Supporting information for

Synthesis and properties of cyclic olefin polymers by ring-opening metathesis (co)polymerization of α-methyl-substituted norbornene lactones

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EXPERIMENTAL SECTION

Instrumentation

^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance III HD spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C). The chemical shifts were reported in ppm relative to tetramethylsilane in $CDCl_3$ (0.00 ppm for ^{1}H), and the residual solvent $CDCl_3$ (77.10 ppm for ^{13}C). Size exclusion chromatography (SEC) was performed using a JASCO EXTREMA system with a RI-4035 (JASCO) detector using $CHCl_3$ as the eluent at 40 °C with a flow rate of 0.3 mL/min. Two tandem HK-404L columns (Shodex) were calibrated against polystyrene standards (the molecular weights ranging from 1.20×10^3 to 2.61×10^6). Gas chromatography (GC) analysis was performed on a GC-2014 (Shimadzu) system equipped with a flame ionization detector and a ZB-5 fused-silica capillary column (Zebron). The thermogravimetric analysis (TGA) was carried out with a DTG-60 (Shimadzu) instrument at a heating rate of 10 °C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) measurement was performed on a DSC60-Plus (Shimadzu) apparatus operating with a heating rate of 10 °C/min under a nitrogen atmosphere (FC-60A, Shimadzu). Glass transition temperature (T_g) was determined at the onset of the transition during the second heating scan. Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku SmartLab SE X-ray diffractometer with monochromatic Cu-Kα radiation of 60 kV and 60 mA. Scanning was performed in 0.01° steps at a speed of 1.5 °/min in 2θ angle ranging from 5 to 30°. The samples were measured without heat hysteresis unless otherwise noted. The samples of water contact angle were prepared by the spin-coating (1000 rpm for 60 sec and 5000 rpm for 10 sec) of the polymer in $CHCl_3$ (4.0 mg/0.5 mL) on a glass plate and then drying at 100 °C under reduced pressure for 2 h. Raman spectra were obtained with NRS-3300 (JASCO) with the excitation wavelength of 532.08 nm. Refractive indexes were measured by immersion liquid method. For the measurement of the birefringence, Δn, sample films were uniaxially stretched with a drawn ratio of 2.0 at $T_g + 20$ °C. The retardation (Re) was measured by

RET-100 instrument (Osaka Electonics) at 600 nm, and Δn was calculated by the equation $\Delta n = \mathrm{Re}/d$, where d is thickness of the polymer film.

Materials

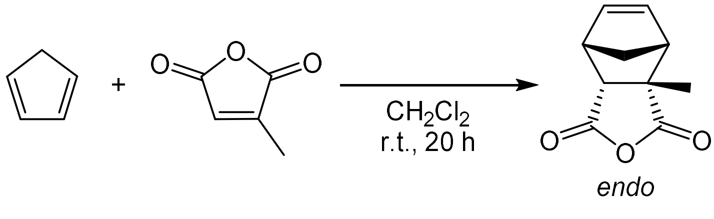
Monomers (*endo*-NBL[1] and *exo*-NBL[1], *endo*-MNBL[2]) were synthesized according to the previous report with slightly modified procedure. Dicyclopentadiene (Aldrich), maleic anhydride (Kanto Chemical, >99%), citraconic anhydride (Tokyo Chemical Industry, >98%), sodium borohydride (Kishida Chemical, >97%), 2-norbornene (Tokyo Chemical Industry, >99%), *endo*-*anti*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene (Tokyo Chemical Industry, >96%), ethyl vinyl ether (Tokyo Chemical Industry, 98%), Grubbs Catalyst® 1st Generation (G1) (Aldrich, 97%), Grubbs Catalyst® 2nd Generation (G2) (Aldrich), Grubbs Catalyst® 3rd Generation (G3) (Aldrich), $RuHCl(CO)(PPh_3)_3$ (Aldrich), *p*-toluenesulfonyl hydrazide (TSH, Tokyo Chemical Industry, >98%) were used as received. Dry solvents such as THF, CH_2Cl_2, and DMF (Kanto chemical) were used as received. 1,1,2,2-Tetrachloroethane (Kishida Chemical, 97%) was distilled from P_2O_5 and stored over Molecular Sieves 4Å. *o*-Xylene and DMAc were distilled from CaH_2 and stored over Molecular Sieves 4Å.

General

All reactions and polymerizations were carried out under nitrogen atmosphere using standard Schlenk techniques or a grove box.

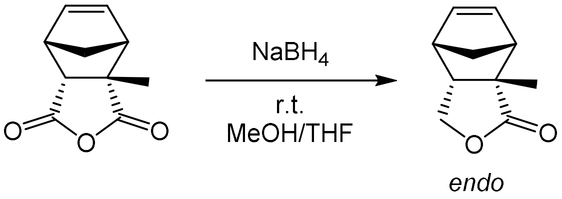
Monomer Synthesis

Synthesis of endo-2-methyl-5-norbornene-2,3-dicarboxylic anhydride[2]



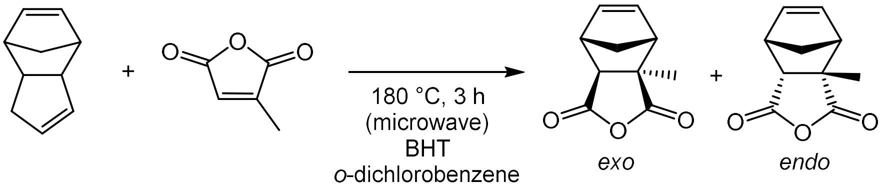
Freshly distilled cyclopentadiene (4.90 g, 74.2 mmol) was added to a solution of citraconic anhydride (7.95 g, 72.2 mmol) in CH_2Cl_2 (40 mL) at 0 °C. The reaction mixture was stirred for 20 h at room temperature under dark conditions. The volatiles were evaporated under vacuum, and the recrystallization from methanol gave *endo*-2-methyl-5-norbornene-2,3-dicarboxylic anhydride as a white solid in 85% yield (10.9 g, 61.2 mmol). For ^{1}H and ^{13}C NMR data, see reference 2.

Synthesis of 2-methyl-4-oxa-endo-tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (endo-MNBL)[2]



A solution of *endo*-2-methyl-5-norbornene-2,3-dicarboxylic anhydride (13.3 g, 74.6 mmol) in a mixed solvent of THF (40 mL) and methanol (3 mL) was added dropwise to a suspended solution of $NaBH_4$ (2.8 g, 75 mmol) in THF (54 mL) at 0 °C. After stirring for 1 h at room temperature, the reaction mixture was neutralized by the addition of HCl aq (2.0 M) at 0 °C. The volatiles were evaporated under vacuum, and the mixture was extracted with CH_2Cl_2, washed with water and brine, and dried over anhydrous $MgSO_4$. After sublimation and recrystallization from methanol, *endo*-MNBL was obtained as a white solid in 39% yield (4.79 g, 29.2 mmol). For ^{1}H and ^{13}C NMR data, see reference 2.

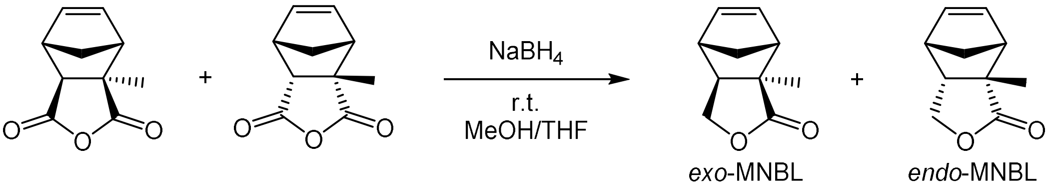
Synthesis of endo/exo-2-methyl-5-norbornene-2,3-dicarboxylic anhydride



Dicyclopentadiene (2.96 g, 22.4 mmol), citraconic anhydride (5.24 g, 46.8 mmol) and a trace amount of 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) were dissolved in *o*-dichlorobenzene (5.0 mL). The solution was stirred under microwave irradiation at 180 °C for 3 h. After the volatiles were evaporated under vacuum and subsequent sublimation, the mixture of *endo/exo*-2-methyl-5-norbornene-2,3-

dicarboxylic anhydride (3.74 g, 21.0 mmol) was obtained as a white solid in 47% yield (*endo/exo*, 45:55). The ratio of *endo/exo* was calculated by the ^{1}H NMR integral ratio of methyl groups (1.62 ppm for *endo*-MNBL, 1.32 ppm for *exo*-MNBL).

Synthesis of 2-methyl-4-oxa-endo/exo-tricyclo[5.2.1.$0^{2,6}$]dec-8-en-3-one (endo/exo-MNBL)



A solution of the mixture *endo*/*exo*-2-methyl-5-norbornene-2,3-dicarboxylic anhydride (*endo/exo*, 45:55) (5.47 g, 30.7 mmol) in THF (16 mL) and methanol (1.2 mL) was added dropwise to a suspended solution of $NaBH_4$ (1.1 g, 31 mmol) in THF (22 mL) at 0 °C. After stirring for 1 h at room temperature, the reaction mixture was neutralized by the addition of HCl aq (2.0 M) at 0 °C. The volatiles were evaporated under vacuum, and the mixture was extracted with CH_2Cl_2, washed with water and brine, and dried over anhydrous $MgSO_4$. The Kugelrohr distillation gave *endo/exo*-MNBL (2.44 g, 14.9 mmol) as a white solid in 49% yield (*endo/exo,* 30:70). ^{1}H NMR for *exo*-MNBL ($CDCl_3$, 400 MHz): δ 6.29–6.25 (m, 2H), 4.48 (dd, $J = 9.7, 8.8$ Hz, 1H), 4.00 (dd, $J = 9.7, 3.0$ Hz, 1H), 2.95–2.91 (m, 1H), 2.90–2.86 (m, 1H), 2.00 (m, 1H), 1.56–1.53 (m, 2H), 1.22 (s, 3H). ^{13}C NMR for *exo*-MNBL ($CDCl_3$, 100 MHz): δ 181.8 (C=O), 137.6 (CH=), 136.0 (CH=), 70.7 (CH_2), 53.4 (C_q), 50.5 (CH), 49.7 (CH), 47.6 (CH), 45.4 (CH_2), 21.3 (CH_3).

Polymerizations

ROMP of endo-MNBL (entry 3, Table 1)

A solution of *endo*-MNBL (84 mg, 0.51 mmol) in CH_2Cl_2 (1.0 mL) was added to a solution of G3 (4.4 mg, 5.0 μmol) in CH_2Cl_2 (1.0 mL) at room temperature. After stirring for 1 h at room temperature, a few drops of ethyl vinyl ether were added to terminate the polymerization. The mixture was stirred for additional 30 min. The solvent was then evaporated under vacuum. A small aliquot was sampled and subjected to ^{1}H NMR measurement to estimate the monomer conversion. The mixture was dissolved in a small quantity of CH_2Cl_2 and reprecipitated into methanol. The product was dried under vacuum at 100 °C for 3 h to give 74 mg of poly(*endo*-MNBL) as a white solid in 89% yield.

ROMCP of endo-MNBL and NB (entry 8, Table 2)

The *endo*-MNBL (84 mg, 0.47 mmol) in CH_2Cl_2 (1.0 mL) was added to the solution of G3 (8.8 mg, 10 μmol) in CH_2Cl_2 (2.0 mL). At the same time, a solution of NB (47 mg, 0.49 mmol) in CH_2Cl_2 (1.0 mL) was added dropwise to the polymerization mixture over 5 min using a micro-syringe pump. After stirring for 1 h at room temperature, a few dops of ethyl vinyl ether were added, and the mixture was stirred for additional 30 min. Then, the solvent was partially evaporated, and the solution was reprecipitated into methanol. The product was dried under vacuum at 100 °C for 3 h to give 99 mg of poly(*endo*-MNBL-*ran*-NB) as a white solid in 76% yield.

Chain extension polymerization of endo-MNBL

The ROMP was carried out by the addition of a solution of *endo*-MNBL (81 mg, 0.45 mmol) in CH_2Cl_2 (1.0 mL) at 0 °C to the solution of G3 (4.4 mg) in CH_2Cl_2 (1.0 mL). The mixture was stirred at 0 °C for 2 h. A small aliquot was sampled from the mixture and quenched with a few drops of ethyl vinyl ether at 0 °C. The quantitative conversion of the monomer was confirmed by ^{1}H NMR. A solution of *endo*-MNBL (80 mg, 0.45 mmol) in CH_2Cl_2 (1.0 mL) at 0 °C was added to the polymerization mixture. After stirring at 0 °C for 3 h, a few drops of ethyl vinyl ether were added, and the mixture was stirred for additional 30 min. The solvent was evaporated under vacuum, and the conversion was estimated by ^1H NMR. The mixture was dissolved in a small quantity of CH_2Cl_2 and reprecipitated into methanol. The product was dried under vacuum at 100 °C for 3 h and subjected to the SEC measurement.

Kinetic study on the ROMCP of endo-MNBL and exo-MNBL

A solution of a mixture of *endo*-MNBL and *exo*-MNBL (1/1) (83 mg, 0.47 mmol), and 1,1,2,2-tetrachloroethane (63 mg, 0.38 mmol) as an internal standard in CH_2Cl_2 (1.0 mL) was added to G3 (4.4 mg, 5.0 μmol) in CH_2Cl_2 (1.0 mL) at −20 °C. During the ROMCP, aliquots were sampled at different time points and immediately quenched by a few drops of ethyl vinyl ether at −20 °C. The conversions were determined by the GC analysis.

Hydrogenation

Hydrogenation of poly(endo-MNBL) with H_2/$RuHCl(CO)(PPh_3)_3$

Poly(*endo*-MNBL) (50 mg) was dispersed in a mixed solvent of *N*,*N*-dimethylacetamide (DMAc) (1.0 mL) and *o*-xylene (2.0 mL) in a glass reaction tube. $RuHCl(CO)(PPh_3)_3$ (3 mg, 3 μmol) was added to the glass reaction tube. The reaction tube was transferred to a stainless-steel autoclave reactor, and nitrogen substitution was performed. Hydrogenation was carried out under the hydrogen pressure of 0.75 MPa at 135 °C for 6 h. After the reaction, the mixture was precipitated into methanol. The product was dried under vacuum at 100 °C for 3 h to give 47 mg of H-poly(*endo*-MNBL) in 93% yield. The conversions were determined by ^1H NMR.

Hydrogenation of poly(endo-MNBL) with TSH

Poly(*endo*-MNBL) (98 mg) and TSH (1.1 g, 5.9 mmol, 10 equivalent relative to the double bond) was dispersed in a solvent of *N*,*N*-dimethylformamide (DMF) (1.5 mL). After stirring for 5 h at 135 °C, the reaction mixture was precipitated into methanol. The product was dried under vacuum at

100 °C for 3 h to give 94 mg of H-poly(*endo*-MNBL) as a white solid in 95% yield. The conversions were determined by ^{1}H NMR.

Table S1. Hydrogenation of poly(*endo*-MNBL) and poly(*endo*-MNBL-*co*-*exo*-MNBL).

entry	poly(MNBL)[a] *endo*/*exo*	cat. or reagent[b]	solvent[c] (v/v)	temp. °C	time h	conv.[d] %	$10^{-3}M_n$[e]	M_w/M_n[e]	T_g[f] °C
1	100/0	H_2/RuHCl(CO)$(PPh_3)_3$	*o*-xylene	135	6	60	26	1.09	-
2	100/0	H_2/RuHCl(CO)$(PPh_3)_3$	*o*-xylene	165	6	57	25	1.11	-
3	100/0	H_2/RuHCl(CO)$(PPh_3)_3$	*o*-xylene/DMAc (2/1)	135	6	81	25	1.11	-
4	100/0	H_2/RuHCl(CO)$(PPh_3)_3$	*o*-xylene/DMAc (2/1)	135	12	88	25	1.12	-
5	100/0	TSH (10 eq.)	DMF	135	5	95	24	1.12	192
6	30/70	TSH (10+20 eq.)	DMF	150	5+5	92	27	1.13	173
7	50/50	TSH (10+20 eq.)	DMF	135	5+5	95	27	1.10	173
8	71/29	TSH (10+20 eq.)	DMF	150	5+5	95	28	1.10	184
9	poly(*endo*-NBL)	TSH (10 eq.)	DMF	135	5	>99	27[g]	1.53[g]	-

[a] 50 mg. [b] Ru cat.: 3 mg (entries 1-4). [c] 2 mL (entries 1, 2; insoluble), 3 mL (entries 3, 4; soluble), 1.5 mL (entries 5-9). [d] by ^1H NMR ($CDCl_3$). [e] by GPC ($CHCl_3$, PSt std.). [f] by DSC. [g] by GPC (DMF, PMMA std.).

Table S2. Hydrogenation of poly(*endo*-NBL-*co*-TCD) and poly(*exo*-NBL-*co*-TCD).

entry	polymer[a]	cat. or reagent[b]	solvent		temp.	time	conv.[c]	$10^{-3}M_n$[d]	M_w/M_n[d]	T_g[e]
			type	mL	°C	h	%			°C
1	poly(*endo*-NBL-*grad*-TCD)	H_2/RuHCl(CO)$(PPh_3)_3$	*o*-xylene	2.0	135	6 h	(>99)[f]	(22)[f]	(1.25)[f]	168
2	poly(*endo*-NBL-*ran*-TCD)	H_2/RuHCl(CO)$(PPh_3)_3$	*o*-xylene	2.0	135	6 h	(>99)[f]	(27)[f]	(1.59)[f]	168
3	poly(*endo*-NBL-*ran*-TCD)	TSH (10 eq.)	DMF	1.5	135	5 h	(>99)[f]	(22)[f]	(1.63)[f]	-
4	poly(*exo*-NBL-*ran*-TCD)	H_2/RuHCl(CO)$(PPh_3)_3$	*o*-xylene	2.0	135	6 h	97	54	1.09	142
5	poly(*exo*-NBL-*ran*-TCD)	TSH (10 eq.)	DMF	1.5	135	5 h	97	41	1.37	-

[a] 50 mg. [b] 3 mg of RuHCl(CO)$(PPh_3)_3$. [c] by ^1H NMR ($CDCl_3$). [d] by GPC ($CHCl_3$, PSt std.). [e] by DSC. [f] soluble fraction.

Table S3. Hydrogenation of poly(*endo*-MNBL-*co*-NB)[a]

entry	polymer[b]	conv.[c] %	$10^{-3}M_n$[d]	M_w/M_n[d]	T_g[e] °C
1	poly(*endo*-MNBL-*grad*-NB)	98	24	1.14	-
2	poly(*endo*-MNBL-*block*-NB)	97	20	1.34	*m.p.*
3	poly(*endo*-MNBL-*ran*-NB)	98	23	1.26	102

[a] with TSH (10 eq.) in DMF (1.5 mL) at 135 °C for 5 h. [b] 50 mg. [c] by ^{1}H NMR ($CDCl_3$). [d] by GPC ($CHCl_3$, PSt std.). [e] by DSC.

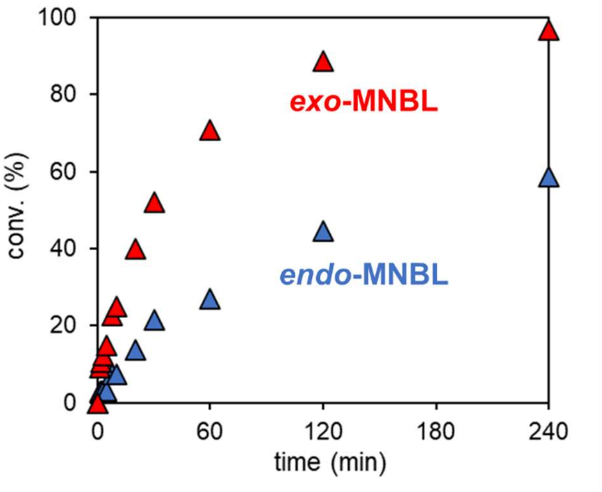


Figure S1. Time-conversion plots of the copolymerization of *endo*-MNBL and *exo*-MNBL by G3 in CH_2Cl_2 at −20 °C (Kinetic plots of ln([M_0]/[M]) versus time is shown in Figure 2).

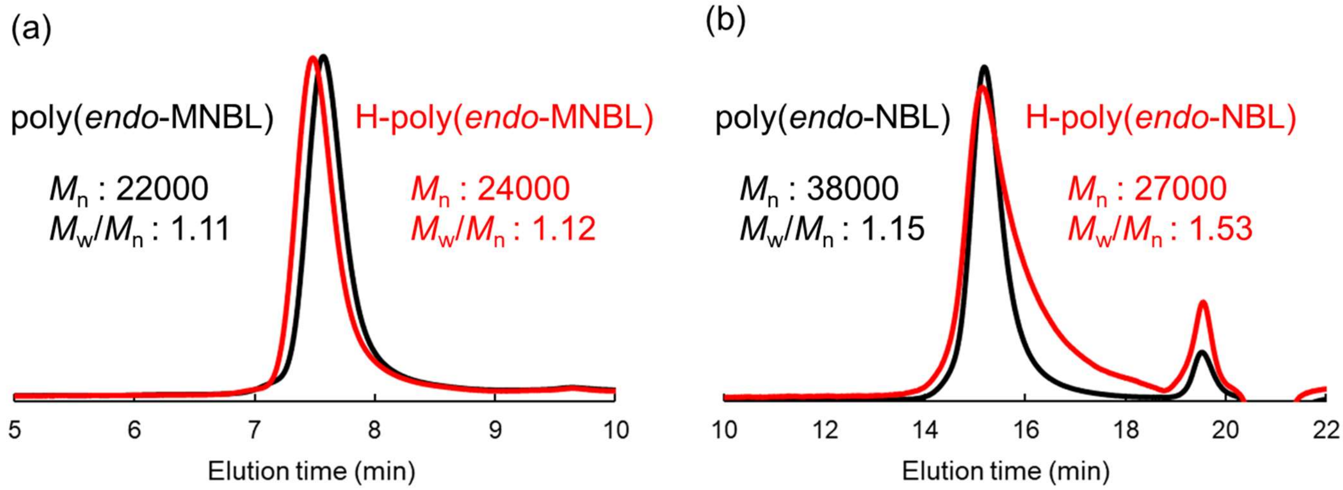


Figure S2. SEC profiles of before and after the hydrogenation of (a) poly(*endo*-MNBL) ($CHCl_3$ as the eluent) and (b) poly(*endo*-NBL) (DMF as the eluent).

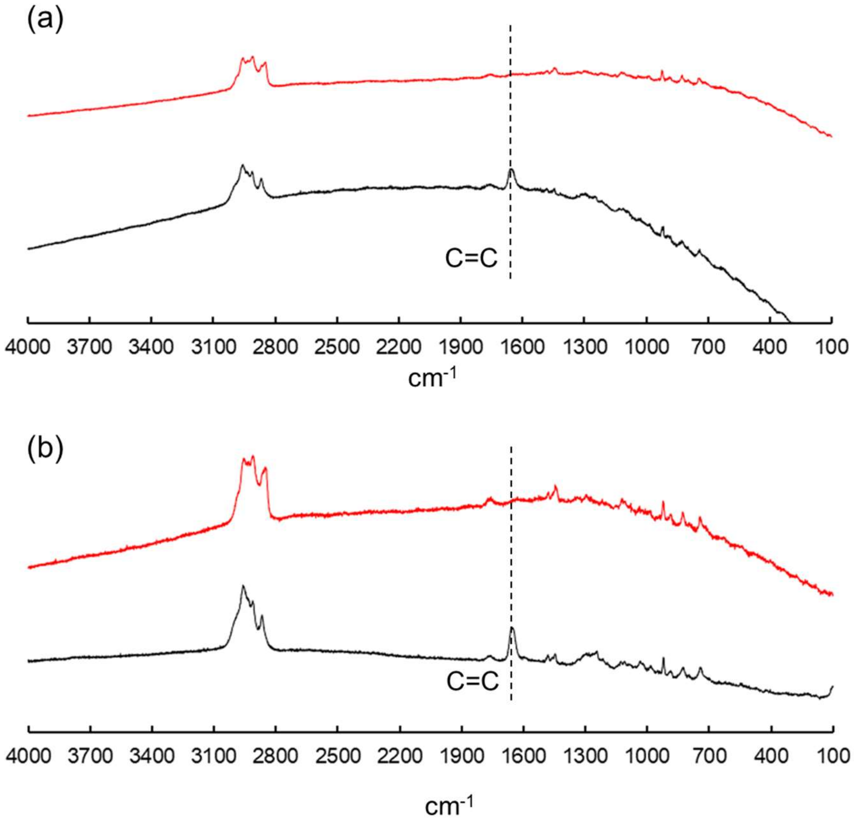


Figure S3. Raman spectra of before (black) and after (red) the hydrogenation of (a) poly(*endo*-NBL-*grad*-TCD) (entry 1, Table 2) and (b) poly(*endo*-NBL-*ran*-TCD) (entry 2, Table 2).

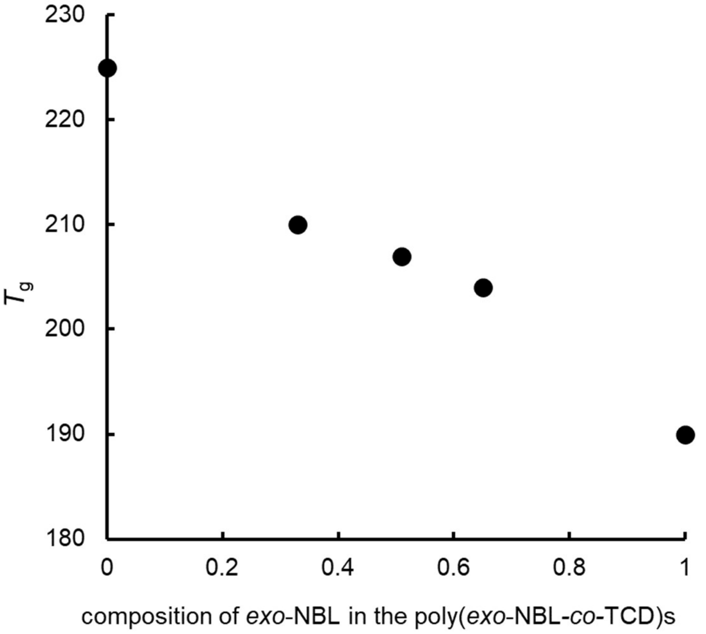


Figure S4. T_g **values of poly(*exo*-NBL-*co*-TCD)s at various compositions of *exo*-NBL unit.**

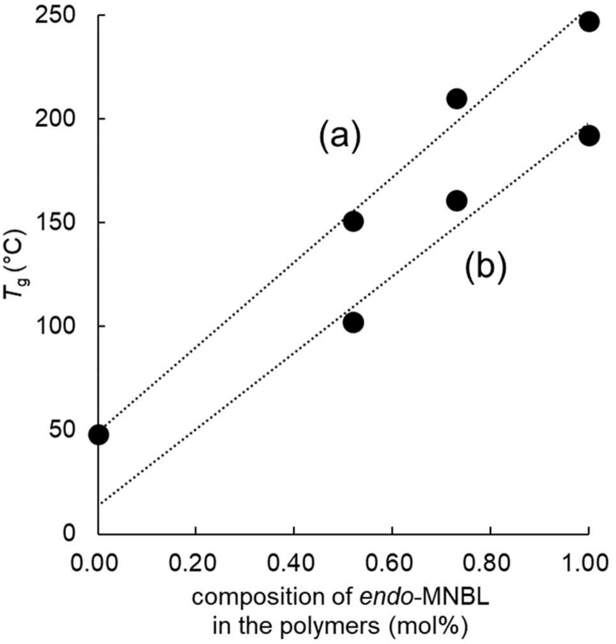


Figure S5. T_g **values of (a) poly(*endo*-MNBL-*ran*-NB)s and (b) H-poly(*endo*-MNBL-*ran*-NB)s at various compositions of *endo*-MNBL unit.**

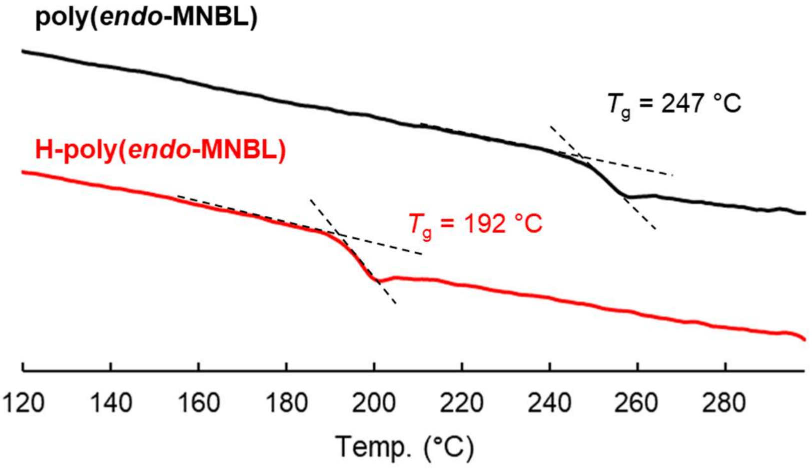


Figure S6. DSC curves and T_g values of poly(*endo*-MNBL) and H-poly(*endo*-MNBL).

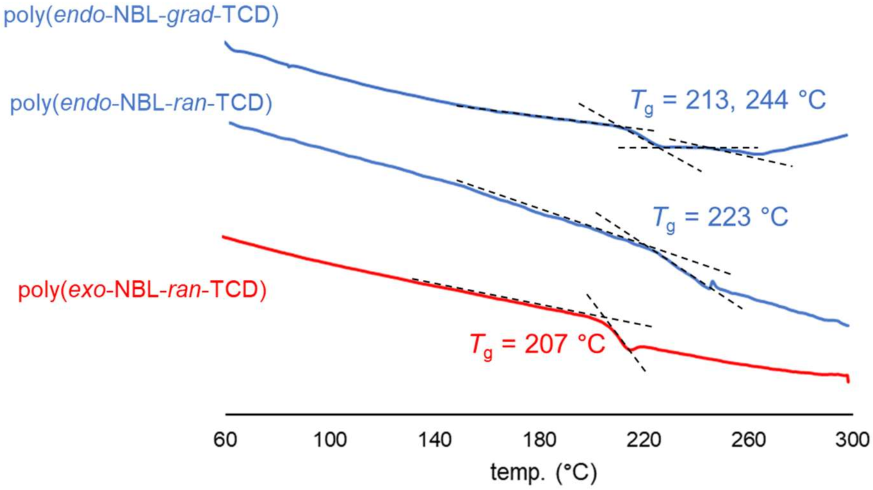


Figure S7. DSC curves and T_g values of poly(*endo*-NBL-*grad*-TCD) (entry 1 in Table 2), poly(*endo*-NBL-*ran*-TCD) (entry 2 in Table 2) and poly(*exo*-NBL-*ran*-TCD) (entry 4 in Table 2).

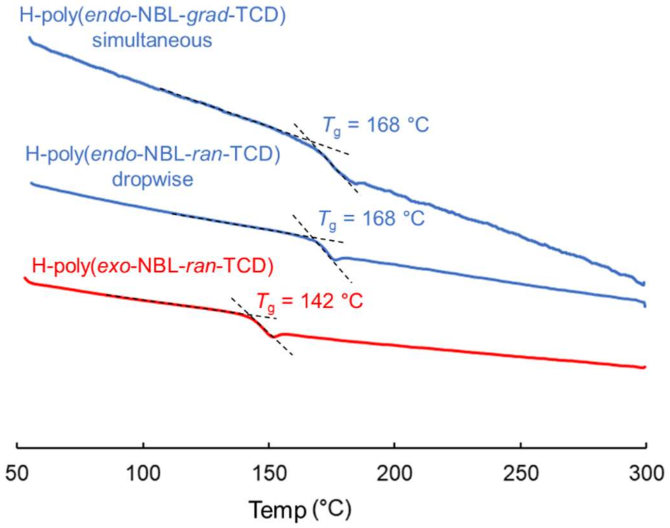


Figure S8. DSC curves and T_g values of H-poly(*endo*-NBL-*grad*-TCD) (entry 1 in Table S2), H-poly(*endo*-NBL-*ran*-TCD) (entry 2 in Table S2), and H-poly(*exo*-NBL-*ran*-TCD) (entry 4 in Table S2).

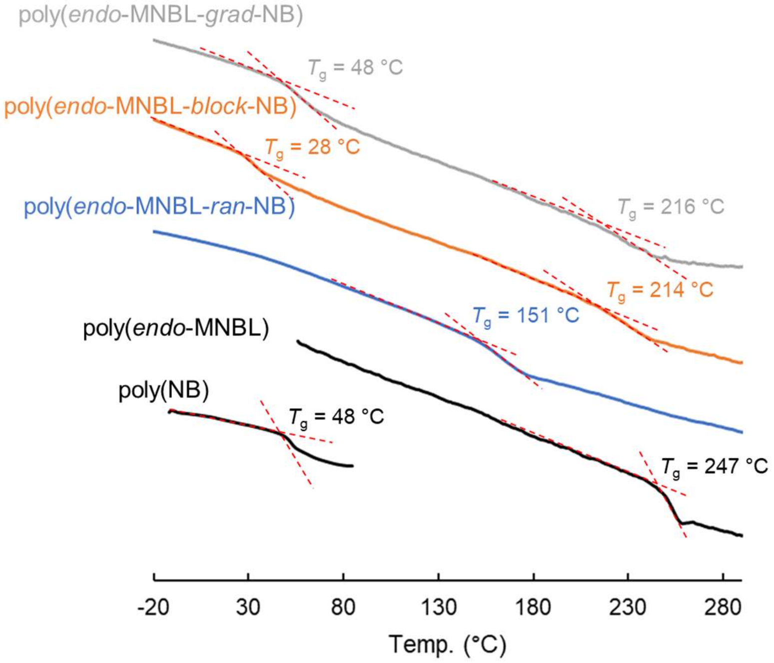


Figure S9. DSC curves and T_g values of poly(*endo*-MNBL-*co*-NB)s compared with the corresponding homopolymers.

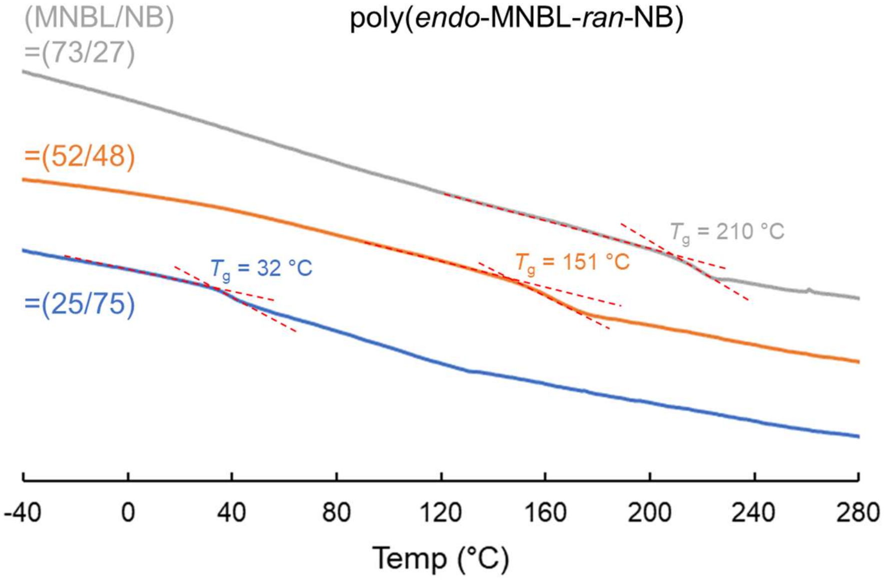


Figure S10. DSC curves and T_g values of poly(*endo*-MNBL-*ran*-NB)s with various compositions.

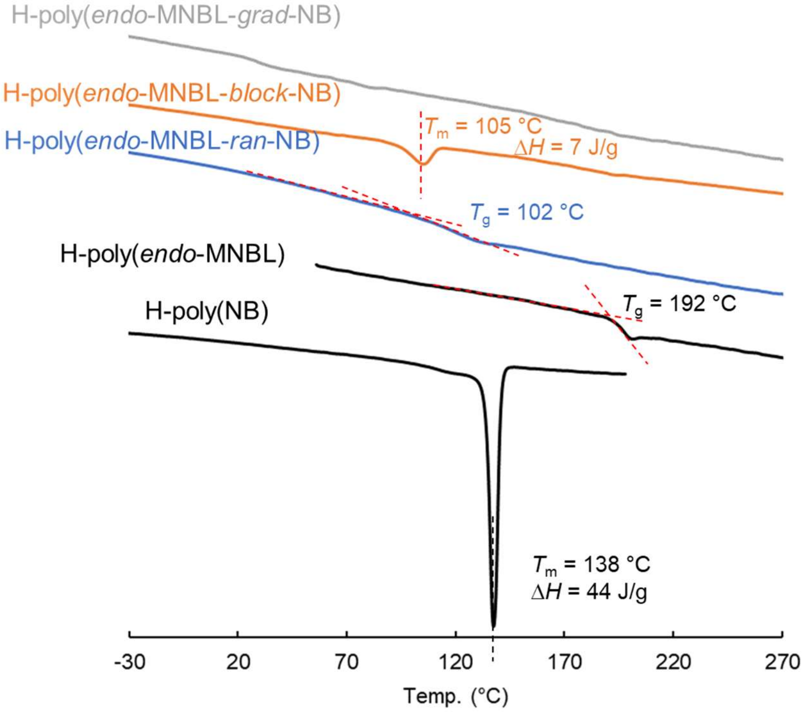


Figure S11. DSC curves and T_g values of H-poly(*endo*-MNBL-*co*-NB)s compared with the corresponding homopolymers.

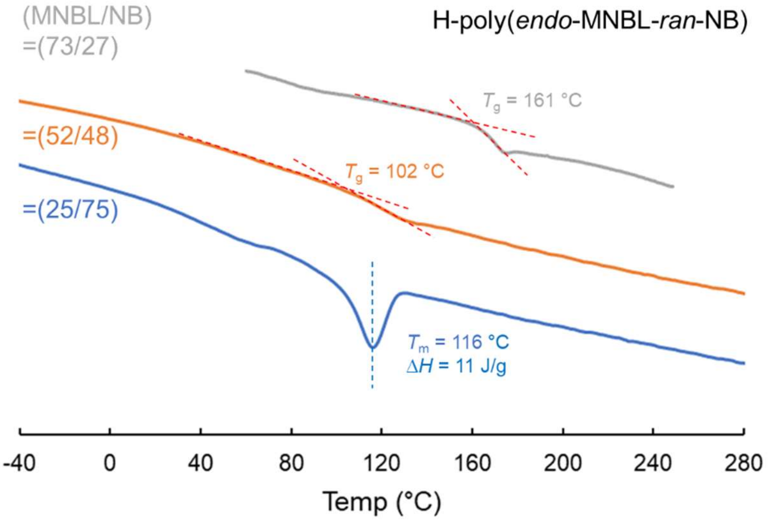


Figure S12. DSC curves and T_g values of H-poly(*endo*-MNBL-*ran*-NB)s with various compositions.

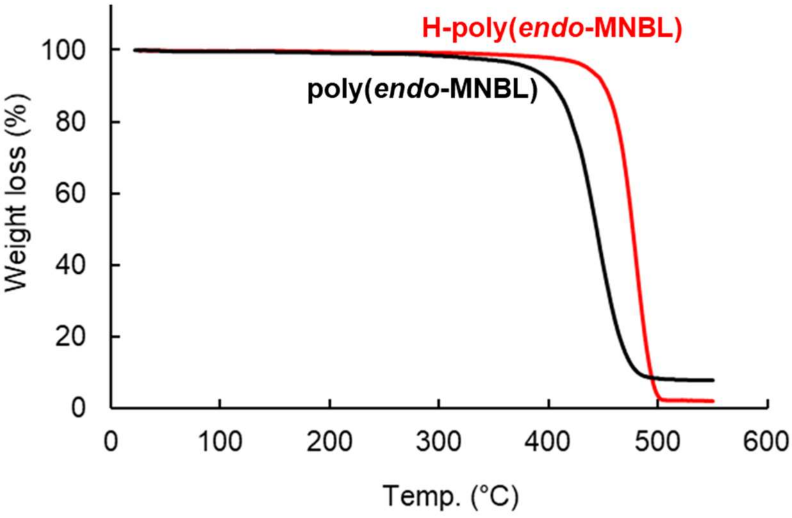


Figure S13. TGA curves of poly(*endo*-MNBL) and H-poly(*endo*-MNBL)

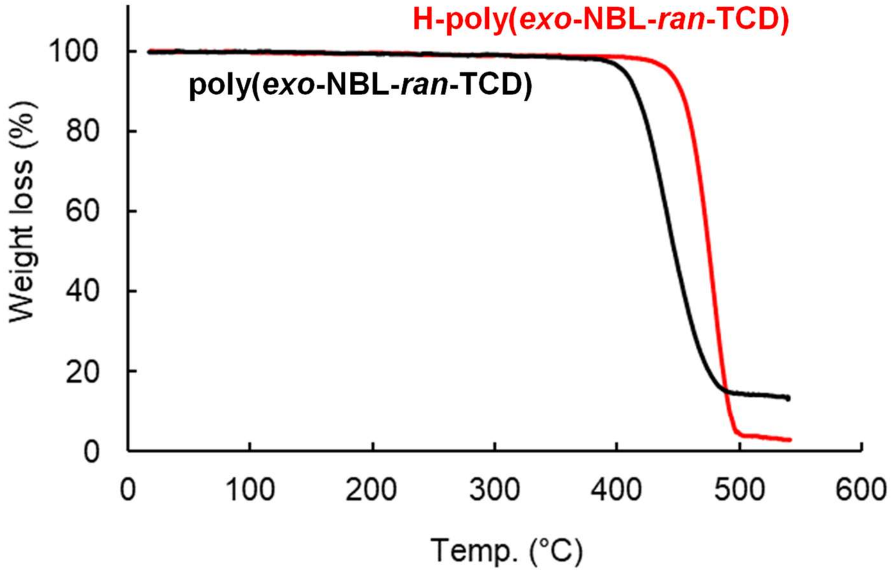


Figure S14. TGA curves of poly(*exo*-NBL-*ran*-TCD) and H-poly(*exo*-NBL-*ran*-TCD) (NBL/TCD = 53/47)

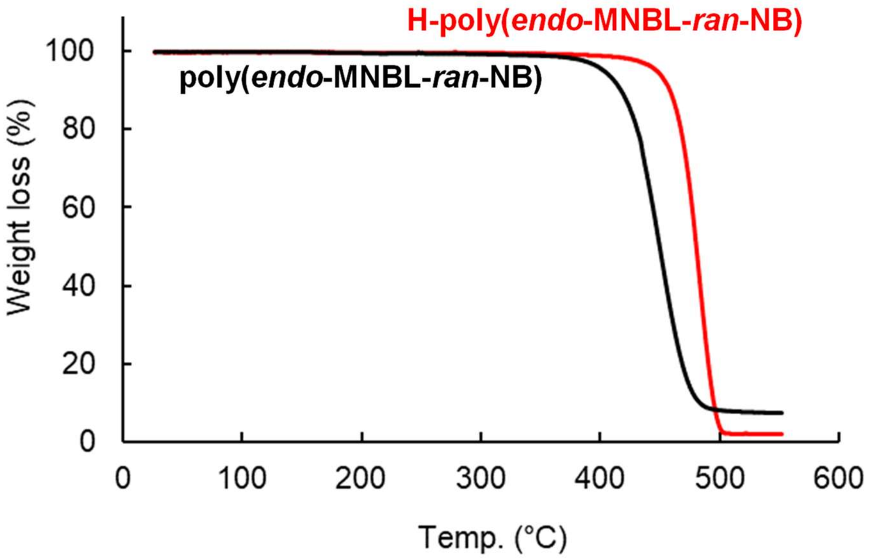


Figure S15. TGA curves of poly(*endo*-MNBL-*ran*-NB) and H-poly(*endo*-MNBL-*ran*-NB) (*endo*-MNBL /NB = 52/48)

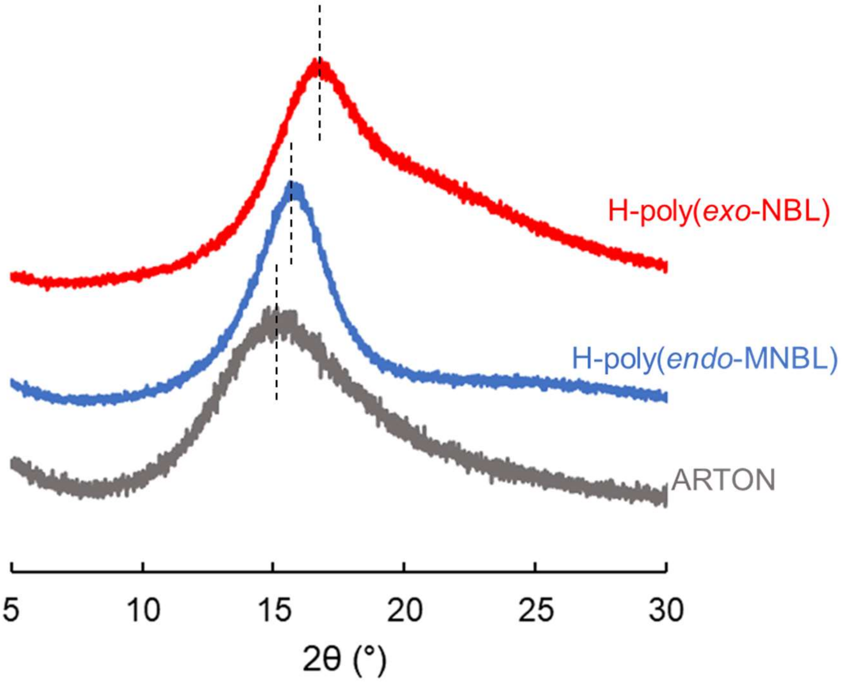


Figure S16. XRD patterns of H-poly(NBL)s and ARTON.

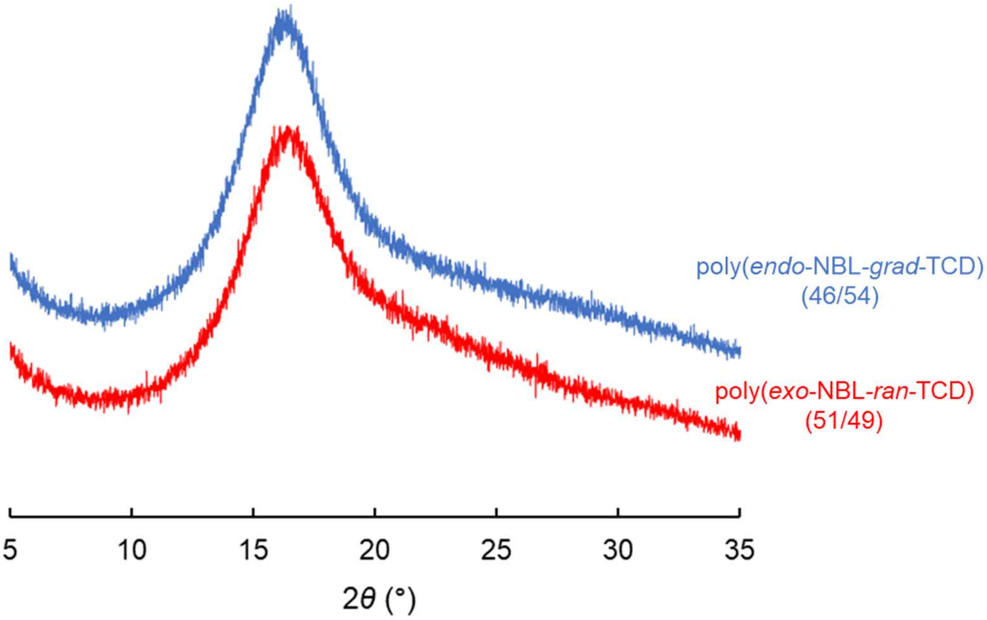


Figure S17. XRD patterns of poly(NBL-*co*-TCD)s.

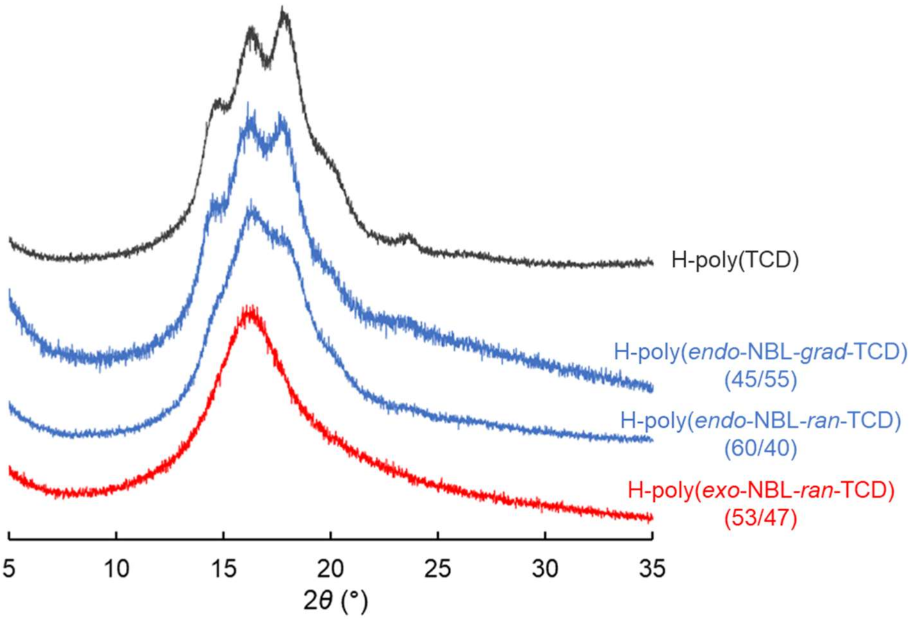


Figure S18. XRD patterns of H-poly(NBL-*co*-TCD)s compared with H-poly(TCD).

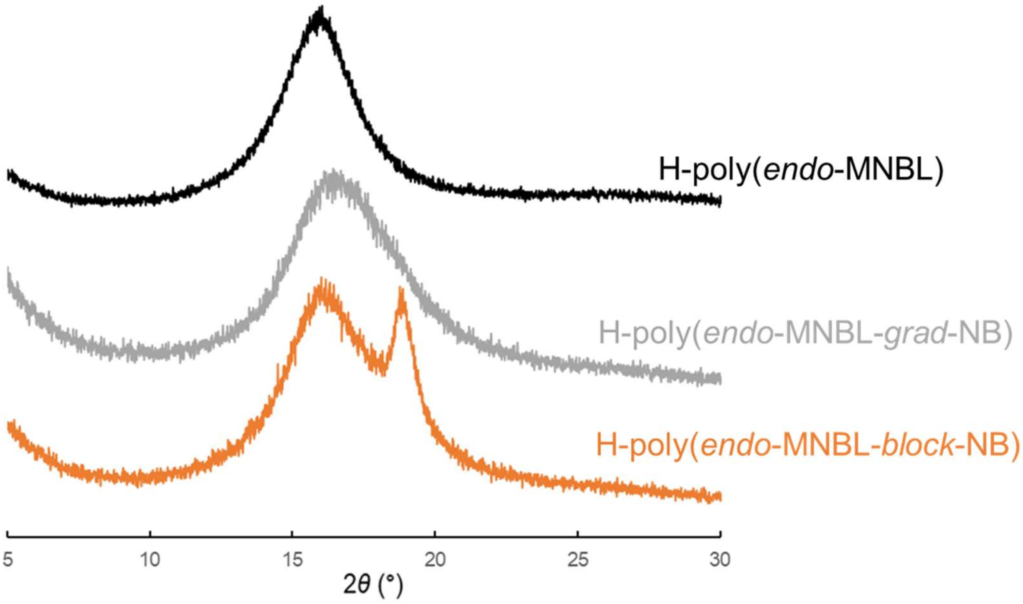


Figure S19. XRD patterns of H-poly(*endo*-MNBL) and H-poly(MNBL-*co*-NB)s with heat hysteresis (annealed at 200 °C for 30 min).

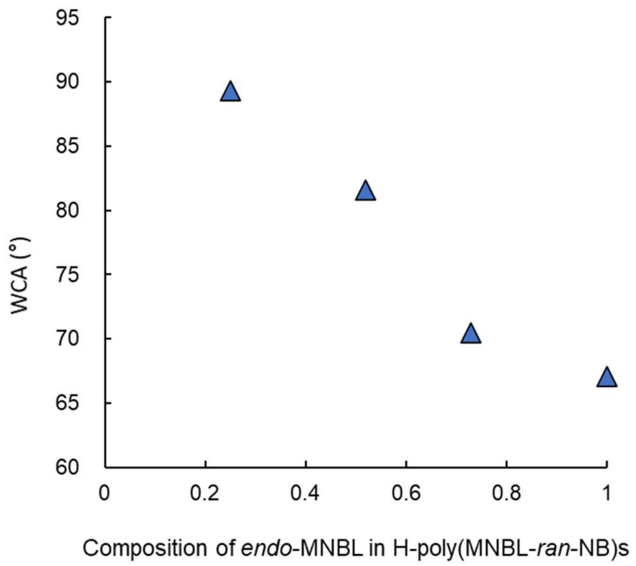
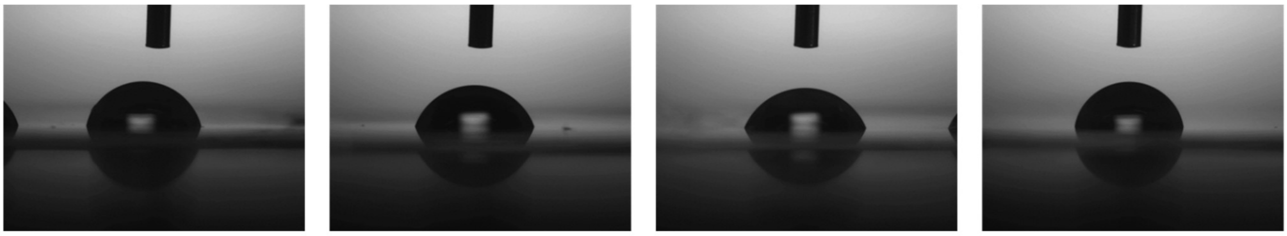
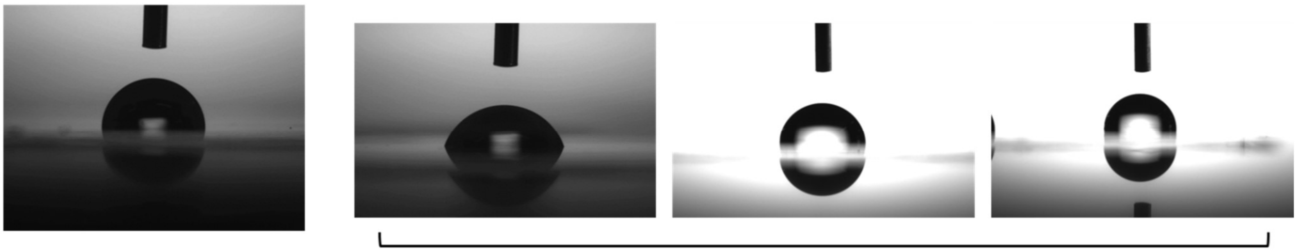


Figure S20. Water contact angle (°) at various compositions of *endo*-MNBL in H-poly(MNBL-*ran*-NB)s.



H-poly(*endo*-NBL) H-poly(*exo*-NBL) H-poly(*endo*-MNBL) ARTON®



H-poly(*exo*-NBL-*ran*-TCD)
(*exo*-NBL/TCD = 1/1)

H-poly(*endo*-MNBL-*ran*-NB)
(*endo*-MNBL/NB = 73/27) (52/48) (25/75)

Figure S21. Pictures of water contact angle measurement.

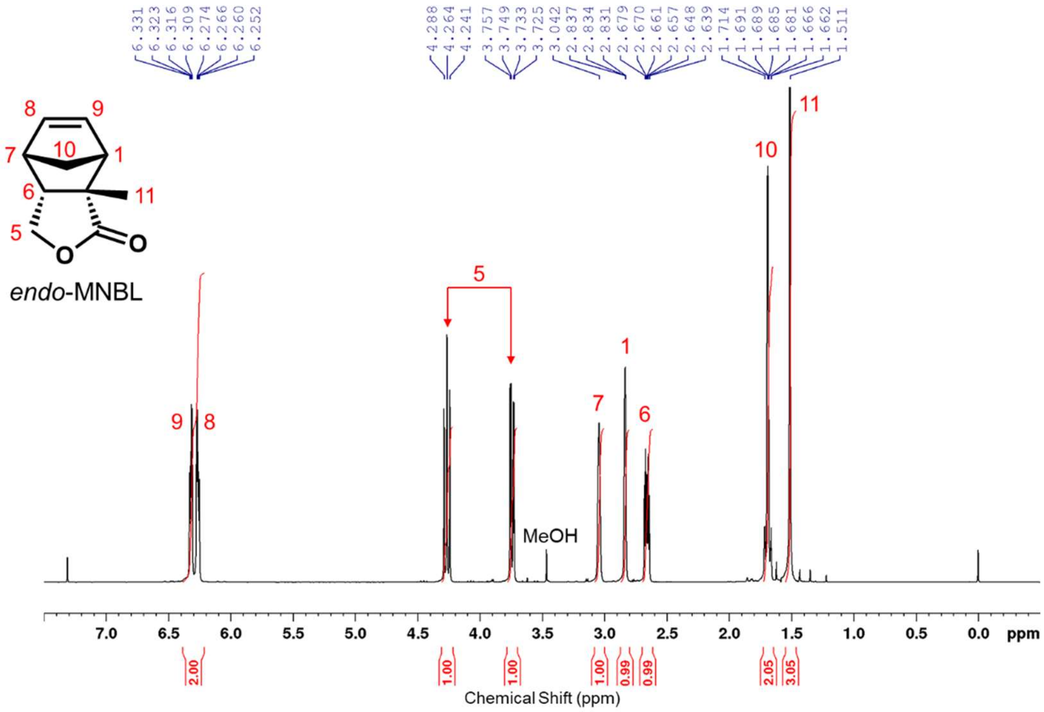


Figure S22. ^{1}H NMR spectrum of *endo*-MNBL.

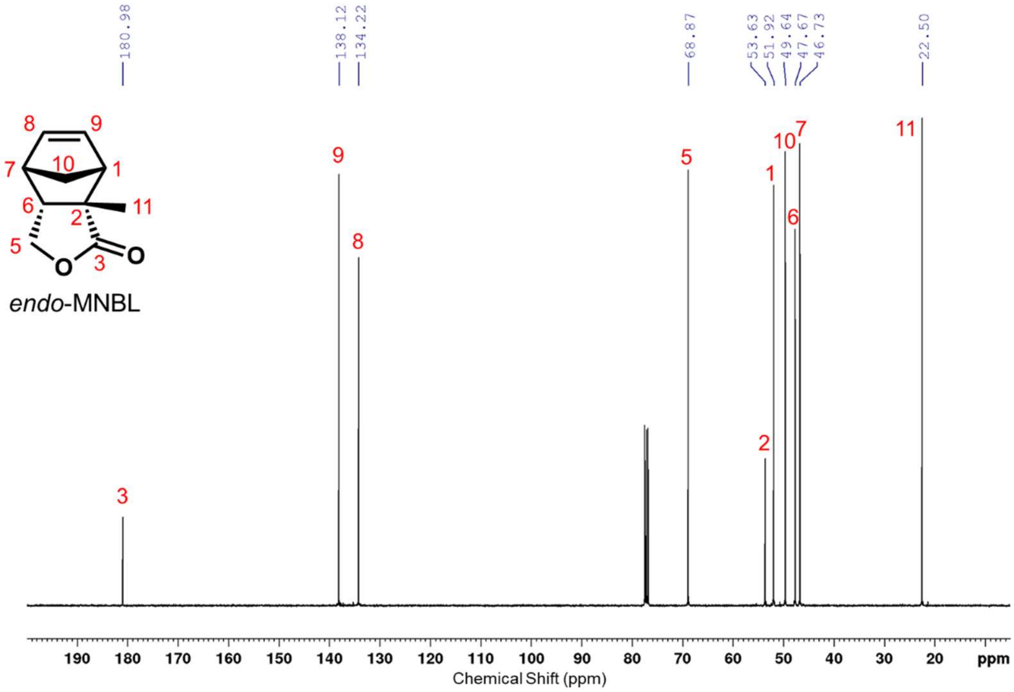


Figure S23. ^{13}C NMR spectrum of *endo*-MNBL.

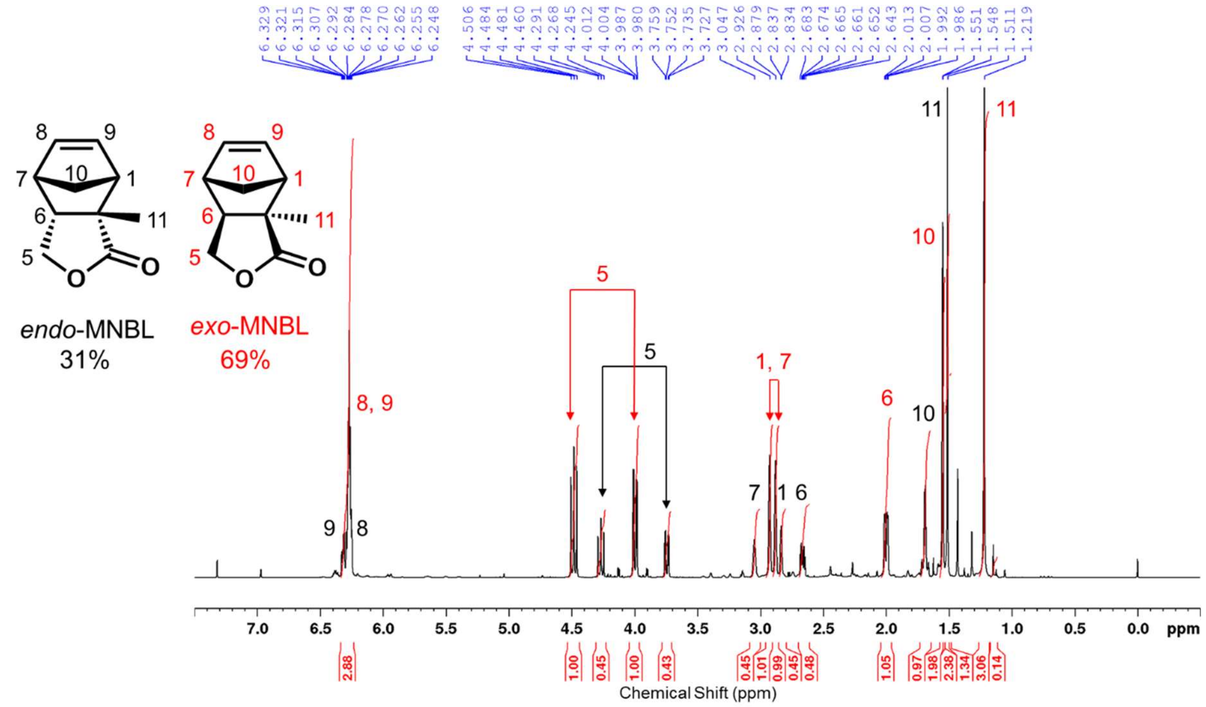


Figure S24. ^{1}H NMR spectrum of a mixture of *exo*-MNBL and *endo*-MNBL.

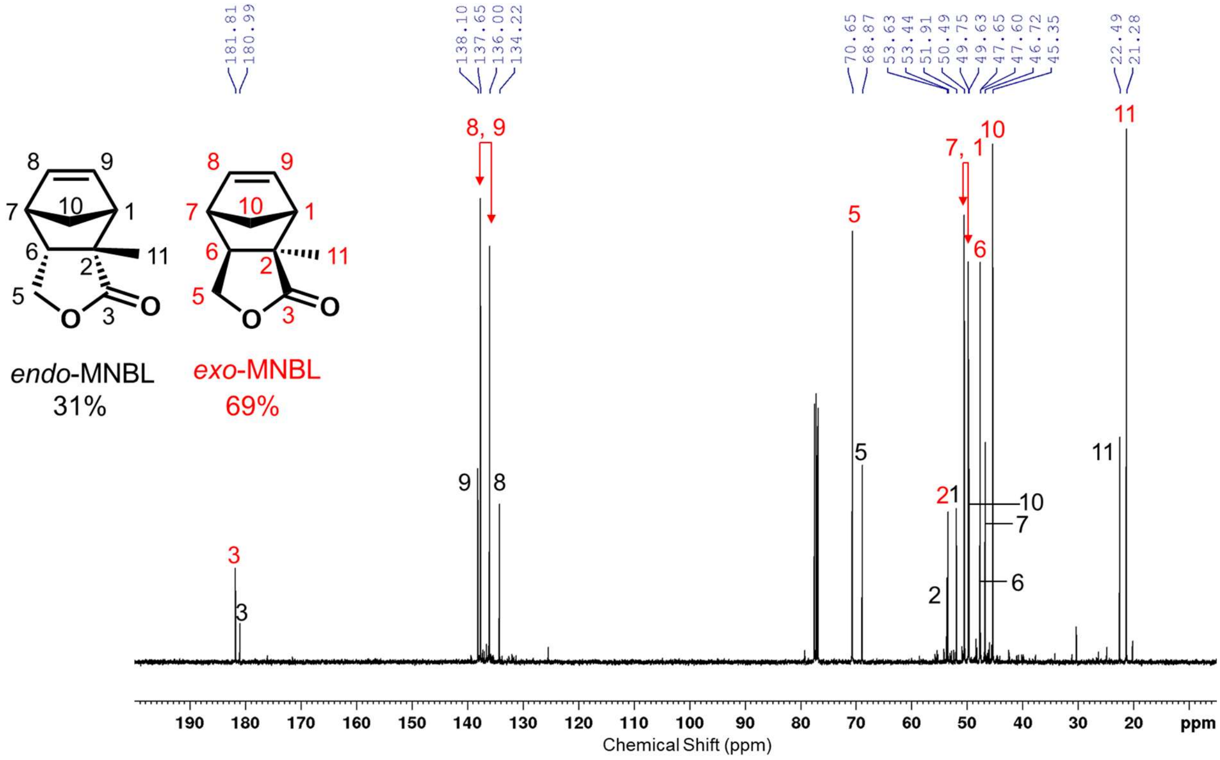


Figure S25. ^{13}C NMR spectrum of a mixture of *exo*-MNBL and *endo*-MNBL.

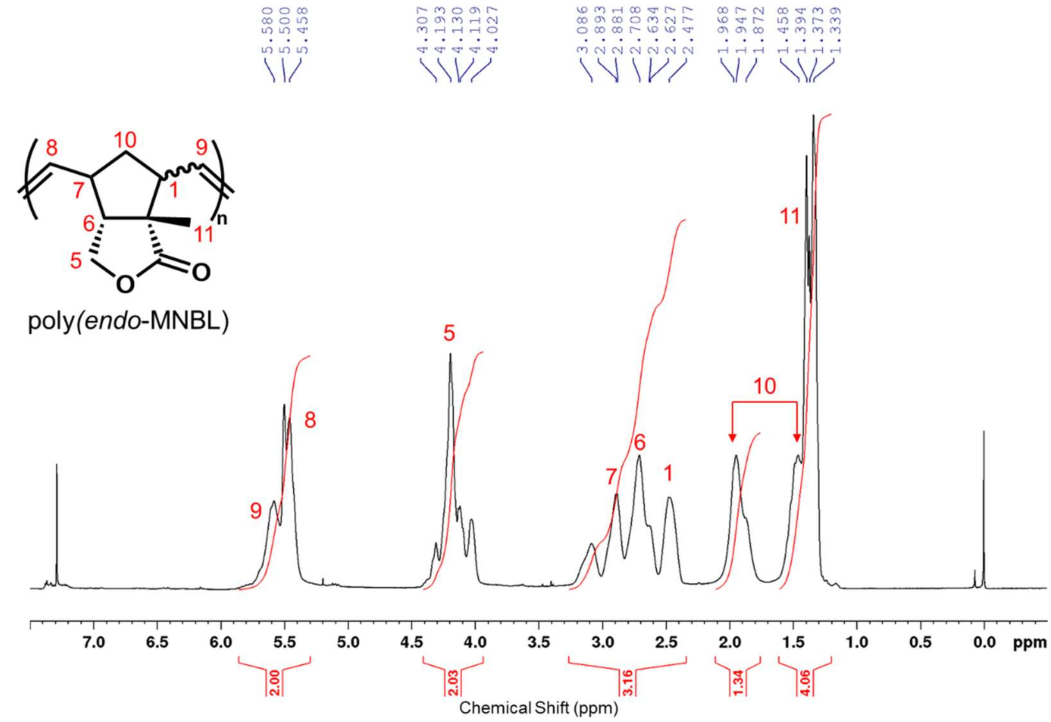


Figure S26. ^{1}H NMR spectrum of poly(*endo*-MNBL).

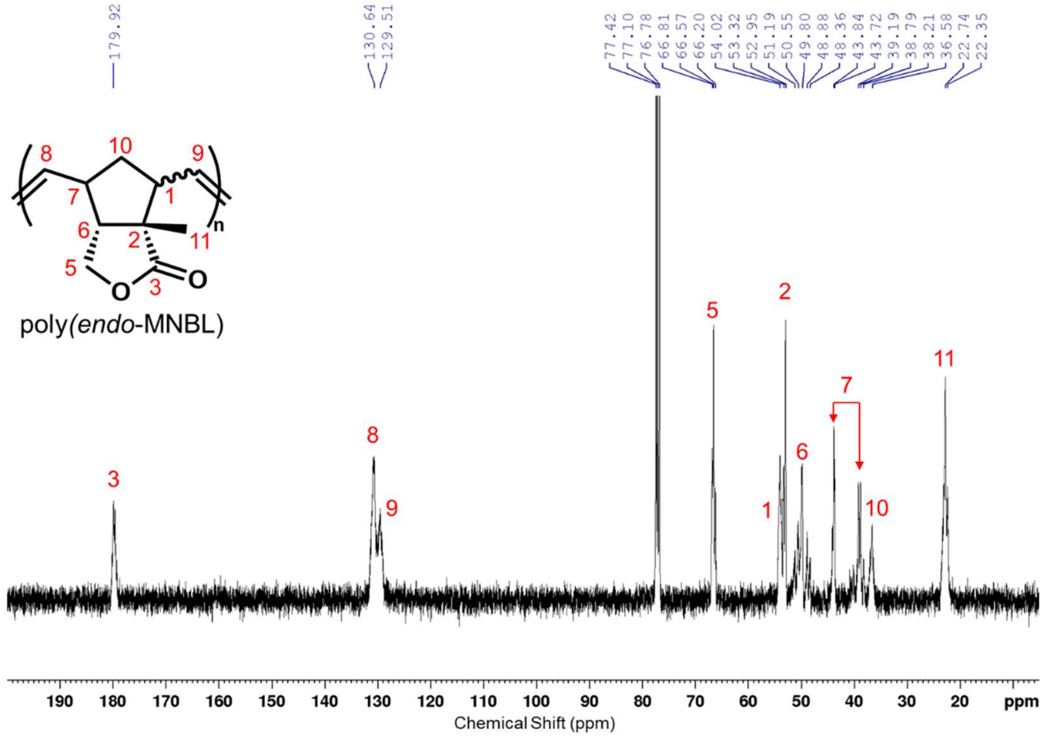


Figure S27. ^{13}C NMR spectrum of poly(*endo*-MNBL).

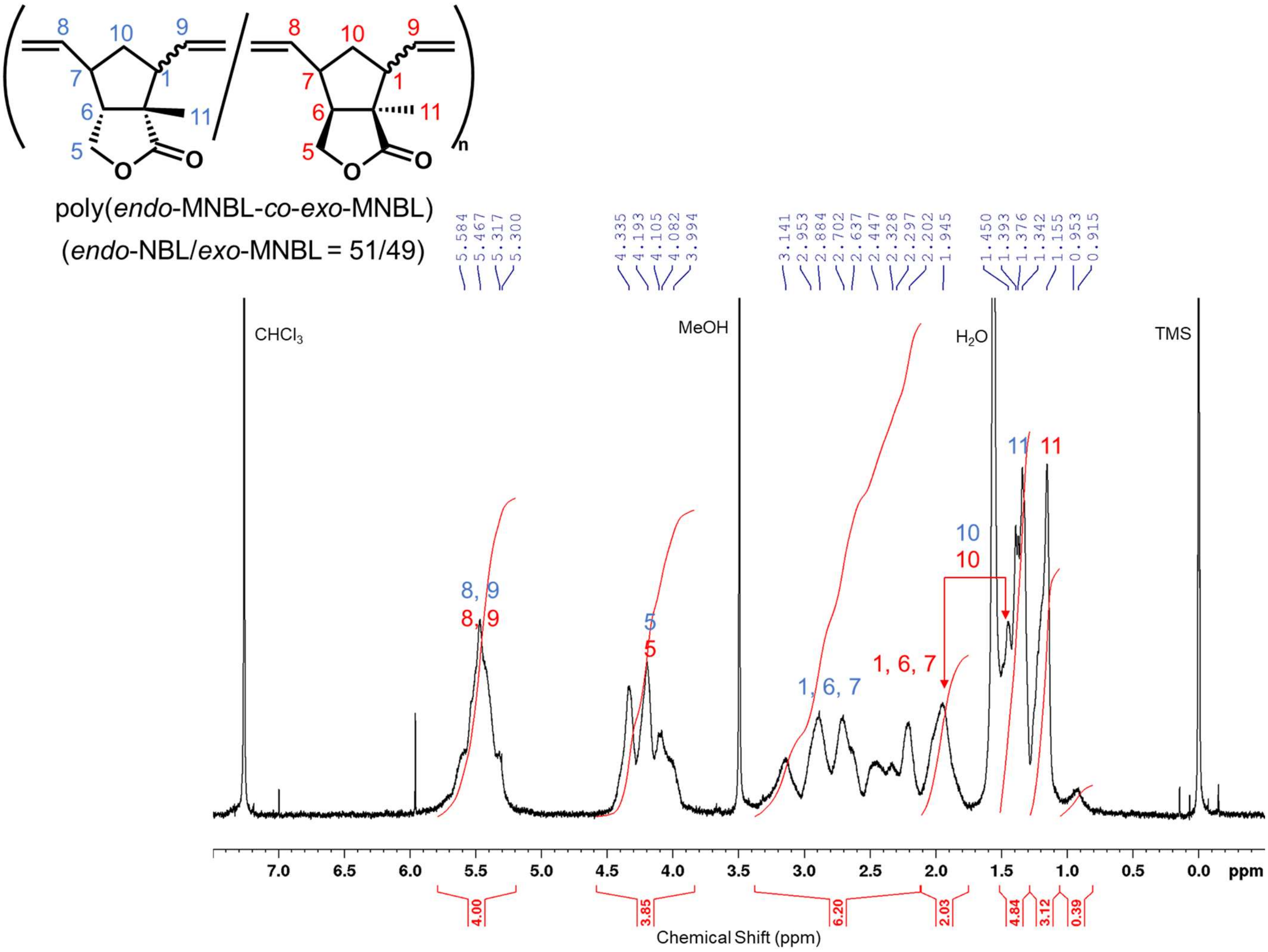


Figure S28. ^{1}H NMR spectrum of poly(*endo*-MNBL-*co*-*exo*-MNBL).

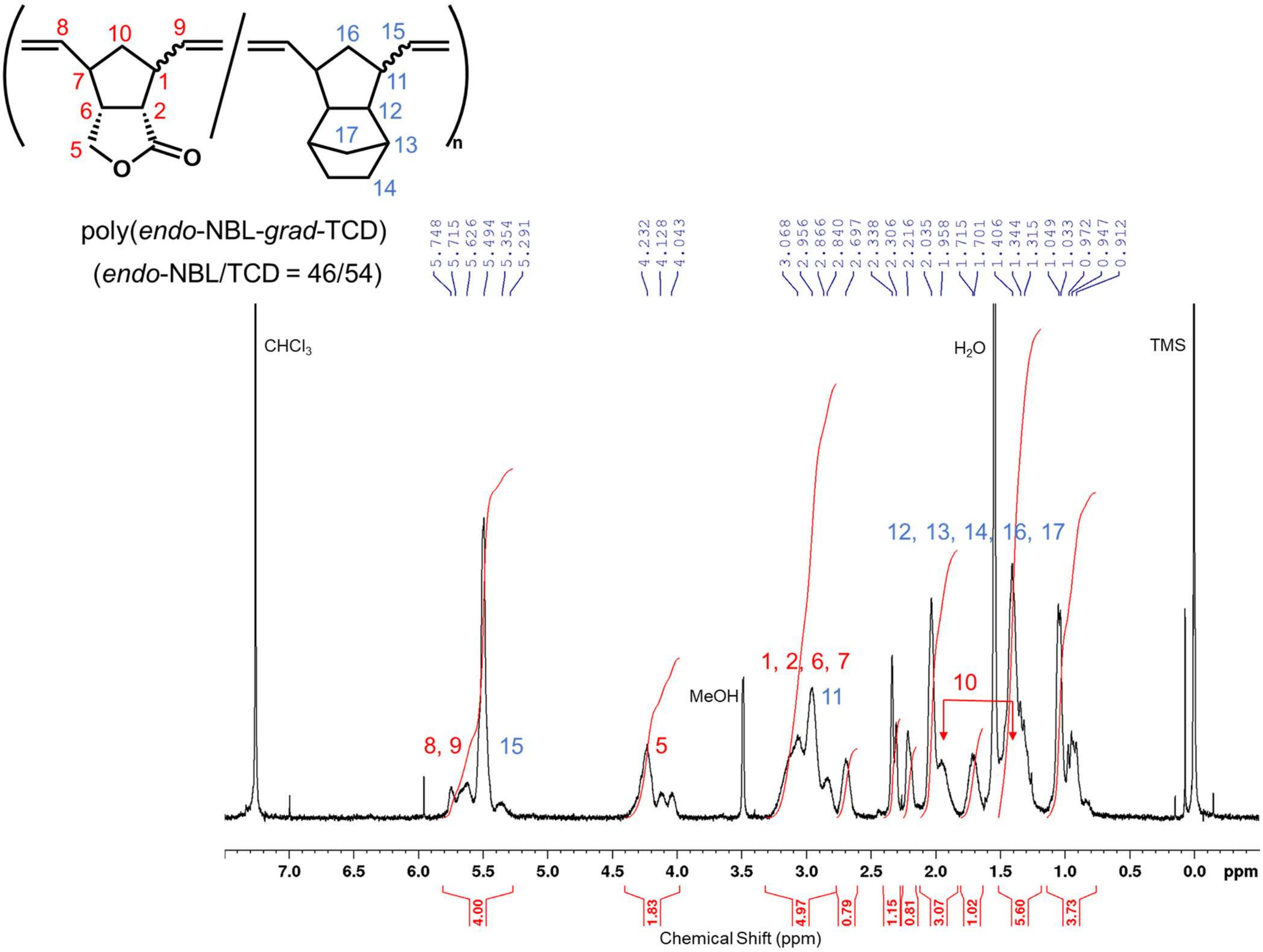


Figure S29. ^{1}H NMR spectrum of poly(*endo*-NBL-*grad*-TCD).

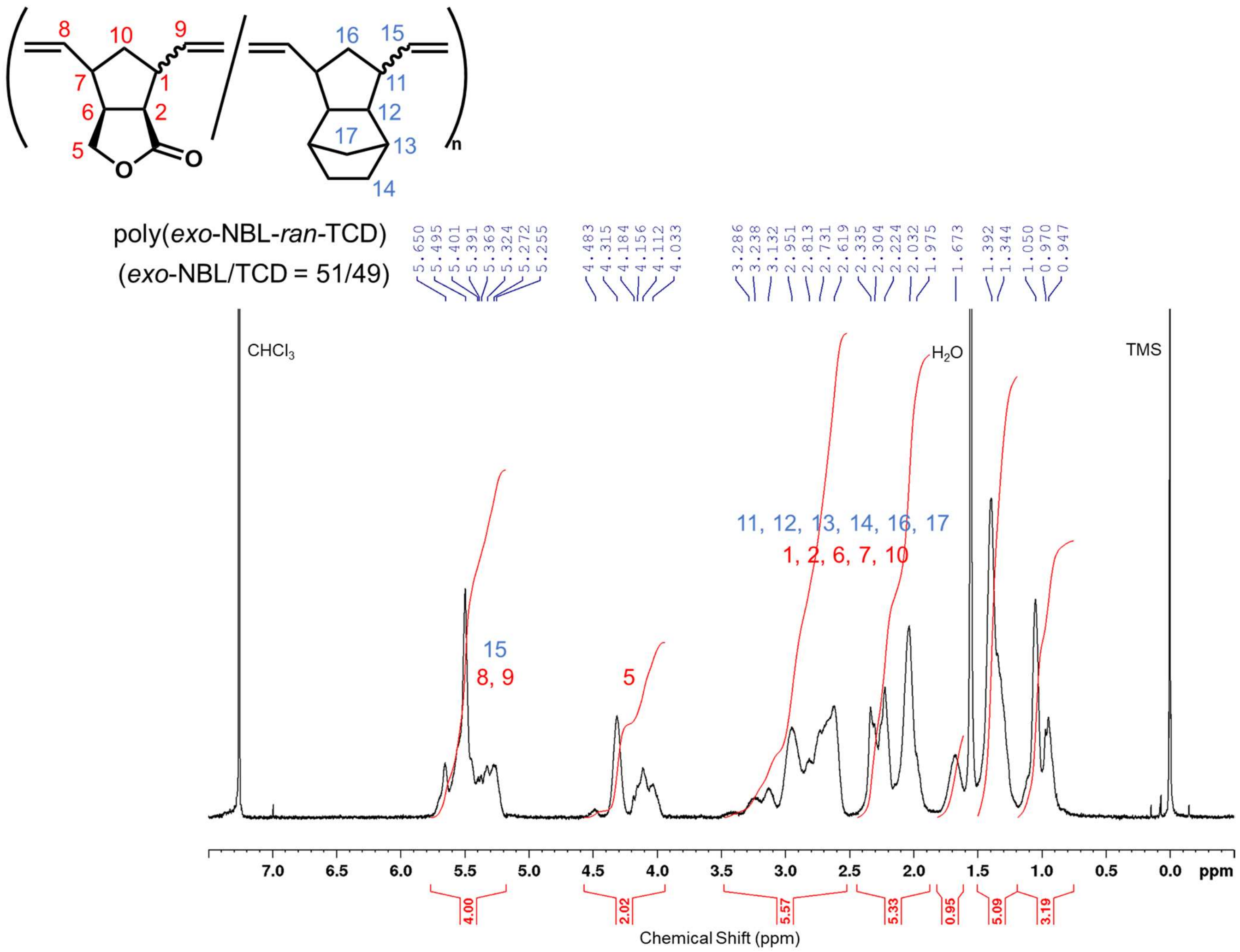


Figure S30. ^{1}**H NMR spectrum of poly(*exo*-NBL-*ran*-TCD).**

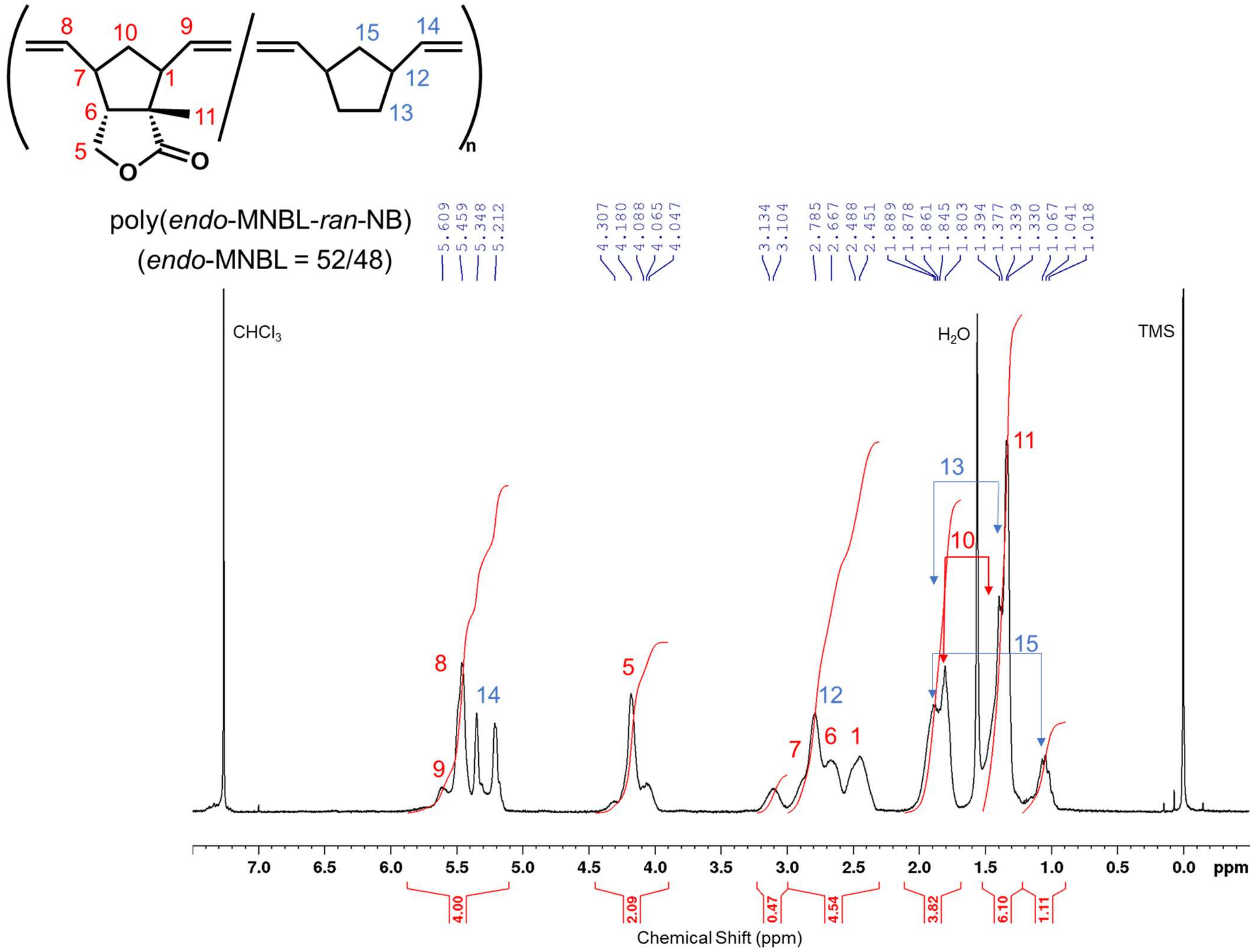


Figure S31. ^{1}H NMR spectrum of poly(*endo*-MNBL-*ran*-NB).

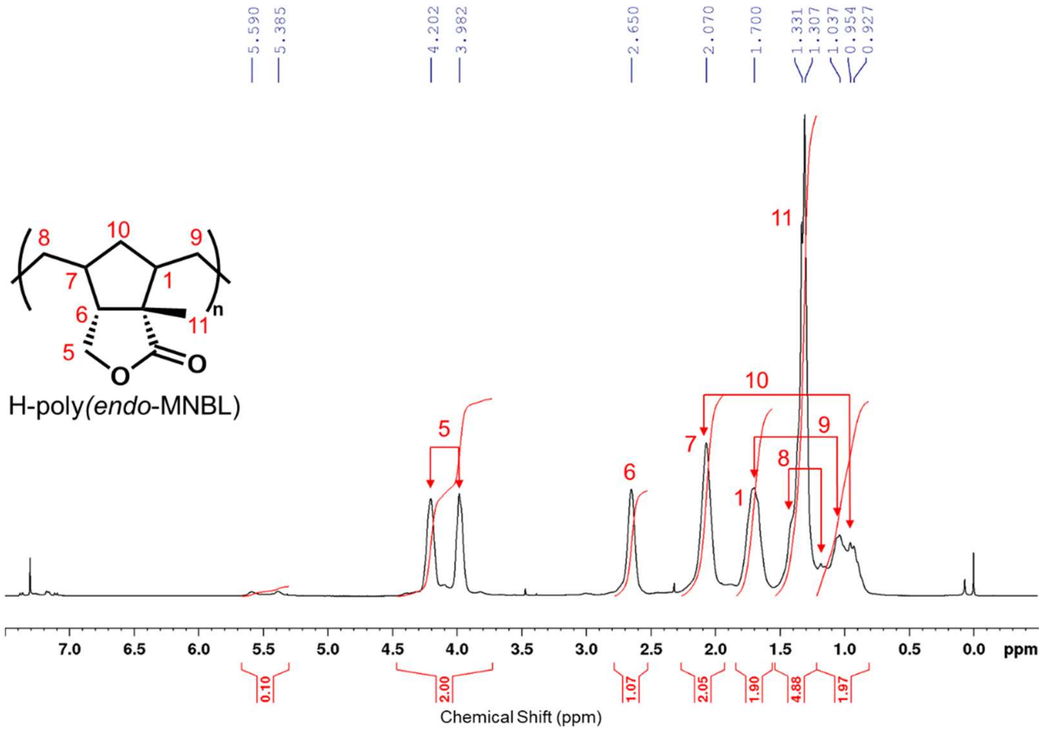


Figure S32. ^{1}H NMR spectrum of H-poly(*endo*-MNBL).

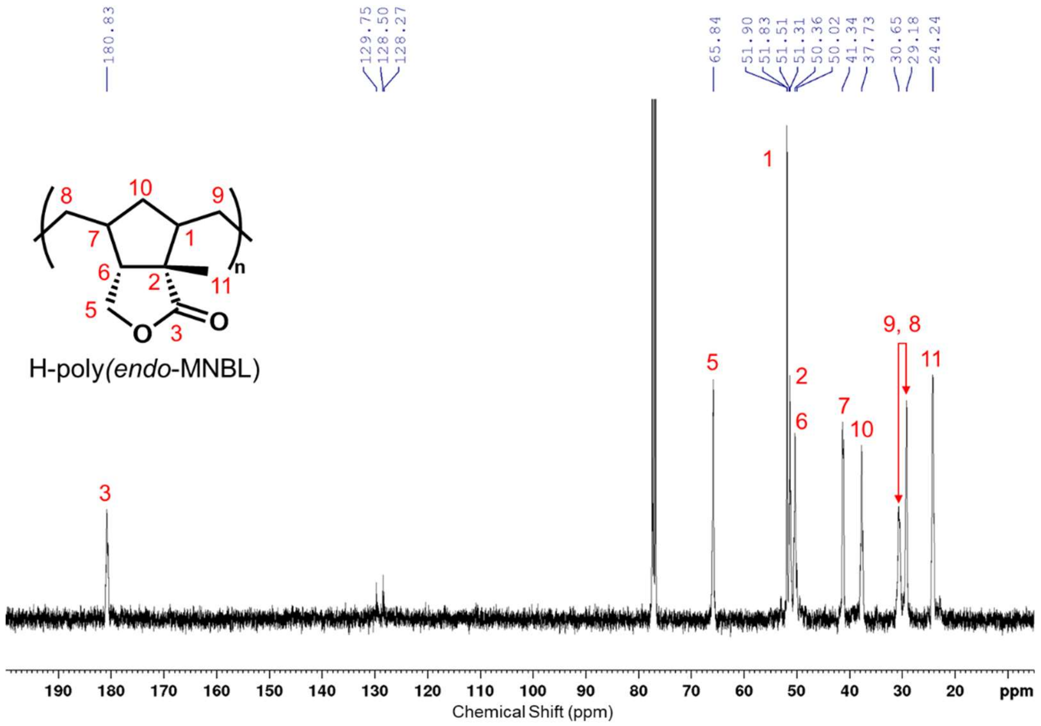


Figure S33. ^{13}C NMR spectrum of H-poly(*endo*-MNBL).

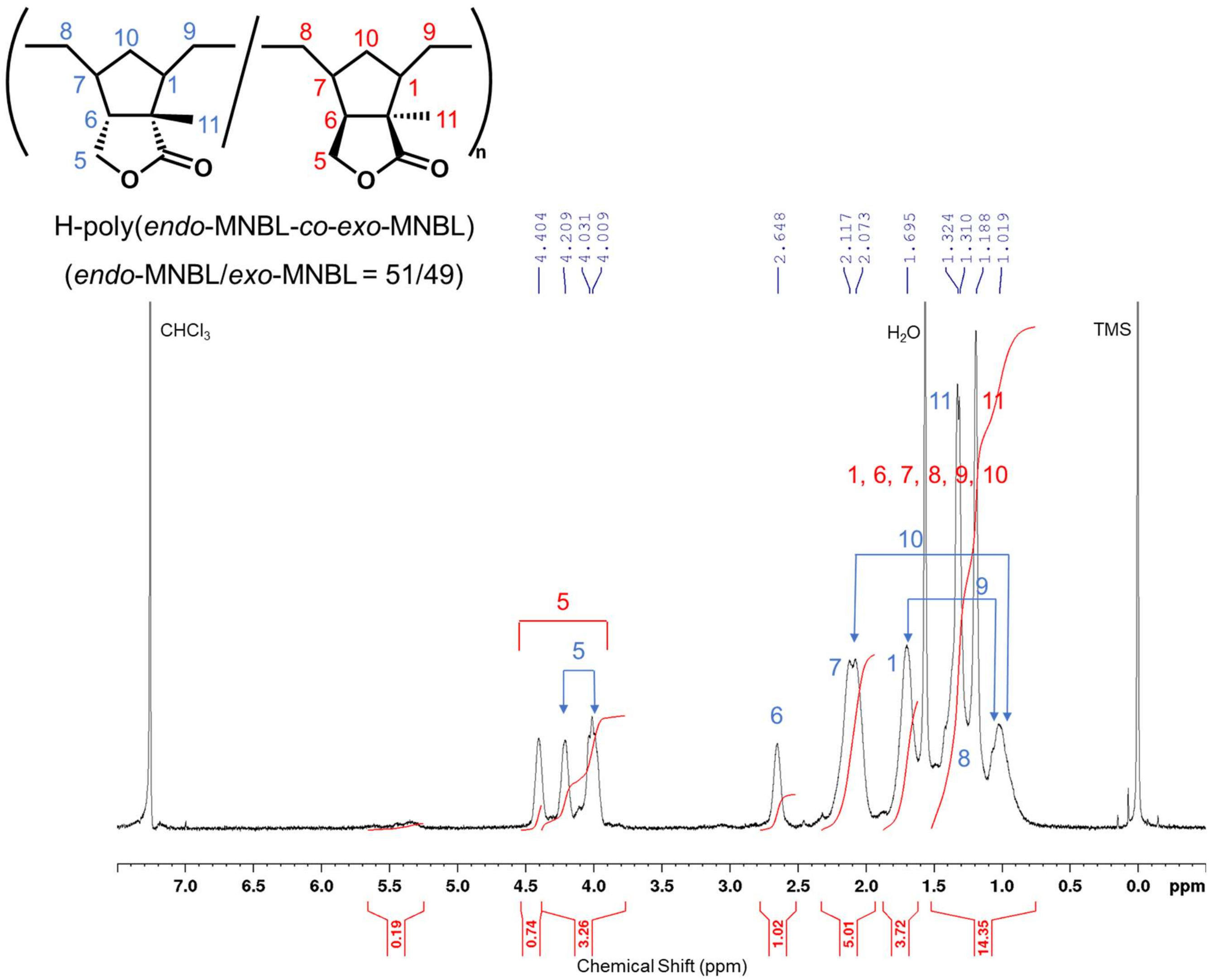


Figure S34. ^{1}H NMR spectrum of H-poly(*endo*-MNBL-*co*-*exo*-MNBL).

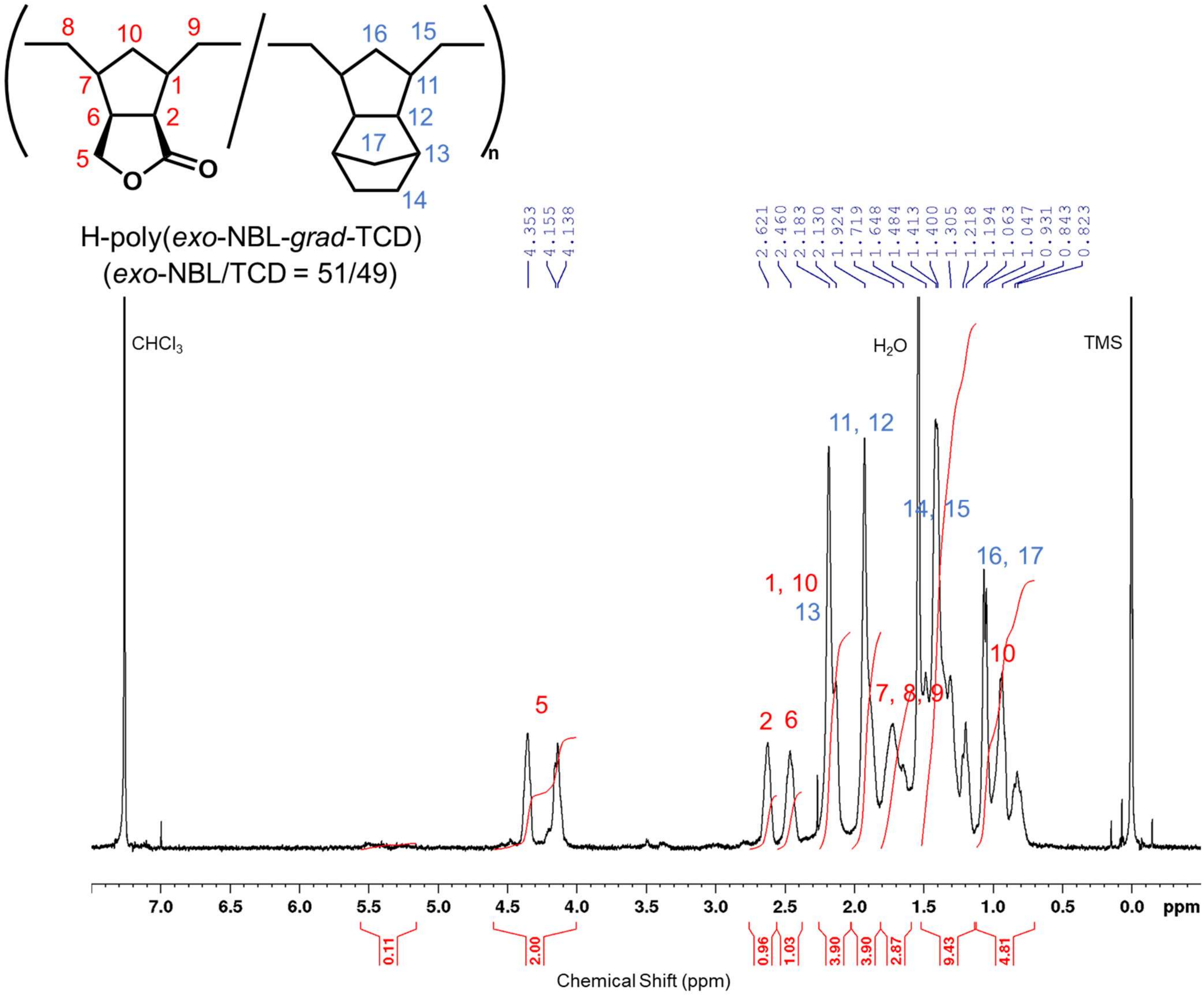


Figure S35. ^{1}H NMR spectrum of H-poly(*exo*-NBL-*grad*-TCD).

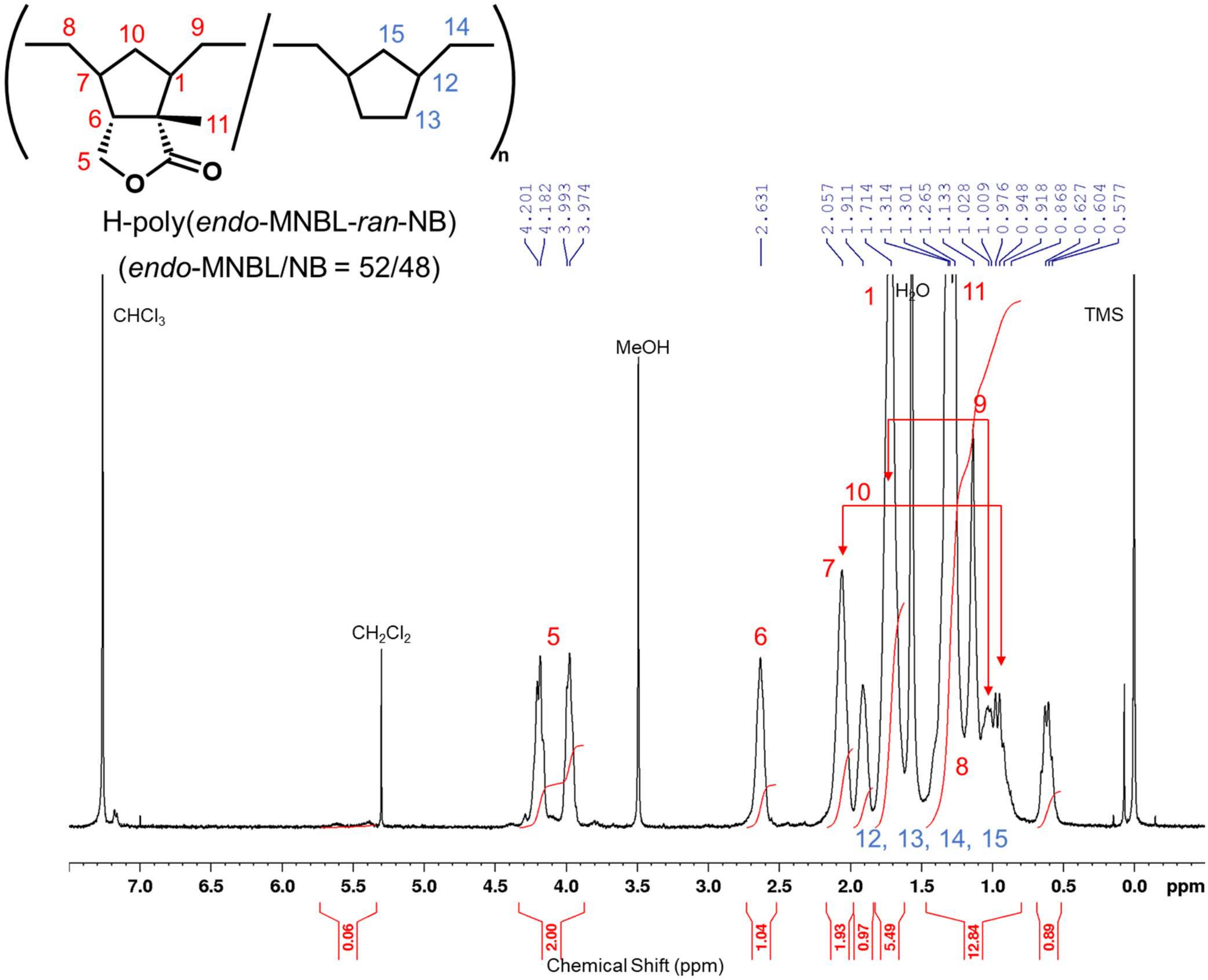


Figure S36. ^{1}H NMR spectrum of H-poly(*endo*-MNBL-*ran*-NB).

Reference

1) Miyasako, N.; Matsuoka, S.; Suzuki, M., *Macromol. Rapid Commun.* **2021**, *42*, 2000326.

2) Citron, C. A.; Wickel, S. M.; Schulz, B.; Draeger, S.; Dickschat, J. S. *Eur. J. Org. Chem*. **2012**, 6636–6646.