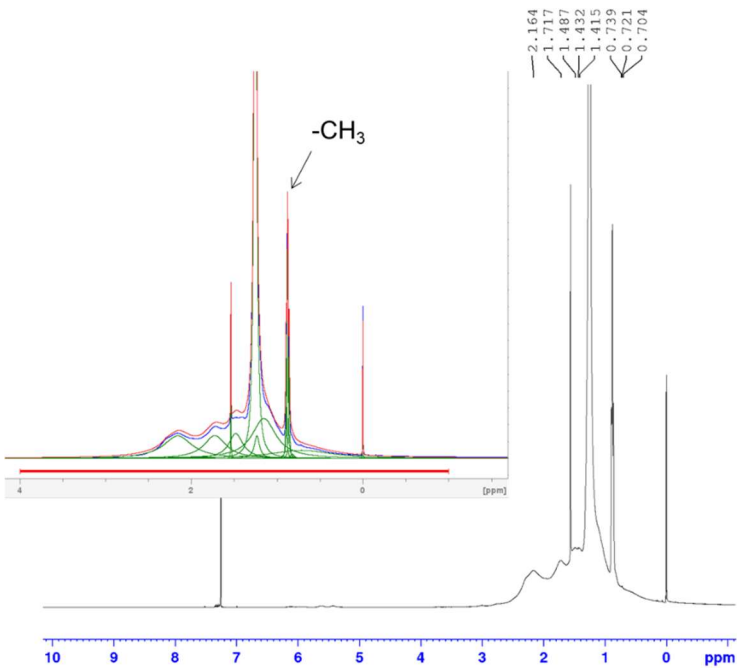

Fig S11. ^{1}H NMR spectrum of poly(**1**-*co*-**3**).
(entry 3, Table 2)
The integral ratio was estimated by deconvolution of the overlapping methyl signal.

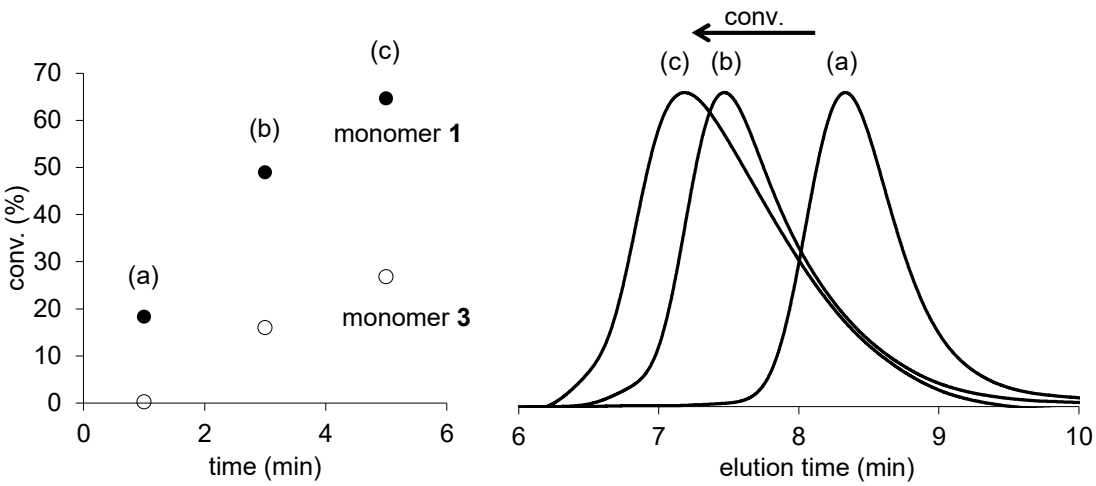

Fig S12. Time versus conversion plots and SEC traces of poly(**1**-*co*-**3**).
under similar conditions of entry 3 in Table 2.

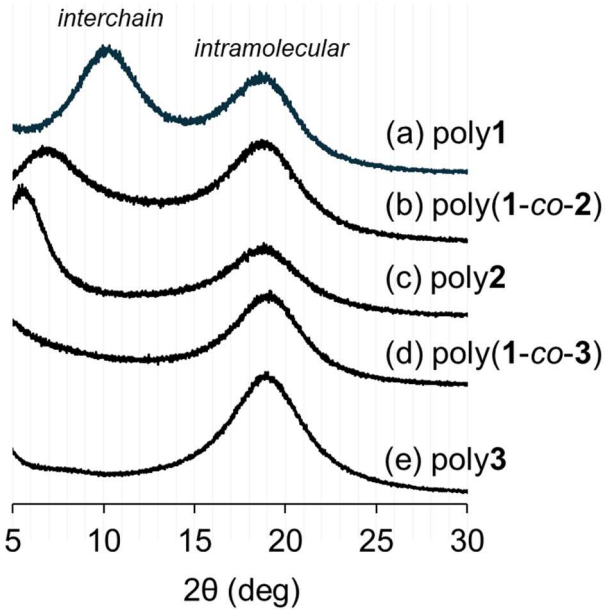

Fig S13. XRD patterns.
(a) entry 5 in Table 1, (b) entry 1, Table S3, (c) entry 12, Table 1, (d) entry 3, Table 2, and (e) entry 17, Table 1.

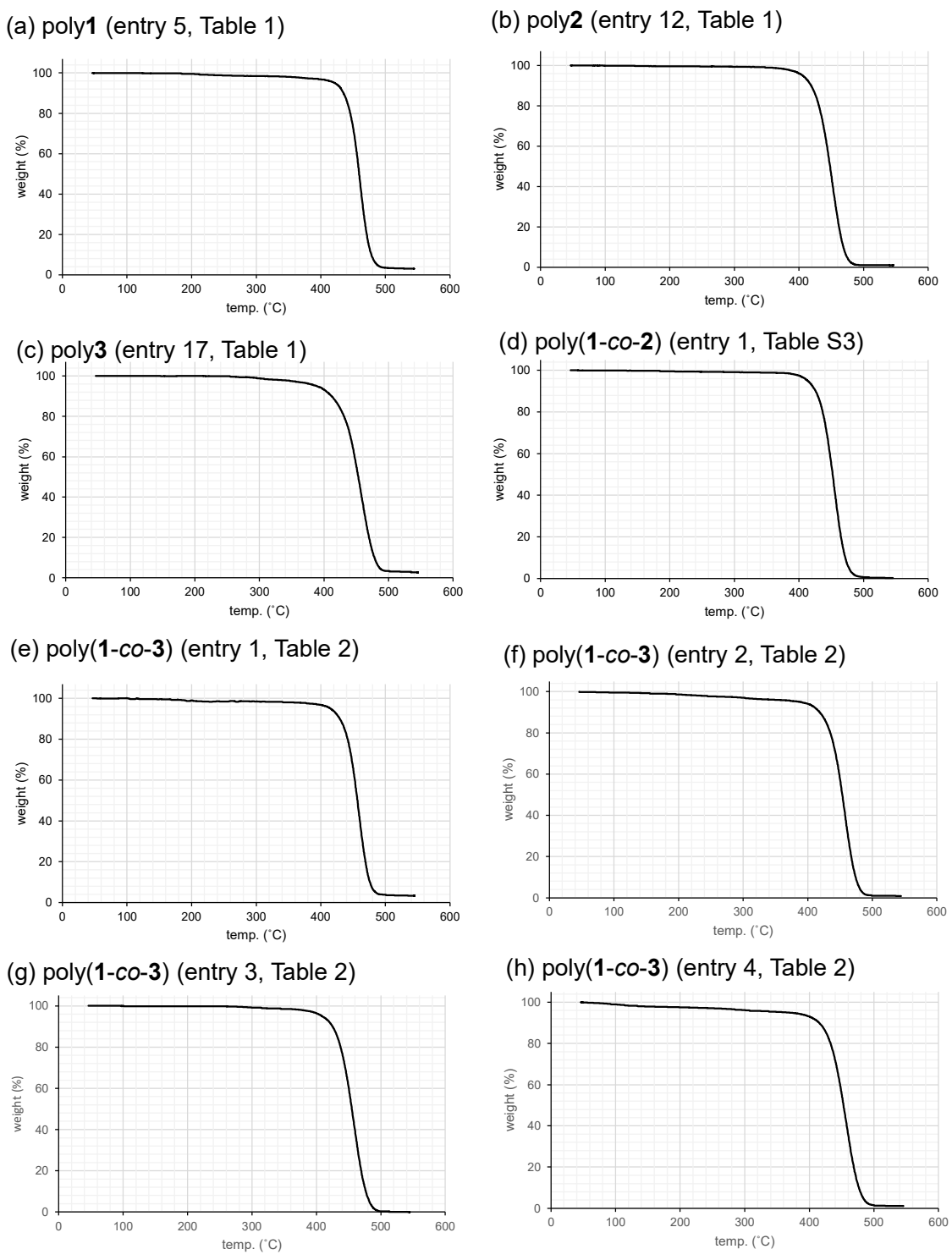

Fig S14. TGA curves.

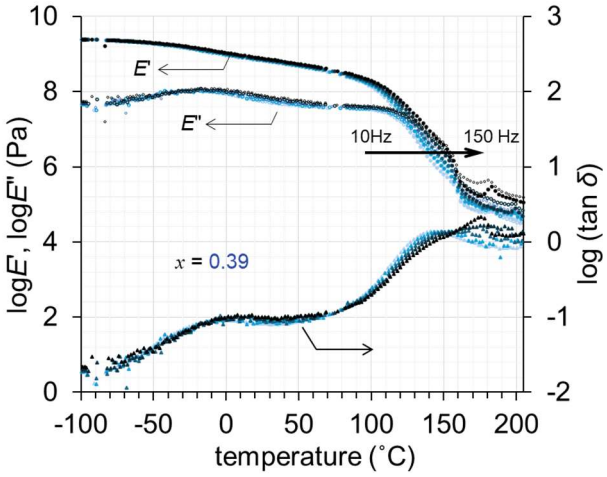

Fig S15. DMA thermograms of poly(**1**-*co*-**3**).

(entry 3 in Table 2)

The measurements were performed at various frequencies, 10.0, 19.7, 38.7, 76.0, and 150 Hz, scanning from −100 °C.

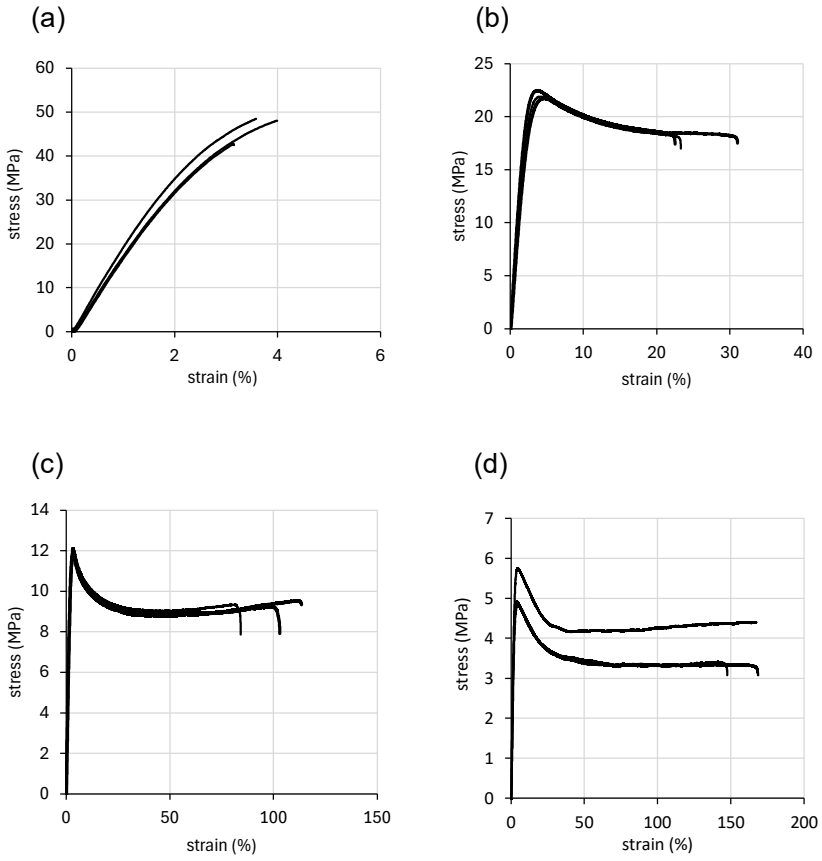

Fig S16. Tensile properties of poly(**1**-*co*-**3**).

(a) entry 1, (b) entry 2, (c) entry 3, and (d) entry 4 in Table 2. The averages of Young's modulus, σ_y, σ_B, ε_y, and ε_B shown in Tables 2 and S5 were estimated from these data.

Table S5. Summary of the thermal and mechanical properties of poly(**1**-*co*-**3**).

entry		T_g (DMA)	Young's modulus	σ_y[b]	σ_B[c]	ε_y[d]	ε_B[e]	toughness
		°C	MPa	MPa	MPa	%	%	MJ/m^3
1	poly(**1**-*co*-**3**) (x = 0.10)	263	1820±73	-	46.4±2.7	-	3.6±0.3	1.0±0.2
2	poly(**1**-*co*-**3**) (x = 0.29)	163	1040±81	22.0±0.3	17.4±0.2	4.2±0.4	26±4	4.8±0.7
3	poly(**1**-*co*-**3**) (x = 0.39)	127	634±19	11.9±0.1	8.4±0.7	3.4±0.1	100±12	9.2±1.0
4	poly(**1**-*co*-**3**) (x = 0.53)	103	266±11	5.2±0.4	3.4±0.7	4.3±0.2	161±10	6.1±0.9
5	poly(**1**-*co*-ethylene)[f]	159	2095±47	-	71±2.5	-	2.5±0.09	0.70±0.05

[a]The polymers in the entries 1-4 correspond to those of the entries in Table 2. For reference, the data of T_g (DMA), Young's modulus, and toughness are reproduced from Table 2. [b]tensile yield stress. [c]tensile stress at break. [d]tensile yield strain. [e]tensile strain at break. [f]a conventional cyclic olefin copolymer (APEL 5514ML, Mitsui Chemicals).

References

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