Electronic Supplementary Information (ESI)

Synthesis of Macro-rotaxanes via Direct Trapping of Multicyclic Poly(*n*-butyl acrylate) in a Cross-linked Network

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S1. Materials

Grubbs third-generation catalyst (G3) and ethylene bis(2-bromoisobutyrate) (EBBiB) were prepared according to reported method.[1,2] Ethyl vinyl ether (TCI, >98.0%), *exo*-5-norbornenecarboxylic acid (*exo*-NB-COOH; Aldrich, 97%), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU; TCI, >98.0%), dichloromethane (CH_2Cl_2, Junsei Chemical Co., Ltd., >99.0%), methanol (Aldrich, ≥99.8%), chloroform-d_1 ($CDCl_3$; Kanto Chemical Co., Inc., 99.8 atom % D with 0.03 vol% tetramethylsilane (TMS)), anisole (Sigma Aldrich, 99.7%,), acetone (>99.0%, Kanto Chemical Co., Inc.), chloroform ($CHCl_3$; Junsei Chemical Co., Ltd., ≥99.0%,), toluene (Junsei Chemical Co., Ltd., >99.8%), copper(I) bromide (CuBr; Sigma Aldrich, 99.999%), copper(II) bromide ($CuBr_2$; Sigma Aldrich, 99.999%), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA; TCI, >99.0%), aluminum oxide (≤100%, Sigma Aldrich), hydrochloric acid (HCl; FUJIFILM Wako Pure Chemical Corp., Ltd., 63.0–65.0% in water), sodium hydrogen carbonate ($NaHCO_3$; Kanto Chemical Co., Inc., >99.0%), 2,2-diethoxyacetophenone (DEAP; TCI, >95.0%), dry *N,N*-dimethylformamide (dry DMF; Kanto Chemical Co., Inc., >99.5%, water content, <0.001%), dry toluene (Kanto Chemical Co., Inc., >99.5%), and dry CH_2Cl_2 (Kanto Chemical Co., Inc., >99.5%, water content, <0.001%) were used as receives. *n*-Butyl acrylate (BA; TCI, >99.0%) and ethylene glycol dimethacrylate (EGDM; TCI, >97.0%) were purified by passing through a short column of aluminum oxide.

S2. Instruments

^{1}H (600 MHz) NMR spectra were recorded at 25 °C on a JEOL JNM-ECS 600 instrument using $CDCl_3$ as the solvent and TMS as the internal reference.

The SEC using $CHCl_3$ as the eluent was performed at 40 °C (flow rate, 1.0 mL min^{-1}) using a Jasco high-performance liquid chromatography system (PU-4180 HPLC pump, AS-4550 auto sampler, and CO-4060 column oven) equipped with a Shodex K-800D guard column (8.0 mm × 100 mm; particle size, 10 μm), two Shodex columns (K-806L and K-804L; linear, 8.0 mm × 100 mm; particle size, 10 μm). The polystyrene standard curve ranging from 1,990 to 1,330,000 was used for calibration to achieve the molecular weight ($M_{n,SEC}$) and polydispersity index ($Đ$) of the polymers.

The absolute number-average molecular weights ($M_{n,MALS}$) and the dispersities ($Đ_{MALS}$) of the samples were determined by SEC with multi-angle light scattering and viscometry (SEC-MALS-Visco) in $CHCl_3$ (flow rate, 1.0 mL min^{-1}) at 40 °C using a Jasco high-performance liquid chromatography system (PU-4180 HPLC pump, AS-4550 auto sampler, and CO-4060 column oven) equipped with a Shodex K-800D guard column (8.0 mm × 100 mm; particle size, 10 μm), two Shodex columns (K-806L and K-804L; linear, 8.0 mm × 100 mm; particle size, 10 μm), a DAWN 8 multiangle laser light scattering detector (Wyatt Technology), a Viscostar viscosity detector (Wyatt Technology), and an RI-501 refractive index detector (Shodex).

The preparative SEC was performed at 25 °C in $CHCl_3$ (flow rate, 10.0 mL min^{-1}) using LaboACE LC-7080 Plus Ⅱ liquid chromatography system (Japan Analytical Industry Co. Ltd. (JAI)) equipped with a JAIGEL HR-P guard column (8 mm × 40 mm, JAI), a JAIGEL-2HR column (linear, 20.0 mm × 600 mm; exclusion limit, 5.0×10^3 , JAI), a JAIGEL-2.5HR column (linear, 20.0 mm × 600 mm; exclusion limit, 2.0×10^4 , JAI), a JAIGEL-3HR column (linear, 20.0 mm × 600 mm; exclusion limit, 7.0×10^4 , JAI) , and a JAIGEL-4HR column (linear, 20.0 mm × 600 mm; exclusion limit, 5.0×10^5 , JAI).

The dynamic viscoelastic measurement of the acrylic rubbers was conducted using an MCR-702e rheometer (Anton Paar) with P-PTD220 Peltier-type temperature controller. The samples were placed under a 12 mm-diameter parallel plate. In the strain sweep tests, the shear strain (γ) was from 0.01 to 10% at the frequency of 10 rad s^{-1} and temperature of 25 °C. In the frequency sweep measurements, the angular frequency (ω) was from 0.1 to 10 rad s^{-1} at specified temperatures from −45 to 25 °C by 5 °C step. The obtained master curve was calculated for a reference temperature of 25 °C by using RheoCompass^{TM} software.

The indentation tests were carried out using an AUTOGRAPH AG-X plus (Shimadzu Corp.) equipped with a spherical indenter (diameter: 1 mm). The measurements were performed at a constant displacement rate of 1 mm min^{-1} at r.t.. The thickness of the samples ranged from 490 to 620 μm. The force–displacement curves were recorded, and the Young's modulus (E) was determined from the slope of the applied force (F) versus the indentation depth to the power of 3/2 ($l^{3/2}$) in the linear region (indentation depth: 0–ca. 20 μm) based on the Hertz contact theory. The relationship is expressed as:

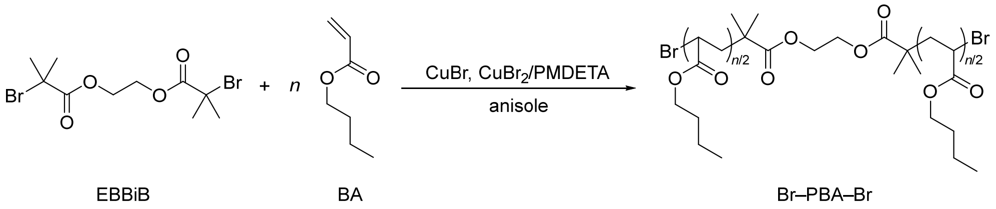
$$E=\frac{3(1-\nu^2)}{4R^{1/2}}\times\frac{F}{l^{3/2}}$$

where the F is the applied force, ν is the Poisson's ratio (0.5), l is the indentation depth, and R is the radius of the indenter.

S3. Synthesis Details

Synthesis of dibromo-terminated PBA (Br–PBA$_{10k}$–Br)

Scheme S1. Synthesis of Br–PBA–Br



A typical procedure for the atom transfer radical polymerization (ATRP) of BA is as follows (method A): A Schlenk flask (Flask A) was charged with CuBr (236 mg, 1.65 mmol, 0.95 eq.) and purged with argon. Another Schlenk flask (Flask B) was charged with BA (50.0 g, 390 mmol, 224 eq.), EBBiB (626 mg, 1.74 mmol, 1.00 eq.), a CuBr$_2$/PMDETA/dry DMF solution (19.3 mg, 86.4 μmol, 0.05 eq. / 331 mg, 191 μmol, 1.10 eq. / 1.00 mL), and anisole (13.1 mL). The mixture was subjected to freeze–pump–thaw cycles to remove dissolved gases. The degassed solution in the flask B was transferred into the flask A under an argon atmosphere, and the polymerization was initiated by heating the mixture at 70 °C. After stirring for 2.5 h, the reaction was terminated by exposing the mixture to air. The resulting solution was diluted with acetone and then passed through a short column of aluminum oxide to remove copper residues, and the solvent was removed under reduced pressure to give Br–PBA$_{10k}$–Br (16.6 g) as a pale green viscous product. Yield: 33.2%. ^{1}H NMR ($\mathrm{CDCl_3}$, 600 MHz): δ (ppm) 0.94 (t, J = 7.2 Hz, 3H × n, $\mathrm{–CH_2CH(C(=O)OCH_2CH_2CH_2C}\mathit{H}_3\mathrm{))}$), 1.10–1.16 (m, 12H, $\mathrm{–OC(=O)C(C}\mathit{H}_3\mathrm{)_2–}$), 1.31–1.44 (br, 2H × n, $\mathrm{–CH_2CH(C(=O)OCH_2CH_2C}\mathit{H}_2\mathrm{CH_3))}$), 1.55–1.79 (br, 2H × n, $\mathrm{–CH_2CH(C(=O)OCH_2C}\mathit{H}_2\mathrm{CH_2CH_3))}$), 1.21–2.11 (br, 2H × n, $\mathrm{–C}\mathit{H}_2\mathrm{CH(C(=O)OCH_2CH_2CH_2CH_3))}$), 2.14–2.49 (br, 1H × ($n$ − 2), $\mathrm{–CH_2C}\mathit{H}\mathrm{(C(=O)OCH_2CH_2CH_2CH_3))}$), 3.84–4.29 (br, 2H × ($n$ + 3), $\mathrm{–CH_2CH(C(=O)OC}\mathit{H}_2\mathrm{CH_2CH_2CH_3)}$, $\mathrm{–C}\mathit{H}\mathrm{Br}$, $\mathrm{–CH(C(=O)OC}\mathit{H}_2\mathrm{CH_2CH_2CH_3)Br}$, $\mathrm{–(C}\mathit{H}_2\mathrm{)_2OC(=O)–}$). $M_{\mathrm{n,NMR}}$ = 11,600 g mol^{-1} ($\mathrm{CDCl_3}$); $M_{\mathrm{n,SEC}}$ = 10,400 g mol^{-1} (THF); $Đ$ = 1.07.

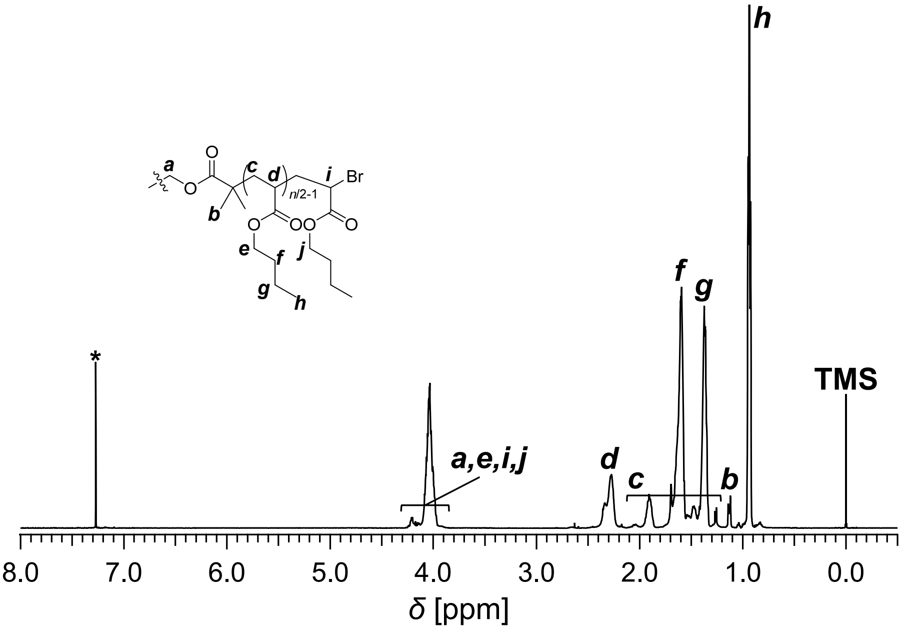


Figure S1. ^{1}H NMR spectrum of Br–PBA$_{10k}$–Br (solvent, CDCl$_3$; 600 MHz). The asterisk denotes solvent peak.

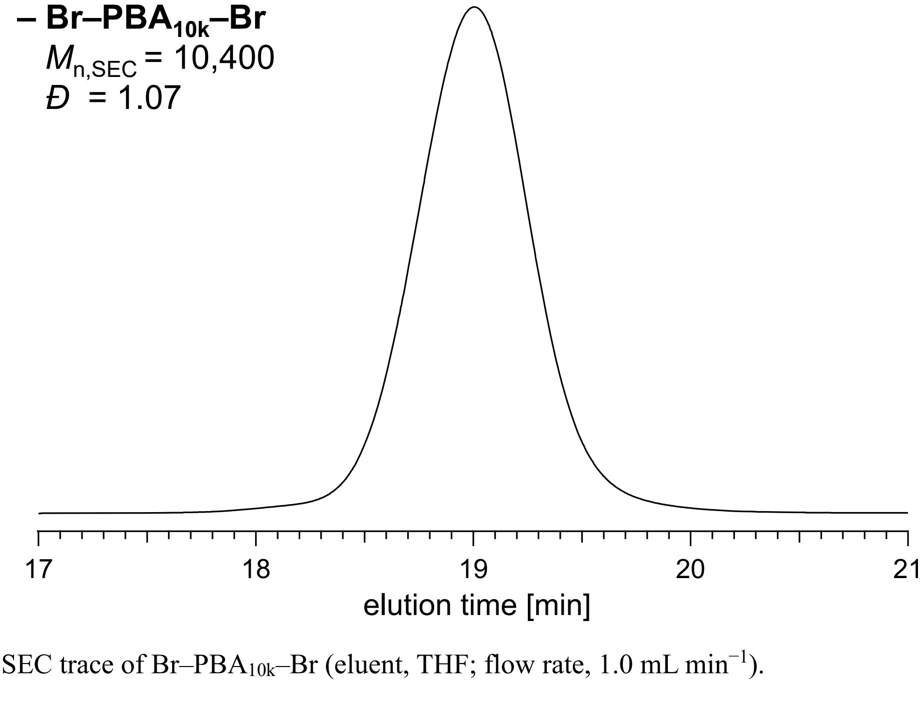


Figure S2. SEC trace of Br–PBA$_{10k}$–Br (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of Br–PBA$_{19k}$–Br

Method A was used for the ATRP of BA (50.0 g, 390 mmol, 511 eq.) with CuBr (104 mg, 726 μmol, 0.95 eq.), EBBiB (275 mg, 763 μmol, 1.00 eq.), CuBr$_2$ (8.6 mg, 38.5 μmol, 0.05 eq.), PMDETA (146 mg, 840 μmol, 1.10 eq.), dry DMF solution (1.00 mL), and anisole (13.1 mL) for 7.0 h to give Br–PBA$_{19k}$–Br (15.2 g) as a pale green viscous product. Yield: 30.4%. ^{1}H NMR (CDCl$_3$, 600 MHz): δ(ppm) 0.94 (t, J =

7.5 Hz, 3H × *n*, $-CH_2CH(C(=O)OCH_2CH_2CH_2C\mathit{H}_3))$, 1.10–1.17 (m, 12H, $-OC(=O)C(C\mathit{H}_3)_2-$), 1.32–1.44 (br, 2H × *n*, $-CH_2CH(C(=O)OCH_2CH_2C\mathit{H}_2CH_3))$, 1.55–1.80 (br, 2H × *n*, $-CH_2CH(C(=O)OCH_2C\mathit{H}_2CH_2CH_3))$, 1.17–2.09 (br, 2H × *n*, $-C\mathit{H}_2CH(C(=O)OCH_2CH_2CH_2CH_3))$, 2.14–2.46 (br, 1H × (*n* − 2), $-CH_2C\mathit{H}(C(=O)OCH_2CH_2CH_2CH_3))$, 3.88–4.27 (br, 2H × (*n* + 3), $-CH_2CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)$, $-C\mathit{H}Br$, $-CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)Br$, $-(C\mathit{H}_2)_2OC(=O)-$). $M_{\mathrm{n,NMR}}$ = 23,400 g mol^{-1} ($CDCl_3$); $M_{\mathrm{n,SEC}}$ = 20,900 g mol^{-1} (THF); $Đ$ = 1.07.

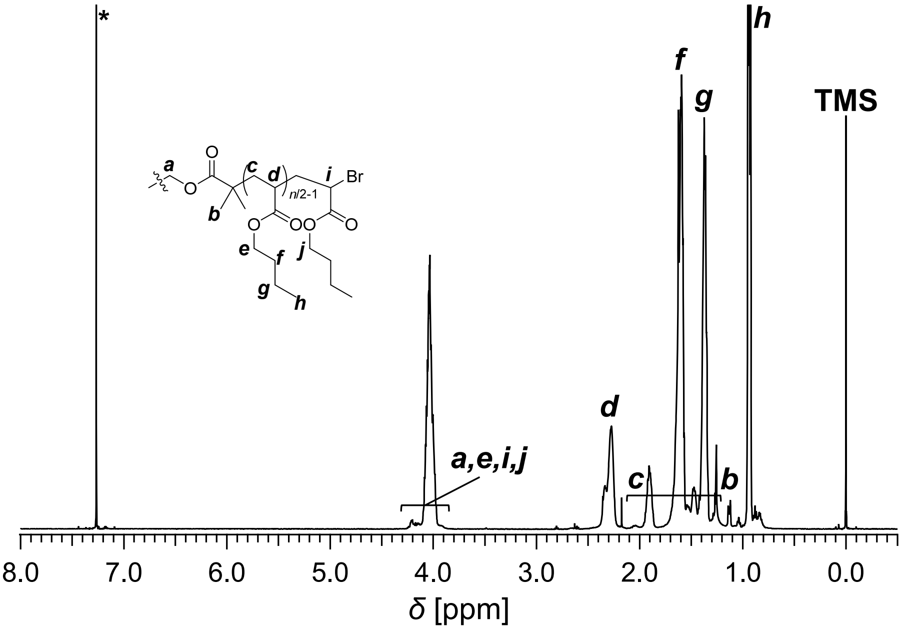


Figure S3. ^{1}H NMR spectrum of Br–PBA$_{19k}$–Br (solvent, $CDCl_3$; 600 MHz). The asterisk denotes solvent peak.

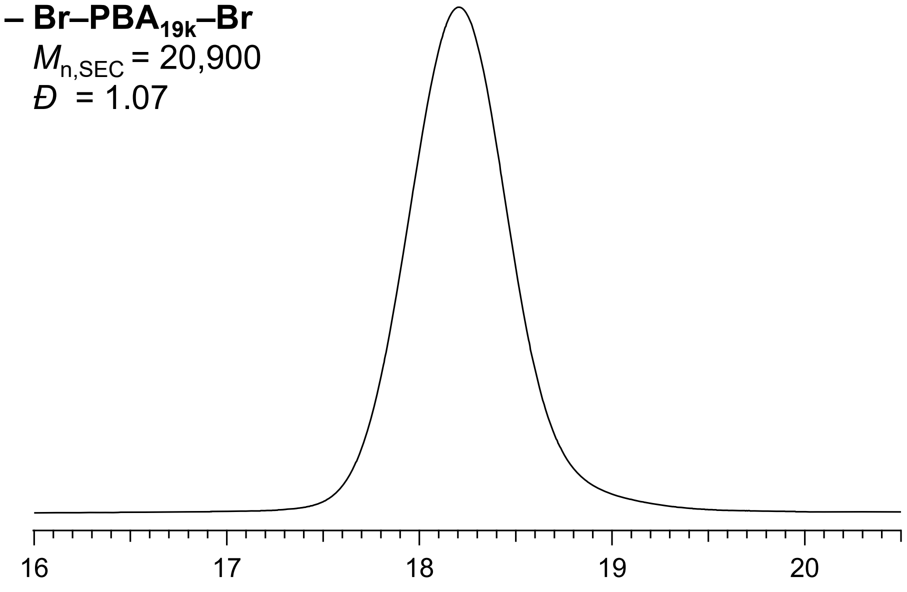


Figure S4. SEC trace of Br–PBA$_{19k}$–Br (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of Br–PBA$_{32k}$–Br

Method A was used for the ATRP of BA (150 g, 1.17 mol, 770 eq.) with CuBr (207 mg, 144 μmol, 0.95 eq.), EBBiB (547 mg, 152 μmol, 1.00 eq.), CuBr$_2$ (17.0 mg, 76.1 μmol, 0.05 eq.), PMDETA (289 mg, 167 μmol, 1.10 eq.), dry DMF solution (1.00 mL), and anisole (39.2 mL) for 13 h to give Br–PBA$_{32k}$–Br (54.5 g) as a pale green viscous product. Yield: 36.3%. ^{1}H NMR (CDCl$_3$, 600 MHz): δ(ppm) 0.94 (t, J = 7.2 Hz, 3H × n, –CH$_2$CH(C(=O)OCH$_2$CH$_2$CH$_2$CH_3)), 1.10–1.17 (m, 12H, –OC(=O)C(CH_3)$_2$–), 1.31–1.44 (br, 2H × n, –CH$_2$CH(C(=O)OCH$_2$CH$_2$CH_2CH$_3$)), 1.55–1.80 (br, 2H × n, –CH$_2$CH(C(=O)OCH$_2$CH_2CH$_2$CH$_3$)), 1.19–2.11 (br, 2H × n, –CH_2CH(C(=O)OCH$_2$CH$_2$CH$_2$CH$_3$)), 2.12–2.55 (br, 1H × (n − 2), –CH$_2$CH(C(=O)OCH$_2$CH$_2$CH$_2$CH$_3$)), 3.86–4.27 (br, 2H × (n + 3), –CH$_2$CH(C(=O)OCH_2CH$_2$CH$_2$CH$_3$), –CHBr, –CH(C(=O)OCH_2CH$_2$CH$_2$CH$_3$)Br, –(CH_2)$_2$OC(=O)). $M_{n,NMR}$ = 41,900 g mol^{-1} (CDCl$_3$); $M_{n,SEC}$ = 35,000 g mol^{-1} (THF); $Đ$ = 1.10.

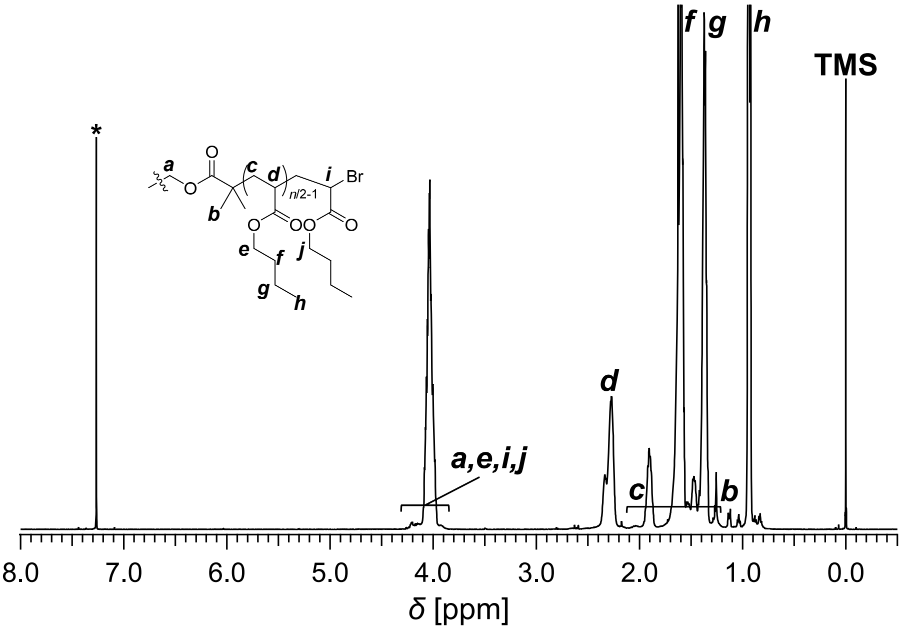


Figure S5. ^{1}H NMR spectrum of Br–PBA$_{32k}$–Br (solvent, CDCl$_3$; 600 MHz). The asterisk denotes solvent peak.

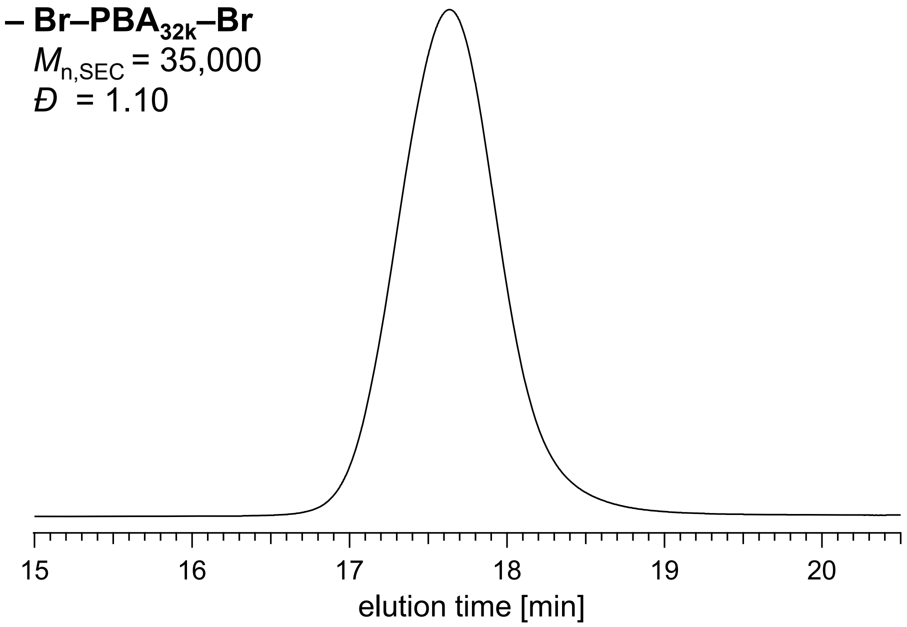


Figure S6. SEC trace of Br–PBA$_{32k}$–Br (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of Br–PBA$_{175k}$–Br

Method A was used for the ATRP of BA (30.0 g, 234 mmol, 5735 eq.) with CuBr (33.3 mg, 232 µmol, 5.69 eq.), EBBiB (14.7 mg, 40.8 µmol, 1.00 eq.), $CuBr_2$ (2.8 mg, 13 µmol, 0.32 eq.), PMDETA (47.2 mg, 272 µmol, 6.67 eq.), dry DMF solution (1.00 mL), and anisole (7.8 mL) for 42 h to give Br–PBA$_{175k}$–Br (9.0 g) as a pale green viscous product. Yield: 30.0%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 0.94 (t, J = 7.2 Hz, 3H × n, $–CH_2CH(C(=O)OCH_2CH_2CH_2C\mathit{H}_3)$), 1.11–1.17 (m, 12H, $–OC(=O)C(C\mathit{H}_3)_2–$), 1.30–1.44 (br, 2H × n, $–CH_2CH(C(=O)OCH_2CH_2C\mathit{H}_2CH_3)$), 1.55–1.80 (br, 2H × n, $–CH_2CH(C(=O)OCH_2C\mathit{H}_2CH_2CH_3)$), 1.17–2.10 (br, 2H × n, $–C\mathit{H}_2CH(C(=O)OCH_2CH_2CH_2CH_3)$), 2.11–2.50 (br, 1H × ($n$ − 2), $–CH_2C\mathit{H}(C(=O)OCH_2CH_2CH_2CH_3)$), 3.86–4.22 (br, 2H × ($n$ + 2), $–CH_2CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)$, $–C\mathit{H}Br$, $–CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)Br$, $–(C\mathit{H}_2)_2OC(=O)–$). $M_{n,NMR}$ = 252,600 g mol^{-1} ($CDCl_3$); $M_{n,SEC}$ = 201,300 g mol^{-1} (THF); $Đ$ = 1.21; $M_{n,MALS}$ = 174,800; $Đ_{MALS}$ = 1.05 ($CHCl_3$).

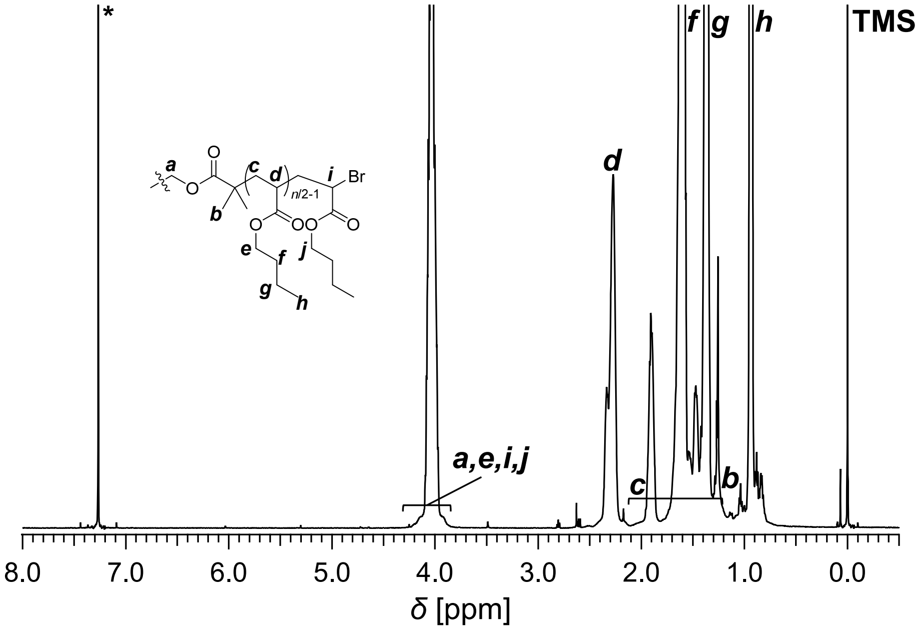


Figure S7. ^{1}H NMR spectrum of Br–PBA$_{175k}$–Br (solvent, CDCl$_3$; 600 MHz). The asterisk denotes solvent peak.

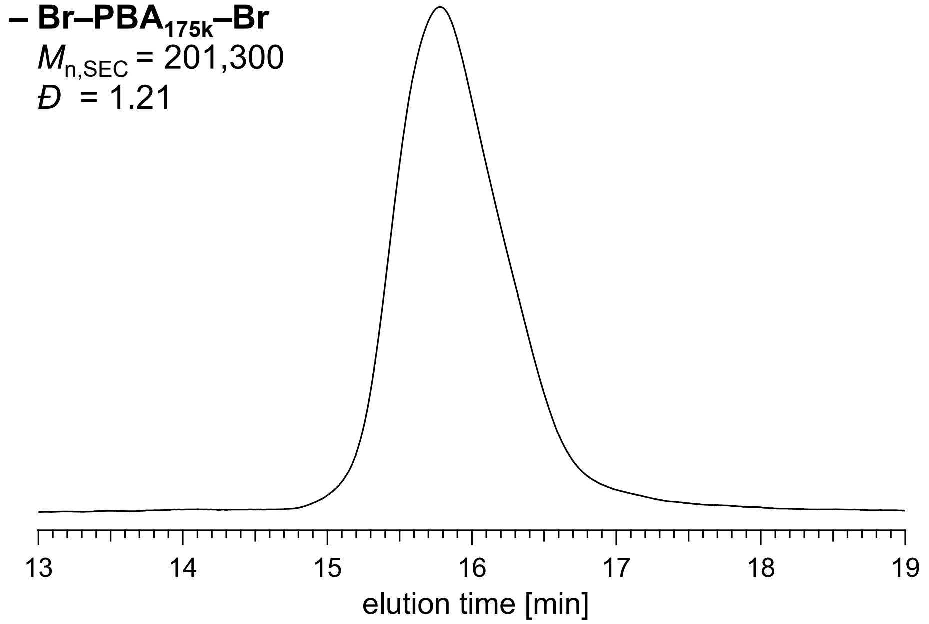
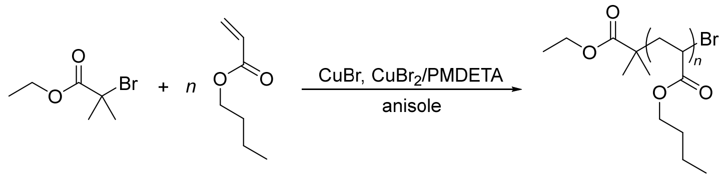


Figure S8. SEC trace of Br–PBA$_{175k}$–Br (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of PBA$_{15k}$–Br

Scheme S2. Synthesis of PBA–Br



EBiB BA PBA–Br

Method A was used for the ATRP of BA (50.0 g, 390 mmol, 461 eq.) with CuBr (116 mg, 809 μmol, 0.96 eq.), EBBiB (165 mg, 846 μmol, 1.00 eq.), CuBr$_2$ (9.4 mg, 42 μmol, 0.05 eq.), PMDETA (161 mg, 927 μmol, 1.10 eq.), dry DMF solution (1.00 mL), and anisole (13.1 mL) for 5.5 h to give PBA$_{15k}$–Br (14.6 g) as a pale green viscous product. Yield: 29.2%. ^{1}H NMR (CDCl$_3$, 600 MHz): δ(ppm) 0.94 (t, J = 7.2 Hz, 3H × n, $\mathrm{–CH_2CH(C(=O)OCH_2CH_2CH_2C}H_3\mathrm{))}$), 1.09–1.17 (m, 6H, $\mathrm{–OC(=O)C(C}H_3\mathrm{)_2–}$), 1.22–1.29 (m, 3H, $\mathrm{C}H_3\mathrm{CH_2OC(=O)–}$), 1.32–1.44 (br, 2H × n, $\mathrm{–CH_2CH(C(=O)OCH_2CH_2C}H_2\mathrm{CH_3))}$), 1.55–1.77 (br, 2H × n, $\mathrm{–CH_2CH(C(=O)OCH_2C}H_2\mathrm{CH_2CH_3))}$), 1.18–2.09 (br, 2H × n, $\mathrm{–C}H_2\mathrm{CH(C(=O)OCH_2CH_2CH_2CH_3))}$), 2.11–2.48 (br, 1H × ($n$ − 1), $\mathrm{–CH_2C}H\mathrm{(C(=O)OCH_2CH_2CH_2CH_3))}$), 3.82–4.32 (br, 2H × ($n$ + 3/2), $\mathrm{–CH_2CH(C(=O)OC}H_2\mathrm{CH_2CH_2CH_3)}$, $\mathrm{–C}H\mathrm{Br}$, $\mathrm{–CH(C(=O)OC}H_2\mathrm{CH_2CH_2CH_3)Br}$, $\mathrm{CH_3C}H_2\mathrm{OC(=O)–}$). $M_{\mathrm{n,NMR}}$ = 20,300 g mol^{-1} (CDCl$_3$); $M_{\mathrm{n,SEC}}$ = 19,500 g mol^{-1} (THF); $Đ$ = 1.06.

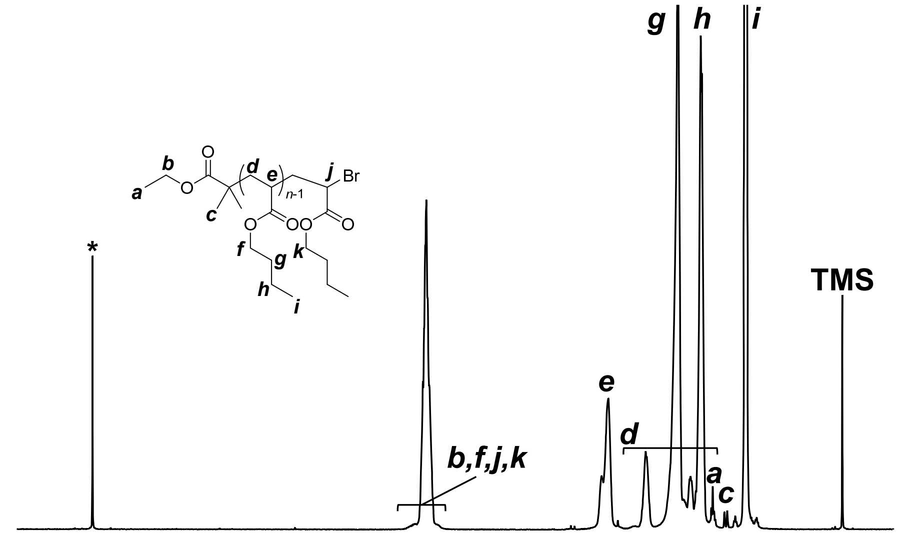


Figure S9. ^{1}H NMR spectrum of PBA$_{15k}$–Br (solvent, CDCl$_3$; 600 MHz). The asterisk denotes solvent peak.

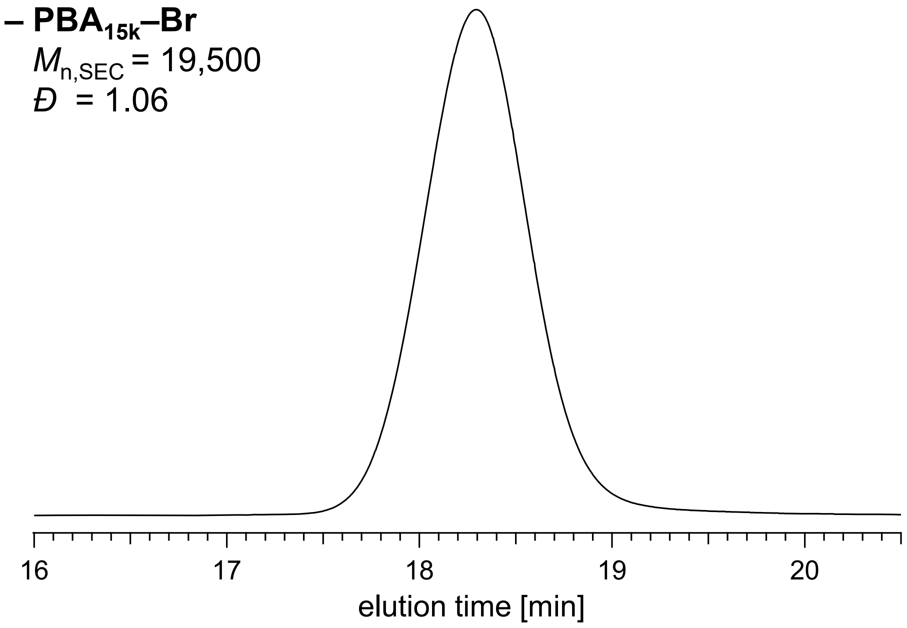
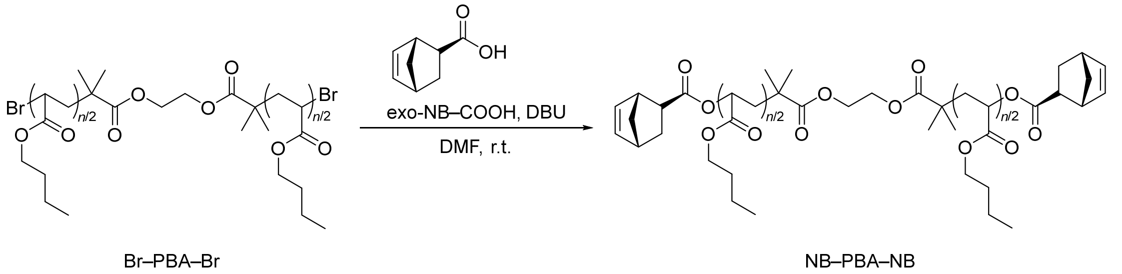


Figure S10. SEC trace of $\mathrm{PBA_{15k}}$–Br (eluent, THF; flow rate, 1.0 mL $\mathrm{min^{-1}}$).

Synthesis of *α*,*ω*-end norbornenyl-functionalized PBA (NB–$\mathrm{PBA_{10k}}$–NB)

Scheme S3. Synthesis of NB–PBA–NB



A typical procedure for the condensation reaction is as follows (Method B): In a round-bottom flask, Br–$\mathrm{PBA_{10k}}$–Br ($M_{\mathrm{n,NMR}}$ = 11,600, 12.0 g, 1.03 mmol, 1.0 eq.), *exo*-NB–COOH (570 mg, 4.13 mmol, 4.0 eq.), and DBU (616 µL, 4.13 mmol, 4.0 eq.) were dissolved in dry DMF (120 mL), and the mixture was stirred at r.t. for 166 h. The mixture was then poured into MeOH to give NB–$\mathrm{PBA_{10k}}$–NB (10.8 g) as a yellow viscous product. Yield: 90.0%. Note that NB–$\mathrm{PBA_{32k}}$–NB and $\mathrm{PBA_{15k}}$–NB were purified by washing with 1 M HCl solution, brine, and saturated aqueous $\mathrm{NaHCO_3}$ solution. ^{1}H NMR ($\mathrm{CDCl_3}$, 600 MHz): δ(ppm) 0.94 (t, J = 7.2 Hz, 3H × n, $-\mathrm{CH_2CH(C(=O)OCH_2CH_2CH_2C}\mathit{H}_3))$, 1.10–1.17 (m, 12H, $-\mathrm{OC(=O)C(C}\mathit{H}_3)_2-)$, 1.31–1.44 (br, 2H × n, $-\mathrm{CH_2CH(C(=O)OCH_2CH_2C}\mathit{H}_2\mathrm{CH_3}))$, 1.55–1.80 (br, 2H × n, $-\mathrm{CH_2CH(C(=O)OCH_2C}\mathit{H}_2\mathrm{CH_2CH_3}))$, 1.08–1.82 (m, 6H, *endo*-C*H*– of $-\mathrm{CH-C}\mathit{H}_2\mathrm{-CH-CO-}$ in norbornene ring, bridge head $-\mathrm{C}\mathit{H}_2-$ in norbornene ring), 1.19–2.10 (br, 2H × n, $-\mathrm{C}\mathit{H}_2\mathrm{CH(C(=O)OCH_2CH_2CH_2CH_3)})$, 2.12–2.45 (br, 1H × ($n$ − 2), $-\mathrm{CH_2C}\mathit{H}\mathrm{(C(=O)OCH_2CH_2CH_2CH_3)})$, 1.82–2.68 (m, 4H, *exo*-C*H*– of $-\mathrm{CH-C}\mathit{H}_2\mathrm{-CH-CO-}$, $-\mathrm{CO-CH-CH_2-C}\mathit{H}$ in norbornene ring), 2.88–3.21 (m, 4H, $-\mathrm{C}\mathit{H}\mathrm{-CH_2-CH-CO-}$ in norbornene ring, $-\mathrm{C}\mathit{H}\mathrm{-CH-CO-}$ in norbornene ring), 3.83–4.29 (br, 2H × (n + 2), $-\mathrm{CH_2CH(C(=O)OC}\mathit{H}_2\mathrm{CH_2CH_2CH_3})$, $-\mathrm{CH(C(=O)OC}\mathit{H}_2\mathrm{CH_2CH_2CH_3)OC(=O)NB}$, $-(\mathrm{C}\mathit{H}_2)_2\mathrm{OC(=O)}-)$, 4.90–

5.03 (br, 2H, –C*H*OC(=O)NB), 6.06–6.21 (m, 4H, –C*H*=C*H*– in norbornene ring). $M_{\mathrm{n,NMR}}$ = 12,000 g mol^{-1} ($CDCl_3$); $M_{\mathrm{n,SEC}}$ = 10,900 g mol^{-1} (THF); $Đ$ = 1.07; $M_{\mathrm{n,MALS}}$ =10,200; $Đ_{\mathrm{MALS}}$ = 1.15 ($CHCl_3$).

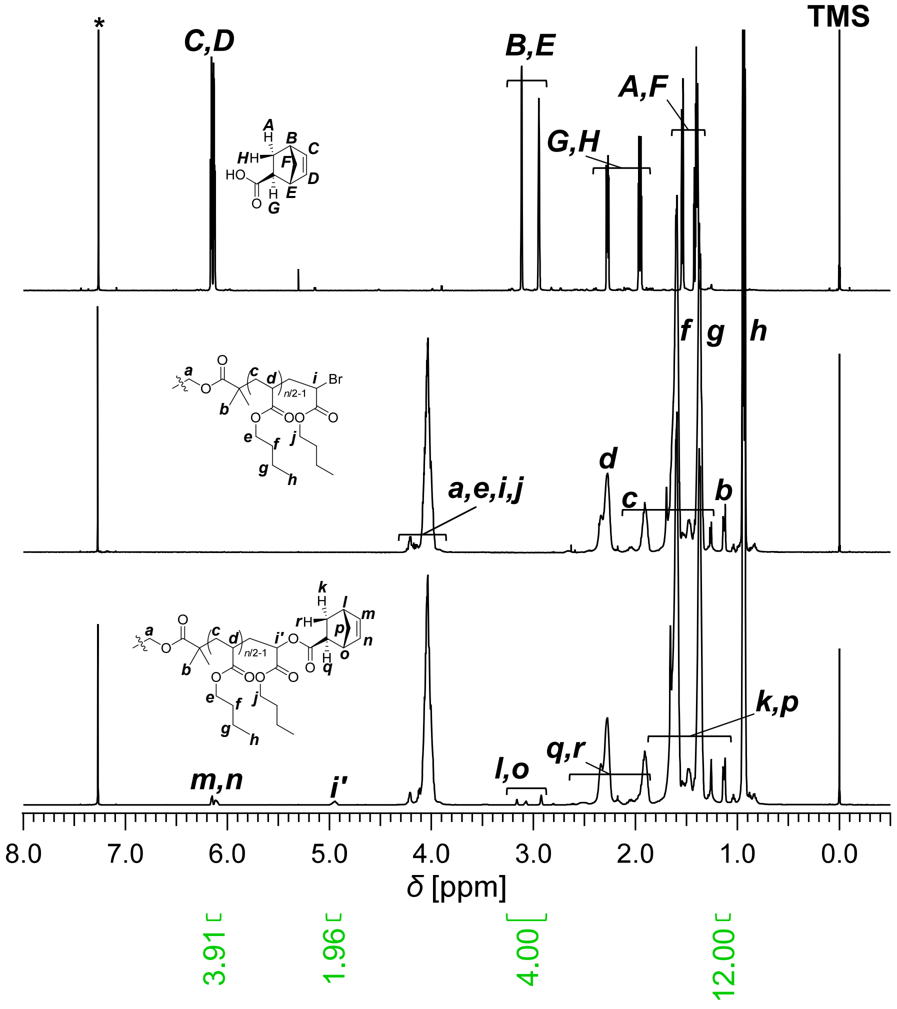


Figure S11. ^{1}H NMR spectra of *exo*-NB–COOH (upper), Br–PBA$_{10k}$–Br (middle), and NB–PBA$_{10k}$–NB (lower) (solvent, $CDCl_3$; 400 or 600 MHz). The asterisk denotes the solvent peak.

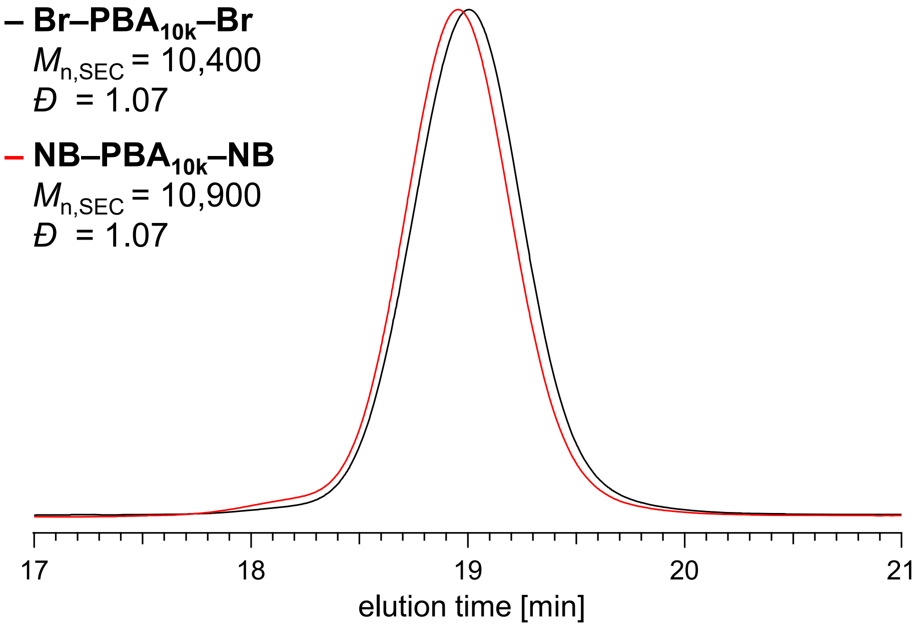


Figure S12. SEC traces of Br–PBA$_{10k}$–Br (black) and NB–PBA$_{10k}$–NB (red) (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of NB–PBA$_{19k}$–NB

Method B was used for the reaction of Br–PBA$_{19k}$–Br ($M_{n,NMR}$ = 23,400, 12.0 g, 513 µmol, 1.0 eq.) with *exo*-NB–COOH (302 mg, 2.19 mmol, 4.3 eq.) and DBU (314 µL, 2.11 mmol, 4.1 eq.) in dry DMF (120 mL) for 161 h to give NB–PBA$_{19k}$–NB (10.7 g) as a yellow viscous product. Yield: 89.2%. ^{1}H NMR (600 MHz, CDCl$_3$): δ (ppm) 0.94 (t, J = 7.5 Hz, 3H × n, –CH$_2$CH(C(=O)OCH$_2$CH$_2$CH$_2$CH_3)), 1.10–1.17 (m, 12H, –OC(=O)C(CH_3)$_2$–), 1.32–1.44 (br, 2H × n, –CH$_2$CH(C(=O)OCH$_2$CH$_2$CH_2CH$_3$)), 1.55–1.82 (br, 2H × n, –CH$_2$CH(C(=O)OCH$_2$CH_2CH$_2$CH$_3$)), 1.09–1.83 (m, 6H, *endo*-C*H*– of –CH–CH_2–CH–CO– in norbornene ring, bridge head –CH_2– in norbornene ring), 1.17–2.10 (br, 2H × n, –CH_2CH(C(=O)OCH$_2$CH$_2$CH$_2$CH$_3$)), 2.11–2.64 (br, 1H × (n − 2), –CH$_2$C*H*(C(=O)OCH$_2$CH$_2$CH$_2$CH$_3$)), 1.83–2.70 (m, 4H, *exo*-C*H*– of –CH–CH_2–CH–CO–, –CO–CH–CH$_2$–C*H* in norbornene ring), 2.90–3.20 (m, 4H, –C*H*–CH$_2$–CH–CO– in norbornene ring, –C*H*–CH–CO– in norbornene ring), 3.79–4.34 (br, 2H × (n + 2), –CH$_2$CH(C(=O)OCH_2CH$_2$CH$_2$CH$_3$), –CH(C(=O)OCH_2CH$_2$CH$_2$CH$_3$)OC(=O)NB, –(CH_2)$_2$OC(=O)–), 4.89–5.02 (br, 2H, –C*H*OC(=O)NB), 6.06–6.19 (m, 4H, –C*H*=C*H*– in norbornene ring). $M_{n,NMR}$ = 24,300 g mol^{-1} (CDCl$_3$); $M_{n,SEC}$ = 21,500 g mol^{-1} (THF); $Đ$ = 1.08; $M_{n,MALS}$ =19,200; $Đ_{MALS}$ = 1.05 (CHCl$_3$).

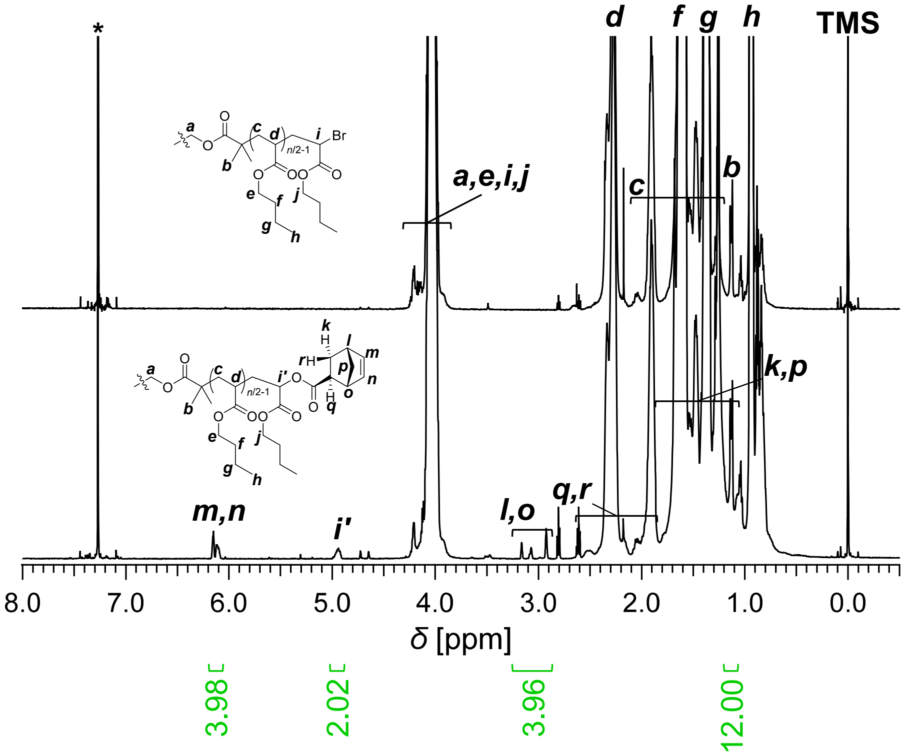


Figure S13. ^{1}H NMR spectra of Br–PBA$_{19k}$–Br (upper) and NB–PBA$_{19k}$–NB (lower) (solvent, $CDCl_3$; 600 MHz). The asterisk denotes the solvent peak.

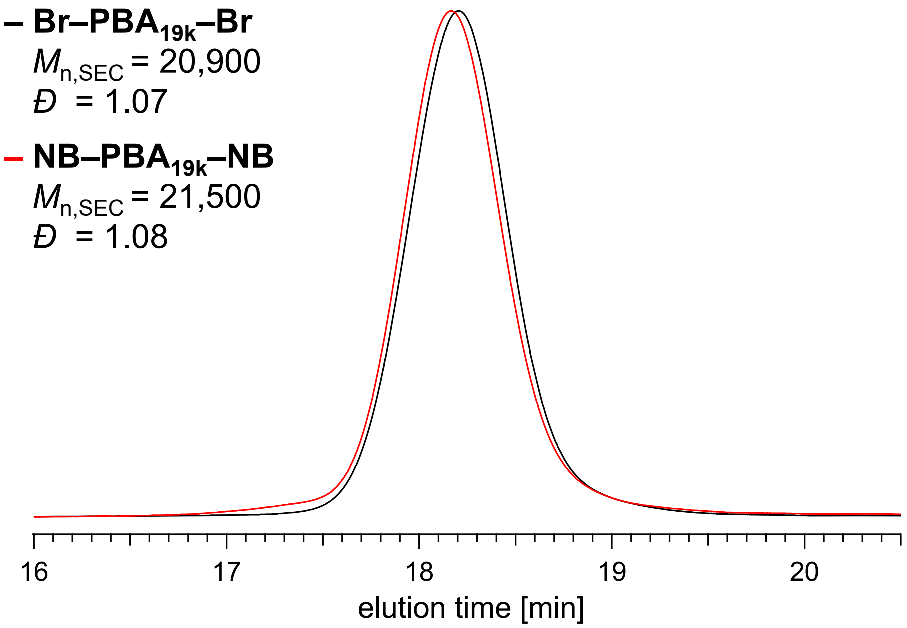


Figure S14. SEC traces of Br–PBA$_{19k}$–Br (black) and NB–PBA$_{19k}$–NB (red) (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of NB–PBA$_{32k}$–NB

Method B was used for the reaction of Br–PBA$_{32k}$–Br ($M_{\mathrm{n,NMR}}$ = 41,900, 25.5 g, 609 µmol, 1.0 eq.) with *exo*-NB–COOH (350 mg, 2.53 mmol, 4.2 eq.) and DBU (375 µL, 2.51 mmol, 4.1 eq.) in dry DMF (255 mL) for 138 h to give NB–PBA$_{32k}$–NB (23.8 g) as a yellow viscous product. Yield: 93.3%. ^{1}H NMR (600 MHz, CDCl$_3$): δ (ppm) 0.94 (t, J = 7.2 Hz, 3H × *n*, –CH$_2$CH(C(=O)OCH$_2$CH$_2$CH$_2$C*H*$_3$)), 1.09–1.16 (m, 12H, –OC(=O)C(C*H*$_3$)$_2$–), 1.30–1.44 (br, 2H × *n*, –CH$_2$CH(C(=O)OCH$_2$CH$_2$C*H*$_2$CH$_3$)), 1.55–1.80 (br, 2H × *n*, –CH$_2$CH(C(=O)OCH$_2$C*H*$_2$CH$_2$CH$_3$)), 1.07–1.82 (m, 6H, *endo*-C*H*– of –CH–C*H*$_2$–CH–CO– in norbornene ring, bridge head –C*H*$_2$– in norbornene ring), 1.21–2.09 (br, 2H × *n*, –C*H*$_2$CH(C(=O)OCH$_2$CH$_2$CH$_2$CH$_3$)), 2.10–2.68 (br, 1H × (*n* − 2), –CH$_2$C*H*(C(=O)OCH$_2$CH$_2$CH$_2$CH$_3$)), 1.82–2.69 (m, 4H, *exo*-C*H*– of –CH–C*H*$_2$–CH–CO–, –CO–CH–CH$_2$–C*H* in norbornene ring), 2.90–3.19 (m, 4H, –C*H*–CH$_2$–CH–CO– in norbornene ring, –C*H*–CH–CO– in norbornene ring), 3.73–4.34 (br, 2H × (*n* + 2), –CH$_2$CH(C(=O)OC*H*$_2$CH$_2$CH$_2$CH$_3$), –CH(C(=O)OC*H*$_2$CH$_2$CH$_2$CH$_3$)OC(=O)NB, –(C*H*$_2$)$_2$OC(=O)–), 4.90–5.00 (br, 2H, –C*H*OC(=O)NB), 6.07–6.21 (m, 4H, –C*H*=C*H*– in norbornene ring). $M_{\mathrm{n,NMR}}$ = 39,700 g mol^{-1} (CDCl$_3$); $M_{\mathrm{n,SEC}}$ = 37,100 g mol^{-1} (THF); $Đ$ = 1.10; $M_{\mathrm{n,MALS}}$ =31,500; $Đ_{\mathrm{MALS}}$ = 1.03 (CHCl$_3$).

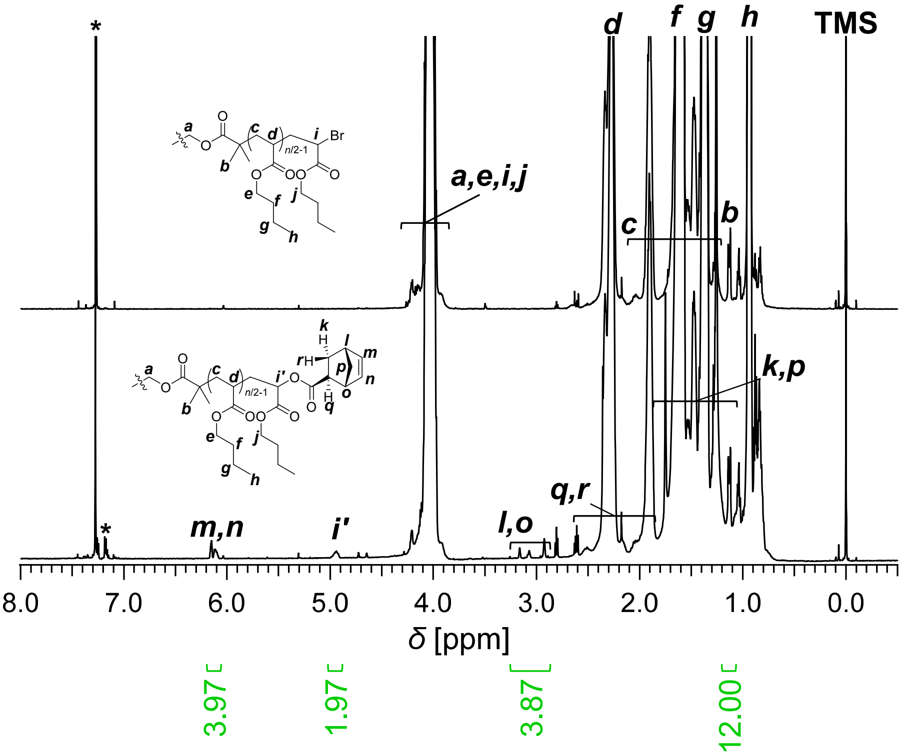


Figure S15. ^{1}H NMR spectra of Br–PBA$_{32k}$–Br (upper) and NB–PBA$_{32k}$–NB (lower) (solvent, CDCl$_3$; 600 MHz). The asterisks denote the solvent peaks.

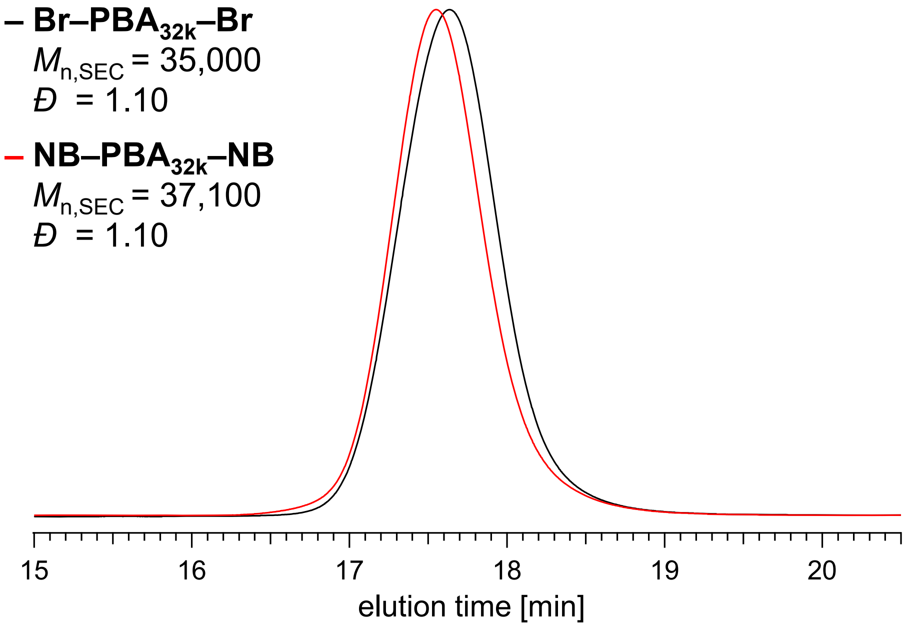
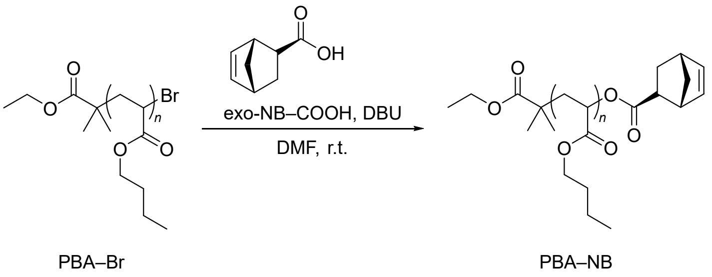


Figure S16. SEC traces of $Br–PBA_{32k}–Br$ (black) and $NB–PBA_{32k}–NB$ (red) (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of PBA_{15k}–NB

Scheme S4. Synthesis of PBA–NB



Method B was used for the reaction of PBA_{15k}–Br ($M_{n,NMR}$ =20,300, 8.00 g, 394 μmol, 1.0 eq.) with *exo*-NB–COOH (241 mg, 1.74 mmol, 4.4 eq.) and DBU (265 μL, 1.74 mmol, 4.4 eq.) in dry DMF (80 mL) for 189 h to give PBA_{15k}–NB (4.43 g) as a yellow viscous product. Yield: 55.4%. ^{1}H NMR (600 MHz, $CDCl_3$): *δ* (ppm) 0.94 (t, *J* = 7.2 Hz, 3H × *n*, $–CH_2CH(C(=O)OCH_2CH_2CH_2C\mathit{H}_3)$), 1.09–1.18 (m, 6H, $–OC(=O)C(C\mathit{H}_3)_2–$), 1.21–1.29 (m, 3H, $C\mathit{H}_3CH_2OC(=O)–$), 1.30–1.44 (br, 2H × *n*, $–CH_2CH(C(=O)OCH_2CH_2C\mathit{H}_2CH_3)$), 1.55–1.78 (br, 2H × *n*, $–CH_2CH(C(=O)OCH_2C\mathit{H}_2CH_2CH_3)$), 1.07–1.82 (m, 3H, *endo*-C*H*– of $–CH–C\mathit{H}_2–CH–CO–$ in norbornene ring, bridge head $–C\mathit{H}_2–$ in norbornene ring), 1.18–2.06 (br, 2H × *n*, $–C\mathit{H}_2CH(C(=O)OCH_2CH_2CH_2CH_3)$), 2.10–2.69 (br, 1H × (*n* − 1), $–CH_2C\mathit{H}(C(=O)OCH_2CH_2CH_2CH_3)$), 1.81–2.73 (m, 2H, *exo*-C*H*– of $–CH–C\mathit{H}_2–CH–CO–$, $–CO–CH–CH_2–C\mathit{H}$ in norbornene ring), 2.89–3.20 (m, 2H, $–C\mathit{H}–CH_2–CH–CO–$ in norbornene ring, $–C\mathit{H}–CH–CO–$ in norbornene ring), 3.80–4.33 (br, 2H × (*n* + 1), $–CH_2CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)$, $–CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)NB$, $CH_3C\mathit{H}_2OC(=O)–$), 4.89–5.02 (br, 1H, $–C\mathit{H}OC(=O)NB$), 6.06–6.20 (m, 2H, $–C\mathit{H}=C\mathit{H}–$ in norbornene ring). $M_{n,NMR}$ = 21,500 g mol^{-1} ($CDCl_3$); $M_{n,SEC}$ = 19,800 g mol^{-1} (THF); *Đ* =

1.06; $M_{\mathrm{n,MALS}}$ =15,000; $Đ_{\mathrm{MALS}}$ = 1.08 ($CHCl_3$).

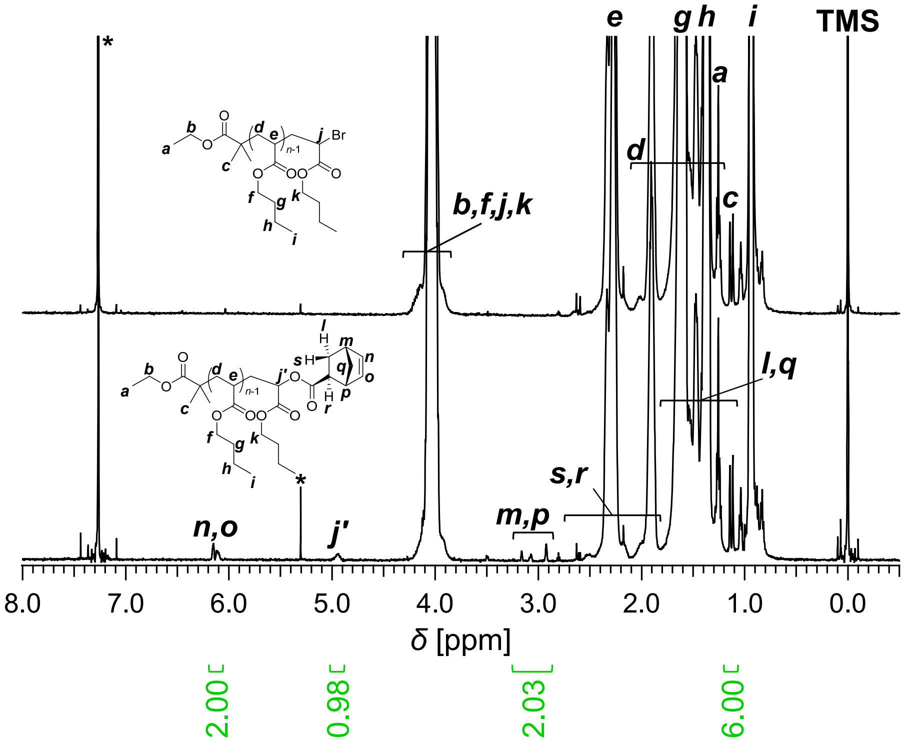


Figure S17. ^{1}H NMR spectra of PBA_{15k}–Br (upper) and PBA_{21k}–NB (lower) (solvent, $CDCl_3$; 600 MHz). The asterisk denotes solvent peak.

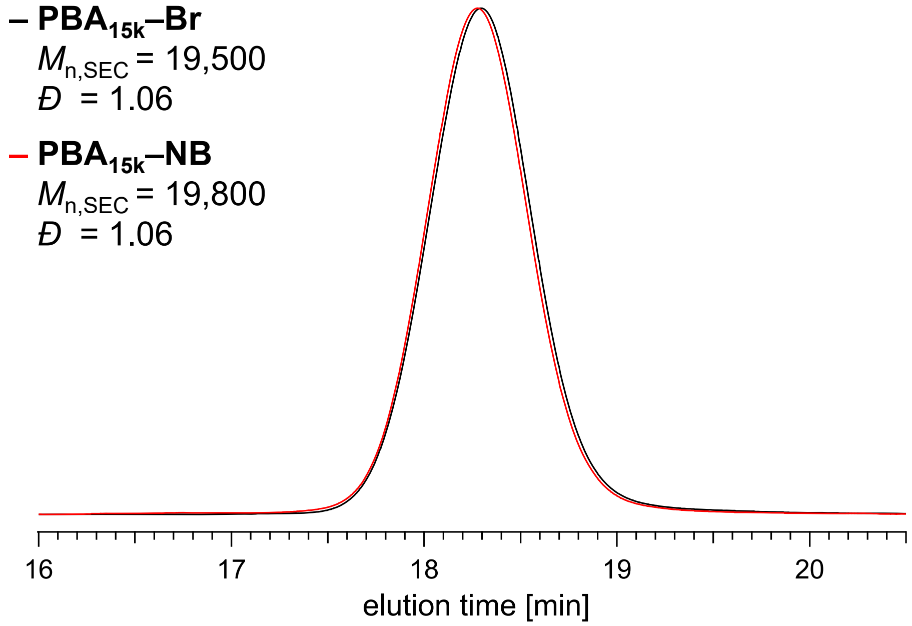
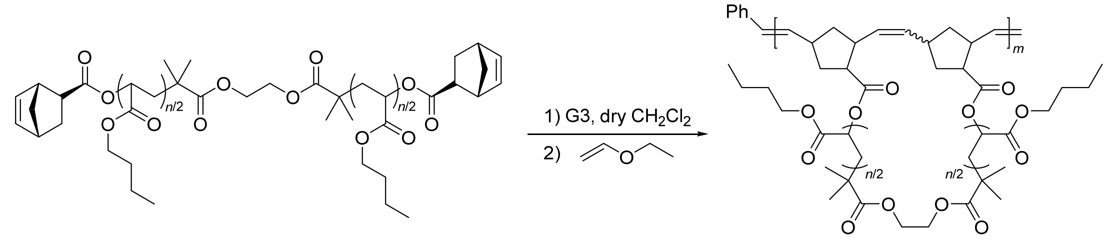


Figure S18. SEC traces of PBA_{15k}–Br (black) and PBA_{15k}–NB (red) (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of Multicyclic PBA (8c-PBA$_{10k}$)

Scheme S5. Synthesis of mc-PBA



NB–PBA–NB

mc-PBA

A typical ring-opening metathesis polymerization (ROMP) procedure is as follows (method C): Under an argon atmosphere, a stock solution of G3 (31.0 mg, 35.0 mmol, 1.0 eq. as a 8.0 mmol L^{-1} solution in CH_2Cl_2) was added to a stirred mixture of NB–PBA$_{10k}$–NB (3.00 g, 294 µmol, 8.4 eq.) in dry CH_2Cl_2 (2.80 L). After 1.5 h, ethyl vinyl ether was added to the reacting mixture to terminate the ROMP. The mixture was purified by preparative SEC to remove the catalyst residue and mc-PBA species containing fewer cyclic units, affording mc-PBA as a brown viscous product (2.07 g). Yield: 69.0%. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 0.94 (t, J = 7.2 Hz, 3H × n, $-CH_2CH(C(=O)OCH_2CH_2CH_2C\mathit{H}_3)$), 1.10–1.16 (m, 12H, $-OC(=O)C(C\mathit{H}_3)_2-$), 1.31–1.44 (br, 2H × n, $-CH_2CH(C(=O)OCH_2CH_2C\mathit{H}_2CH_3)$), 1.51–1.80 (br, 2H × n, $-CH_2CH(C(=O)OCH_2C\mathit{H}_2CH_2CH_3)$), 1.17–2.19 (br, 2H × n, $-C\mathit{H}_2CH(C(=O)OCH_2CH_2CH_2CH_3)$), 2.20–2.69 (br, 1H ×($n$ − 2), $-CH_2C\mathit{H}(C(=O)OCH_2CH_2CH_2CH_3)$), 3.71–4.40 (br, 2H × ($n$ + 2), $-CH_2CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)$, $-CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)OC(=O)-$, $-(C\mathit{H}_2)_2OC(=O)-$), 2.00–4.36 (br, alkenyl of poly(norbornene) backbone), 4.75–5.01 (br, 2H, $-C\mathit{H}OC(=O)CH-$), 4.74–5.62 (br, alkenyl of poly(norbornene) backbone). $M_{n,SEC}$ = 48,600 g mol^{-1} (THF); $Đ$ = 1.16; $M_{n,MALS}$ =83,200; $Đ_{MALS}$ = 1.15 ($CHCl_3$).

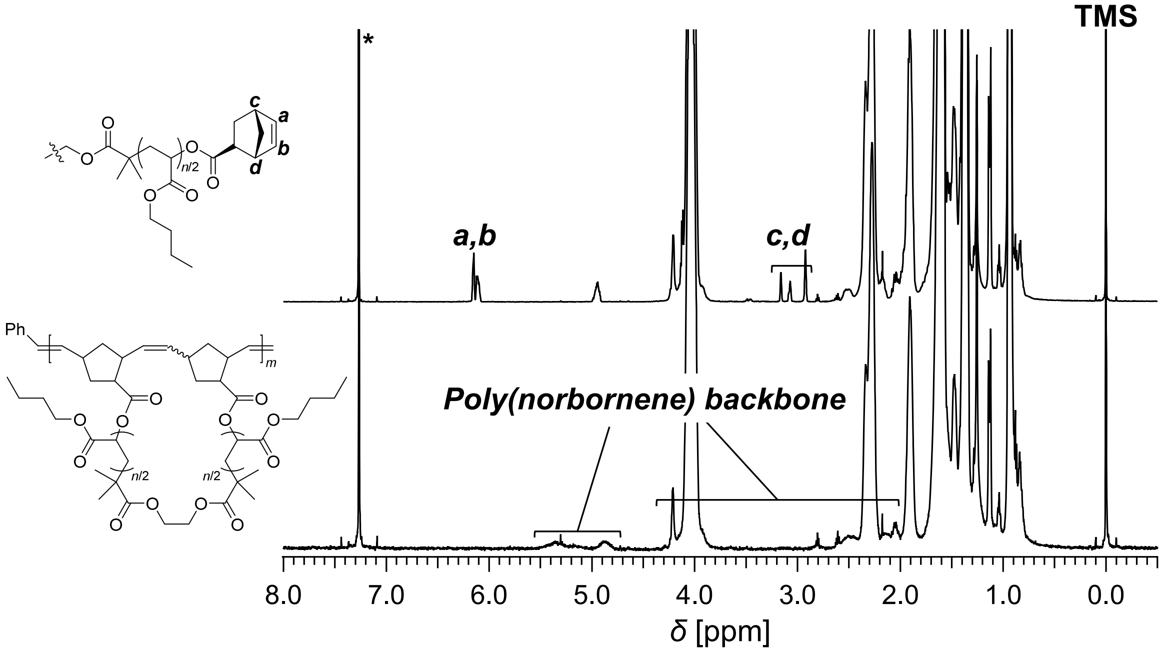


Figure S19. ^{1}H NMR spectra of NB–PBA$_{10k}$–NB (upper) and 8c-PBA$_{10k}$ (lower) (solvent, $CDCl_3$; 600 MHz). The asterisk denotes the solvent peak.

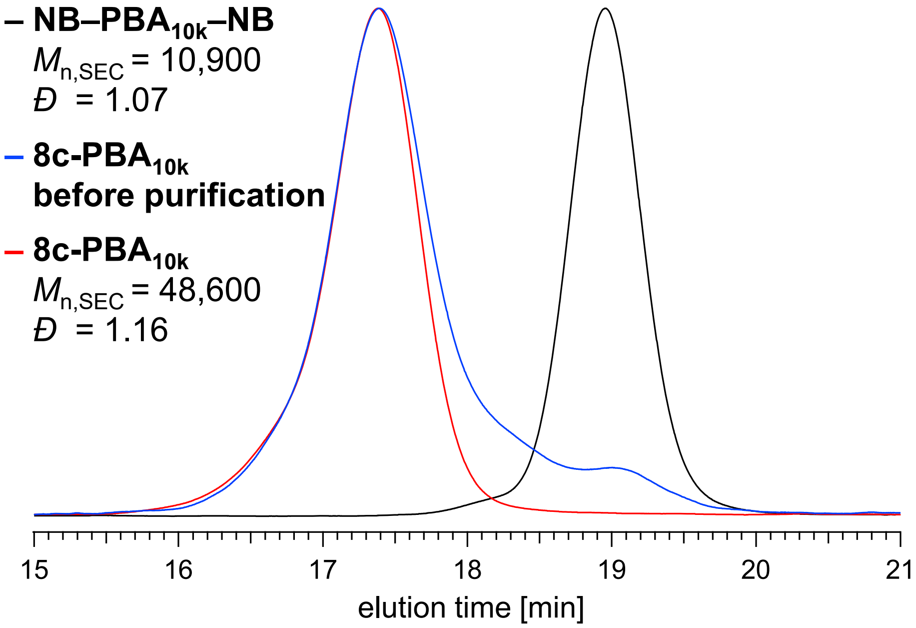


Figure S20. SEC traces of NB–PBA$_{10k}$–NB (black), 8c-PBA$_{10k}$ before purification (blue), and 8c-PBA$_{10k}$ (red) (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of 34c-PBA$_{10k}$

Method C was used for the ROMP of NB–PBA$_{10k}$–NB (3.00 g, 294 µmol, 48 eq.) with G3 (5.4 mg, 6.1 µmol, 1.0 eq. as a 8.0 mmol L^{-1} solution in CH_2Cl_2) in CH_2Cl_2 (2.8 L) to give 34c-PBA$_{10k}$ as a pale brown viscous product (1.50 g). Yield: 50.0%. ^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm) 0.94 (t, J = 7.2 Hz, 3H × n, –$CH_2CH(C(=O)OCH_2CH_2CH_2C\mathit{H}_3)$), 1.11–1.17 (m, 12H, –$OC(=O)C(C\mathit{H}_3)_2$–), 1.32–1.44 (br, 2H × n, –$CH_2CH(C(=O)OCH_2CH_2C\mathit{H}_2CH_3)$), 1.51–1.82 (br, 2H × n, –$CH_2CH(C(=O)OCH_2C\mathit{H}_2CH_2CH_3)$), 1.17–2.19 (br, 2H × n, –$C\mathit{H}_2CH(C(=O)OCH_2CH_2CH_2CH_3)$), 2.19–2.69 (br, 1H ×($n$ − 2), –$CH_2C\mathit{H}(C(=O)OCH_2CH_2CH_2CH_3)$), 3.79–4.40 (br, 2H × ($n$ + 2), –$CH_2CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3$), –$CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)OC(=O)$–, –$(C\mathit{H}_2)_2OC(=O)$–), 2.00–4.53 (br, alkenyl of poly(norbornene) backbone), 4.75–5.03 (br, 2H, –$C\mathit{H}OC(=O)CH$–), 4.74–5.61 (br, alkenyl of poly(norbornene) backbone). $M_{n,SEC}$ = 110,200 g mol^{-1} (THF); $Đ$ = 1.34; $M_{n,MALS}$ =348,300; $Đ_{MALS}$ = 1.62 ($CHCl_3$).

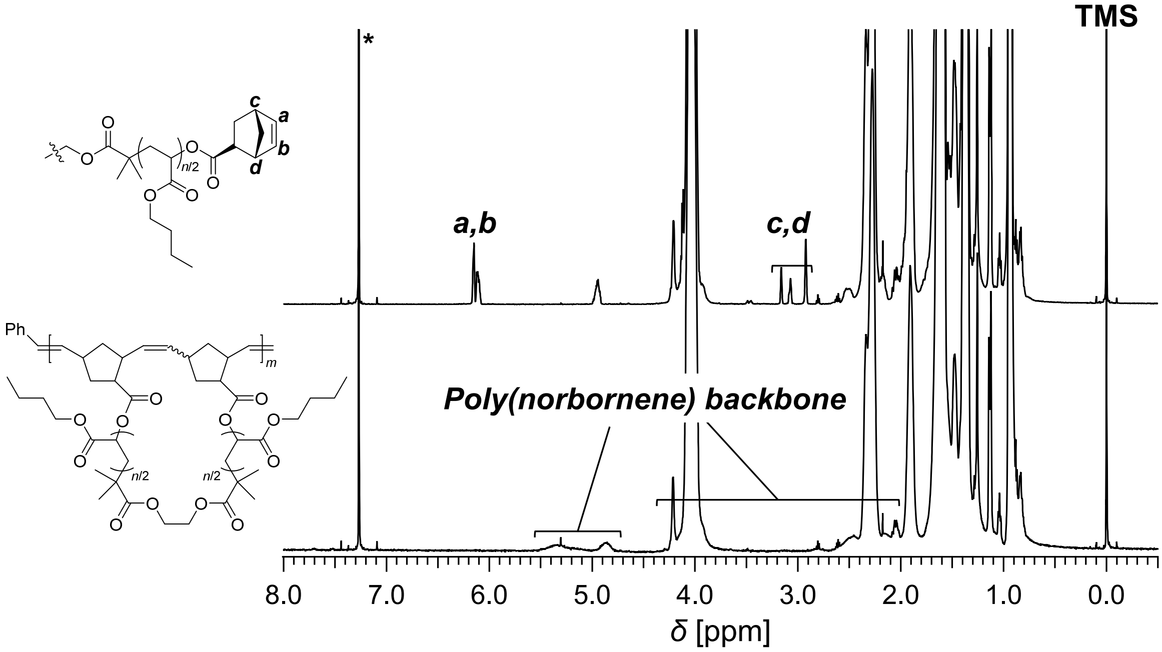


Figure S21. ^{1}H NMR spectra of NB–PBA$_{10k}$–NB (upper) and 34c-PBA$_{10k}$ (lower) (solvent, $CDCl_3$; 600 MHz). The asterisk denotes the solvent peak.

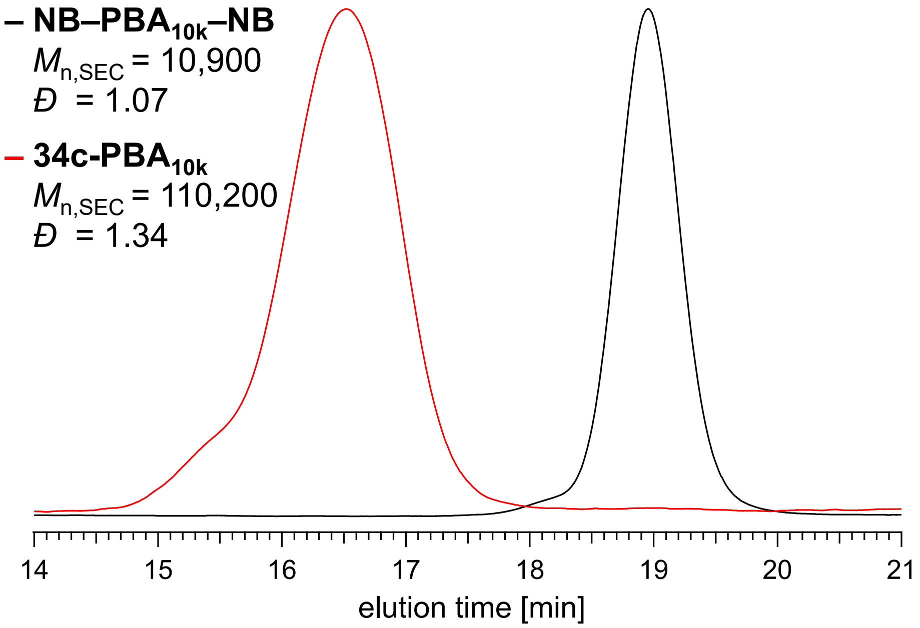


Figure S22. SEC traces of NB–PBA$_{10k}$–NB (black) and 34c-PBA$_{10k}$ (red) (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of 12c-PBA$_{19k}$

Method C was used for the ROMP of NB–PBA$_{19k}$–NB (2.00 g, 104 µmol, 15 eq.) with G3 (6.3 mg, 7.1 µmol, 1.0 eq. as a 8.0 mmol L^{-1} solution in CH_2Cl_2) in CH_2Cl_2 (1.00 L) to give 12c-PBA$_{19k}$ as a pale brown viscous product (1.36 g). Yield: 68.0%. ^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm) 0.94 (t, J = 7.2 Hz, 3H × n, $-CH_2CH(C(=O)OCH_2CH_2CH_2C\mathit{H}_3)$), 1.09–1.17 (m, 12H, $-OC(=O)C(C\mathit{H}_3)_2-$), 1.29–1.44 (br, 2H × n, $-CH_2CH(C(=O)OCH_2CH_2C\mathit{H}_2CH_3)$), 1.51–1.80 (br, 2H × n, $-CH_2CH(C(=O)OCH_2C\mathit{H}_2CH_2CH_3)$), 1.17–2.19 (br, 2H × n, $-C\mathit{H}_2CH(C(=O)OCH_2CH_2CH_2CH_3)$), 2.19–2.69 (br, 1H ×($n$ − 2), $-CH_2C\mathit{H}(C(=O)OCH_2CH_2CH_2CH_3)$), 3.78–4.33 (br, 2H × ($n$ + 2), $-CH_2CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)$, $-CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)OC(=O)-$, $-(C\mathit{H}_2)_2OC(=O)-$), 2.00–4.36 (br, alkenyl of poly(norbornene) backbone), 4.75–5.02 (br, 2H, $-C\mathit{H}OC(=O)CH-$), 4.71–5.74 (br, alkenyl of poly(norbornene) backbone). $M_{n,SEC}$ = 108,300 g mol^{-1} (THF); $Đ$ = 1.40; $M_{n,MALS}$ = 222,400; $Đ_{MALS}$ = 1.75 ($CHCl_3$).

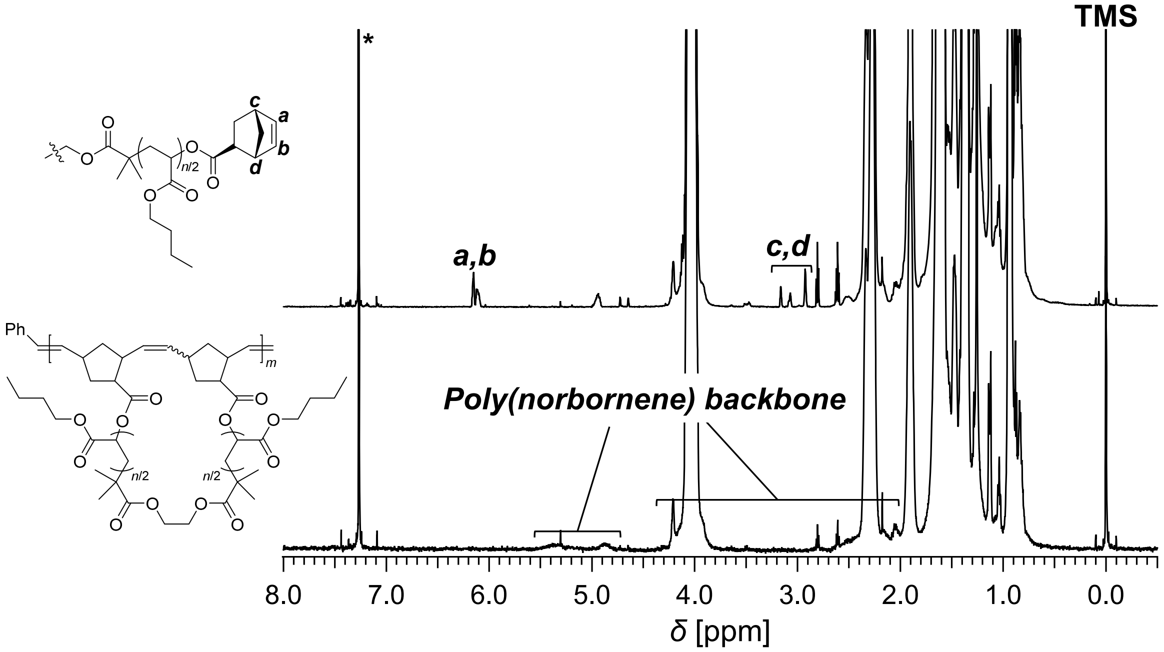


Figure S23. ^{1}H NMR spectra of NB–PBA$_{19k}$–NB (upper) and 12c-PBA$_{19k}$ (lower) (solvent, $CDCl_3$; 600 MHz). The asterisk denotes the solvent peak.

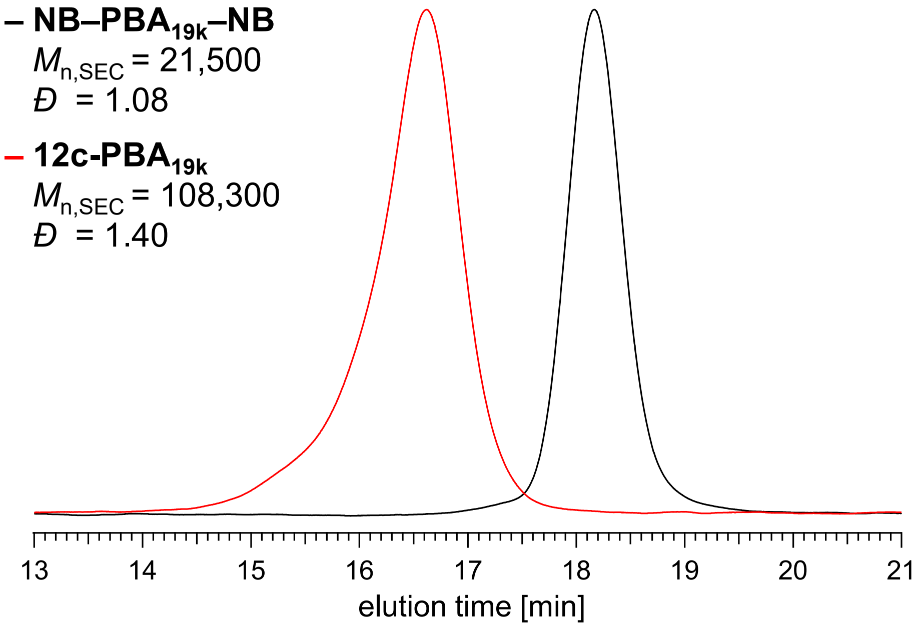


Figure S24. SEC traces of NB–PBA$_{19k}$–NB (black) and 12c-PBA$_{19k}$ (red) (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of 5c-PBA$_{32k}$

Method C was used for the ROMP of NB–PBA$_{32k}$–NB (7.00 g, 222 μmol, 3.9 eq.) with G3 (50.7 mg, 57.3 μmol, 1.0 eq. as a 8.0 mmol L^{-1} solution in CH_2Cl_2) in CH_2Cl_2 (3.44 L) to give 5c-PBA$_{32k}$ as a pale brown viscous product (4.32 g). Yield: 61.7%.^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm) 0.94 (t, J = 7.2 Hz, 3H × n, $–CH_2CH(C(=O)OCH_2CH_2CH_2C\mathit{H}_3)$), 1.08–1.17 (m, 12H, $–OC(=O)C(C\mathit{H}_3)_2–$), 1.29–1.44 (br, 2H × n, $–CH_2CH(C(=O)OCH_2CH_2C\mathit{H}_2CH_3)$), 1.54–1.81 (br, 2H × n, $–CH_2CH(C(=O)OCH_2C\mathit{H}_2CH_2CH_3)$), 1.17–2.19 (br, 2H × n, $–C\mathit{H}_2CH(C(=O)OCH_2CH_2CH_2CH_3)$), 2.18–2.71 (br, 1H ×($n$ − 2), $–CH_2C\mathit{H}(C(=O)OCH_2CH_2CH_2CH_3)$), 3.77–4.33 (br, 2H × ($n$ + 2), $–CH_2CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)$, $–CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)OC(=O)–$, $–(C\mathit{H}_2)_2OC(=O)–$), 2.00–4.35 (br, alkenyl of poly(norbornene) backbone), 4.81–4.96 (br, 2H, $–C\mathit{H}OC(=O)CH–$), 4.78–5.63 (br, alkenyl of poly(norbornene) backbone). $M_{n,SEC}$ = 118,100 g mol^{-1} (THF); $Đ$ = 1.39; $M_{n,MALS}$ = 162,100; $Đ_{MALS}$ = 1.27 ($CHCl_3$).

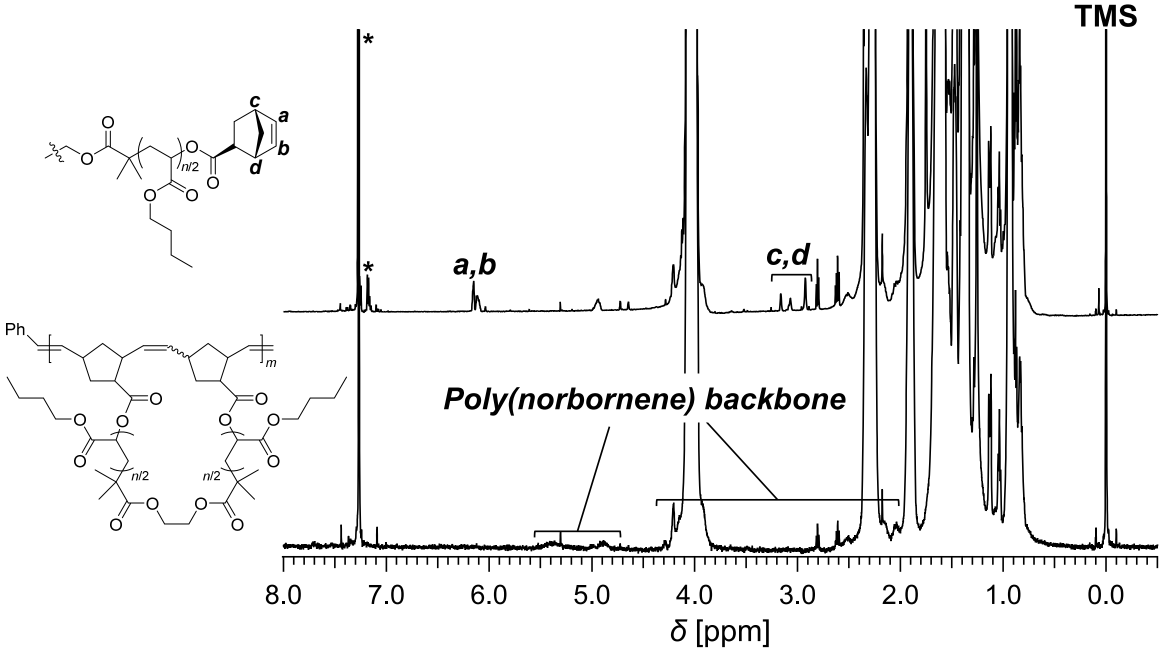


Figure S25. ^{1}H NMR spectra of NB–PBA$_{32k}$–NB (upper) and 5c-PBA$_{32k}$ (lower) (solvent, CDCl$_3$; 600 MHz). The asterisks denote the solvent peaks.

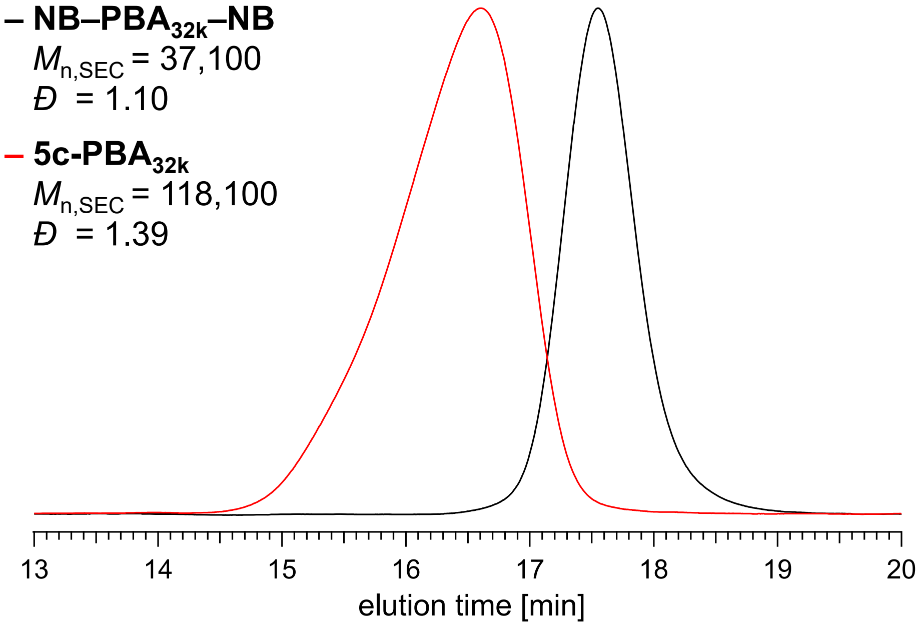


Figure S26. SEC traces of NB–PBA$_{32k}$–NB (black) and 5c-PBA$_{32k}$ (red) (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of 8c-PBA$_{32k}$

Method C was used for the ROMP of NB–PBA$_{32k}$–NB (4.00 g, 127 μmol, 7.5 eq.) with G3 (15.0 mg, 16.9 μmol, 1.0 eq. as a 8.0 mmol L^{-1} solution in CH_2Cl_2) in CH_2Cl_2 (1.94 L) to give 8c-PBA$_{32k}$ as a pale brown viscous product (2.24 g). Yield: 56.0%. ^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm) 0.94 (t, J = 7.2 Hz, 3H × n, $-CH_2CH(C(=O)OCH_2CH_2CH_2C\mathit{H}_3))$), 1.11–1.16 (m, 12H, $-OC(=O)C(C\mathit{H}_3)_2-$), 1.31–1.44 (br, 2H × n, $-CH_2CH(C(=O)OCH_2CH_2C\mathit{H}_2CH_3))$), 1.51–1.81 (br, 2H × n, $-CH_2CH(C(=O)OCH_2C\mathit{H}_2CH_2CH_3))$), 1.16–2.19 (br, 2H × n, $-C\mathit{H}_2CH(C(=O)OCH_2CH_2CH_2CH_3))$), 2.19–2.67 (br, 1H ×($n$ − 2), $-CH_2C\mathit{H}(C(=O)OCH_2CH_2CH_2CH_3))$), 3.77–4.34 (br, 2H × ($n$ + 2), $-CH_2CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)$, $-CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)OC(=O)-$, $-(C\mathit{H}_2)_2OC(=O)-$), 1.99–4.34 (br, alkenyl of poly(norbornene) backbone), 4.75–5.11 (br, 2H, $-C\mathit{H}OC(=O)CH-$), 4.66–5.66 (br, alkenyl of poly(norbornene) backbone). $M_{n,SEC}$ = 159,000 g mol^{-1} (THF); $Đ$ = 1.43; $M_{n,MALS}$ = 256,100; $Đ_{MALS}$ = 1.47 ($CHCl_3$).

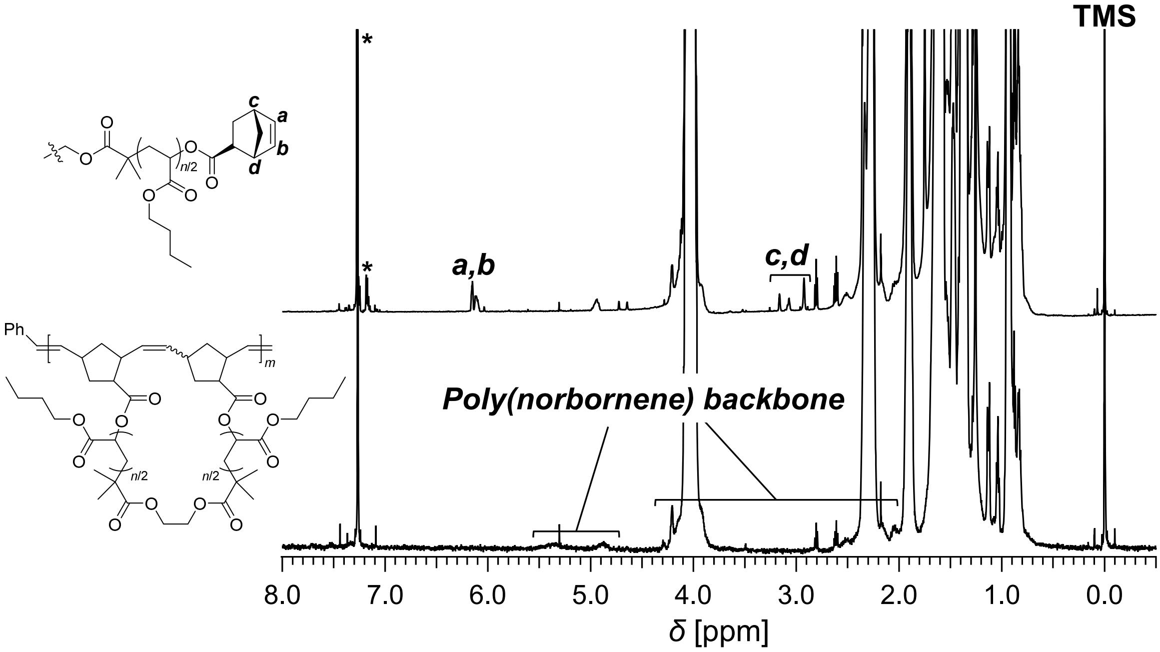


Figure S27. ^{1}H NMR spectra of NB–PBA$_{32k}$–NB (upper) and 8c-PBA$_{32k}$ (lower) (solvent, $CDCl_3$; 600 MHz). The asterisks denote the solvent peaks.

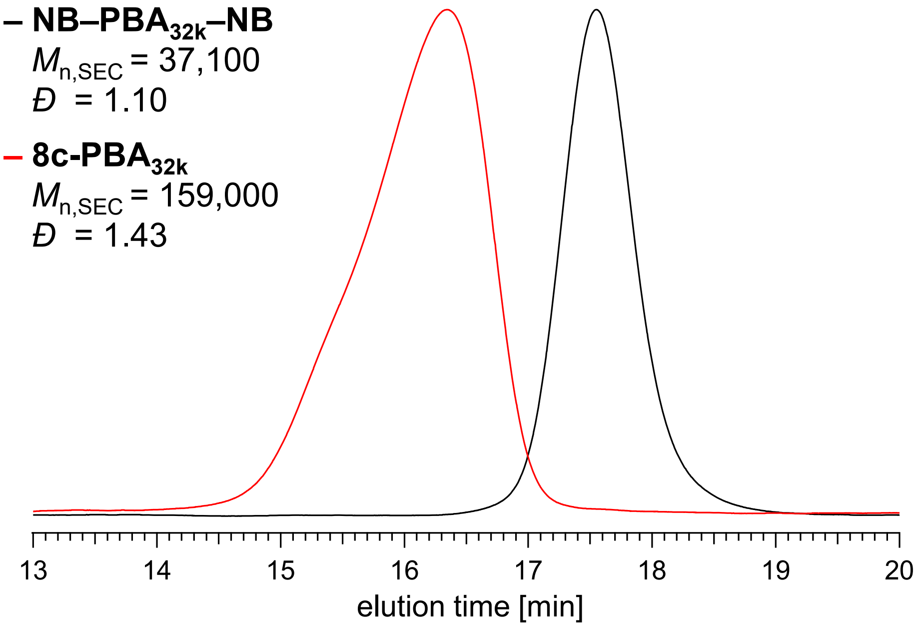


Figure S28. SEC traces of NB–PBA$_{32k}$–NB (black) and 8c-PBA$_{32k}$ (red) (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of 13c-PBA$_{32k}$

Method C was used for the ROMP of NB–PBA$_{32k}$–NB (3.00 g, 95.2 µmol, 18.7 eq.) with G3 (4.5 mg, 5.1 µmol, 1.0 eq. as a 8.0 mmol L^{-1} solution in CH_2Cl_2) in CH_2Cl_2 (1.45 L) to give 13c-PBA$_{32k}$ as a pale brown viscous product (1.37 g). Yield: 45.7%.^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm) 0.94 (t, J = 7.2 Hz, 3H × n, $–CH_2CH(C(=O)OCH_2CH_2CH_2C\mathit{H}_3)$), 1.09–1.16 (m, 12H, $–OC(=O)C(C\mathit{H}_3)_2–$), 1.30–1.44 (br, 2H × n, $–CH_2CH(C(=O)OCH_2CH_2C\mathit{H}_2CH_3)$), 1.50–1.80 (br, 2H × n, $–CH_2CH(C(=O)OCH_2C\mathit{H}_2CH_2CH_3)$), 1.17–2.11 (br, 2H × n, $–C\mathit{H}_2CH(C(=O)OCH_2CH_2CH_2CH_3)$), 2.11–2.70 (br, 1H ×($n$ − 2), $–CH_2C\mathit{H}(C(=O)OCH_2CH_2CH_2CH_3)$), 3.77–4.42 (br, 2H × ($n$ + 2), $–CH_2CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)$, $–CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3)OC(=O)–$, $–(C\mathit{H}_2)_2OC(=O)–$), 2.01–4.42 (br, alkenyl of poly(norbornene) backbone), 4.77–5.01 (br, 2H, $–C\mathit{H}OC(=O)CH–$), 4.77–5.64 (br, alkenyl of poly(norbornene) backbone). $M_{n,SEC}$ = 221,700 g mol^{-1} (THF); $Đ$ = 1.58; $M_{n,MALS}$ = 403,800; $Đ_{MALS}$ = 2.38 ($CHCl_3$).

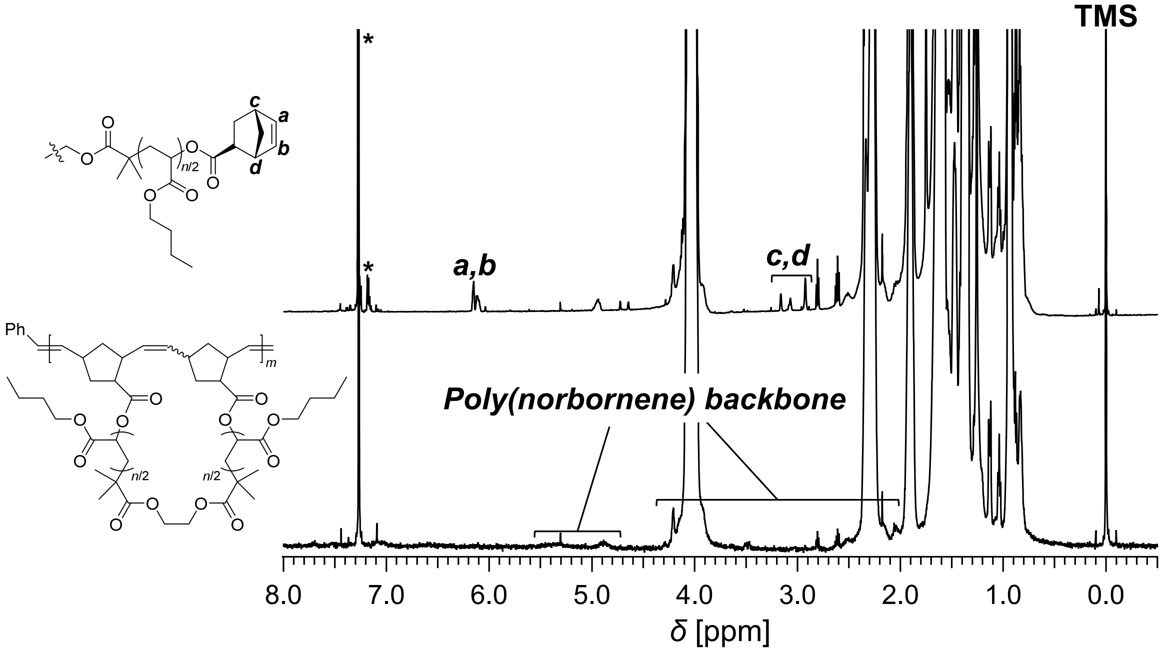


Figure S29. ^{1}H NMR spectra of NB–PBA$_{32k}$–NB (upper) and 13c-PBA$_{32k}$ (lower) (solvent, CDCl$_3$; 600 MHz). The asterisks denote the solvent peaks.

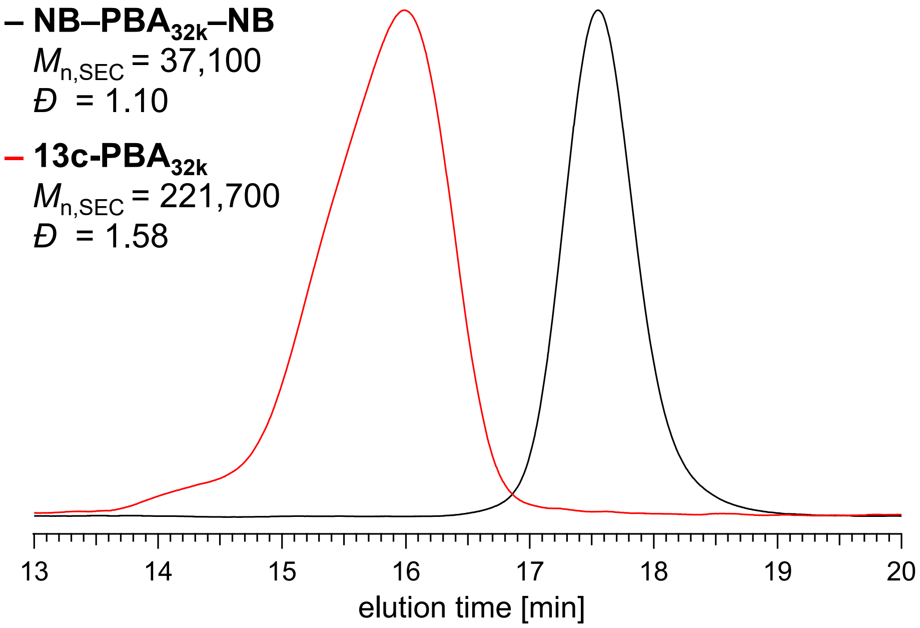
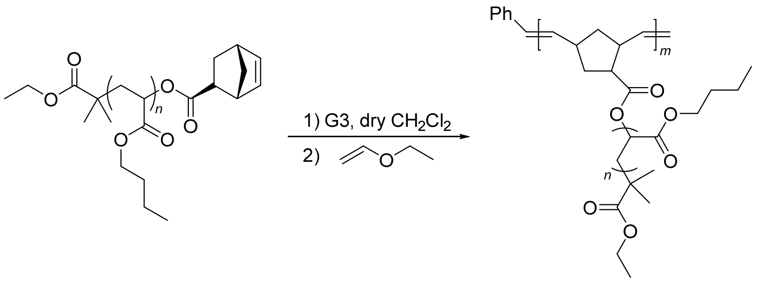


Figure S30. SEC traces of NB–PBA$_{32k}$–NB (black) and 13c-PBA$_{32k}$ (red) (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of graft PBA (19g-PBA$_{15k}$)

Scheme S6. Synthesis of g-PBA



PBA–NB g-PBA

Method C was used for the ROMP of PBA$_{15k}$–NB (3.00 g, 200 μmol,) with G3 (9.0 mg, 10.2 μmol, 19.6 eq. as a 8.0 mmol L^{-1} solution in CH_2Cl_2) in CH_2Cl_2 (70.5 mL) to give 19g-PBA$_{15k}$ as a pale brown viscous product (2.06 g). Yield: 68.7%. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 0.94 (t, $J = 7.2$ Hz, 3H × n, $–CH_2CH(C(=O)OCH_2CH_2CH_2C\mathit{H}_3)$), 1.10–1.16 (m, 6H, $–OC(=O)C(C\mathit{H}_3)_2–$), 1.20–1.31 (m, 3H, $C\mathit{H}_3CH_2OC(=O)–$), 1.31–1.44 (br, 2H × n, $–CH_2CH(C(=O)OCH_2CH_2C\mathit{H}_2CH_3)$), 1.55–1.81 (br, 2H × n, $–CH_2CH(C(=O)OCH_2C\mathit{H}_2CH_2CH_3)$), 1.17–2.10 (br, 2H × n, $–C\mathit{H}_2CH(C(=O)OCH_2CH_2CH_2CH_3)$), 2.10–2.57 (br, 1H ×($n$ − 1), $–CH_2C\mathit{H}(C(=O)OCH_2CH_2CH_2CH_3)$), 3.80–4.33 (br, 2H × ($n$ + 1), $–CH_2CH(C(=O)OC\mathit{H}_2CH_2CH_2CH_3$, $CH_3C\mathit{H}_2OC(=O)–$), 1.98–4.35 (br, alkenyl of poly(norbornene) backbone), 4.63–5.03 (br, 1H, $–C\mathit{H}OC(=O)CH–$), 4.63–5.67 (br, alkenyl of poly(norbornene) backbone). $M_{n,SEC}$ = 153,900 g mol^{-1} (THF); $Đ$ = 1.09; $M_{n,MALS}$ = 280,200; $Đ_{MALS}$ = 1.02 ($CHCl_3$).

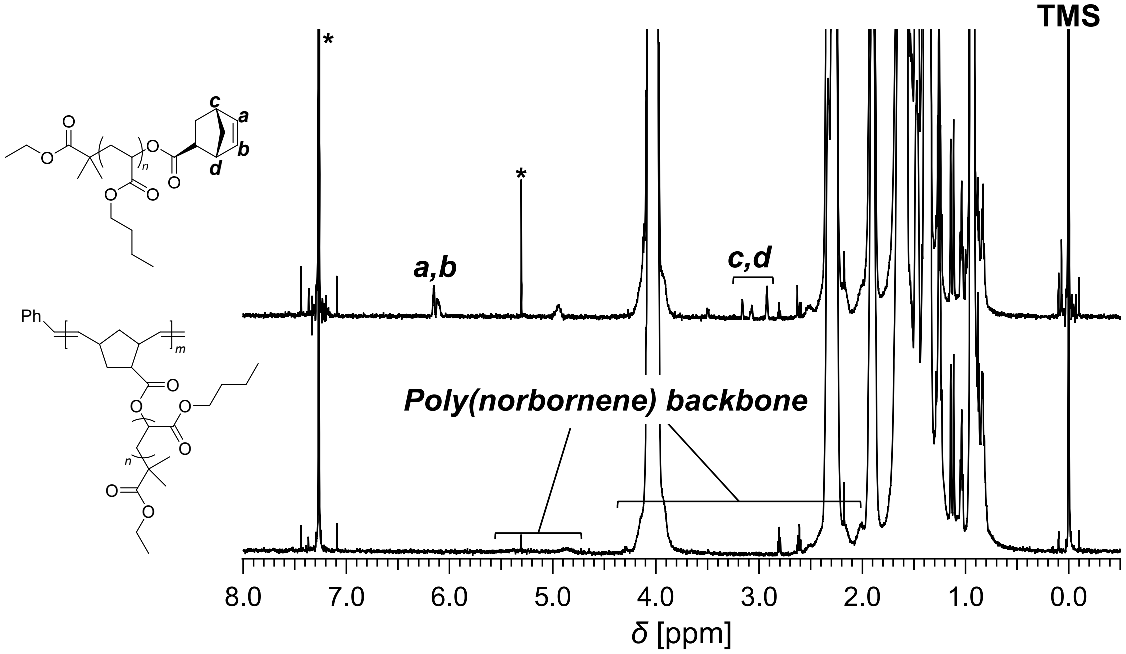


Figure S31. ^{1}H NMR spectra of PBA$_{15k}$–NB (upper) and 19g-PBA$_{15k}$ (lower) (solvent, $CDCl_3$; 600 MHz). The asterisks denote the solvent peaks.

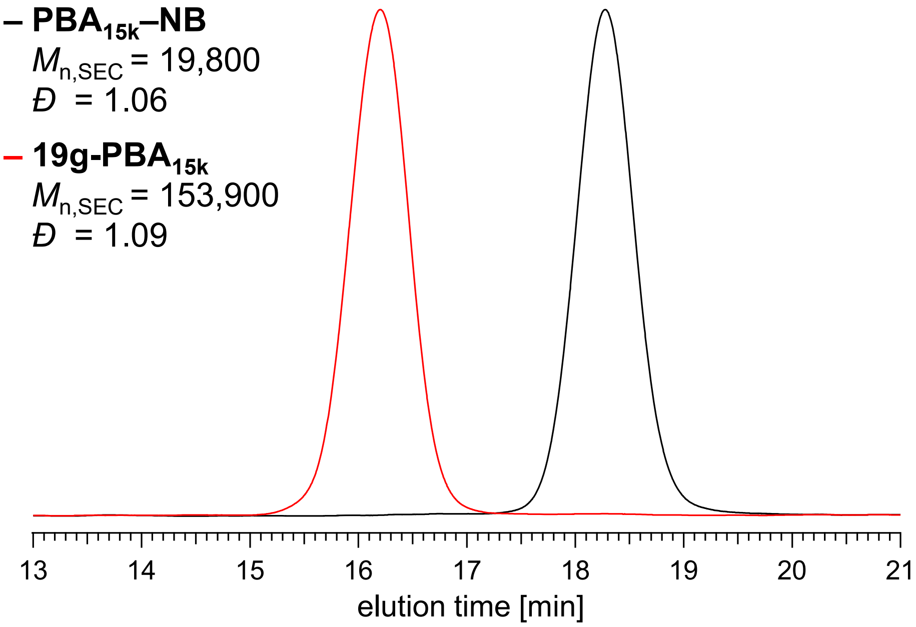


Figure S32. SEC traces of PBA_{15k}–NB (black) and 19g-PBA_{15k} (red) (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of mc-PBA-blended PBA network

Scheme S7. Synthesis of mc-PBA-blended PBA network

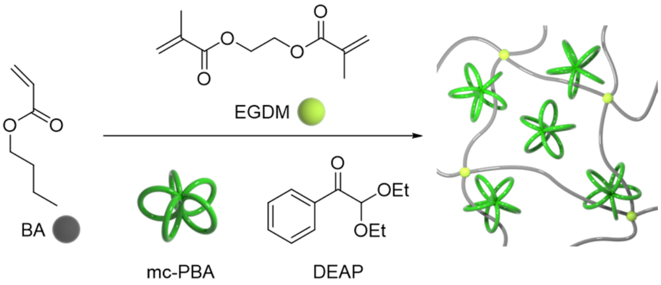


Figure S33. Photograph of the UV lump and mold used for synthesis of mc-PBA-blended PBA network.

The network formation was achieved by photoradical polymerization of BA in the presence of EGDM as the cross-linker and DEAP as the photoinitiator. The reaction was conducted in a mold consisting of two 10 cm × 10 cm × 5 mm quartz plates separated by a 500 µm-thick silicone spacer under UV irradiation (352 nm, FL15BLB, Sankyo-denki Co., Ltd.) at room temperature for 1 h. mc-PBA was incorporated into the BA/EGDM/DEAP mixture (97/3/1, w/w/w) at loadings of 20, 40, and 60 wt%. The resulting networks were dried for 1 d in a vacuum of 80 °C to remove unreacted monomers.

Polymerization of BA with 60 wt% 8c-PBA$_{32k}$ in the absence of EGDM

To test whether the chemical cross-linking is essential to retain the macro-rotaxane structure, a polymerization of BA with 60 wt% 8c-PBA$_{32k}$ was carried out in the absence of EGDM, which afforded a highly viscous liquid rather than a rubber-like solid. The resulting product was then analyzed by SEC (Figure S34). As a result, elution peaks attributable to the added 8c-PBA$_{32k}$ and linear PBA were separately observed. This result suggests that, without chemical cross-linking, the tentatively formed macro-pseudorotaxane of mc-PBA and linear PBA undergoes dethreading.

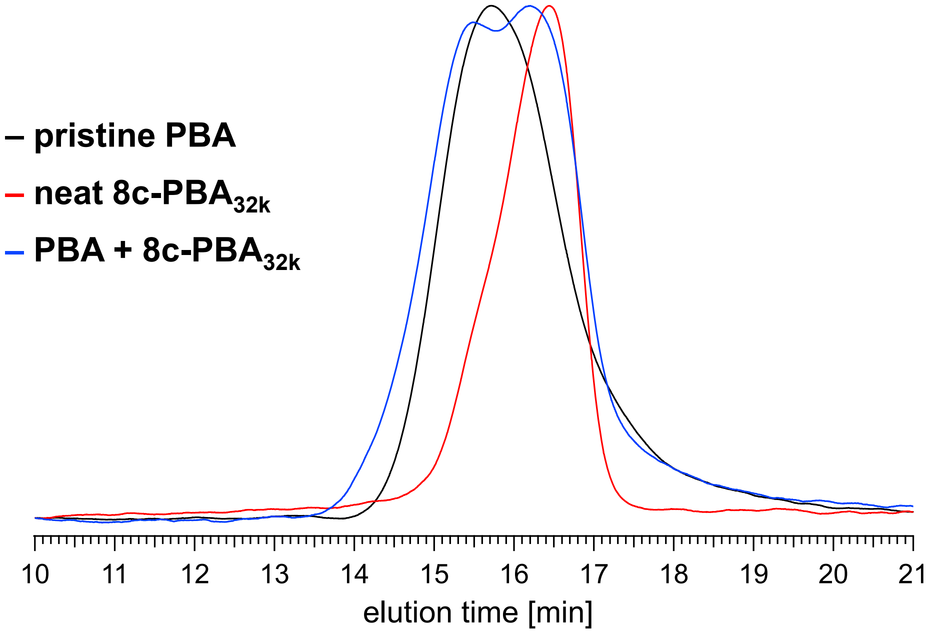


Figure S34. SEC traces of PBA synthesized without cross-linker (black), neat 8c-PBA$_{32k}$ (red), and PBA synthesized in the presence of 60 wt% 8c-PBA$_{32k}$ without cross-linker (blue).

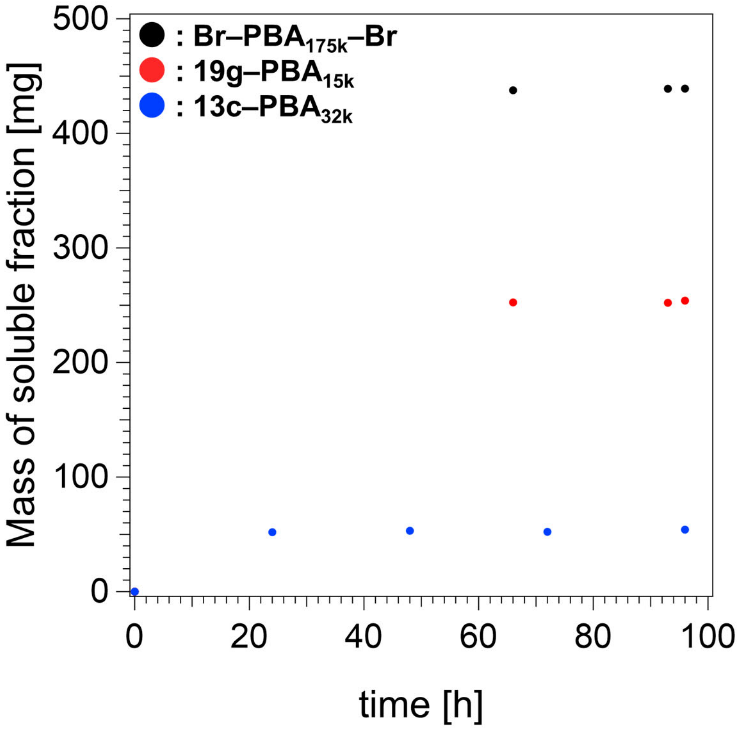


Figure S35. Time course of accumulated toluene-soluble fraction of Br–PBA$_{175k}$–Br, 19g-PBA$_{15k}$, and 13c-PBA$_{32k}$-blended PBA network during Soxhlet extraction

Swelling tests

The swelling experiments were conducted to evaluate the network structure of the samples. The specimens were first dried under vacuum at 80 °C for 1 d to obtain the initial dry weight (W_d). Subsequently, the dried samples were immersed in anhydrous toluene at room temperature for 48 h until equilibrium was reached. The swollen samples were then removed, and the excess solvent on the surface was gently wiped off using filter paper. The swollen weight (W_s) was immediately measured. The swelling ratio Q was calculated as

$$Q=\frac{W_s}{W_d}$$

In addition, the molecular weight between crosslinks (M_c) was determined using the Flory–Rehner equation, assuming a toluene density of 0.867 g cm^{-3}, a PBA density of 1.06 g cm^{-3}, a polymer–solvent interaction parameter (χ) of 0.34 (for PBA/toluene), and a molar volume of toluene of 106.3 cm^3 mol^{-1}.[3]

Table S1. Swelling tests performed on pristine and 60 wt% mc-PBA-blended PBA networks after Soxhlet extraction[a]

run	additive	*Q*	M_c
1	-	4.58	6,700
2	5c-PBA$_{32k}$	7.75	20,500
3	8c-PBA$_{32k}$	7.64	19,900
4	13c-PBA$_{32k}$	7.10	17,100

[a] Polymerization conditions: Temperature, r.t.; BA/EGDM/DEAP = 97:3:1 (w/w/w); mixture of BA, EGDM, and DEAP/additive = 100:60 (w/w).

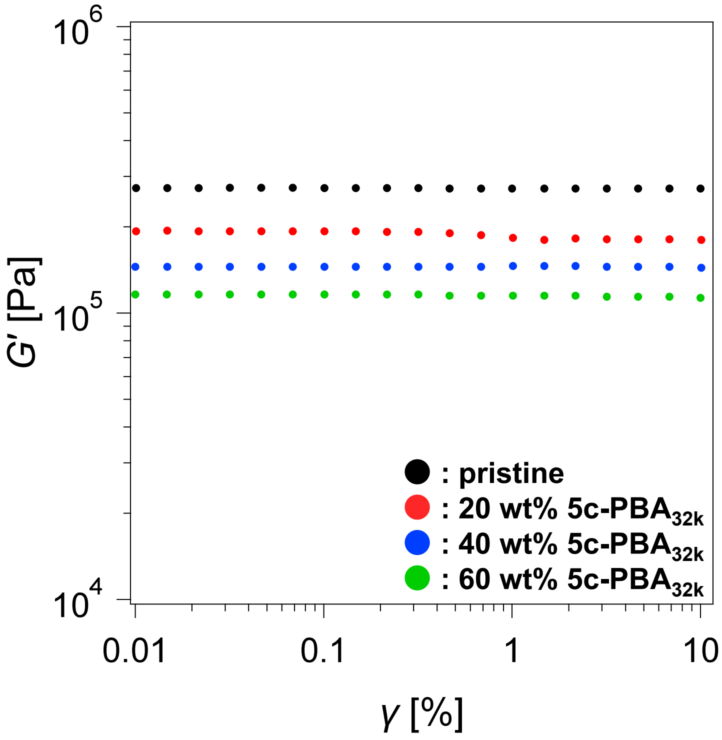
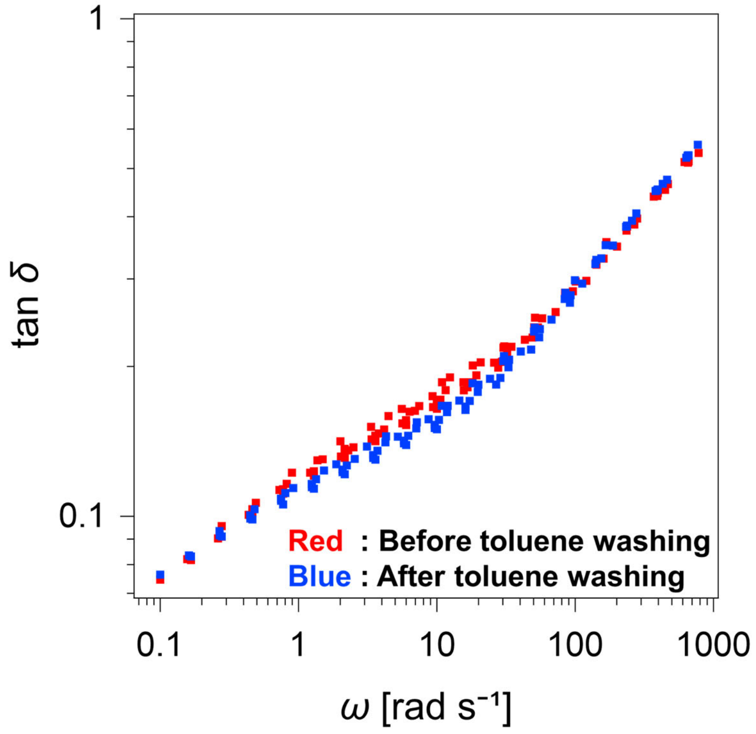


Figure S36. Strain dependence of *G′* at 25 °C of pristine PBA network (black), 20 wt% 5c-PBA$_{32k}$ (red), 40 wt% 5c-PBA$_{32k}$ (blue), and 60 wt% 5c-PBA$_{32k}$ (blue)-blended PBA networks.

(a) 13c-PBA$_{32k}$



(b) 19g-PBA$_{15k}$

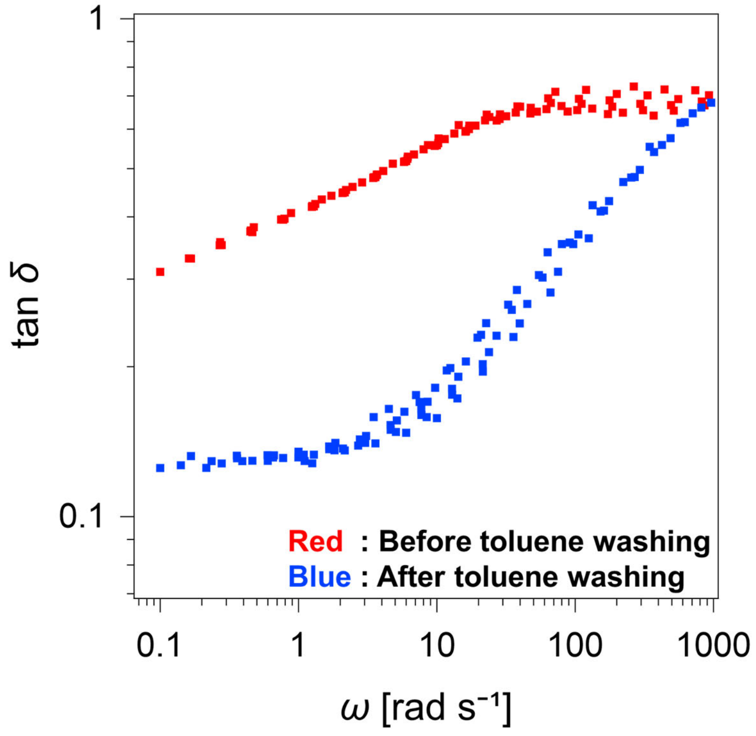


Figure S37. Master curves of tan δ at 25 °C as a reference temperature for (a) 60 wt% 13c-PBA$_{32k}$ (red), toluene washed 60 wt% 13c-PBA$_{32k}$ (blue), (b) 60 wt% 19g-PBA$_{15k}$ (red), and toluene washed 60 wt% 19g-

PBA_{15k} (blue)-blended networks.

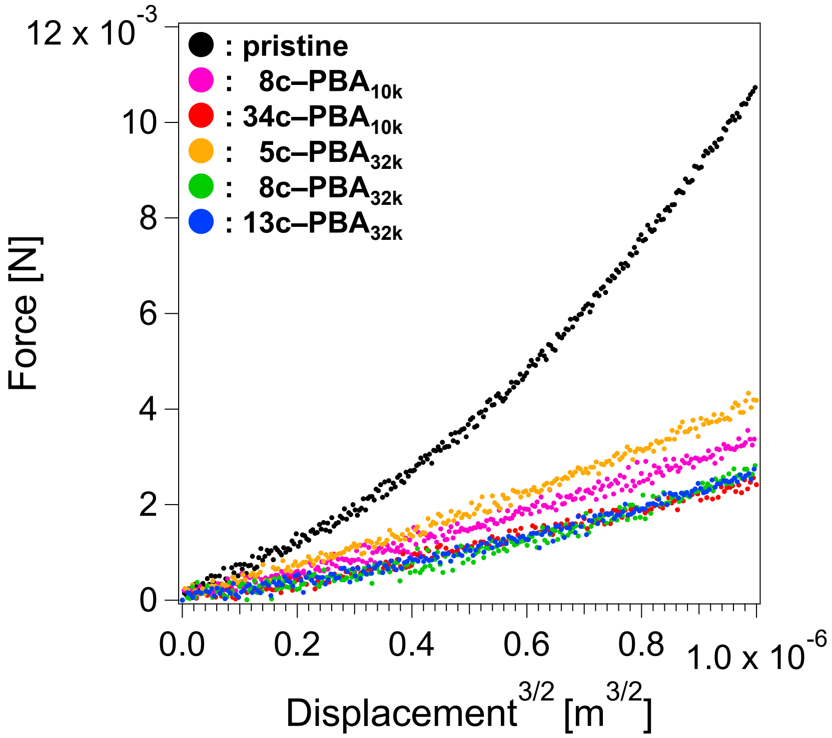


Figure S38. Force-displacement curves for the pristine PBA network (black), 60 wt% 8c-PBA_{10k} (pink), 60 wt% 34c-PBA_{10k} (red), 60 wt% 5c-PBA_{32k} (orange), 60 wt% 8c-PBA_{32k} (green), and 60 wt% 13c-PBA_{32k} (red).

Table S2. Indentation tests performed on pristine, 60 wt% mc-PBA, and 60 wt% g-PBA-blended PBA networks[a]

run	additive	*E* [MPa]
1	-	0.122 ± 0.008
2	8c-PBA_{10k}	0.062 ± 0.006
3	34c-PBA_{10k}	0.047 ± 0.004
4	5c-PBA_{32k}	0.080 ± 0.015
5	8c-PBA_{32k}	0.049 ± 0.016
6	13c-PBA_{32k}	0.045 ± 0.009

[a] Polymerization conditions: Temperature, r.t.; BA/EGDM/DEAP = 97:3:1 (w/w/w); mixture of BA, EGDM, and DEAP/additive = 100:60 (w/w).

S4. Reference

1. T. L. Choi and R. H. Grubbs, *Angew. Chem. Int. Ed.* **2003**, *42*, 1743–1746.
2. A. Simula, V. Nikolaou, A. Anastasaki, F. Alsubaie, G. Nurumbetov, P. Wilson, K. Kempe, and D. M. Haddleton, *Polym. Chem.* **2015**, *6*, 2226–2223.
3. S. D. Tobing and A. Klein, *J. Appl. Polym. Sci.* **2001**, 79, 2230–2244.