Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

for

Synthesis and Properties of Block Gradient Copolymers Composed of Norbornene and Higher *α*-Olefins Using *ansa*-Fluorenylamidodimethyltitanium-[Ph_3C][$B(C_6F_5)_4$] Catalyst System

by

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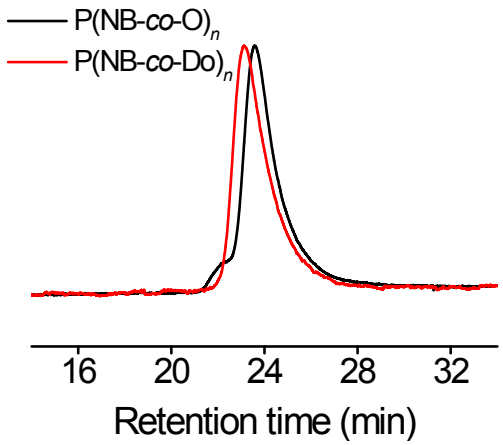

Fig. S1 GPC curves of NB/O and NB/Do pseudo-random copolymers

The shoulder peak in GPC curve of P(NB-*co*-O)$_n$ was an experimental error caused by manual monomer dropping operation during copolymerization.

2. Weight fractions of NB/*α*-olefin block copolymers in obtained post polymers

The weight fractions of NB/O and NB/Do block copolymers in the obtained post polymers were calculated from their integral areas of the corresponding peaks in GPC curves. Each GPC curve was fitted with a sum of Gaussian functions using Igor Pro 8 software. The fitting error of the peak area was less than ±2.5%.

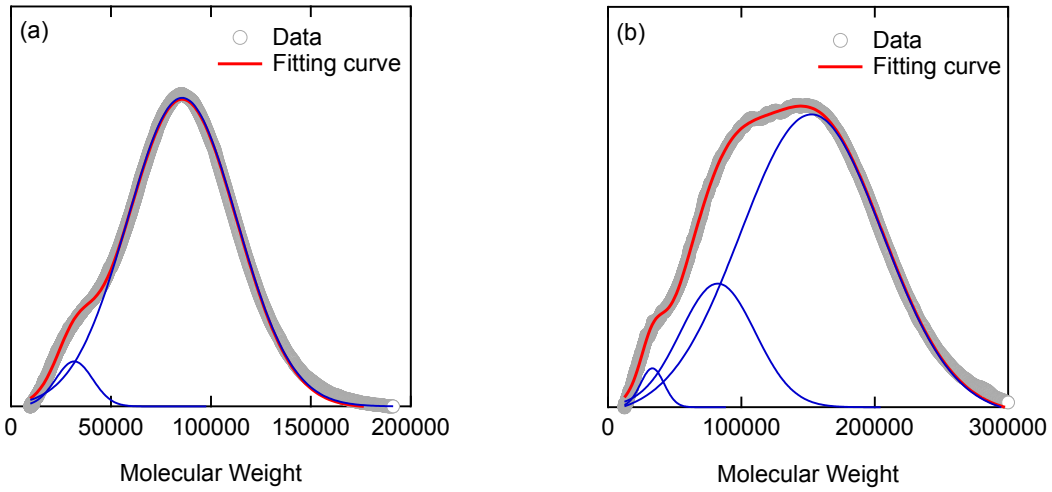

Fig. S2 Fitting results of molecular weight distribution curves of P(NB-*co*-O)$_2$-1 (a) and P(NB-*co*-O)$_3$-1 (b). The red line represents the fitting curve from a sum of Gaussian functions (blue lines).

Table S1 Weight fractions of NB/*α*-olefin block copolymers in obtained post polymers

sample	Gradient content (wt.%)	Diblock content (wt.%)	Triblock content (wt.%)
P(NB-*co*-O)$_2$-1	12	89	–
P(NB-*co*-O)$_2$-2	11	89	–
P(NB-*co*-O)$_2$-3	15	85	–
P(NB-*co*-O)$_2$-4	17	83	–
P(NB-*co*-O)$_3$-1	6	27	68
P(NB-*co*-O)$_3$-2	6	25	69
P(NB-*co*-Do)$_2$	17	83	–

Determined from the relative peak area of each fraction after converting the *y* axis of Fig. S2 to the logarithmic scale.

3. Visible light transmittance curves of diblock- and triblock-gradient NB/O copolymer films

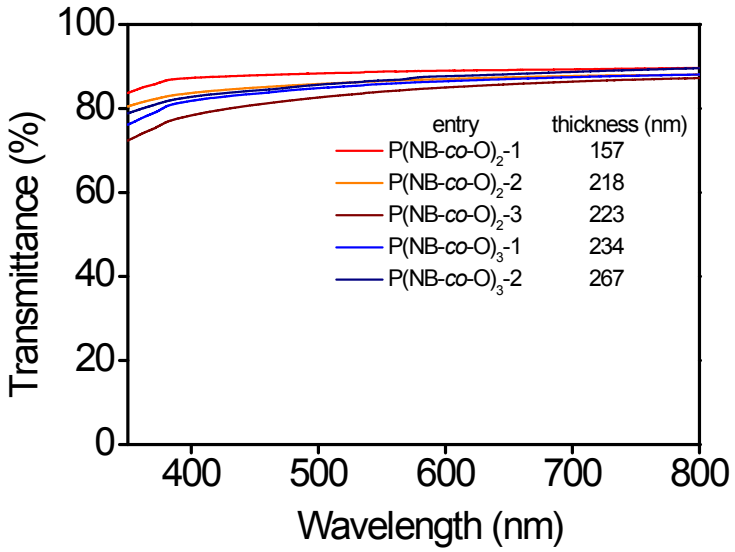

Fig. S3 Visible light transmittance curves (350 ~ 800 nm) of diblock- and triblock NB/O copolymer films.

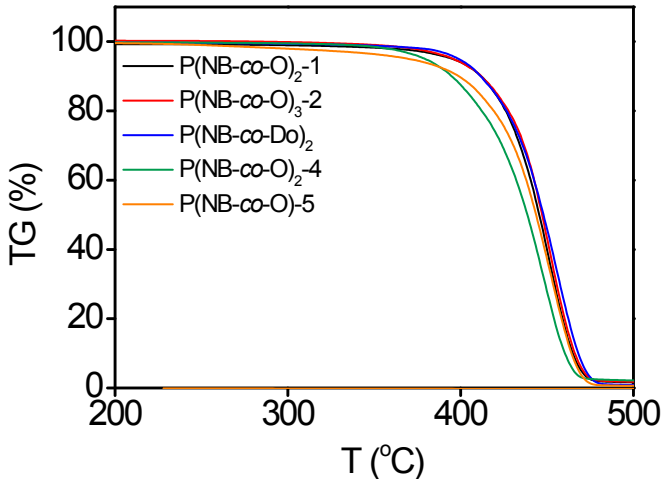

Fig. S4 TGA curves of NB/*α*-olefin copolymers.

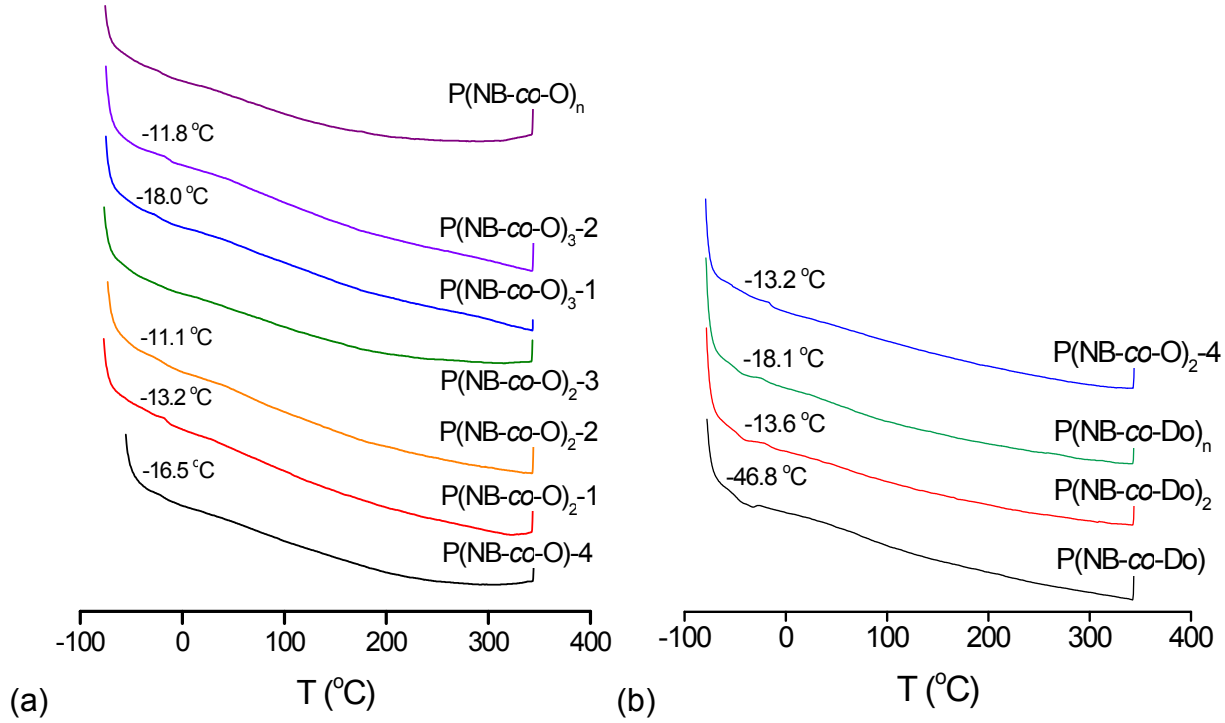

Fig. S5 DSC curves of NB/*α*-olefin copolymers. (a) gradient, di- and triblock NB/O copolymers; (b) gradient, diblock and pseudo-random NB/Do copolymers.

4. TGA and DSC curves of NB/*α*-olefin copolymers

5. One-dimensional SAXS results of NB/O copolymer films

Experimental

One-dimensional small-angle X-ray scattering (SAXS) measurements were performed using a Nano-Viewer SAXS system (Rigaku, Japan) with Cu*Ka* radiation (40 kV and 30 mA). SAXS patterns were measured using an imaging plate with an exposure time of 30 min.

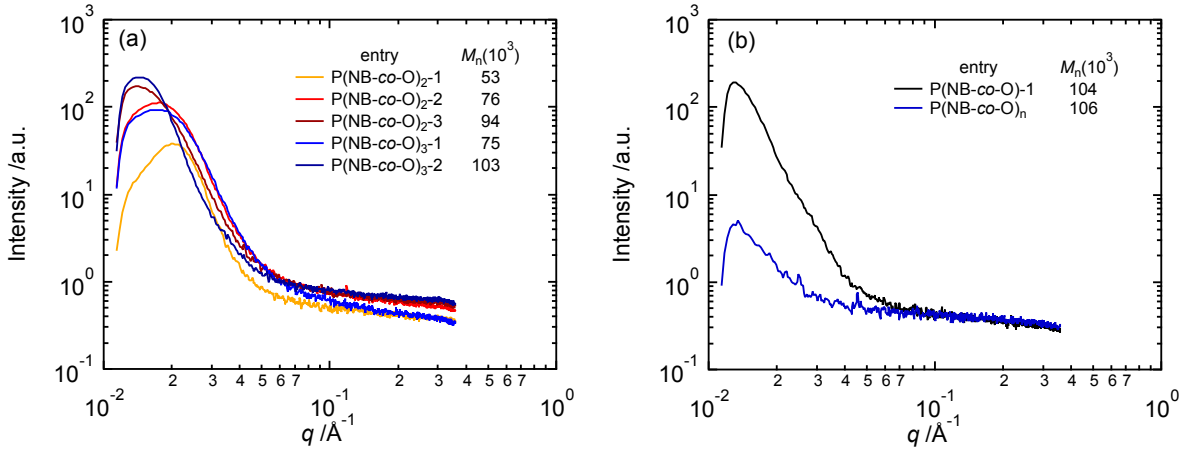

Fig. S6 One-dimensional SAXS profiles of (a) block copolymers and (b) gradient and pseudo-random NB/O copolymers.

6. SPM images of gradient and block NB/O copolymer films

Experimental

Scanning probe microscope (SPM) measurements were performed on a Dimension Icon SPM system (Bruker, America) with a RTESPA-300 probe using standard peak force quantitative nanomechanical mapping (QNM) mode (in air). The scan size was 3 μm, and the scan rate was 0.5 Hz.

The samples were prepared as followed: The copolymer films made by a melt-pressing procedure were first covered by a two-component epoxy resin adhesive, then the samples were cut from the films by a cryomicrotome under -115 °C.

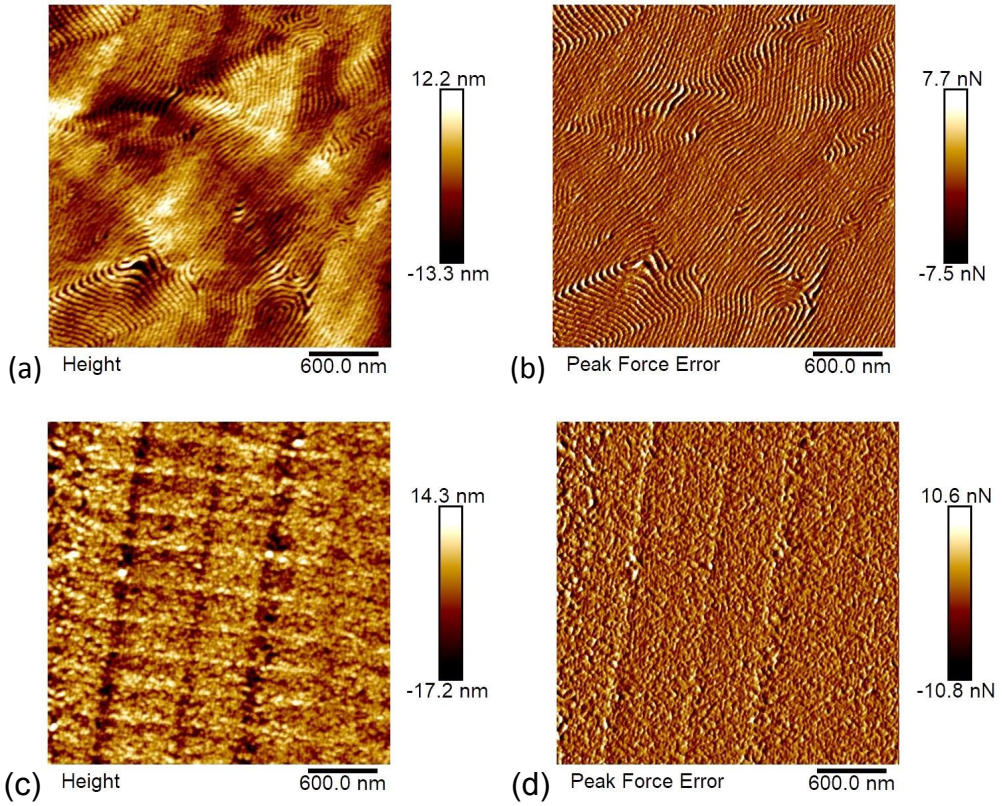

Fig. S7 SPM images of gradient and block NB/O copolymer films. (a) gradient NB/O copolymer film (M_n = 77000, $Đ$ = 1.18), height image; (b) gradient NB/O copolymer film, peak force error image; (c) gradient-block NB/O copolymer film (M_n = 73000, $Đ$ = 1.44), height image; (b) gradient-block NB/O copolymer film, peak force error image.

7. Elongation test results of NB/*α*-olefin copolymer films before annealing

Table S2. Elongation test results of NB/*α*-olefin copolymer films before annealing

Sample	M_n [a] (kg/mol)	Young modulus [b] (MPa)	strength [b] (MPa)	strain at break [b]
P(NB-*co*-O)-4	104	327 ± 14	6.5 ± 0.2	0.03 ± 0.01
P(NB-*co*-O)$_2$-1	53	441 ± 30	17.1 ± 0.2	0.83 ± 0.42
P(NB-*co*-O)$_2$-2	76	358 ± 9	16.2 ± 0.3	0.10 ± 0.01
P(NB-*co*-O)$_2$-3	94	366 ± 5	11.9 ± 1.9	0.06 ± 0.03
P(NB-*co*-O)$_3$-1	75	356 ± 10	16.4 ± 0.1	0.40 ± 0.31
P(NB-*co*-O)$_3$-2	103	335 ± 12	13.6 ± 1.5	0.06 ± 0.01
P(NB-*co*-O)$_n$	106	766 ± 5	21.8 ± 1.6	0.04 ± 0.01
P(NB-*co*-O)-3	141	312 ± 3	9.7 ± 0.3	0.11 ± 0.05
P(NB-*co*-O)$_2$-4	125	239 ± 6	10.0 ± 1.2	1.13 ± 0.05
P(NB-*co*-Do)	124	158 ± 15	4.8 ± 0.2	0.22 ± 0.10
P(NB-*co*-Do)$_2$	114	77 ± 2	7.5 ± 0.1	2.85 ± 0.15
P(NB-*co*-Do)$_n$	129	151 ± 3	6.1 ± 0.4	0.06 ± 0.02

[a] Determined by GPC (THF; 40 °C; polystyrene standards). [b] Determined by elongation test.

annealing

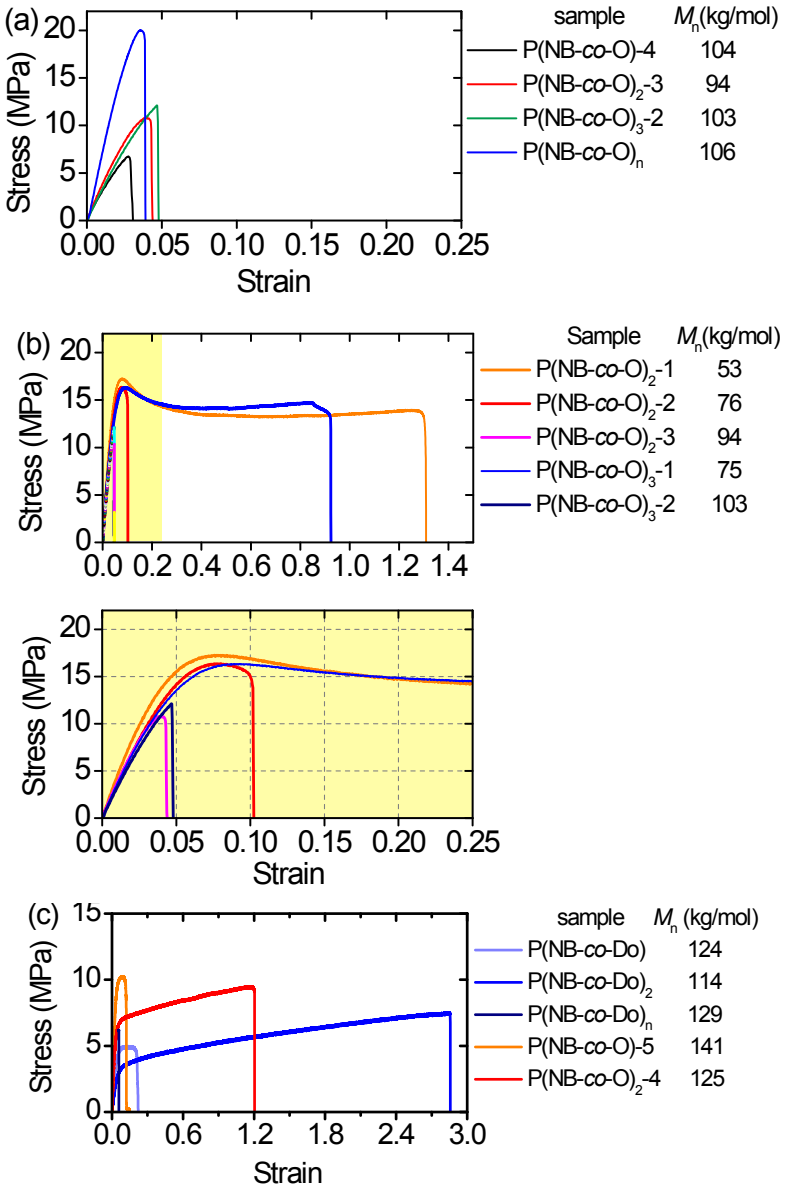

Fig. S8 Stress-strain curves of NB/*α*-olefin copolymer films prepared without annealing procedure. (a) gradient, diblock, triblock and pseudo-random NB/O copolymer films. (NB = 50 mol%) (b) diblock and triblock NB/O copolymer films with different block length. (NB = 50 mol%) (c) NB/Do and NB/O copolymer films with the same NB wt.% (NB = 36 wt.%).

8. Temperature dependences of tangent delta of NB/O block copolymers

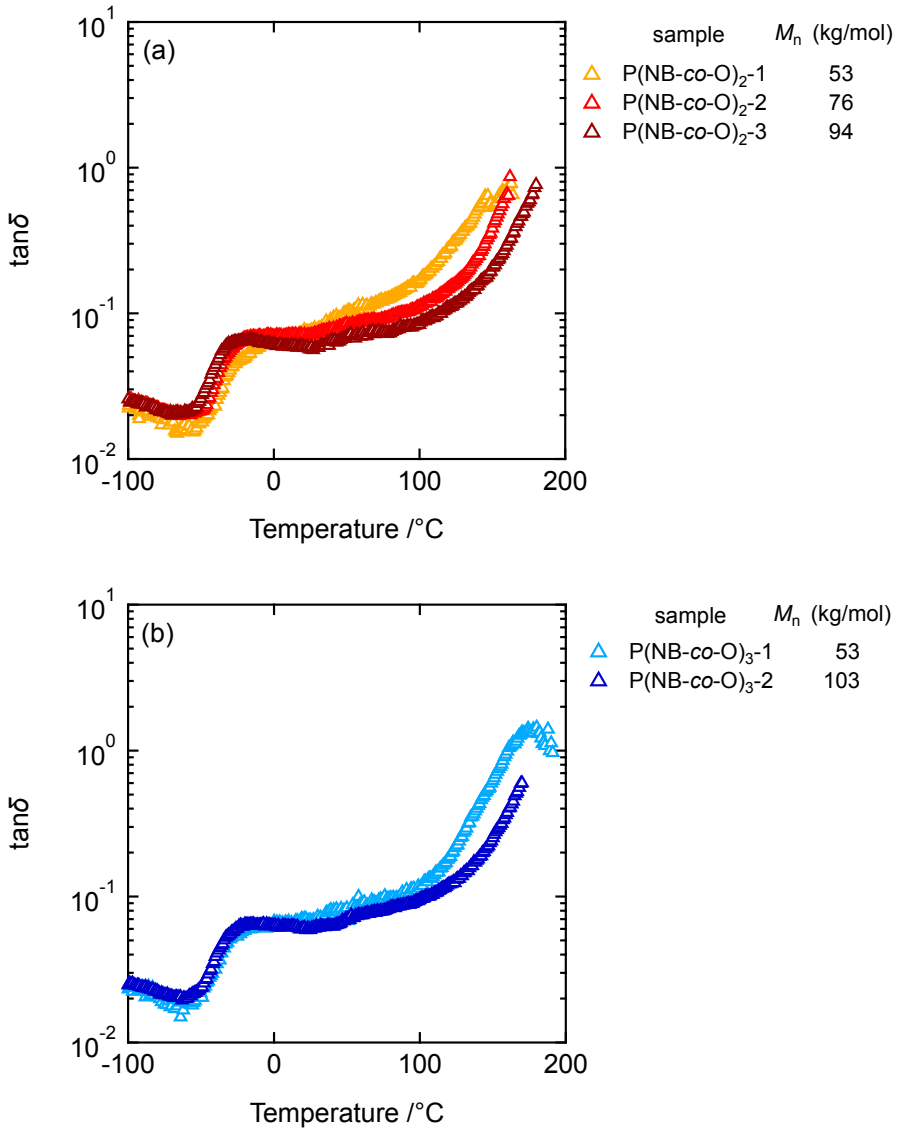

Fig. S9 Temperature dependences of the tangent delt of (a) diblock and (b) triblock NB/O copolymers