Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Intramolecular Olefin Metathesis as a Robust Tool to Synthesize Single-Chain Nanoparticles in a Size-Controlled Manner

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Synthesis of statistic copolymer of BMA and 3BMA ($P(BMA_{0.40}$-*co*-$3BMA_{0.60})_{49k}$). Method A was used for the GTP of BMA (492 mg, 3.46 mmol) and 3BMA (731 mg, 5.19 mmol) with Me-SKA (4.30 mg, 24.7 μmol) and *t*-Bu-P_4 (50.0 μL, 0.500 μmol, 0.0100 mol L^{-1} in toluene) in toluene (7.30 mL) for 6 h to give $P(BMA_{0.30}$-*co*-$3BMA_{0.60})_{49k}$. Yield: 1.05 g (86.1%). $M_{n,SEC}$ = 49,000 g mol^{-1}, $Đ$ = 1.14, F_{3BMA} = 0.60.

Synthesis of homopolymer of 3BMA ($P(3BMA)_{50k}$). Method A was used for the GTP of 3BMA (1.24 g, 8.77 mmol) with Me-SKA (4.30 mg, 24.7 μmol) and *t*-Bu-P_4 (50.0 μL, 0.500 μmol, 0.0100 mol L^{-1} in toluene) in toluene (7.4 mL) for 6 h to give $P(3BMA)_{50k}$. Yield: 1.08 g (87.1%). $M_{n,SEC}$ = 50,200 g mol^{-1}, $Đ$ = 1.21, F_{3BMA} = 1.00.

Synthesis of statistic copolymer of BMA and 3BMA ($P(BMA_{0.30}$-*co*-$3BMA_{0.60})_{24k}$). Method A was used for the GTP of BMA (495 mg, 3.48 mmol) and 3BMA (725 mg, 5.17 mmol) with Me-SKA (8.6 mg, 49.3 μmol) and *t*-Bu-P_4 (50.0 μL, 0.500 μmol, 0.0100 mol L^{-1} in toluene) in toluene (7.3 mL) for 17 h to give $P(BMA_{0.30}$-*co*-$3BMA_{0.60})_{26k}$. Yield: 0.91 g (74.6%). $M_{n,SEC}$ = 23,700 g mol^{-1}, $Đ$ = 1.11, F_{3BMA} = 0.60.

Synthesis of statistic copolymer of BMA and 3BMA ($P(BMA_{0.30}$-*co*-$3BMA_{0.60})_{80k}$). Method A was used for the GTP of BMA (740 mg, 5.20 mmol) and 3BMA (1.09 g, 7.78 mmol) with Me-SKA (4.30 mg, 24.7 μmol) and *t*-Bu-P_4 (50.0 μL, 0.500 μmol, 0.0100 mol L^{-1} in toluene) in toluene (11.0 mL) for 11 h to give $P(BMA_{0.30}$-*co*-$3BMA_{0.60})_{86k}$. Yield: 1.62 g (88.5%). $M_{n,SEC}$ = 79,700 g mol^{-1}, $Đ$ = 1.22,

F_{3BMA} = 0.60.

Synthesis of statistical copolymer of *n*BA and 3BA ($P(BA_{0.50}\text{-}co\text{-}3BA_{0.50})_{120k}$). In the globebox, a stock solution of Me_3SiNTf_2 (120 μL, 12.0 μmol, 1.00 mol L^{-1} in toluene) was added to a solution of *n*BA (2.05 g, 16.0 mmol), 3BA (2.02 g, 16.0 mmol), and *i*Pr-SKA (20.7 μg, 80.0 μmol) in dry-CH_2Cl_2 (27.0 mL) at room temperature (27 °C). After stirring for 4.5 min, the polymerization was quenched by the addition of a small amount of HMTETA. The crude product was purified by dialysis in acetone to give the statistical copolymer of *n*BA and 3BA ($P(BA_{0.50}\text{-}co\text{-}3BA_{0.50})_{120k}$) as a colorless viscous liquid. Yield: 3.76 g (92.4%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.84−5.71 (m, 1H × *m*, $-CH{=}CH_2$), 5.16−5.04 (m, 2H × *m*, $-CH{=}CH_2$), 4.18−3.94 (m, 2H × (*m*+*n*), $-OCH_2(CH_2)_2CH_3$, $-OCH_2CH_2CH{=}CH_2$), 3.63 (s, 3H, $-OCH_3$), 2.44−2.19 (m, 3H × *m* + 1H × *n*, s$-OCH_2CH_2CH{=}CH_2$, $-CH_2CH(COO(CH_2)_3CH_3)-$, $-CH_2CH(COO(CH_2)_2CH = CH_2)-$), 1.99−1.31 (m, 2H × (*m*+*n*), $-CH_2CH(COO(CH_2)_3CH_3)-$, $-CH_2CH(COO(CH_2)_2CH = CH_2)-$), 1.74−1.53 (m, 2H × *n*, $-OCH_2CH_2CH_2CH_3$), 1.43−1.31 (m, 2H × *n*, $-O(CH_2)_2CH_2CH_3$), 1.14 (d, *J* = 11.4, 6H, $-(CH_3OCO)C(CH_3)_2$), 0.93 (t, *J* = 15.1, 3H × *n*, $-O(CH_2)_3CH_3$). $M_{n,SEC}$ = 120,000 g mol^{-1}, $Đ$ = 1.05, F_{3BA} = 0.50.

Synthesis of statistical copolymer of St and BSt ($P(St_{0.43}\text{-}co\text{-}BSt_{0.57})$). In the glovebox, dry-toluene (16.6 mL) and dry-THF (8.30 mL) were placed in a Shlenk flask. After sealing, the flask was taken out from the glovebox. After cooling to -78 °C, *n*-BuLi (50.0 μL, 81.5 μmol as a 1.63 mol L^{-1} stock solution in *n*-hexane) was added to the flask. In a flame dried Shlenk flask, St (0.52 g, 5.0 mmol) and BSt (1.19 g, 7.5 mmol) were mixed together under an argon atmosphere. The mixture was dropwise added to the initiator solution. After completing the monomer addition, the mixture was stirred at -78 °C for 10 h. The polymerization was terminated by the addition of a drop of dry-methanol. The product was purified by reprecipitation in MeOH to give the statistic copolymer of St and BSt ($P(St_{0.43}\text{-}co\text{-}BSt_{0.57})_{20k}$) as a white solid. Yield: 1.62 g (94.7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.20−6.15 (m, 10H × *n* + 8H × *m*, $-C_6H_{10}$, $-C_6H_8-$), 5.93−5.71 (m, 1H × *m*, $-CH{=}CH_2$), 5.10−4.86 (m, 2H × *m*, $-CH{=}CH_2$), 2.73−2.42 (m, 2H × *m*, $-C_6H_8CH_2-$), 2.42−2.15 (m, 2H × *m*, $-C_6H_8CH_2CH_2-$), 2.10−1.62 (m, 1H × (*n*+*m*), $-CHC_6H_{10}$, $-CHC_6H_8-$), 1.62−1.01 (m, 2H × (*m*+*n*), $-CH_2CHC_6H_{10}$, $-CH_2CHC_6H_8-$). $M_{n,SEC}$ = 19,800 g mol^{-1}, $Đ$ = 1.04, F_{BSt} = 0.57.

Synthesis of copolymer of CL and ACL ($P(CL_{0.64}\text{-}co\text{-}ACL_{0.36})_{13k}$). In the glovebox, a stock solution of PPA (40.0 μL, 40.0 μmol, 1.00 mol L^{-1} in toluene) was added to a solution of CL (320 mg, 2.80 mmol), ACL (432 mg, 2.80 mmol), and DPP (10.0 mg, 40.0 μmol) in dry-toluene (2.80 mL) at room temperature (27 °C) in a Shlenk flask. After sealing, the flask was taken out from the glovebox. After stirring for 30 h at 50 °C, the polymerization was quenched by the addition of an excessive amount of Amberlyst® A21. The crude product was purified by dialysis in acetone to give the copolymer of CL and ACL ($P(CL_{0.64}\text{-}co\text{-}ACL_{0.36})_{13k}$) as a colorless viscous liquid. Yield: 432 mg (57.6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.13-7.31 (m, 5H, $-C_6H_5$), 5.63-5.79 (m, 1H × *m*, $-CH{=}CH_2$), 4.99-5.10 (m, 1H × *m*, −

CH=C*H*$_2$), 4.86-4.96 (m, 1H × *m*, −CH$_2$C*H*(CH$_2$−)O−), 3.98-4.11 (m, 2H × *n*, −C*H*$_2$OCO−), 3.59-3.69 (m, 1H, −C*H*(CH$_2$CH=CH$_2$)OH), 2,69 (t, J = 8.4 Hz, 2H, PhC*H*$_2$−), 2.19-2.49 (m, 4H × (*n* + *m*) + 2H × *m*, −COC*H*$_2$−, −CH$_2$CH(C*H*$_2$CH=CH$_2$)O−), 1.90-2.00 (m, 2H, PhCH$_2$C*H*$_2$−), 1.43-1.83 (m, 4H × (*n* + *m*), −COCH$_2$C*H*$_2$CH$_2$C*H*$_2$−), 1.20-1.43 (m, 2H × (*n* + *m*), −COCH$_2$CH$_2$C*H*$_2$CH$_2$−). $M_{\mathrm{n,SEC}}$ = 12,900 g mol^{-1}, $Đ$ = 1.08, F_{ACL} = 0.36.

Synthesis of poly(methacrylate)-based SCNP from P(BMA$_{0.30}$-*co*-3BMA$_{0.60}$)$_{49k}$ (NP$_{\mathrm{BMA}}$2). Method B was used for the intramolecular cross-linking of P(BMA$_{0.30}$-*co*-3BMA$_{0.60}$)$_{49k}$ (117 mg, 0.496 mmol olefin-containing units) with G2 (7.8 mg, 9.2 μmol) in dry-CH$_2$Cl$_2$ (146 mL) for 10 h to give NP$_{\mathrm{BMA}}$2. $M_{\mathrm{n,SEC}}$ = 33,100 g mol^{-1}, $Đ$ = 1.19, conv.$_{\mathrm{olefin}}$. = 95%.

Synthesis of poly(methacrylate)-based SCNP from P(3BMA)$_{50k}$ (NP$_{\mathrm{BMA}}$3). Method B was used for the intramolecular cross-linking of P(3BMA)$_{50k}$ (96.8 mg, 0.691 mmol olefin-containing units) with G2 (11.7 mg, 13.8 μmol) in dry-CH$_2$Cl$_2$ (120mL) for 10 h to give NP$_{\mathrm{BMA}}$3. $M_{\mathrm{n,SEC}}$ = 25,700 g mol^{-1}, $Đ$ = 1.19, conv.$_{\mathrm{olefin}}$ = 94%.

Synthesis of poly(methacrylate)-based SCNP from P(BMA$_{0.40}$-*co*-3BMA$_{0.60}$)$_{24k}$ (NP$_{\mathrm{BMA}}$4). Method B was used for the intramolecular cross-linking of P(BMA$_{0.40}$-*co*-3BMA$_{0.60}$)$_{24k}$ (104 mg, 0.433 mmol olefin-containing units) with G2 (7.4 mg, 8.7 μmol) in mixture of dry-CH$_2$Cl$_2$ and *n*-hexane (dry-CH$_2$Cl$_2$/*n*-hexane = 1/1 (v/v)) (130 mL) for 10 h to give NP$_{\mathrm{BMA}}$4. $M_{\mathrm{n,SEC}}$ = 17,100 g mol^{-1}, $Đ$ = 1.10, conv.$_{\mathrm{olefin}}$ = 97%

Synthesis of poly(methacrylate)-based SCNP from P($\mathbf{BMA_{0.40}}$-*co*-3$\mathbf{BMA_{0.60}}$)$_{\mathbf{80k}}$ ($\mathbf{NP_{BMA}5}$). Method B was used for the intramolecular cross-linking of P($BMA_{0.40}$-*co*-3$BMA_{0.60}$)$_{80k}$ (86.9 mg, 0.366 mmol olefin-containing units) with G2 (6.2 mg, 7.3 μmol) in mixture of dry-CH_2Cl_2 and *n*-hexane (dry-CH_2Cl_2/*n*-hexane = 1/1 (v/v)) (109 mL) for 10 h to give $NP_{BMA}5$. $M_{n,SEC}$ = 46,900 g mol^{-1}, $Đ$ = 1.23, conv.$_{olefin}$ = 95%.

Synthesis of poly(methacrylate)-based SCNP from P($\mathbf{BMA_{0.70}}$-*co*-3$\mathbf{BMA_{0.30}}$)$_{\mathbf{55k}}$ ($\mathbf{NP_{BMA}6}$). Method B was used for the intramolecular cross-linking of P($BMA_{0.70}$-*co*-3$BMA_{0.30}$)$_{55k}$ (56.1 mg, 0.119 mmol olefin-containing units) with G2 (2.0 mg, 2.4 μmol) in a mixture of dry-CH_2Cl_2 and *n*-hexane (dry-CH_2Cl_2/*n*-hexane = 1/1 (v/v)) for 10 h to give $NP_{BMA}6$. $M_{n,SEC}$ = 37,900 g mol^{-1}, $Đ$ = 1.20., conv.$_{olefin}$ = 96%.

Synthesis of poly(methacrylate)-based SCNP from P($\mathbf{BMA_{0.70}}$-*co*-3$\mathbf{BMA_{0.30}}$)$_{\mathbf{55k}}$ ($\mathbf{NP_{BMA}7}$). Method B was used for the intramolecular cross-linking of P($BMA_{0.70}$-*co*-3$BMA_{0.30}$)$_{55k}$ (61.6 mg, 0.131 mmol olefin-containing units) with G2 (2.2 mg, 2.6 μmol) in mixture of dry-CH_2Cl_2 and *n*-hexane (dry-CH_2Cl_2/*n*-hexane = 1/3 (v/v)) (77 mL) for 10 h to give $NP_{BMA}7$. $M_{n,SEC}$ = 33,600 g mol^{-1}, $Đ$ = 1.19, conv.$_{olefin}$ = 97%.

Synthesis of poly(methacrylate)-based SCNP from P($\mathbf{BMA_{0.70}}$-*co*-3$\mathbf{BMA_{0.30}}$)$_{\mathbf{55k}}$ ($\mathbf{NP_{BMA}8}$). Method B was used for the intramolecular cross-linking of P($BMA_{0.70}$-*co*-3$BMA_{0.30}$)$_{55k}$ (100 mg, 0.212 mmol olefin-containing units) with G2 (3.6 mg, 4.2 μmol) in mixture of dry-CH_2Cl_2 and *n*-hexane (dry-CH_2Cl_2/*n*-hexane = 1/5 (v/v)) (125 mL) for 10 h to give $NP_{BMA}8$. $M_{n,SEC}$ = 28,000 g mol^{-1}, $Đ$ = 1.21, conv.$_{olefin}$ = 96%.

Synthesis of poly(acrylate)-based SCNP from $P(BA_{0.50}$-*co*-$3BA_{0.50})_{120k}$ ($NP_{BA}1$). Method B was used for the intramolecular cross-linking of $P(BA_{0.50}$-*co*-$3BA_{0.50})_{120k}$ (40.4 mg, 0.152 mmol olefin-containing units) with G2 (2.6 mg, 3.1 μmol) in dry-CH_2Cl_2 (50 mL) for 10 h to give $NP_{BA}1$. $M_{n,SEC}$ = 106,000 g mol^{-1}, $Đ$ = 1.13, conv.$_{olefin}$ = 54%.

Synthesis of poly(acrylate)-based SCNP from $P(BA_{0.50}$-*co*-$3BA_{0.50})_{120k}$ ($NP_{BA}2$). Method B was used for the intramolecular cross-linking of $P(BA_{0.50}$-*co*-$3BA_{0.50})_{120k}$ (40.2 mg, 0.151 mmol olefin-containing units) with G2 (2.6 mg, 3.1 μmol) in mixture of dry-CH_2Cl_2 and *n*-hexane (dry-CH_2Cl_2/*n*-hexane = 1/2 (v/v)) (50 mL) for 10 h to give $NP_{BA}2$. $M_{n,SEC}$ = 73,000 g mol^{-1}, $Đ$ = 1.23, conv.$_{olefin}$ = 69%.

Synthesis of poly(acrylate)-based SCNP from $P(BA_{0.50}$-*co*-$3BA_{0.50})_{120k}$ ($NP_{BA}3$). Method B was used for the intramolecular cross-linking of $P(BA_{0.50}$-*co*-$3BA_{0.50})_{120k}$ (40.1 mg, 0.150 mmol olefin-containing units) with G2 (2.5 mg, 3.0 μmol) in mixture of dry-CH_2Cl_2 and *n*-hexane (dry-CH_2Cl_2/*n*-hexane = 1/3 (v/v)) (50 mL) for 10 h to give $NP_{BA}3$. $M_{n,SEC}$ = 56,100 g mol^{-1}, $Đ$ = 1.31, conv.$_{olefin}$ = 77%.

Synthesis of poly(acrylate)-based SCNP from $P(BA_{0.50}$-*co*-$3BA_{0.50})_{120k}$ ($NP_{BA}4$). Method B was used for the intramolecular cross-linking of $P(BA_{0.50}$-*co*-$3BA_{0.50})_{120k}$ (40.1 mg, 0.150 mmol olefin-containing units) with G2 (2.6 mg, 3.1 μmol) in mixture of dry-CH_2Cl_2 and *n*-hexane (dry-CH_2Cl_2/*n*-hexane = 1/5 (v/v)) (50 mL) for 10 h to give $NP_{BA}4$. $M_{n,SEC}$ = 36,000 g mol^{-1}, $Đ$ = 1.20, conv.$_{olefin}$ = 89%.

Synthesis of poly(styrene)-based SCNP from P(St$_{0.43}$-*co*-BSt$_{0.57}$)$_{20k}$ (NP$_{St}$1). Method B was used for the intramolecular cross-linking of P(St$_{0.43}$-*co*-BSt$_{0.57}$)$_{20k}$ (266 mg, 1.17 mmol olefin-containing units) with G2 (19.8 mg, 23.4 μmol) in dry-THF (330 mL) for 10 h to give NP$_{St}$1. $M_{n,SEC}$ = 16,500 g mol^{-1}, $Đ$ = 1.08, conv.$_{olefin}$ = 63%.

Synthesis of poly(styrene)-based SCNP from P(St$_{0.43}$-*co*-BSt$_{0.57}$)$_{20k}$ (NP$_{St}$2). Method B was used for the intramolecular cross-linking of P(St$_{0.43}$-*co*-BSt$_{0.57}$)$_{20k}$ (63.0 mg, 0.280 mmol olefin-containing units) with G2 (4.8 mg, 5.6 μmol) in dry-THF and *n*-hexane (dry-THF/*n*-hexane = 2/1 (v/v)) (78.8 mL) for 10 h to give NP$_{St}$2. $M_{n,SEC}$ = 14,500 g mol^{-1}, $Đ$ = 1.08, conv.$_{olefin}$. = 62%.

Synthesis of poly(ester)-based SCNP from P(CL$_{0.64}$-*co*-ACL$_{0.36}$)$_{13k}$ (NP$_{CL}$1). Method B was used for the intramolecular cross-linking of P(CL$_{0.64}$-*co*-ACL$_{0.36}$)$_{13k}$ (38.1 mg, 0.106 mmol olefin-containing units) with G2 (1.8 mg, 2.1 μmol) in dry-CH_2Cl_2 (47.6 mL) for 10 h to give NP$_{CL}$1. $M_{n,SEC}$ = 9,470 g mol^{-1}, $Đ$ = 1.15 , conv.$_{olefin}$ = 78%.

Synthesis of poly(ester)-based SCNP from P(CL$_{0.64}$-*co*-ACL$_{0.36}$)$_{13k}$ (NP$_{CL}$2). Method B was used for the intramolecular cross-linking of P(CL$_{0.64}$-*co*-ACL$_{0.36}$)$_{13k}$ (33.0 mg, 0.0910 mmol olefin-containing units) with G2 (1.5 mg, 1.8 μmol) in mixture of dry-CH_2Cl_2 and *n*-hexane (dry-CH_2Cl_2/*n*-hexane = 1/2 (v/v)) (41.3 mL) for 10 h to give $NP_{CL}2$. $M_{n,SEC}$ = 8,640 g mol^{-1}, $Đ$ = 1.19, conv.$_{olefin}$ = 79%.

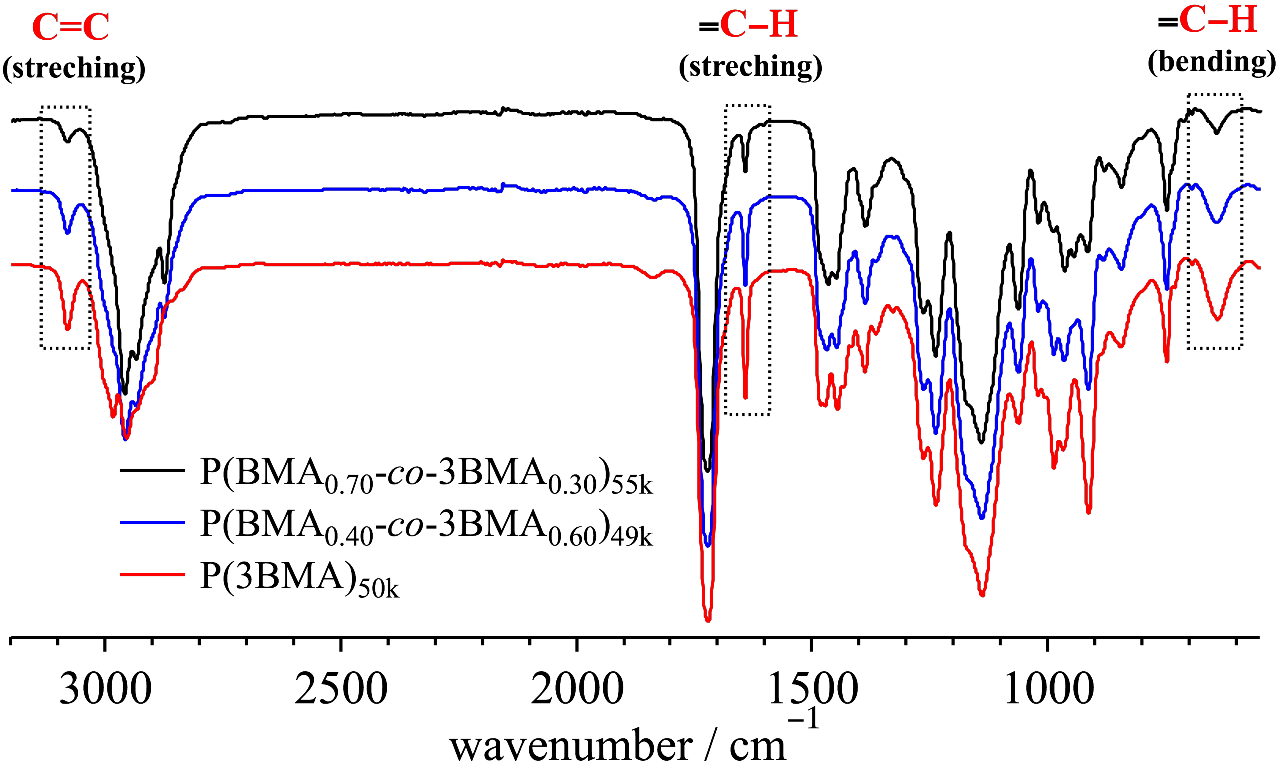

Figure S1. IR spectra of $P(BMA_{0.70}$-*co*-$3BMA_{0.30})_{55k}$ (black), $P(BMA_{0.40}$-*co*-$3BMA_{0.60})_{49k}$ (blue), and $P(3BMA)_{50k}$ (red).

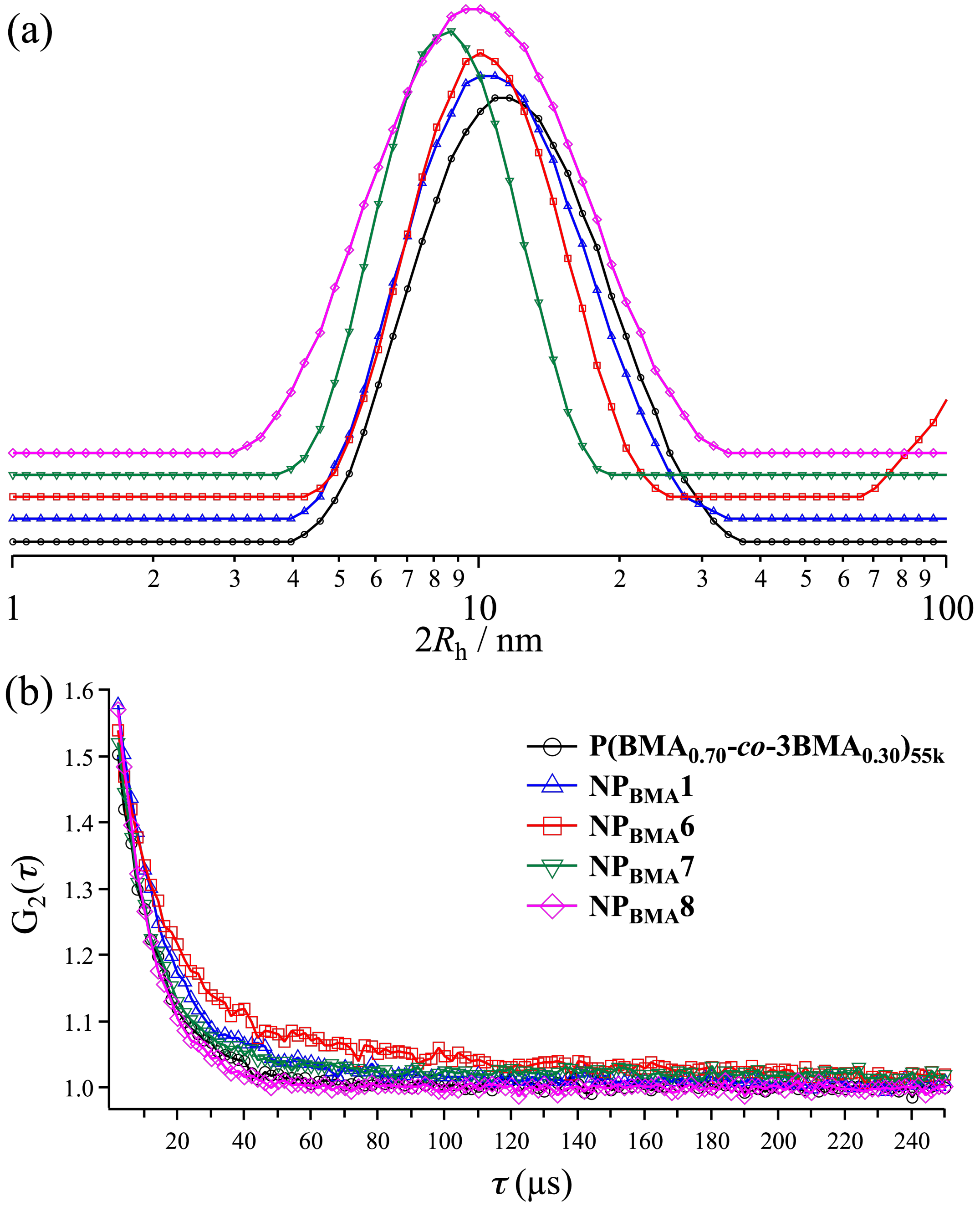

Figure S2. DLS results of P($BMA_{0.70}$-*co*-$3BMA_{0.30}$)$_{55k}$ (black), $NP_{BMA}1$ (blue), $NP_{BMA}6$ (red), $NP_{BMA}7$ (green), and $NP_{BMA}8$ (pink). (a) Intensity-averaged size distributions and (b) autocorrelation functions measured at $\theta = 90°$ at 25 °C in THF ([polymer] = 5 mg mL^{-1}).

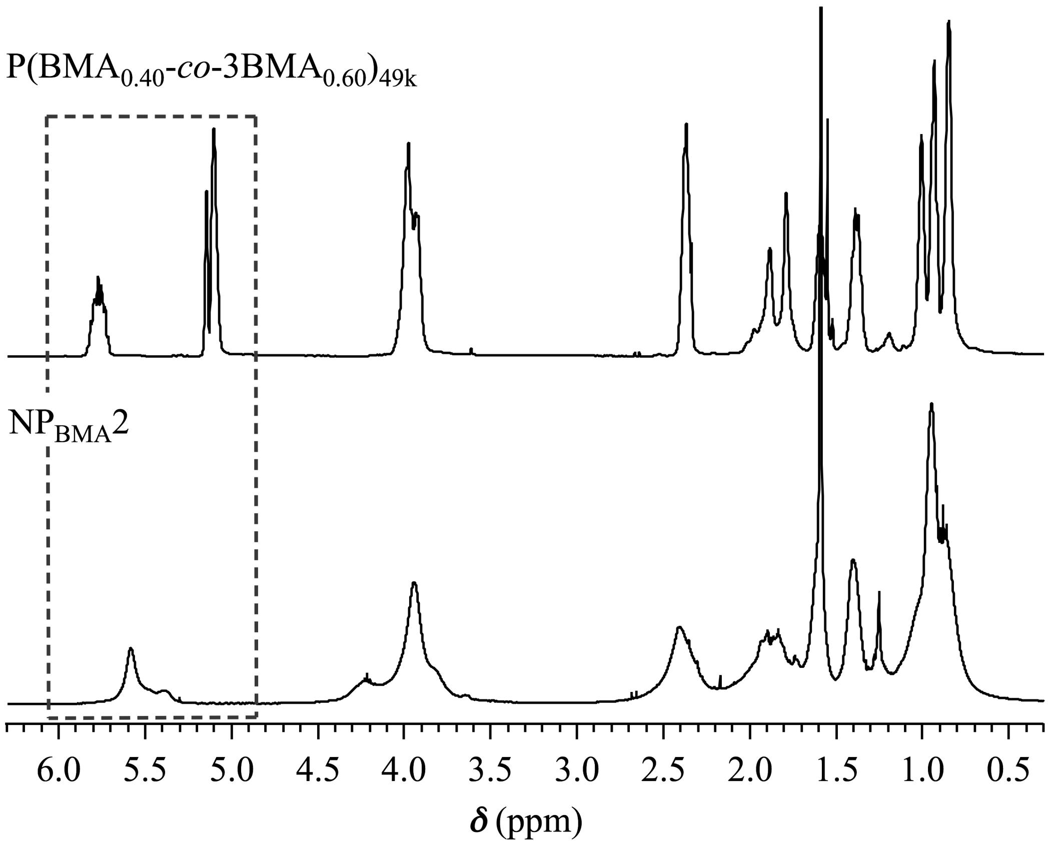

Figure S3. ^{1}H NMR spectra of P($BMA_{0.40}$-*co*-3$BMA_{0.60}$)$_{49k}$ (upper) and NP_{BMA}2 (lower) in $CDCl_3$ (400 MHz).

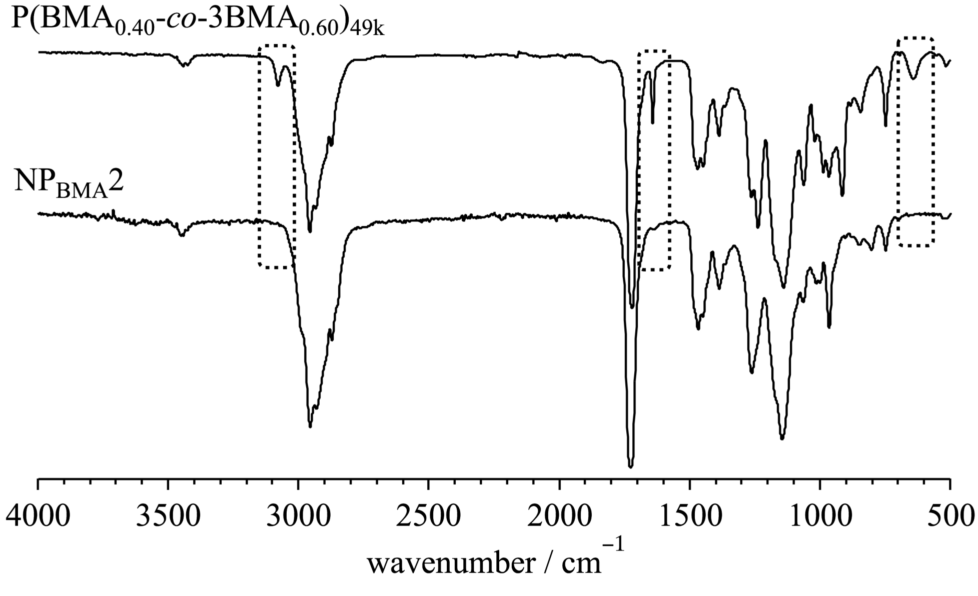

Figure S4. IR spectra of P($BMA_{0.40}$-*co*-3$BMA_{0.60}$)$_{49k}$ (upper) and NP_{BMA}2 (lower).

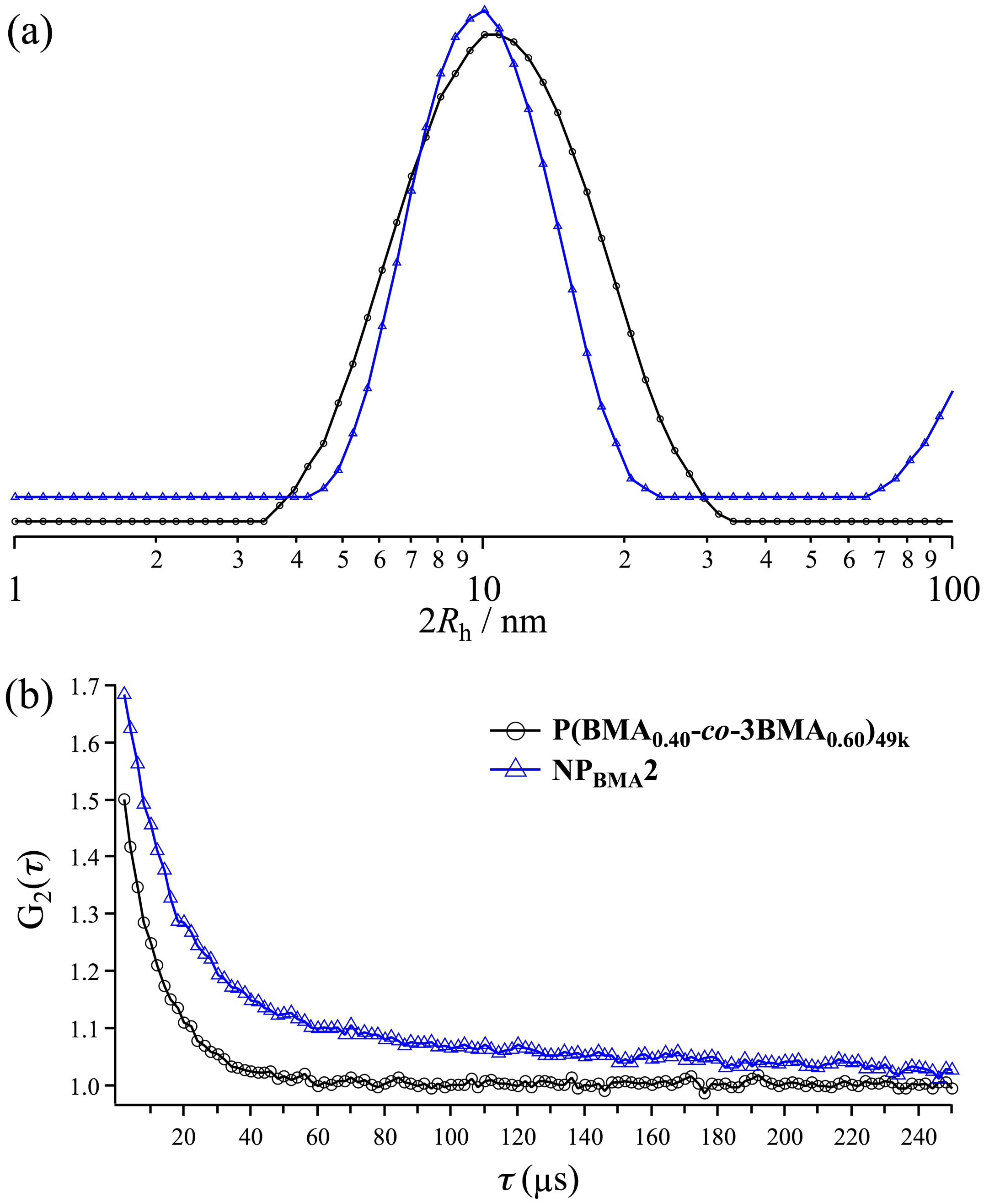

Figure S5. DLS results of P(BMA$_{0.40}$-*co*-3BMA$_{0.60}$)$_{49k}$ (black) and NP$_{BMA}$2 (blue). (a) Intensity-averaged size distributions and (b) autocorrelation functions measured at $\theta = 90°$ at 25 °C in THF ([polymer] = 5 mg mL^{-1}).

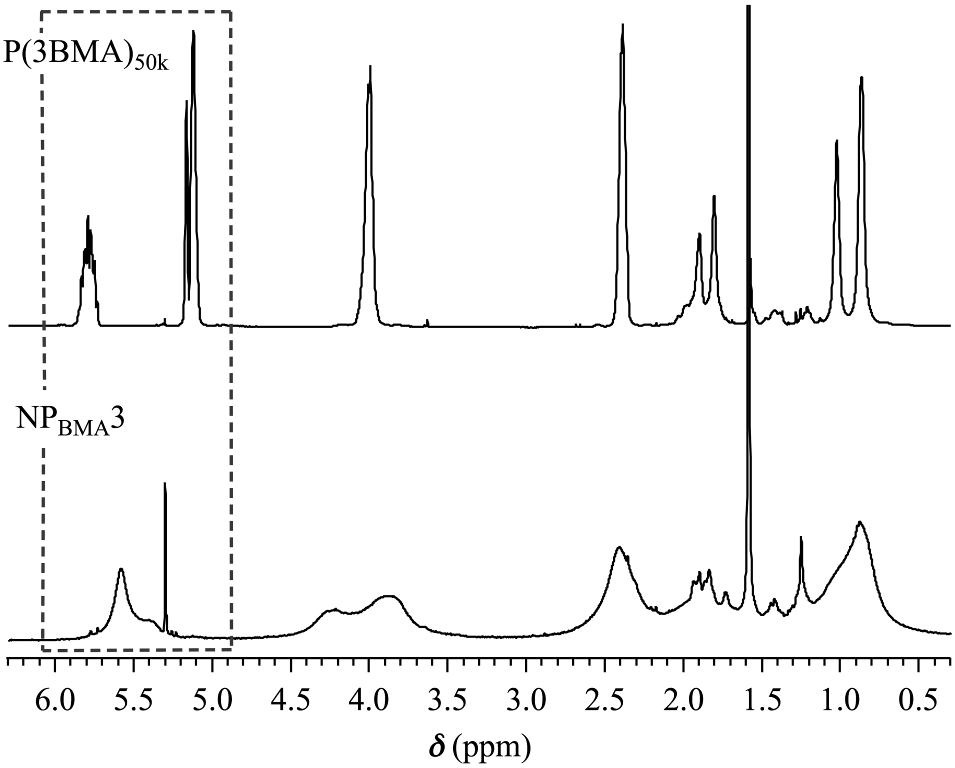

Figure S6. ^{1}H NMR spectra of P(3BMA)$_{55k}$ (upper) and NP$_{BMA}$3 (lower) in CDCl$_3$ (400 MHz).

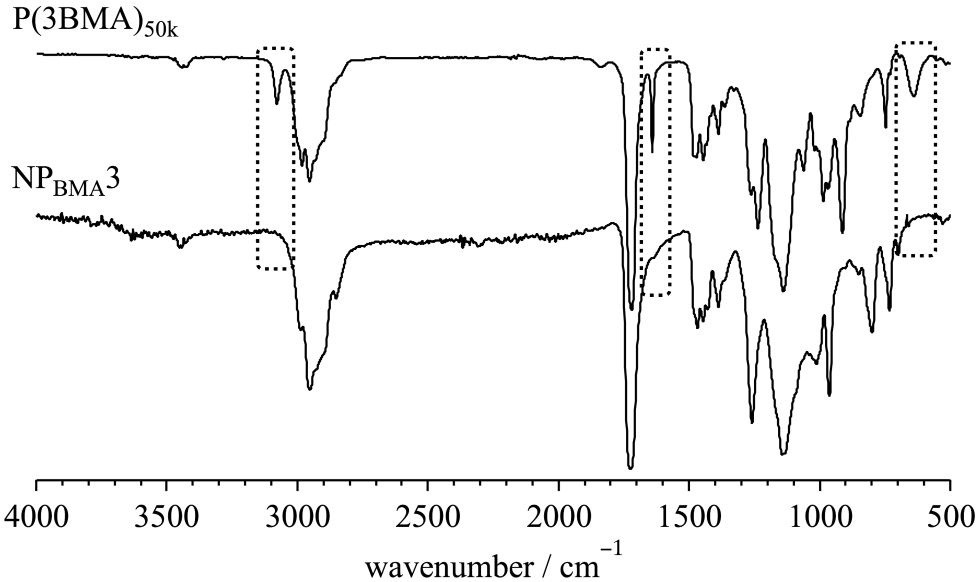

Figure S7. IR spectra of P(3BMA)$_{50k}$ (upper) and NP$_{BMA}$3 (lower).

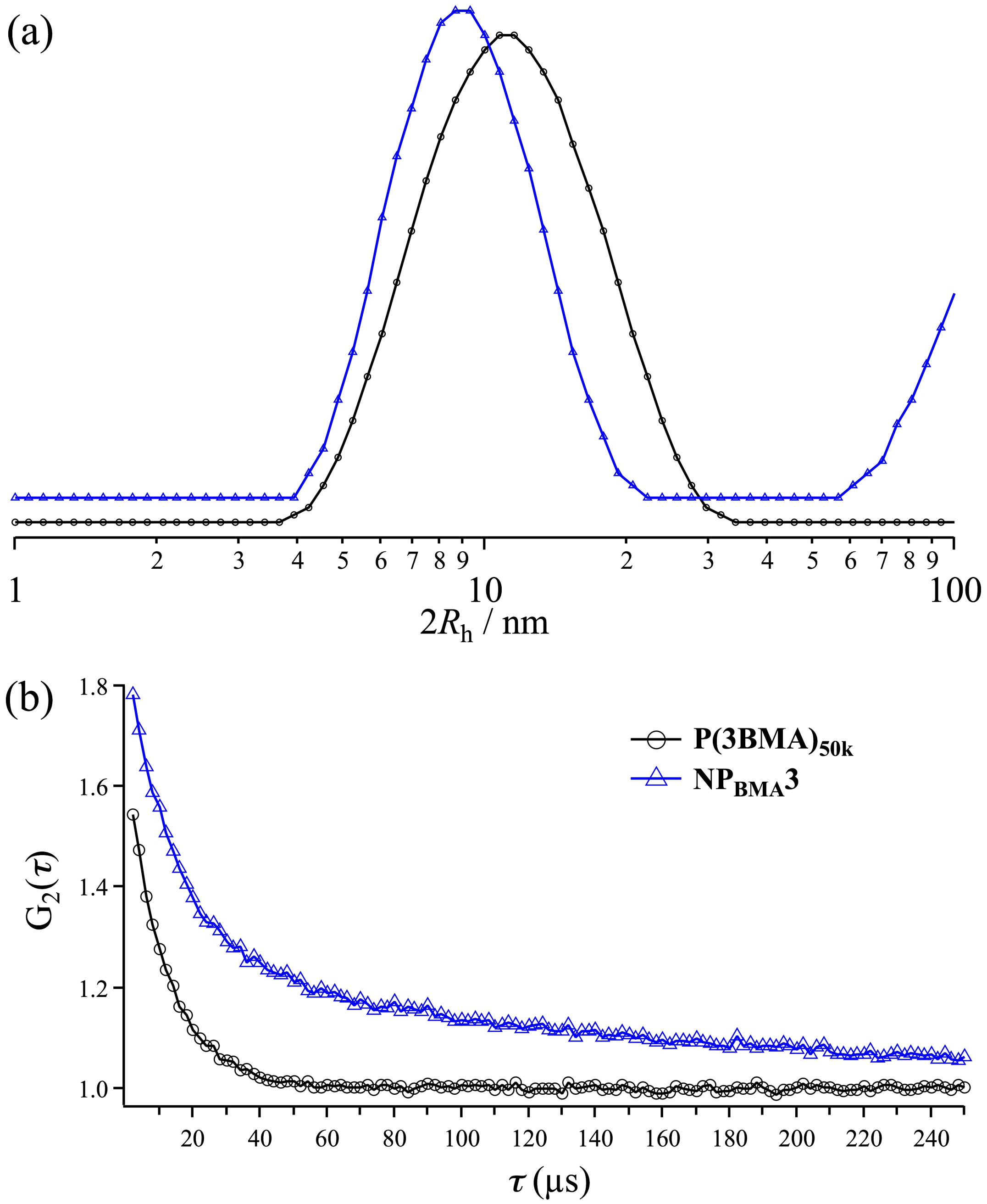

Figure S8. DLS results of $P(3BMA)_{50k}$ (black) and $NP_{BMA}3$ (blue). (a) Intensity-averaged size distributions and (b) autocorrelation functions measured at $\theta = 90°$ at 25 °C in THF ([polymer] = 5 mg mL^{-1}).

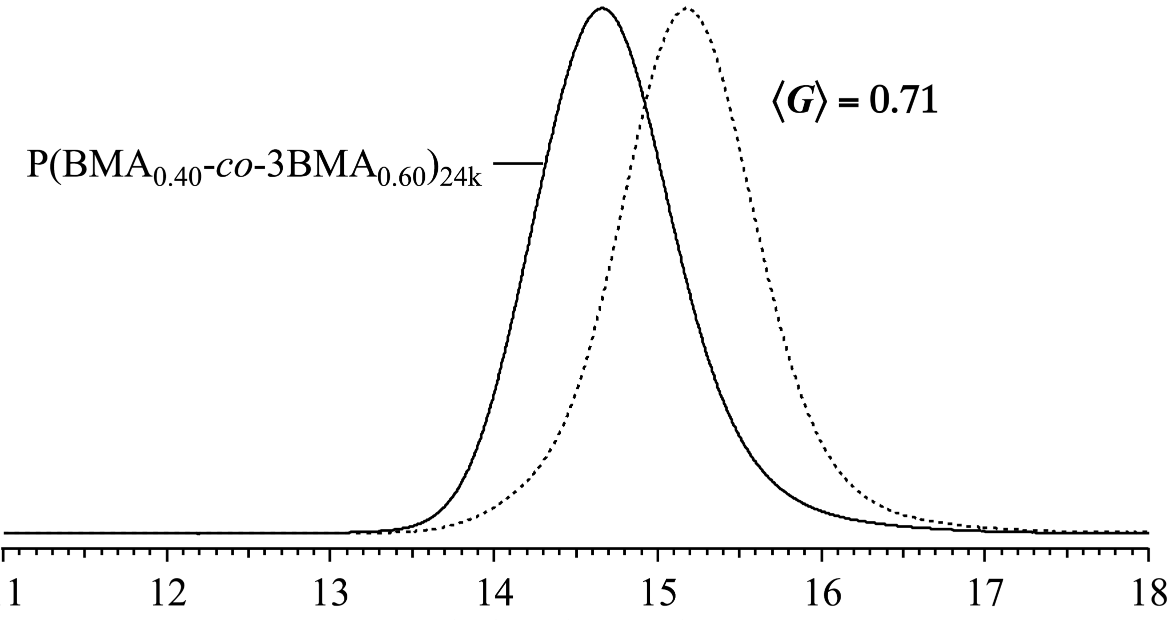

Figure S9. SEC traces of P(BMA$_{0.40}$-*co*-3BMA$_{0.60}$)$_{24k}$ (solid) and NP$_{BMA}$4 (dashed) (eluent, THF; flow rate, 1.0 mL min^{-1}).

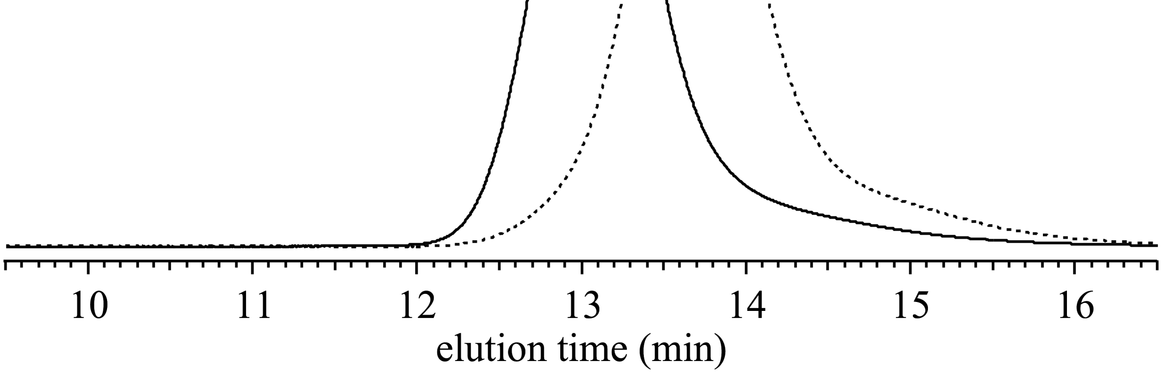

Figure S10. SEC traces of P(BMA$_{0.40}$-*co*-3BMA$_{0.60}$)$_{80k}$ (solid) and NP$_{BMA}$5 (dashed) (eluent, THF; flow rate, 1.0 mL min^{-1}).

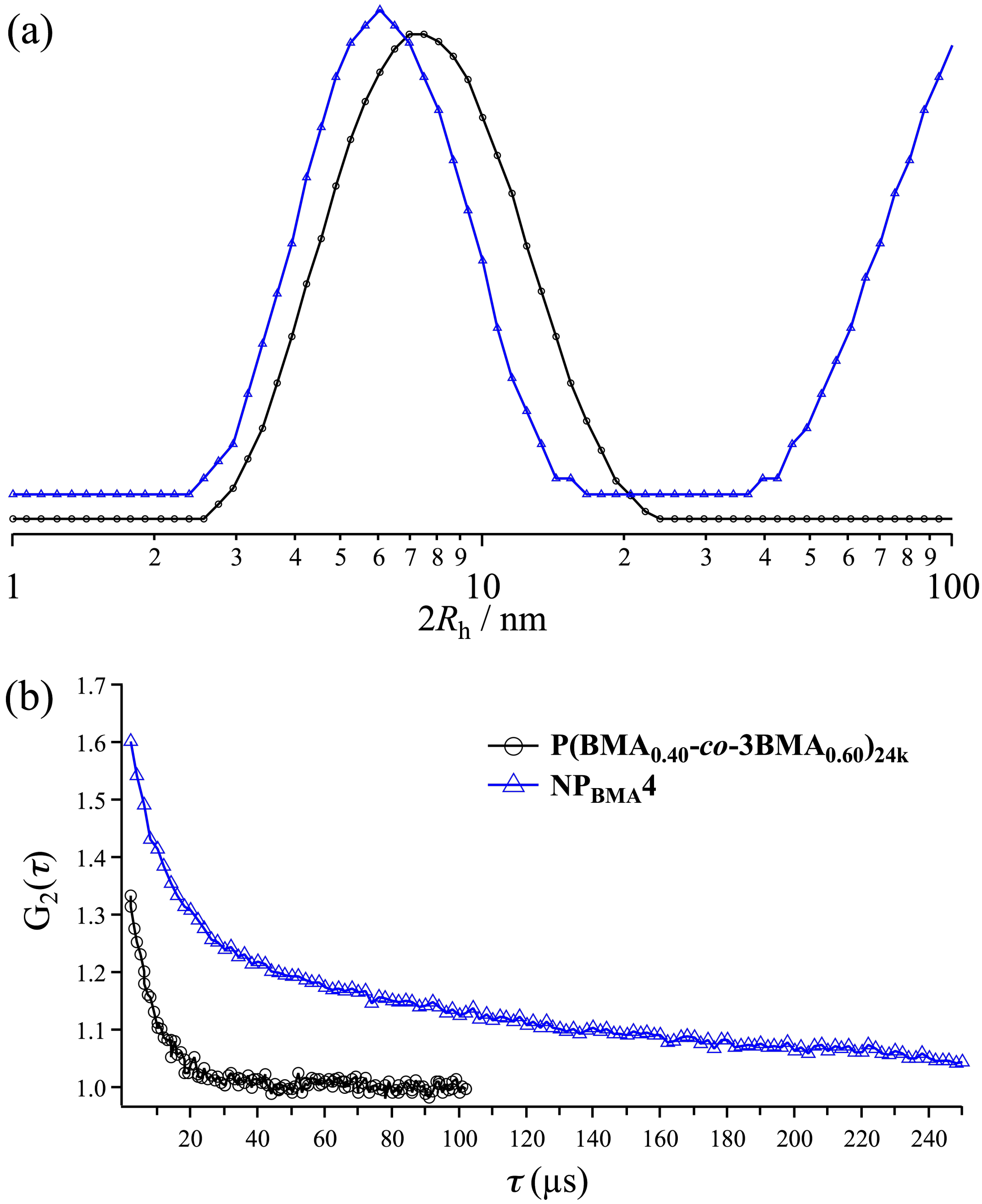

Figure S11. DLS results of P(BMA$_{0.40}$-*co*-3BMA$_{0.60}$)$_{24k}$ (black) and NP$_{BMA}$4 (blue). (a) Intensity-averaged size distributions and (b) autocorrelation functions measured at $\theta = 90°$ at 25 °C in THF ([polymer] = 5 mg mL^{-1}).

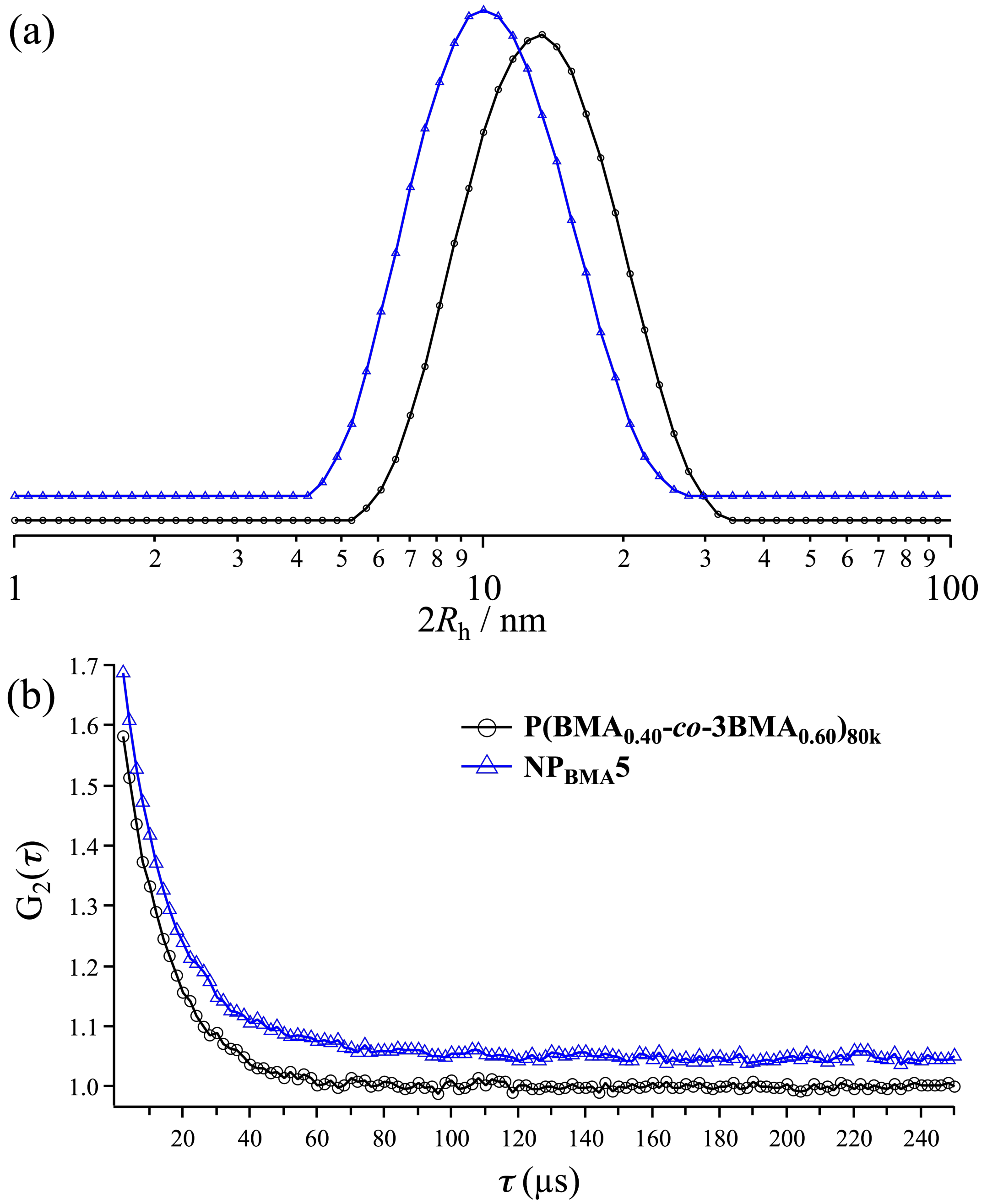

Figure S12. DLS results of P(BMA$_{0.40}$-*co*-3BMA$_{0.60}$)$_{80k}$ (black) and NP$_{BMA}$5 (blue). (a) Intensity-averaged size distributions and (b) autocorrelation functions measured at θ = 90° at 25 °C in THF ([polymer] = 5 mg mL^{-1}).

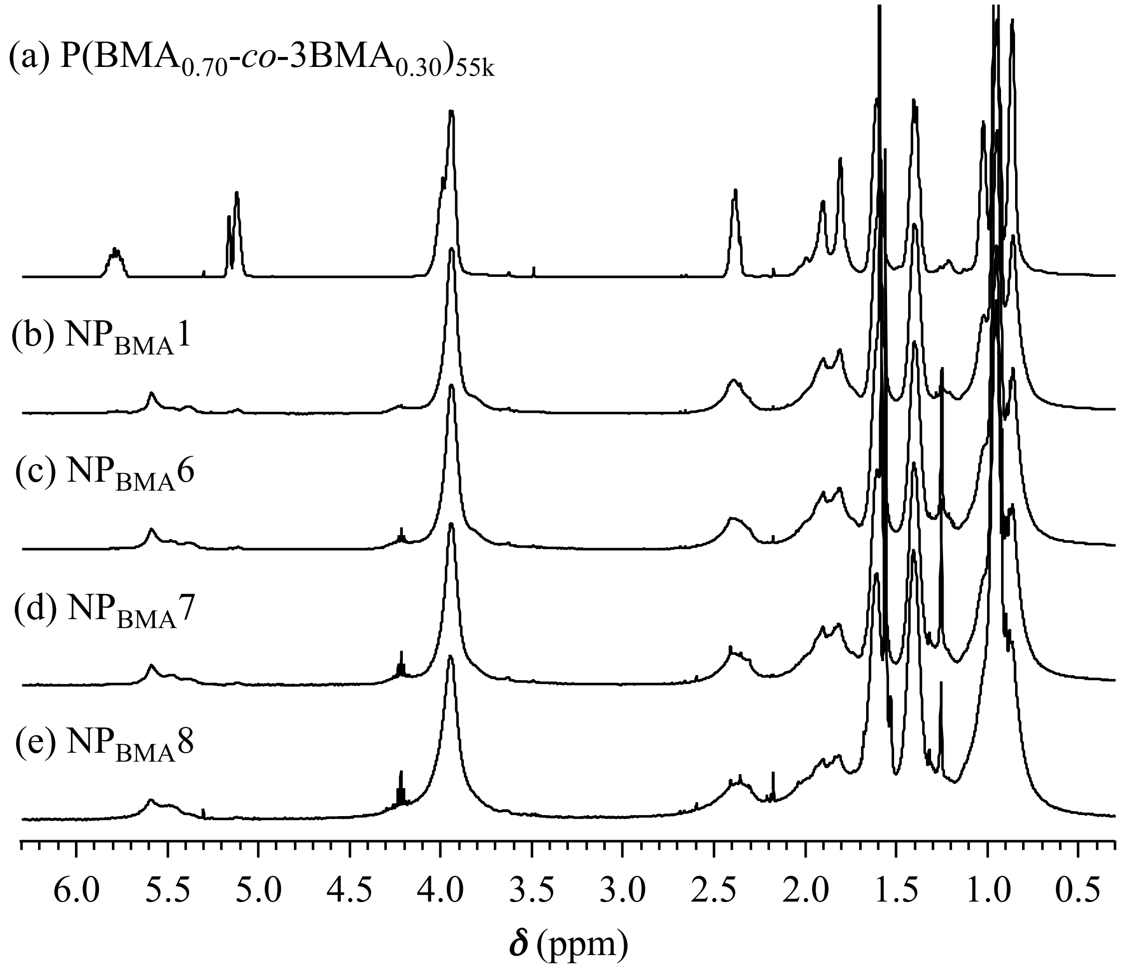

Figure S13. ^{1}H NMR spectra of (a) P(BMA$_{0.70}$-*co*-3BMA$_{0.30}$)$_{55k}$, (b) NP$_{BMA}$1, (c) NP$_{BMA}$6, (d) NP$_{BMA}$7, and (e) NP$_{BMA}$8 in CDCl$_3$ (400 MHz).

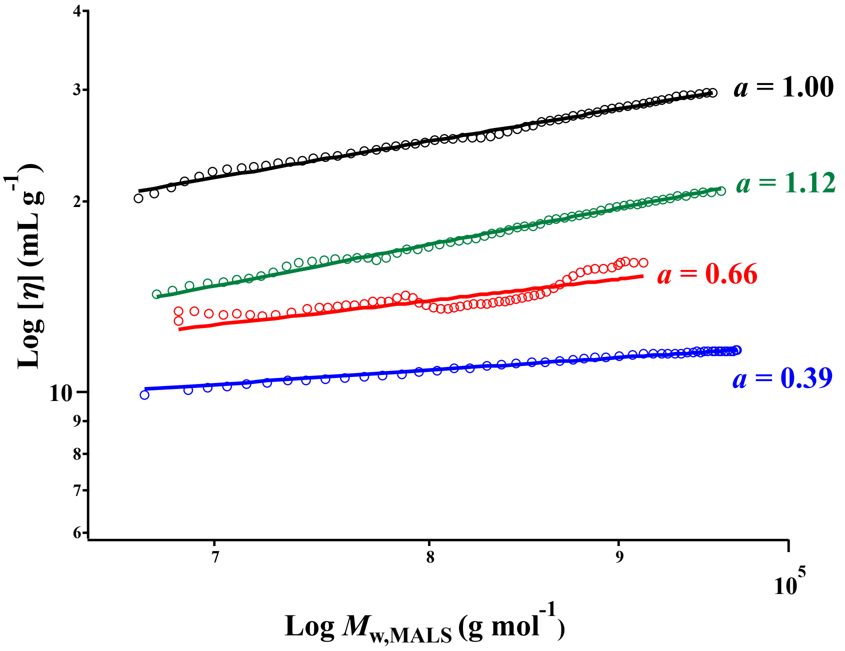

Figure S14. MHS plots for P(BMA$_{0.70}$-*co*-3BMA$_{0.30}$)$_{55k}$ (black), NP$_{BMA}$1 (green), NP$_{BMA}$6 (red), and NP$_{BMA}$7 (blue). Values of a were calculated from MHS equation ($[\eta] = KM^a$).

Table S1. Synthesis of SCNPs from a variety of linear precursors[a]

polymer sample	linear precursor	ϕ_{hexane}	conv.$_{\text{olefin}}$[e] (%)	$M_{\text{n,SEC}}$[f] (g mol^{-1})	$M_{\text{p,SEC}}$[f] (g mol^{-1})	$Đ$[f]	$\langle G \rangle$[g]
NP$_{\text{BA}}$1	P(BA$_{0.50}$-*co*-3BA$_{0.50}$)$_{120\text{k}}$[b]	0.00	54	106,000	119,000	1.13	0.92
NP$_{\text{BA}}$2		0.66	69	73,000	86,300	1.23	0.66
NP$_{\text{BA}}$3		0.75	77	56,100	64,400	1.31	0.50
NP$_{\text{BA}}$4		0.83	89	36,000	37,700	1.20	0.29
NP$_{\text{St}}$1	P(St$_{0.43}$-*co*-BSt$_{0.57}$)$_{20\text{k}}$[c]	0.00	63	16,500	17,100	1.08	0.87
NP$_{\text{St}}$2		0.33	62	14,500	13,900	1.08	0.71
NP$_{\text{CL}}$1	P(CL$_{0.64}$-*co*-ACL$_{0.36}$)$_{13\text{k}}$[d]	0.00	78	9,470	10,000	1.15	0.82
NP$_{\text{CL}}$2		0.67	79	8,640	7,630	1.19	0.62

[a]Reaction conditions: [polymer]$_0$ = 0.80 g L^{-1} in CH_2Cl_2; [3BMA units]/[G2] = 1/0.02; temp., 30 °C. [b]$M_{\text{n,SEC}}$ = 120,000 g mol^{-1}, $M_{\text{p,SEC}}$ = 130,000 g mol^{-1}, $Đ$ = 1.05. [c]$M_{\text{n,SEC}}$ = 19,800 g mol^{-1}, $M_{\text{p,SEC}}$ = 19,600 g mol^{-1}, $Đ$ = 1.04. [d]$M_{\text{n,SEC}}$ = 12,900 g mol^{-1}, $M_{\text{p,SEC}}$ = 12,300 g mol^{-1}, $Đ$ = 1.08. [e]Determined by ^{1}H NMR in $CDCl_3$. [f]Determined by SEC in THF using poly(methyl methacrylate) standards. [g]Determined by $M_{\text{p,SEC}}$(SCNP)/$M_{\text{p,SEC}}$(linear).

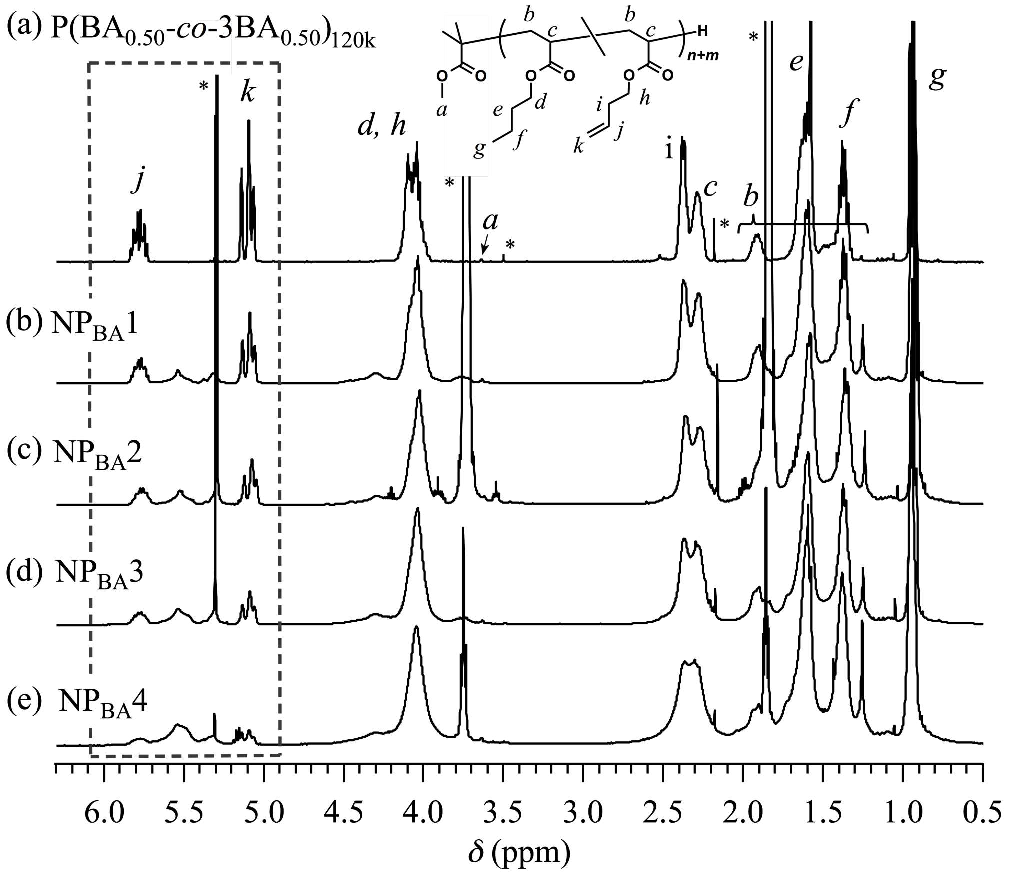

Figure S15. ^{1}H NMR spectra of (a) P(BA$_{0.50}$-*co*-3BA$_{0.50}$)$_{120\text{k}}$, (b) NP$_{\text{BA}}$1, (c) NP$_{\text{BA}}$2, (d) NP$_{\text{BA}}$3, and (e) NP$_{\text{BA}}$4 in $CDCl_3$ (400 MHz).

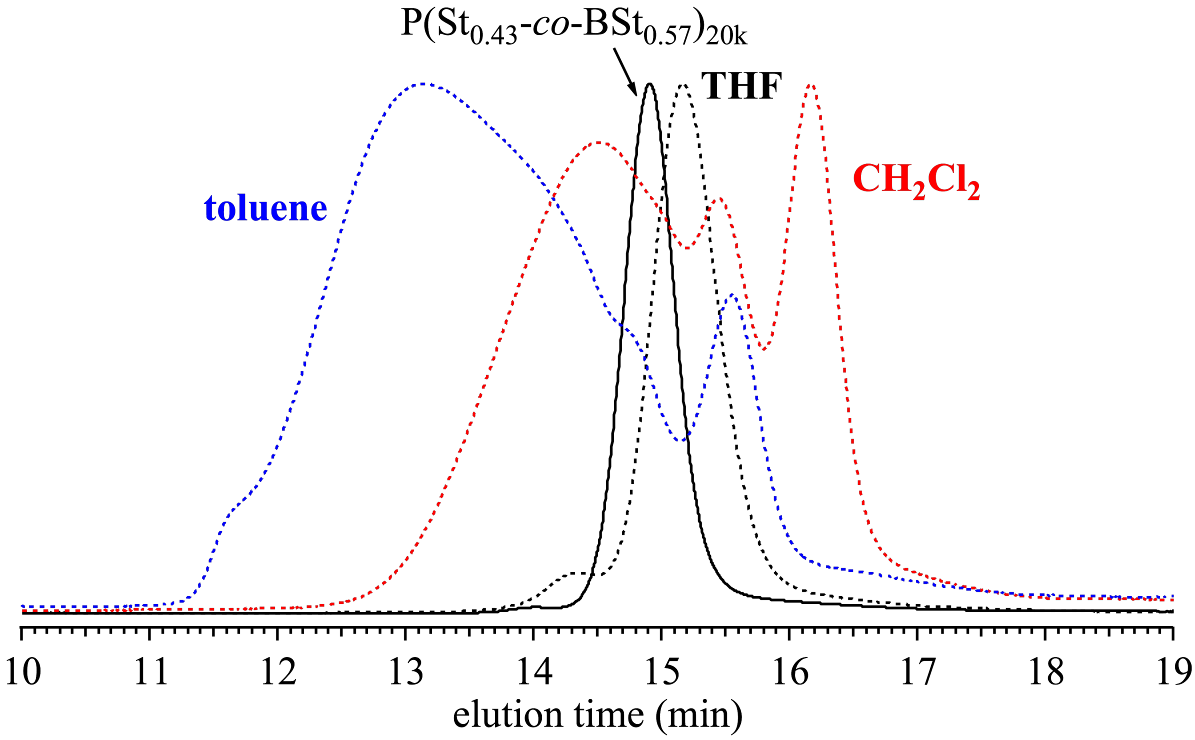

Figure S16. SEC traces of $P(St_{0.43}\text{-}co\text{-}BSt_{0.57})_{20k}$ (solid) and the products obtained by the metathesis reaction (dashed) in CH_2Cl_2 (red), toluene (blue), and THF (black) (eluent, THF; flow rate, 1.0 mL min^{-1}).

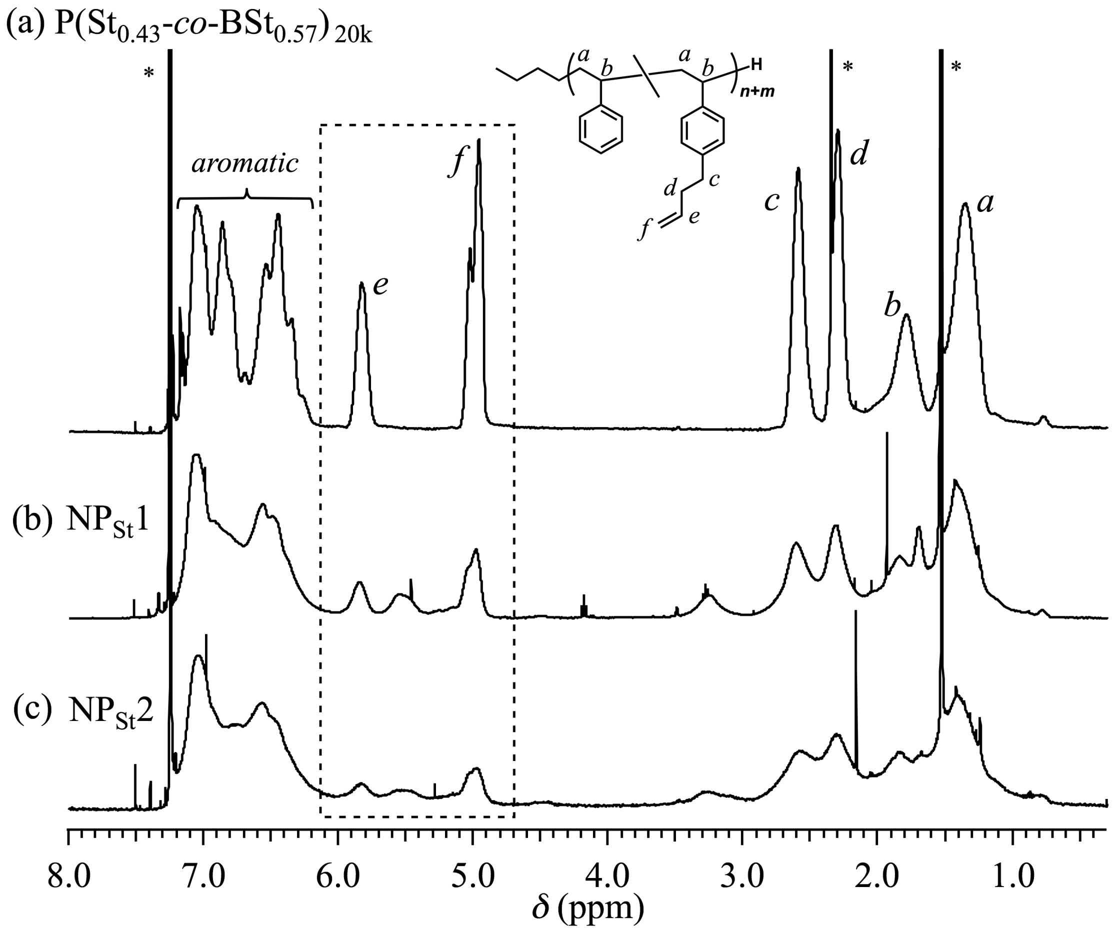

Figure S17. ^{1}H NMR spectra of (a) $P(St_{0.43}\text{-}co\text{-}BSt_{0.57})_{20k}$, (b) $NP_{St}1$, and (c) $NP_{St}2$ in $CDCl_3$ (400 MHz).

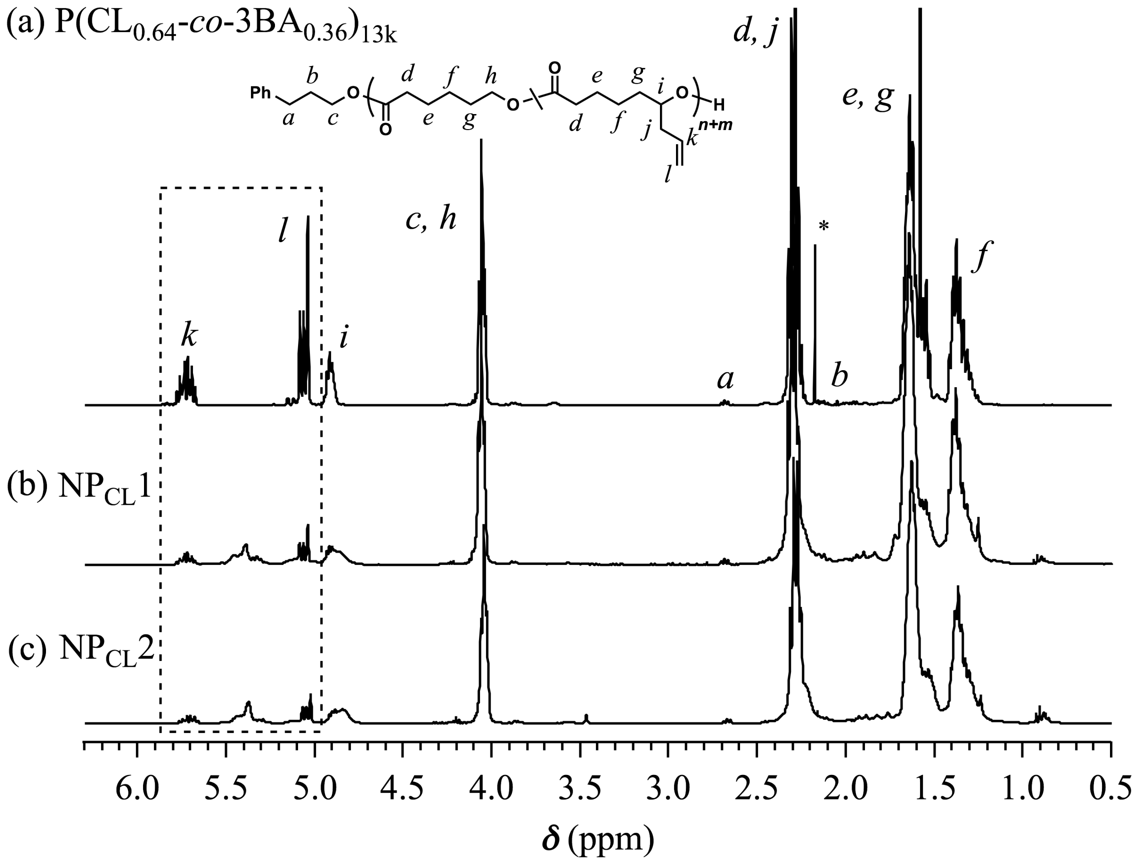

Figure S18. ^{1}H NMR spectra of (a) P(CL$_{0.64}$-*co*-BSt$_{0.36}$)$_{13k}$, (b) NP$_{CL}$1, and (c) NP$_{CL}$2 in CDCl$_3$ (400 MHz).