Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information for:

Janus Bottlebrush Compatibilizers

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Materials

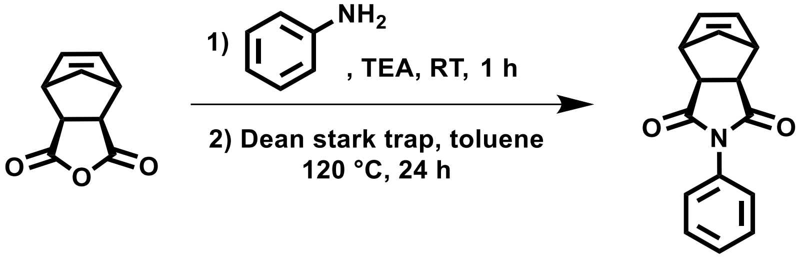
Propagylamine (98%), triethylamine (≥99%, TEA), aniline (ACS reagent, ≥99.5%), ethyl vinyl ether (≥99%, EVE), Grubbs Catalyst M204, pyridine anhydrous (99.8%), sodium azide (*ReagentPlus*®, ≥ 99.5%, NaN_3), *N,N*-dimethylformamide (anhydrous, 99.8%, DMF), ethyl *α*-bromoisobutyrate (98%, EBiB), *tert*-butyl acrylate (contains 10−20 ppm monomethyl ether hydroquinone as inhibitor, 98%, *t*BA), styrene (*ReagentPlus*®, 99.9%) copper (I) bromide (98%, $Cu^{I}Br$), copper (II) bromide (99%, $Cu^{II}Br_2$), *N,N,N′,N″,N″*-pentamethyldiethyltriamine (99%, PMDETA), trifluoroacetic acid (*ReagentPlus*®, 99%, TFA), tetrahydrofuran (anhydrous, ≥99.9%, inhibitor-free, THF) and polystyrene (~280 000g/mol) were purchased from Sigma-Aldrich. *Cis*-5-norbornene-*exo*-2,3- dicarboxylic anhydride was purchased from Oakwood Chemical. Toluene (certified ACS, ≥99.5%) and methanol (MeOH, certified ACS, ≥99.8%) and acetone (certified ACS, ≥99.5%) were purchased from Fisher Scientific. Deuterated styrene (D8, stabilized with 4-*tert*-tutylcatechol (~300 ppm)), deuterated polystyrene (D8, 285 000 g/mol, Đ=1.12), polystyrene (PS, 217 000 g/mol, Đ=1.04), poly(2-vinyl pyridine) (P2VP, 204 000 g/mol, Đ=1.3), and deuterated P2VP (D3, 271 000 g/mol, Đ=1.4) were purchased from Polymer Source, Inc. P2VP (200 000g/mol) was purchased from Scientific Polymer Product Inc. Dialysis membrane tubing (MWCO = 1 kDa, regenerated cellulose, Spectrum™ Lab) was purchased from VWR. DCM and THF were purified by distillation over calcium hydride and sodium benzophenone ketyl, respectively.

Synthesis Characterizations

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-500 spectrometer operating at 500 and 126 MHz respectively, and chemical shifts reported in ppm were calibrated to residual solvent signals. Size-exclusion chromatography (SEC) eluting with THF was performed at 40 ºC at a flow rate of 1.0 mL min^{-1} on an Agilent 1260 infinity system with a G1362A refractive index detector and G1310B isocratic pump, equipped with a PLgel 5 µm mixed-c (7.5 x 300 mm), a PLgel 5 µm mixed-d (7.5 x 300 mm), and a 5 µm guard column (7.5 x 50 mm) calibrated against polystyrene (PS) standards. Multi-angle laser light scattering size-exclusion chromatography (MALLS-SEC) of the BRCPs was carried out in THF with 1.0 vol% of triethylamine (TEA) at 20 ºC on two PLgel 10 µm mixed bed columns and two detectors: multi-angle laser light scattering (MALLS) and differential refractive index (dRI) at a flow rate of 1.0 mL min^{-1}. For GPC analysis, the polymers were first dissolved in THF (3.0 mg mL^{-1}) then passed through a 0.45 µm polytetrafluoroethylene (PTFE) filter. The differential refractive index increment (dn dc^{-1}) was calculated by integrating the differential refractive index signal, assuming 100% mass recovery. The weight-average molar mass (M_w) and polydispersity index (PDI) were determined by constructing a partial Zimm plot for each slice of the elution profile.

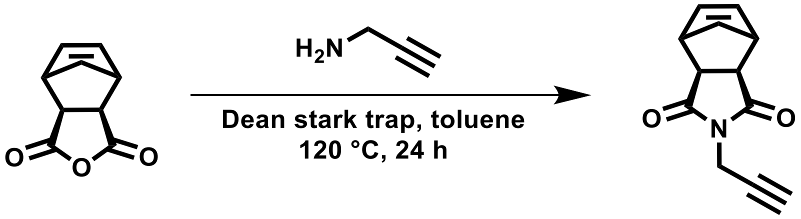
Synthesis

N-(phenyl)-cis-5-norbornene-exo-2,3-dicarboximide (NB-Ph)



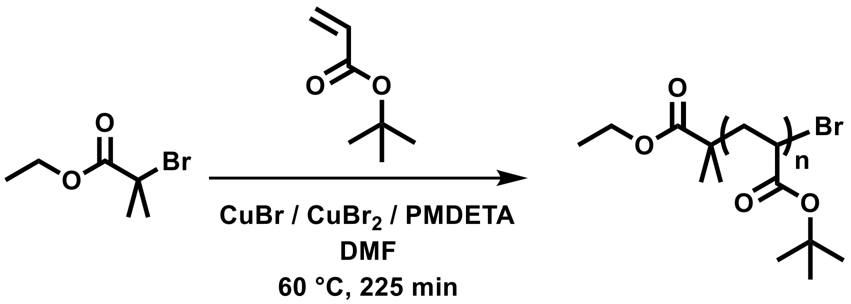
The phenyl product was synthesized according to a published procedure[1] to yield a white crystalline powder (10.4 g, 71.4 % yield). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 7.44-7.49 (m, 2H), 7.36-7.41 (m, 1H), 7.24-7.28 (m, 2H), 6.34 (t, J = 1.5 Hz, 2H), 3.39-3.41 (m, 2H), 2.84-2.87 (m, 2H), 1.59-1.64 (m, 1H), 1.47-1.52 (m, 1H). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 177.20, 138.15, 131.98, 129.32, 128.81, 126.51, 48.02, 45.98, 43.11.

N-(propargyl)-cis-5-norbornene-exo-2,3-dicarboximide



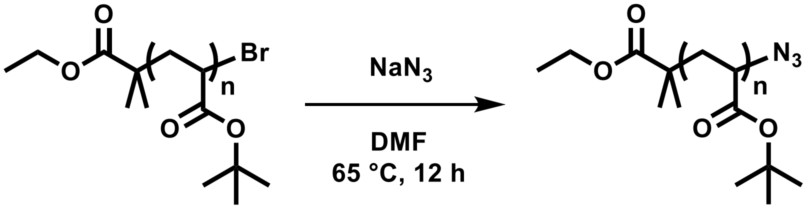
The alkyne product was synthesized according to a published procedure[2] to yield a pale-yellow crystal solid (26.5 g, 90.7 % yield). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 6.28 (s, 2H), 4.21 (m, 2H), 3.26 (m, 2H), 2.70 (s, 2H), 2.17 (m, 1H), 1.51 (d, J = 11 Hz, 1H), 1,27 (d, J = 11 Hz, 1H). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 176.73, 138.10, 76.64, 71.49, 47.94, 45.65, 42.88, 27.69.

PtBA-Br (via atom-transfer radical polymerization)



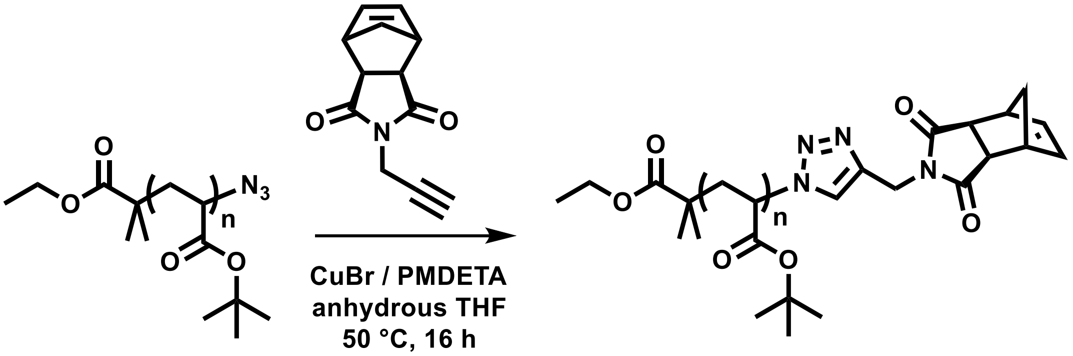
The P*t*BA-Br was synthesized according to a published procedure[2], with slight modifications. Before polymerization, *t*BA was purified by elution through a column of basic alumina to remove inhibitor. Purified *t*BA (100 mL, 688.9 mmol), EBiB (2.0 mL, 13.8 mmol), PMDETA (860 µL, 4.1 mmol), $Cu^{II}Br_2$ (46 mg, 0.2 mmol) and anhydrous DMF (24 mL) were added to a 250 mL Schlenk flask equipped with a magnetic stirring bar. The mixture was degassed by three freeze-pump-thaw cycles. Then, $Cu^{I}Br$ (592 mg, 4.1 mmol) was added to the frozen reaction mixture, and the flask was sealed, evacuated, and backfilled with $N_{2(g)}$ three times. The mixture was allowed to warm to room temperature, then was heated for 225 min in an oil bath pre-set to 60 ºC. The polymerization mixture was cooled to -78 ºC (dry ice/acetone bath) and the crude product was passed through a basic alumina column to remove the copper catalyst. The solution was concentrated under reduced pressure and precipitated into a 4:1 MeOH:H_2O mixture (-78 ºC) three times. The precipitates were dried under vacuum to yield a white powder (58.1 g). ^1H NMR (500 MHz, $CDCl_3$, δ, ppm): 4.10 (br, 2H), 1.39-1.48 (br, 281H). $M_{n,NMR}$ = 4.2 kDa, $M_{n,SEC}$ = 4.2 kDa, PDI = 1.07.

PtBA-N$_3$ (via chain-end substitution)



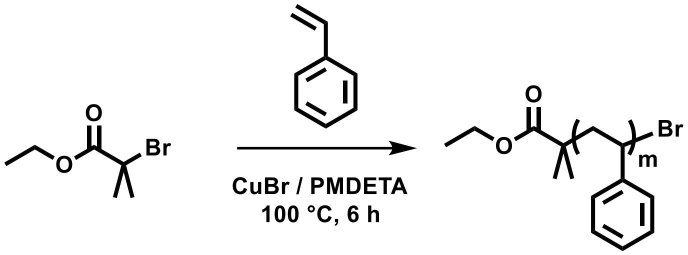
The P*t*BA-N$_3$ was synthesized according to a published procedure[2], with slight modifications. P*t*BA-Br (57.8 g, 13.8 mmol), NaN_3 (2.7 g, 41.3 mmol) and DMF (275 mL) were added to a 500 mL one-neck round-bottom flask equipped with a magnetic stirring bar and a condenser. The reaction was conducted for 24 hours in an oil bath at 70 ºC. The mixture was cooled to room temperature then precipitated into a mixture of 4:1 MeOH:H_2O mixture (-78 ºC) two times. The precipitates were dried under vacuum to yield a white powder (47.1 g). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 4.10 (br, 2H), 3.60-3.78 (br, 1H), 1.28-1.68 (br, 407H).

PtBA macromonomer (NB-PtBA, via Huisgen 1,3-dipolar cycloaddition)



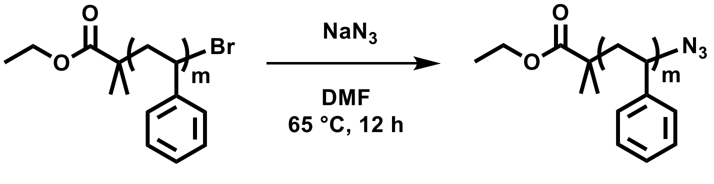
The NB-P*t*BA was synthesized according to a published procedure[2], with slight modifications. PtBA-N_3 (37.8 g, 9.0 mmol), *N*-(propagyl)-*cis*-5-norbornene-*exo*-2,3-dicarboxyimide (2.7 g, 13.5 mmol), PMDETA (560 µL, 2.7 mmol) and anhydrous THF (120 mL) were added to a 250 mL Schlenk flask equipped with a magnetic stirring bar. The mixture was degassed using three freeze-pump-thaw cycles. Then, Cu^{I}Br (387 mg, 2.7 mmol) was quickly added to the frozen reaction mixture, and the flask was sealed, evacuated, and backfilled with $N_{2(g)}$ three times. The mixture was thawed to room temperature and the reaction was conducted in an oil bath pre-set to 50 ºC for 24 h. The crude product was cooled to room temperature, passed through a basic alumina column to remove the copper catalyst, and dialyzed against MeOH (MWCO = 1 kDa) for 3 days. The solvent was removed under reduced pressure to yield a white powder (10.2 g). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.69 (m, 1H), 6.27 (m, 2H), 5.23 (m, 1H), 4.75 (m, 2H), 4.10 (m, 2H), 3.27 (m, 2H), 2.69 (m, 2H), 1.35-1.48 (m, 383H). $M_{n,NMR}$ = 5.8 kDa, $M_{n,SEC}$ = 4.4 kDa, PDI = 1.06.

PS-Br (via atom-transfer radical polymerization)



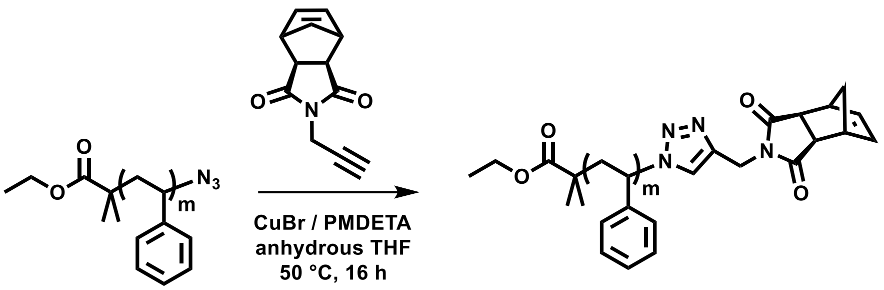
Before polymerization, styrene was purified by elution through a column of basic alumina to remove inhibitor. Purified styrene (100 mL, 872.8 mmol), EBiB (2.6 mL, 17.5 mmol) and PMDETA (1.1 mL, 5.2 mmol) were added to a 100 mL Schlenk flask equipped with a magnetic stirring bar. The mixture was degassed by three freeze-pump-thaw cycles. Then, $Cu^{I}Br$ (750 mg, 5.3 mmol) was added to the frozen reaction mixture, and the flask was sealed, evacuated, and backfilled with $N_{2(g)}$ three times. The mixture was allowed to warm to room temperature, then was heated for 6 h in an oil bath pre-set to 100 °C. The polymerization mixture was cooled to -78 °C (dry ice/acetone bath) and the crude product was passed through a basic alumina column to remove the copper catalyst. The solution was concentrated under reduced pressure and precipitated into MeOH (-78 °C) three times. The precipitates were dried under vacuum to yield a white powder (36.6 g). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.23-7.24 (br, 130H), 4.43 (br, 1H), 3.64 (br, 2H). $M_{n,NMR}$ = 2.9 kDa, $M_{n,SEC}$ = 2.3 kDa, PDI = 1.09.

PS-N₃ (via chain-end substitution)



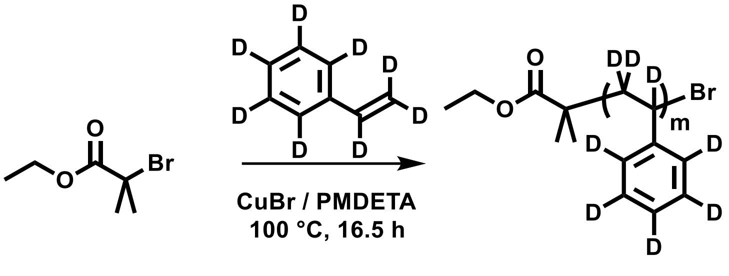
PS-Br (30.0 g, 13.0 mmol), NaN_3 (4.2 g, 65.2 mmol) and DMF (250 mL) were added to a 500 mL one-neck round-bottom flask equipped with a magnetic stirring bar and a condenser. The reaction was conducted for 24 hours in an oil bath at 65 °C. The mixture was cooled to room temperature then precipitated into MeOH (-78 °C). The precipitates were dried under vacuum to yield a white powder (15.9 g). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.23-7.24 (br, 127H), 3.96 (br, 1H), 3.65 (br, 2H).

PS macromonomer (NB-PS, via Huisgen 1,3-dipolar cycloaddition)



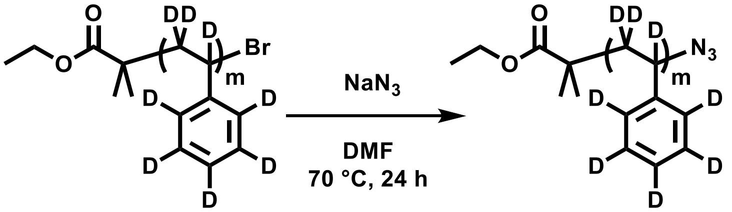
PS-N3 (15.0 g, 6.5 mmol), *N*-(propagyl)-*cis*-5-norbornene-*exo*-2,3-dicarboxyimide (2.0 g, 9.8 mmol), PMDETA (2.0 mL, 9.8 mmol) and anhydrous THF (60 mL) were added to a 250 mL Schlenk flask equipped with a magnetic stirring bar. The mixture was degassed using three freeze-pump-thaw cycles. Then, Cu^IBr (1.4 g, 9.8 mmol) was quickly added to the frozen reaction mixture, and the flask was sealed, evacuated, and backfilled with $N_{2(g)}$ three times. The mixture was thawed to room temperature and the reaction was conducted in an oil bath pre-set to 50 °C for 16 h. The crude product was cooled to room temperature, passed through a basic alumina column to remove the copper catalyst, and precipitated in MeOH (-78 °C) three times. The precipitates were dried under vacuum to yield a white powder (10.9 g). ^1H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.30-7.23 (br, 126H), 6.25 (s, 2H), 5.01 (br, 1H), 4.60 (m, 2H), 3.63 (br, 2H+impurity), 3.23 (s, 2H), 2.64 (m, 2H), $M_{n,NMR}$ = 2.9 kDa, $M_{n,SEC}$ = 2.6 kDa, PDI = 1.07.

DPS-Br (via atom-transfer radical polymerization)



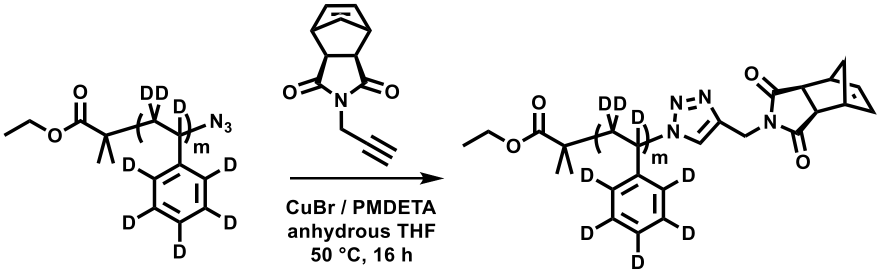
Before polymerization, deuterated styrene was purified by distillation over $CaH_{2(s)}$ to remove inhibitor and water. Purified deuterated styrene (14 mL, 122.1 mmol), EBiB (358.4 μL, 2.4 mmol) and PMDETA (152.6 μL, 0.7 mmol) were added to a 100 mL Schlenk flask equipped with a magnetic stirring bar. The mixture was degassed by three freeze-pump-thaw cycles. Then, Cu^IBr (105.0 mg, 0.7 mmol) was added to the frozen reaction mixture, and the flask was sealed, evacuated, and backfilled with $N_{2(g)}$ three times. The mixture was allowed to warm to room temperature, then was heated for 16.5 h in an oil bath pre-set to 100 °C. The polymerization mixture was cooled to -78 °C (dry ice/acetone bath) and the crude product was passed through a basic alumina column to remove the copper catalyst. The solution was concentrated under reduced pressure and precipitated into MeOH (-78 °C) three times. The precipitates were dried under vacuum to yield a white powder (6.6 g). $M_{n,SEC}$ = 2.5 kDa, PDI = 1.23.

DPS-N₃ (via chain-end substitution)



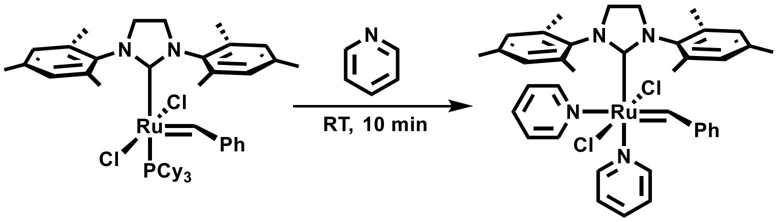
DPS-Br (6.0 g, 2.4 mmol), NaN_3 (780 mg, 12 mmol) and DMF (25 mL) were added to a 100 mL one-neck round-bottom flask equipped with a magnetic stirring bar and a condenser. The reaction was conducted for 24 hours in an oil bath at 70 °C. The mixture was cooled to room temperature then precipitated into MeOH (-78 °C). The precipitates were dried under vacuum to yield a white powder (3.5 g).

DPS macromonomer (NB-DPS, via Huisgen 1,3-dipolar cycloaddition)



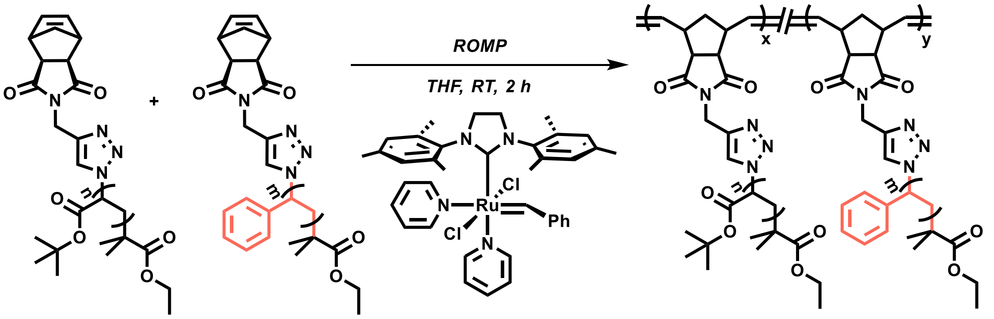
DPS-N_3 (0.9 g, 0.36 mmol), *N*-(propagyl)-*cis*-5-norbornene-*exo*-2,3-dicarboxyimide (109 mg, 0.54 mmol), PMDETA (113 µL, 0.54 mmol) and anhydrous THF (5 mL) were added to a 100 mL Schlenk flask equipped with a magnetic stirring bar. The mixture was degassed using three freeze-pump-thaw cycles. Then, $Cu^{I}Br$ (77 mg, 0.54 mmol) was quickly added to the frozen reaction mixture, and the flask was sealed, evacuated, and backfilled with $N_{2(g)}$ three times. The mixture was thawed to room temperature and the reaction was conducted in an oil bath pre-set to 50 °C for 24 h. The crude product was cooled to room temperature, passed through a basic alumina column to remove the copper catalyst, and precipitated in MeOH (-78 °C) three times. The precipitates were dried under vacuum to yield a white powder (0.8 g). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.25 (m, 2H), 3.64 (m, 2H), 3.22 (s, 2H). $M_{n,SEC}$ = 2.3 kDa, PDI = 1.42.

Grubbs 3rd Generation initiator (G3, ligand substitution)



The G3 was synthesized according to a published procedure.[3] Grubbs Catalyst M204 (500 mg, 0.6 mmol) and pyridine (2.4 mL, 29.4 mmol) were charged in a 20 mL scintillation vial with a magnetic stirring bar under ambient air condition. The mixture was stirred at room temperature for 10 minutes. Pentane (~15 mL) was layered onto the mixture. The vial was capped and kept in a freezer (-20 °C) for 24 hours. The mixture was filtered, and the remaining green solids were washed with pentane (20 mL x 3) and dried under vacuum to yield a green powder (376 mg, 87.8 % yield).

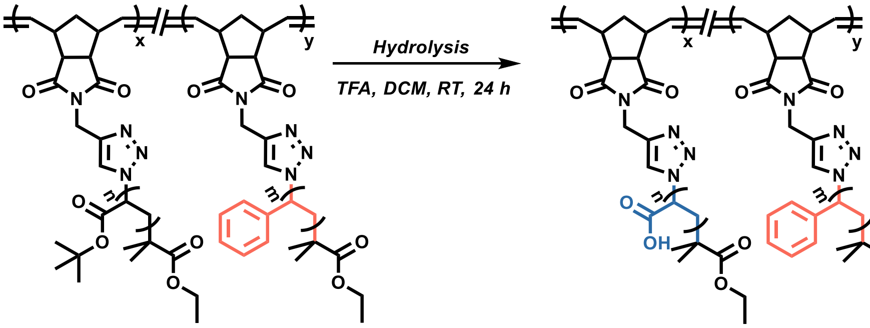
Ring-opening metathesis polymerization (ROMP) of NB-PtBA and NB-(D)PS



NB-P*t*BA (220 mg, 0.05 mmol) and NB-PS (130 mg, 0.05 mmol) were added to a flame-dried 7 mL scintillation vial containing a magnetic stirring bar. The vial was purged with $N_{2(g)}$ and anhydrous THF (2 mL, final [MM] upon injection of G3 stock solution = 0.05 M) (previously purged with $N_{2(g)}$ for 15 min) was added to the vial. In another dry 7 mL scintillation vial, a stock solution of initiator (G3, 0.01 M in anhydrous THF) was prepared under $N_{2(g)}$ atmosphere. The polymerization was initiated by adding the G3 stock solution to the macromonomer solution in stoichiometric amounts intended to yield the desired N_{BB} values. The solution was stirred at room temperature under $N_{2(g)}$ for 2 h. Then, ethyl vinyl ether (0.1 mL) was added to quench the polymerization. The crude products were dried under vacuum to yield a pale brown powder in high conversion (~95 %) and yield (>98 %) and used for the next step without further purification.

For deuterated BRCPs, NB-P*t*BA (88 mg, 0.02 mmol) and NB-DPS (50 mg, 0.02 mmol) were used for the ROMP. Other procedures are identical with the above description.

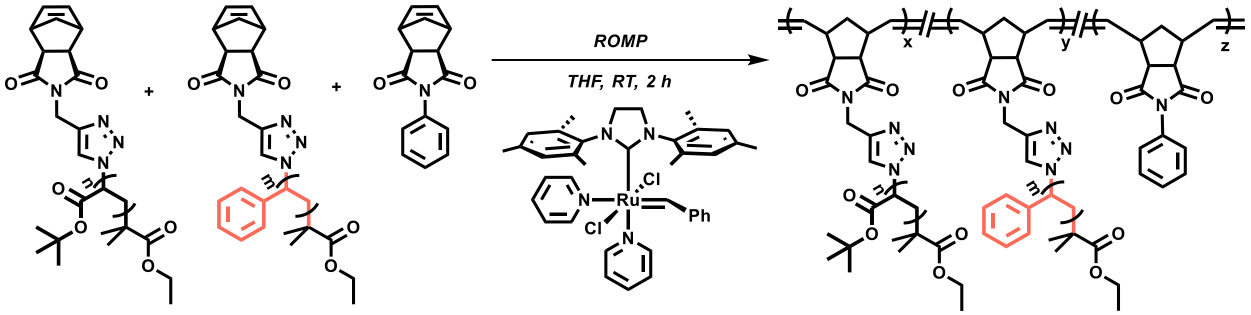
Acid-catalyzed hydrolysis of tBA of ((D)PS-PtBA)$_{N_{BB}}$ BRCPs



(PS-PtBA)$_{N_{BB}}$ (~350 mg, 1 equiv. of *tert*-butyl acrylate repeating unit) and DCM (12 mL) were added in a 20 mL scintillation vial containing a magnetic stirring bar. TFA (1.2 mL, 10 equiv. of *tert*-butyl acrylate repeating unit) was added and the mixture was stirred at room temperature for 24 h, during which time precipitates were observed. The precipitates were collected, washed with DCM (20 mL x 3), and dried under vacuum to yield a pale-yellow powder (~200 mg). FT-IR: 1703 cm^{-1} (carbonyl peak of carboxylic acid).

(DPS-PtBA)$_{N_{BB}}$ were also hydrolyzed under the same acidic conditions to yield a pale-yellow powder (~70 mg).

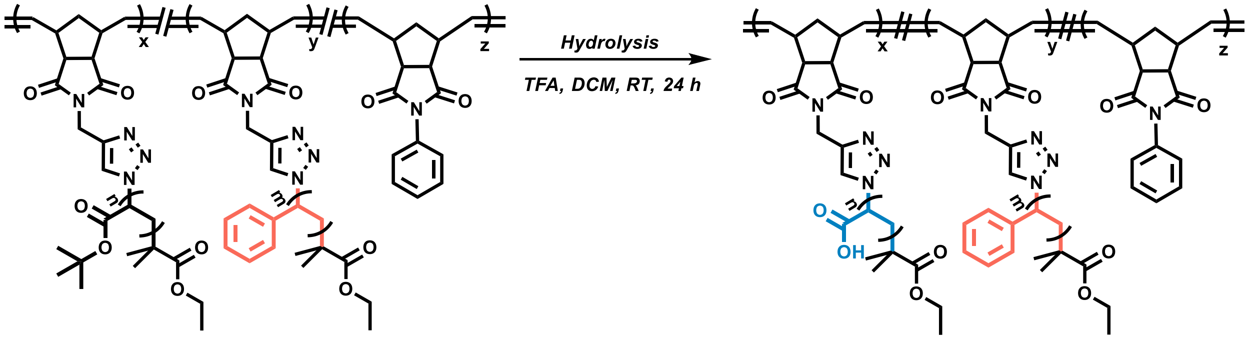
Ring-opening metathesis polymerization (ROMP) of NB-PtBA, NB-(D)PS, and NB-Ph



NB-P*t*BA (220 mg, 0.05 mmol), NB-PS (130 mg, 0.05 mmol), and NB-Ph (in stoichiometric amounts intended to yield the desired GD values) were added to a flame-dried 20 mL scintillation vial containing a magnetic stirring bar. The vial was purged with $N_{2(g)}$ and anhydrous THF (final [MM] upon injection of G3 stock solution = 0.05 M) (previously purged with $N_{2(g)}$ for 15 min) was added to the vial. In another dry 7 mL scintillation vial, a stock solution of initiator (G3, 0.01 M in anhydrous THF) was prepared under $N_{2(g)}$ atmosphere. The polymerization was initiated by adding the G3 stock solution to the macromonomer solution in stoichiometric amounts intended to yield the total N_{BB} = 100. The solution was stirred at room temperature under $N_{2(g)}$ for 2 h. Then, ethyl vinyl ether (0.1 mL) was added to quench the polymerization. The crude products were dried under vacuum to yield a pale brown powder in high conversion (~95 %) and yield (>98 %) and used for the next step without further purification.

For deuterated BRCPs, NB-P*t*BA (88 mg, 0.02 mmol), NB-DPS (50 mg, 0.02 mmol), and NB-Ph (in stoichiometric amounts intended to yield the desired GD values) were used for the ROMP. Other procedures are identical with the above description.

Acid-catalyzed hydrolysis of tBA of ((D)PS-PtBA)$_{N_{BB}\_GD}$ BRCPs



$\mathit{(PS\text{-}PtBA)}_{\mathit{N_{BB}\_GD}}$ (~350 mg, 1 equiv. of *tert*-butyl acrylate repeating unit) and DCM (~5 mL) were added in a 7 mL scintillation vial containing a magnetic stirring bar. TFA (~0.5 mL, 10 equiv. of *tert*-butyl acrylate repeating unit) was added and the mixture was stirred at room temperature for 24 h, during which time precipitates were observed. The precipitates were collected, washed with DCM (10 mL x 3), and dried under vacuum to yield a pale-yellow powder (~200 mg). FT-IR: 1705 cm^{-1} (carbonyl peak of carboxylic acid).

$\mathit{(dPS\text{-}PtBA)}_{\mathit{N_{BB}\_GD}}$ were also hydrolyzed under the same acidic conditions to yield a pale-yellow powder (~70 mg).

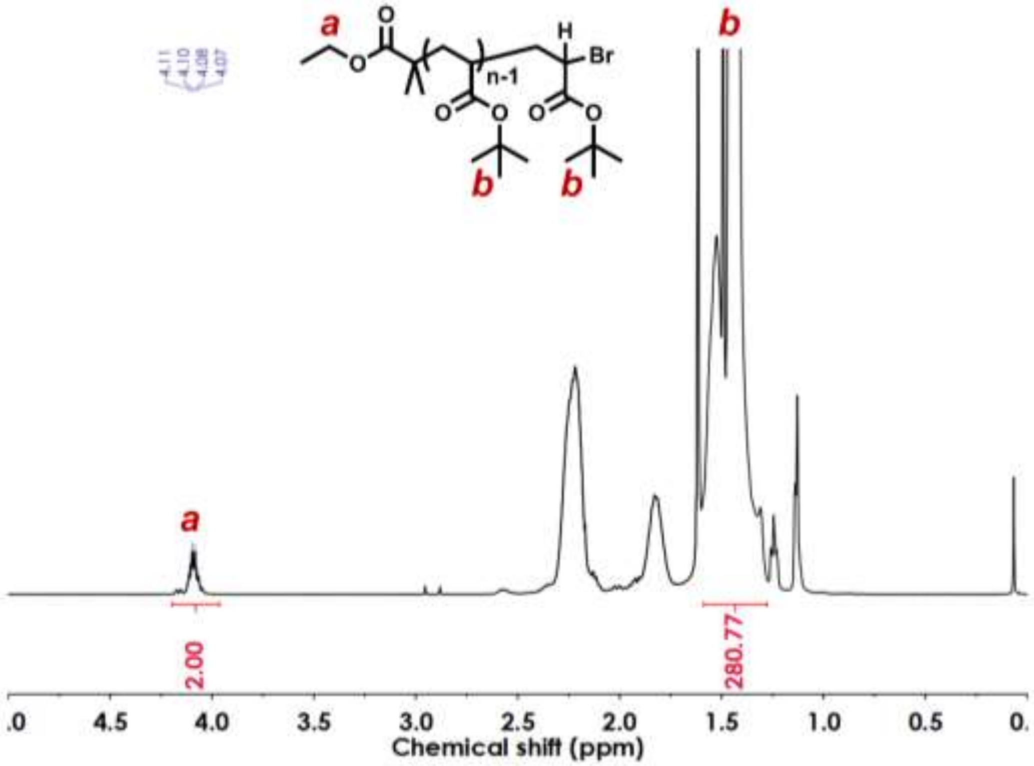


Figure S1. ^{1}H NMR spectrum of **P*t*BA-Br** recorded in $CDCl_3$

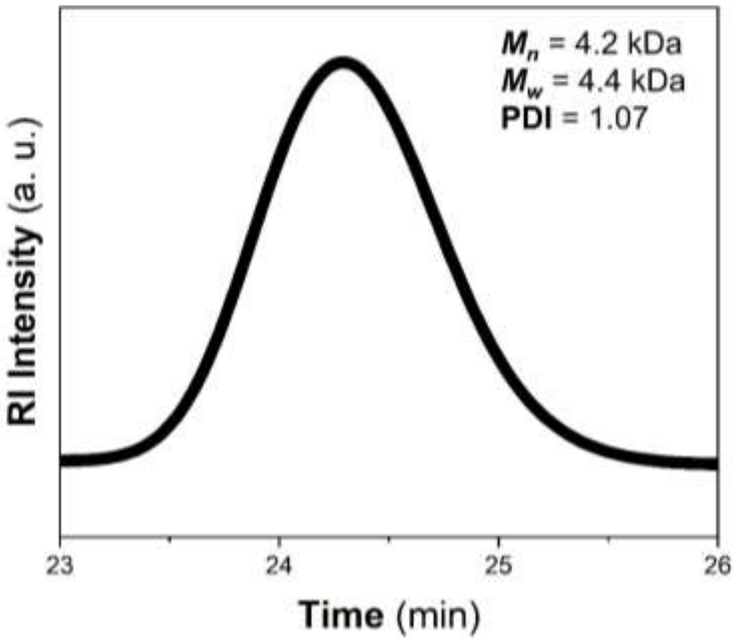


Figure S2. SEC trace of **P*t*BA-Br** eluting with THF

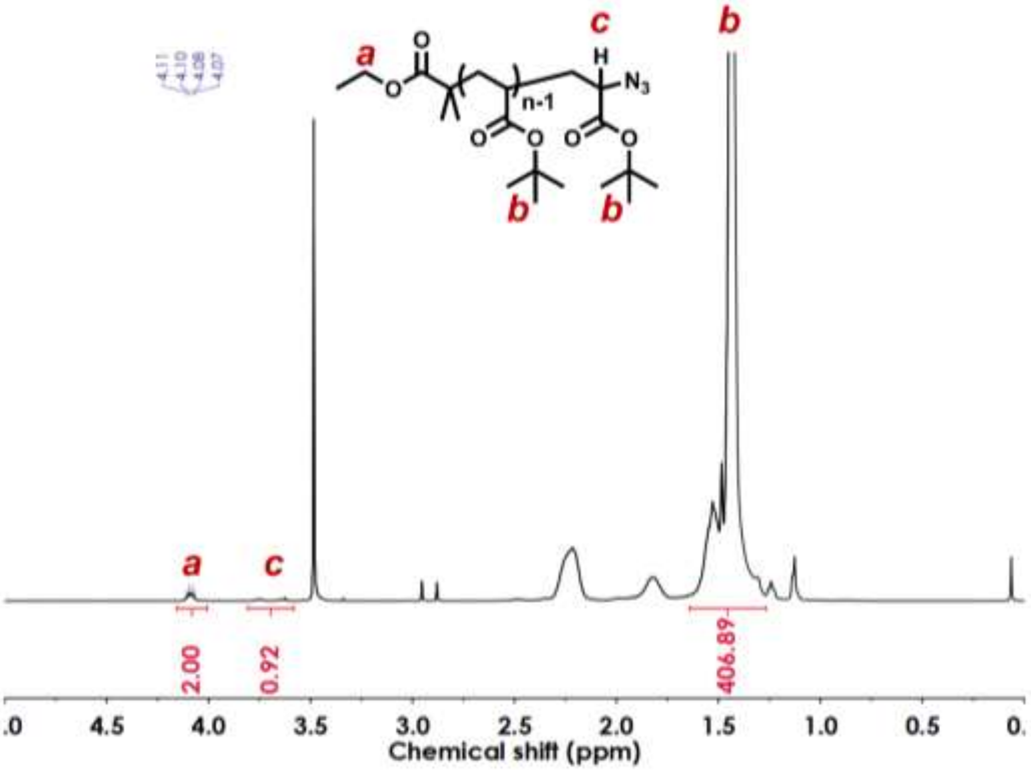


Figure S3. ^{1}H NMR spectrum of **P*t*BA-N$_3$** recorded in CDCl$_3$

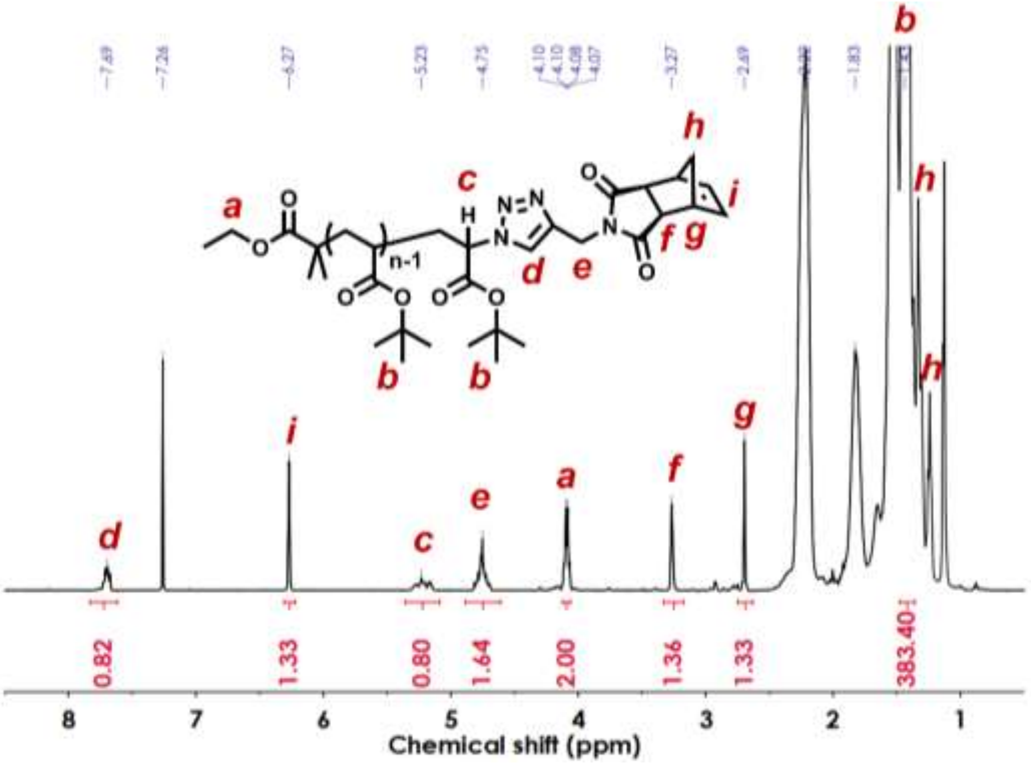


Figure S4. ^{1}H NMR spectrum of **NB-P*t*BA** recorded in CDCl$_3$

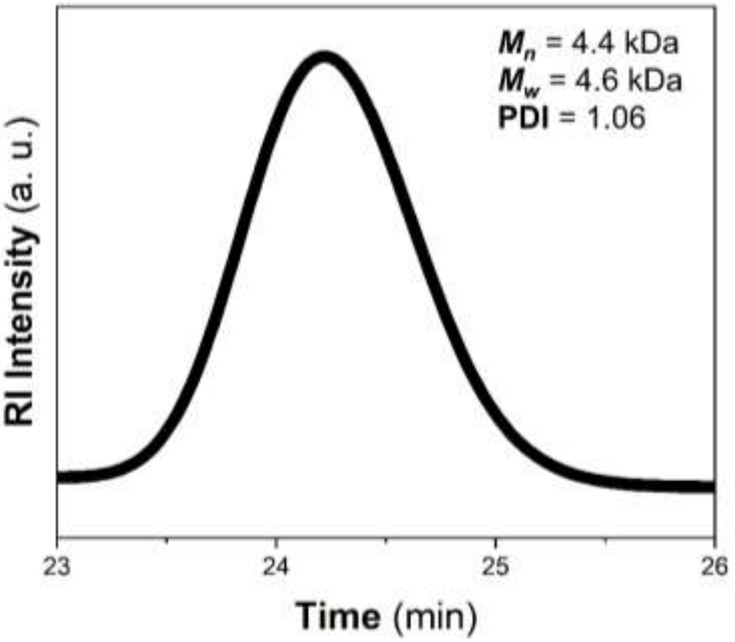


Figure S5. SEC trace of **NB-P*t*BA** eluting with THF

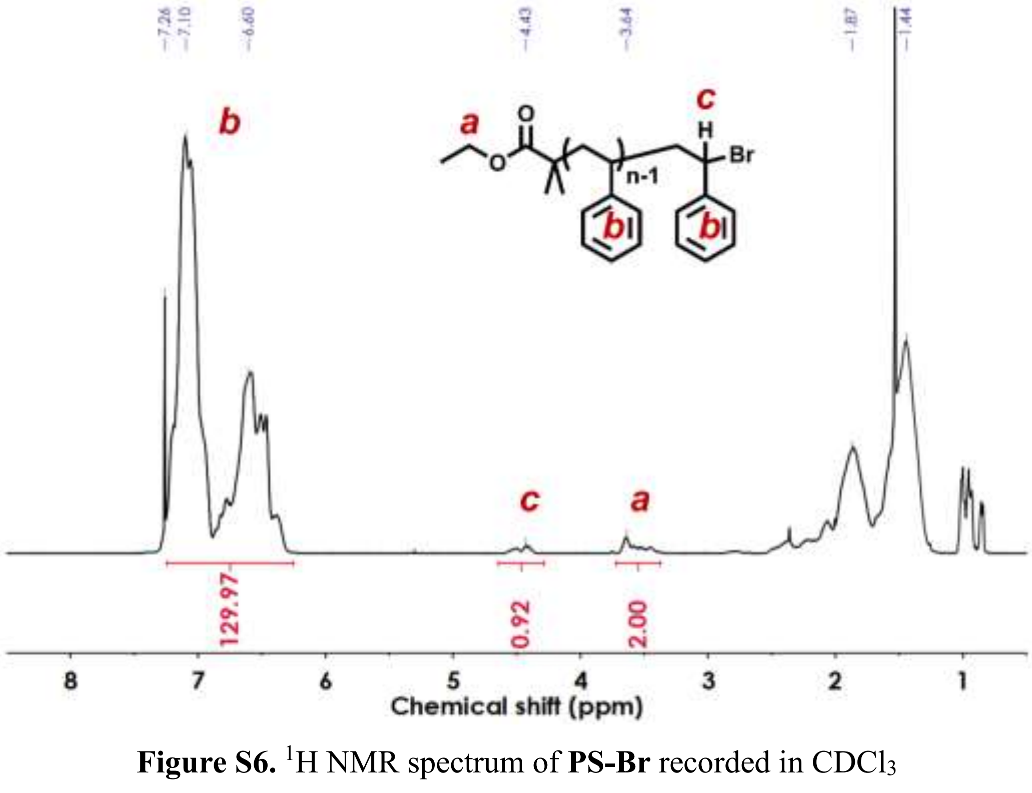


Figure S6. ^{1}H NMR spectrum of **PS-Br** recorded in $CDCl_3$

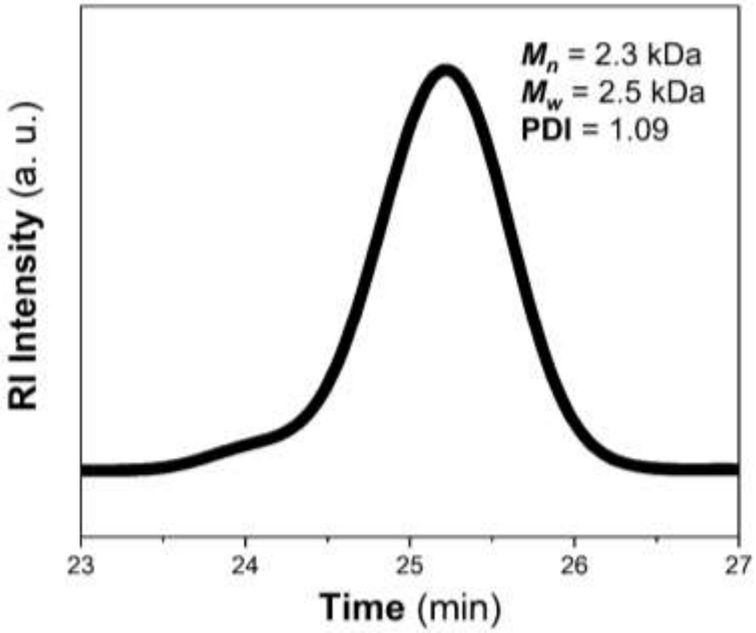


Figure S7. SEC trace of **PS-Br** eluting with THF

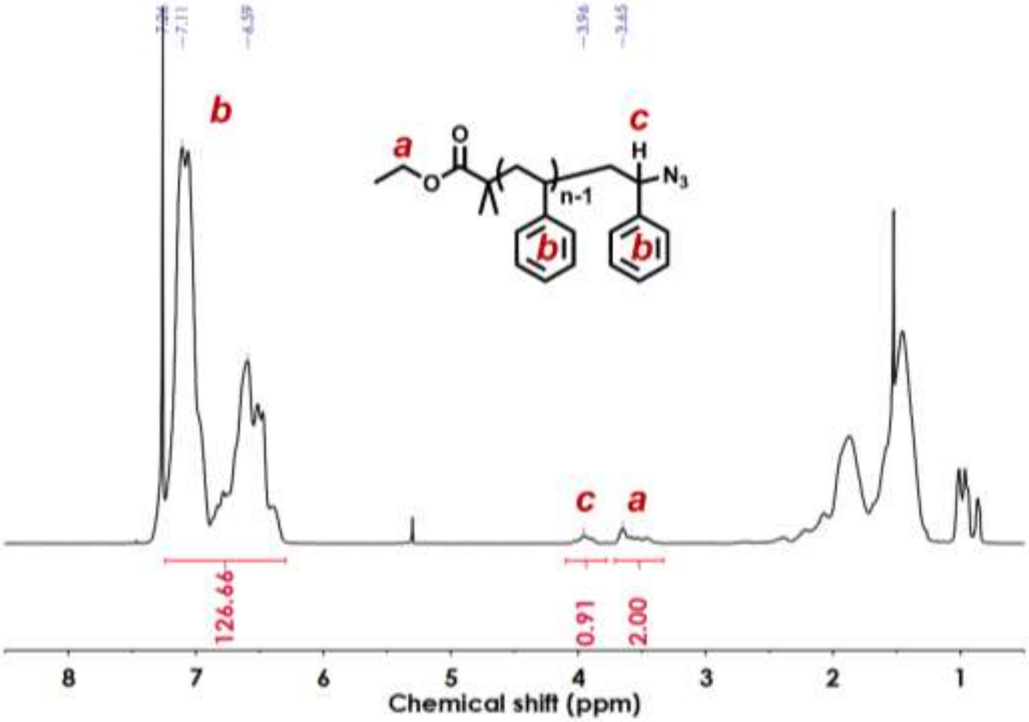


Figure S8. ^{1}H NMR spectrum of **PS-N$_3$** recorded in CDCl$_3$

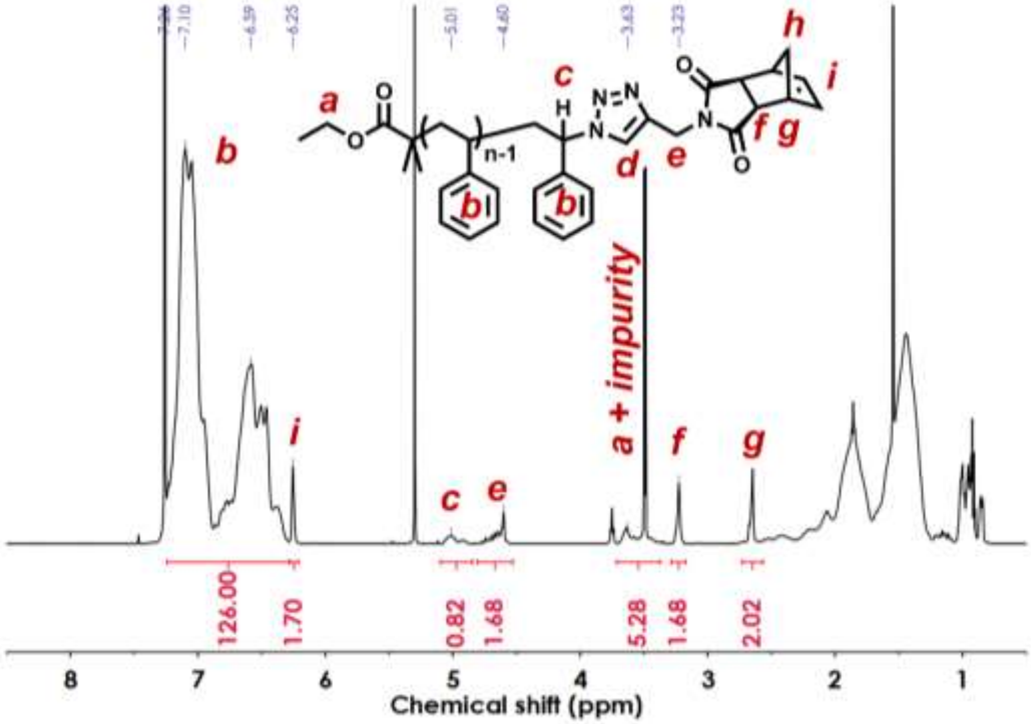


Figure S9. ^{1}H NMR spectrum of **NB-PS** recorded in $CDCl_3$

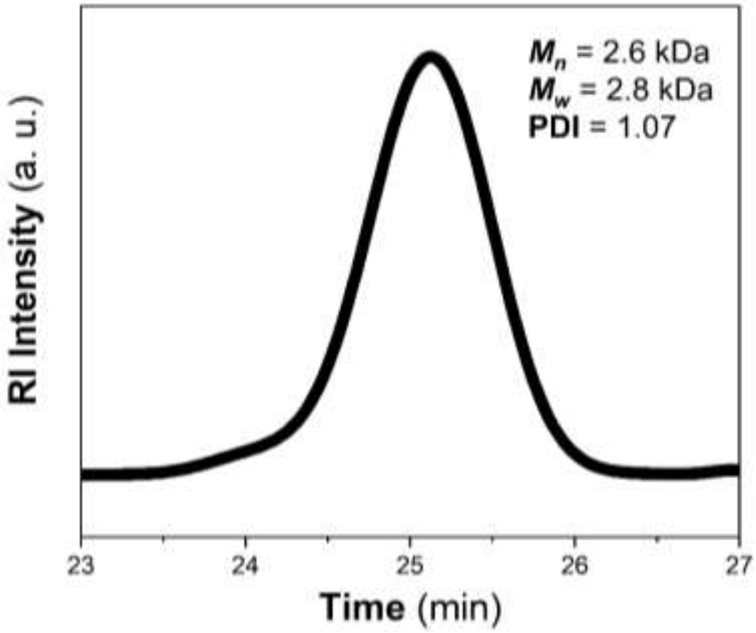


Figure S10. SEC trace of **NB-PS** eluting with THF

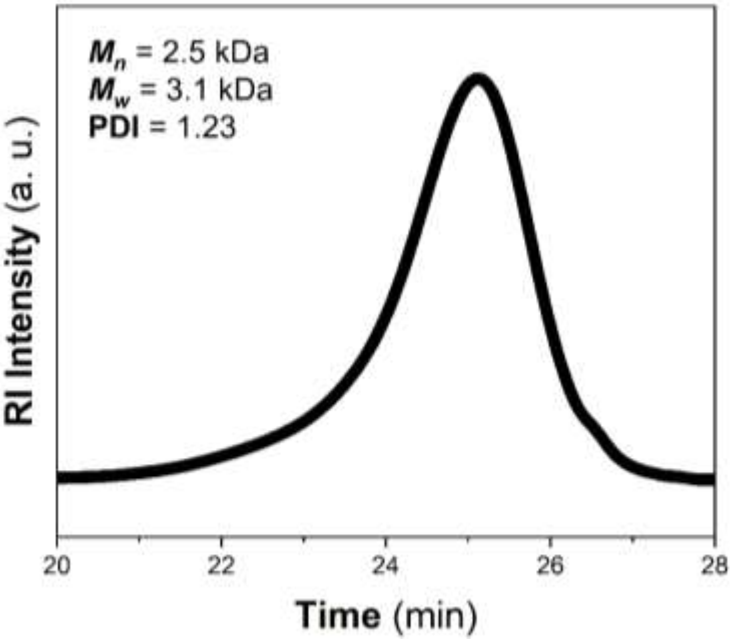


Figure S11. SEC trace of **DPS-Br** eluting with THF

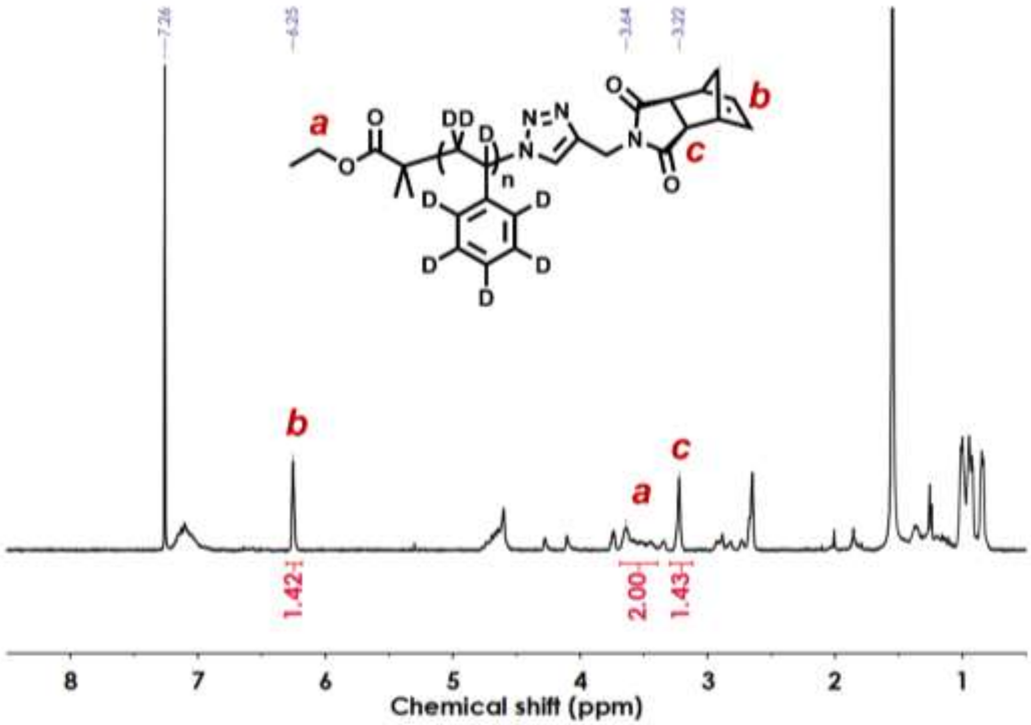


Figure S12. ^{1}H NMR spectrum of **NB-DPS** recorded in $CDCl_3$

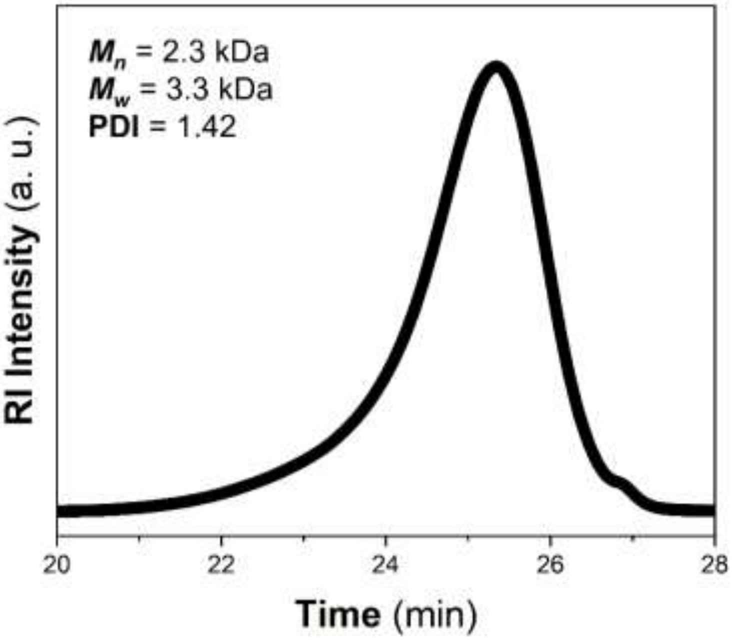


Figure S13. SEC trace of **NB-DPS** eluting with THF

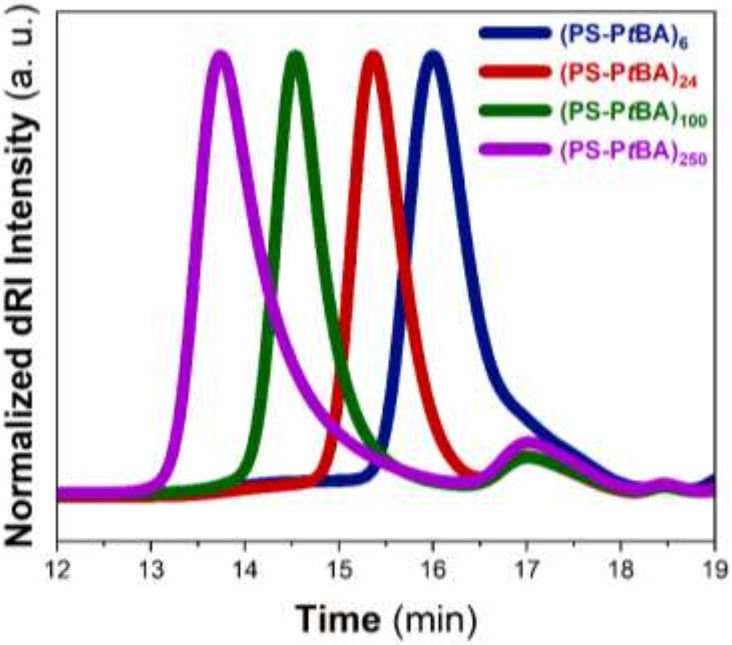


Figure S14. MALLS-SEC traces of hydrogenated JBCPs (@ GD=100 %)

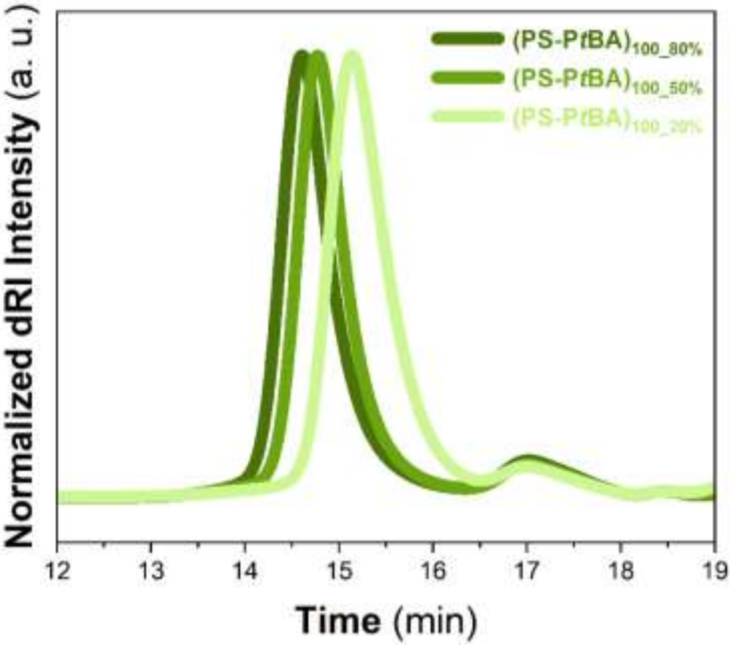


Figure S15. MALLS-SEC traces of hydrogenated JBCPs (@ N_{BB}=100)

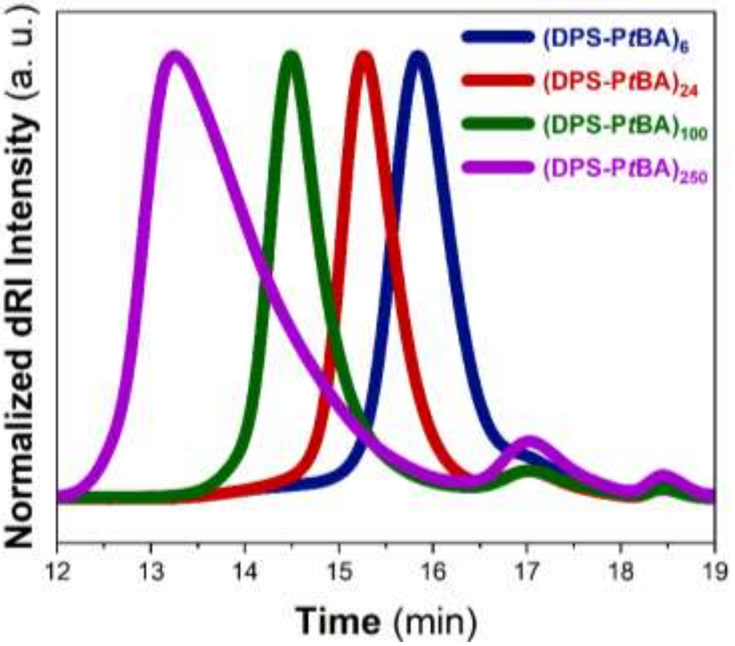


Figure S16. MALLS-SEC traces of deuterated JBCPs (@ GD=100 %)

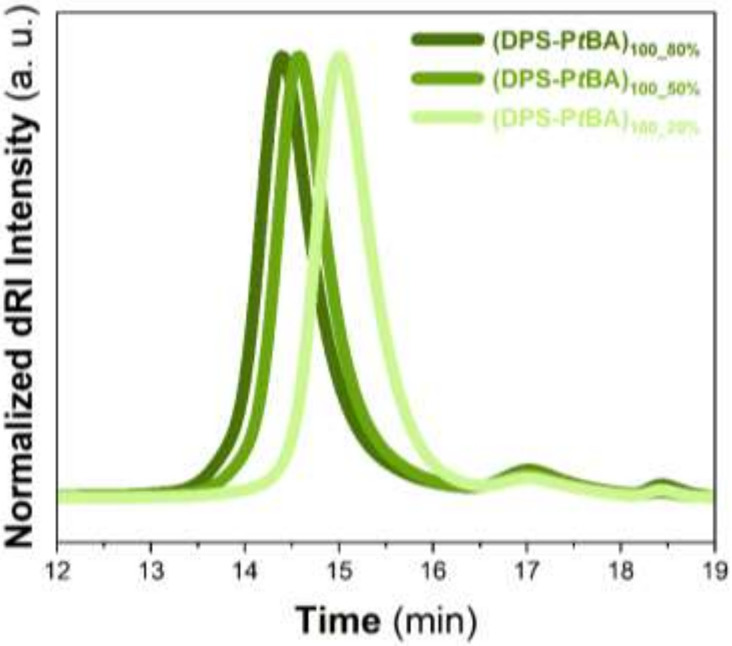


Figure S17. MALLS-SEC traces of deuterated JBCPs (@ N_{BB}=100)

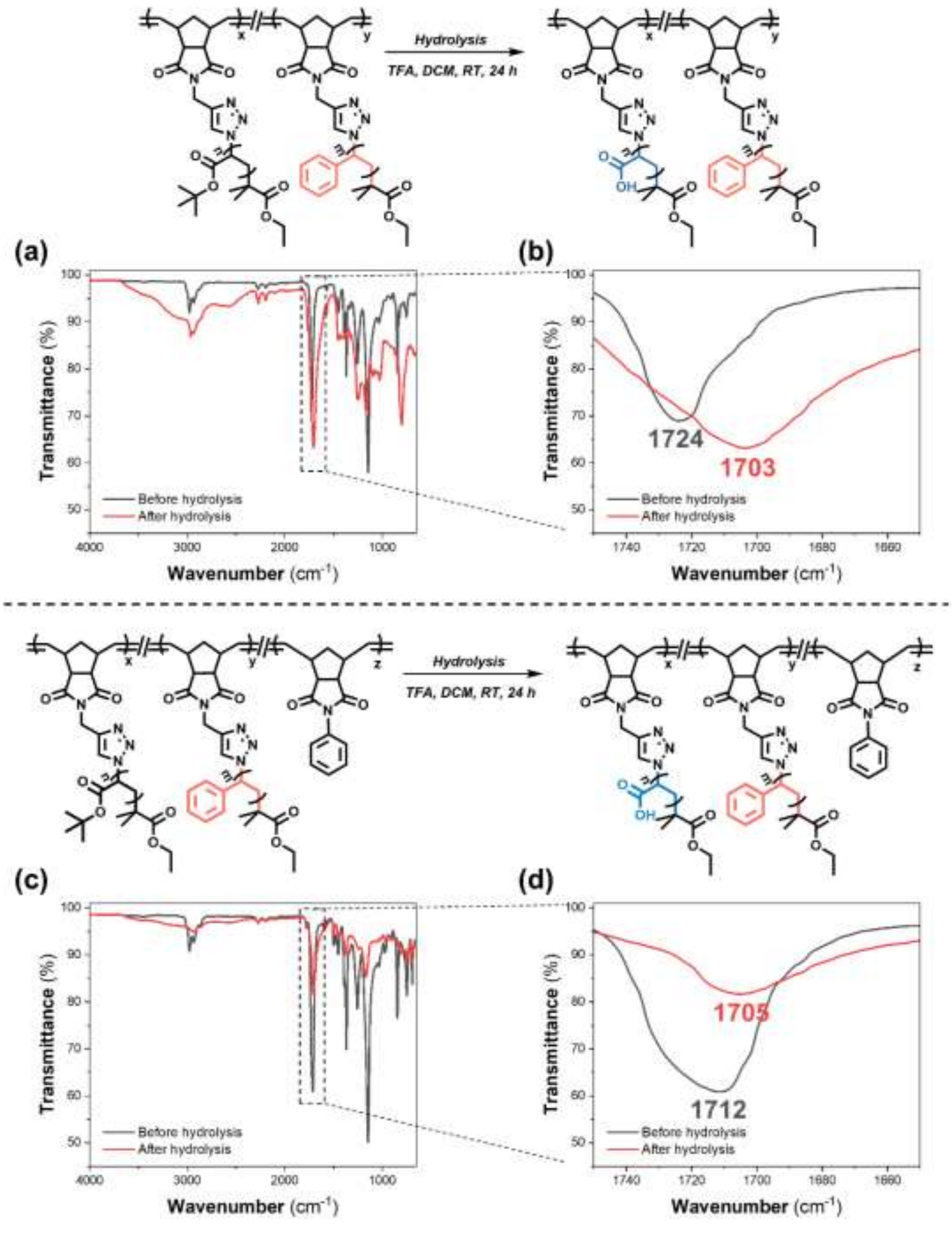


Figure S18. ATR FT-IR result of acid-catalyzed hydrolysis of (a-b) (DPS- P*t*BA)$_{24}$ and (c-d) (DPS- P*t*BA)$_{100\_20\%}$.

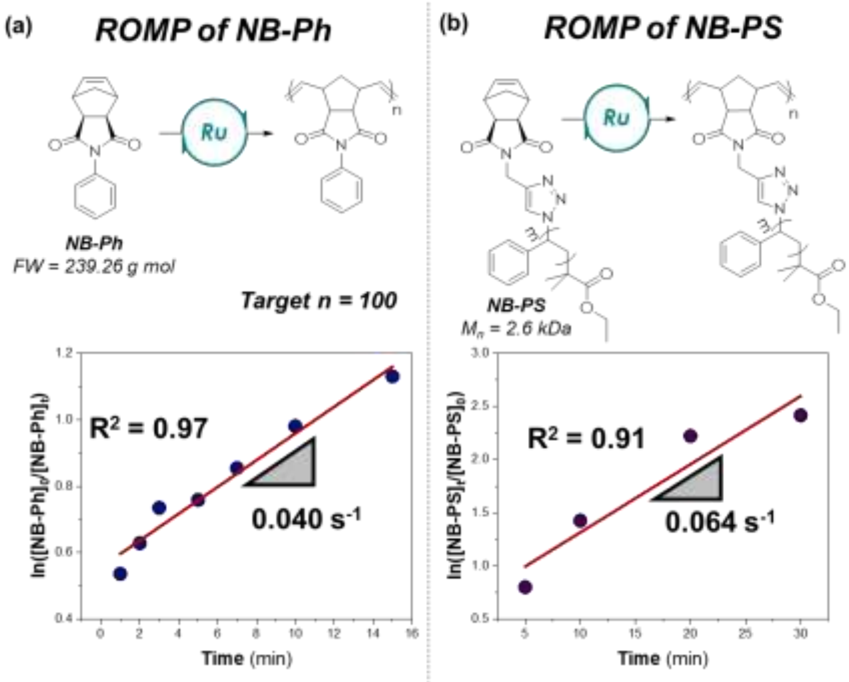


Figure S19. The polymerization kinetics studies of NB-Ph and NB-PS for confirming random distribution of NB-Ph in resulted bottlebrush copolymer.

Table S1. *dn dc*$^{-1}$ values for (D)PS-PtBA JBCPs by MALLS-SEC

entry	*dn dc*$^{-1}$
(PS-P*t*BA)$_6$	0.087
(PS- P*t*BA)$_{24}$	0.086
(PS- P*t*BA)$_{100}$	0.090
(PS- P*t*BA)$_{250}$	0.091
(PS- P*t*BA)$_{100\_80\%}$	0.082
(PS- P*t*BA)$_{100\_50\%}$	0.089
(PS- P*t*BA)$_{100\_20\%}$	0.100
(DPS- P*t*BA)$_6$	0.089
(DPS- P*t*BA)$_{24}$	0.090
(DPS- P*t*BA)$_{100}$	0.085
(DPS- P*t*BA)$_{250}$	0.087
(DPS- P*t*BA)$_{100\_80\%}$	0.082
(DPS- P*t*BA)$_{100\_50\%}$	0.090
(DPS- P*t*BA)$_{100\_20\%}$	0.099

Methods

1. **Trilayer thin films sample preparations for neutron reflectivity:** P2VP (204 kg/mol)or D-P2VP (271 kg/mol)homopolymer was dissolved in tetrahydrofuran (THF) and spin-coated onto wafers (~80nm thickness) after filtration. The first layer thickness was measured using ellipsometry. Random bottlebrush copolymers were dissolved in butyl acetate (orthogonal solvent to P2VP) and the resulted solution was spin-coated onto first layer to give ~5 nm thickness of second layer. The total bilayer thickness was measured, and the second layer thickness was calculated by subtracting the first layer thickness. PS (280 kg/mol) or D-PS (285 kg/mol) homopolymer was dissolved in toluene and spin-coated onto separated glass slides after filtration (~80 nm thickness). The PS film was transferred onto the bilayer samples after scratching the glass edge and transferring it to a water bath. After drying and vacuum treatment, the total layer thickness was measured, yielding the PS layer thickness. The samples were thermally annealed at 178 °C under vacuum for 24 hours, followed by slow cooling to room temperature.

2. **Trilayer beams preparation for adhesion measurements:** PS (280 kg/mol) beam with 1cm * 5cm *3 mm dimension and P2VP (200 kg/mol) beam with 1cm * 5cm *2 mm dimension was melt compressed at 155 °C. Random bottlebrush copolymers were dissolved in butyl acetate and spin-coated onto top of P2VP beam to give thickness ~5 nm. After drying in vacuum, two beams were joint together under slight pressure at 178 °C with nitrogen atmosphere for 2 h, followed by slowly cooling down.

3. **Thin films of polymer blends:** PS (280 kg/mol) homopolymers, P2VP (200 kg/mol) homopolymers (70wt% to 30 wt%) and 10 wt% of random bottlebrush copolymers was

dissolved in THF solvent. The mixed solution was spin-coated onto silicon substrate to give thin films. The sample was thermal annealed at 178 ℃ under vacuum for 24 hours, followed by slowly cooling down. The resulted film was rinsed by ethanol to remove P2VP domain for visualization in polarized optical microscopy (POM) and atomic force microscopy (AFM).

Characterizations

1. **Neutron reflectivity (NR)**: NR was performed at the Oak Ridge National Laboratory (ORNL) Spallation Neutron Source (SNS) on the Liquids Reflectometer (LR, BL-4B). The scattering vector (q) ranged from 0.008 – 0.2 Å^{-1} was achieved from combination of changing neutron wavelength (λ) between 2.55 Å and 18.5 Å with resolution dq/q =0.028 and incident angle comprising 0.6, 1.18 and 2.35°. The q is defined as $q = \frac{\mathbf{4\pi sin(\theta)}}{\lambda}$, where θ is scattering angle, λ is neutron wavelength. Direct incident beam was performed to normalize experiment reflectivity data. The experiment was performed at air with room temperature and neutron counts are 720 000 at q range 0.1~0.2 Å to assure good statistical results. The specular reflection was collected. The NR reflectivity was analyzed by Refnx based on Python.

2. **Polarized optical microscopy (POM):** POM was performed on OLYMPUS BX60 in reflection mode.
3. **Atomic force microscopy (AFM):** AFM was performed on SPM Asylum MFP-3D in tapping mode.
4. **Ellipsometry:** Ellipsometry was performed by Gaertner Scientific Corporation with model number LSE.

5. **Small angle X-ray scattering (SAXS):** SAXS results were measured on Ganesha SAXS-LAB instrument, the incident beam was Cu Kα radiation ($\lambda = 0.1542$ nm). The samples were thermal compressed in steel washer and then sealed both sides using Kapton films. The samples were annealed at 155 °C at vacuum overnight and slowly cooled down.
6. **Scanning electron microscopy (SEM):** SEM was performed on Thermofisher Apreo VolumeScope Variable-Pressure SEM with secondary electron or backscattered electron detector.

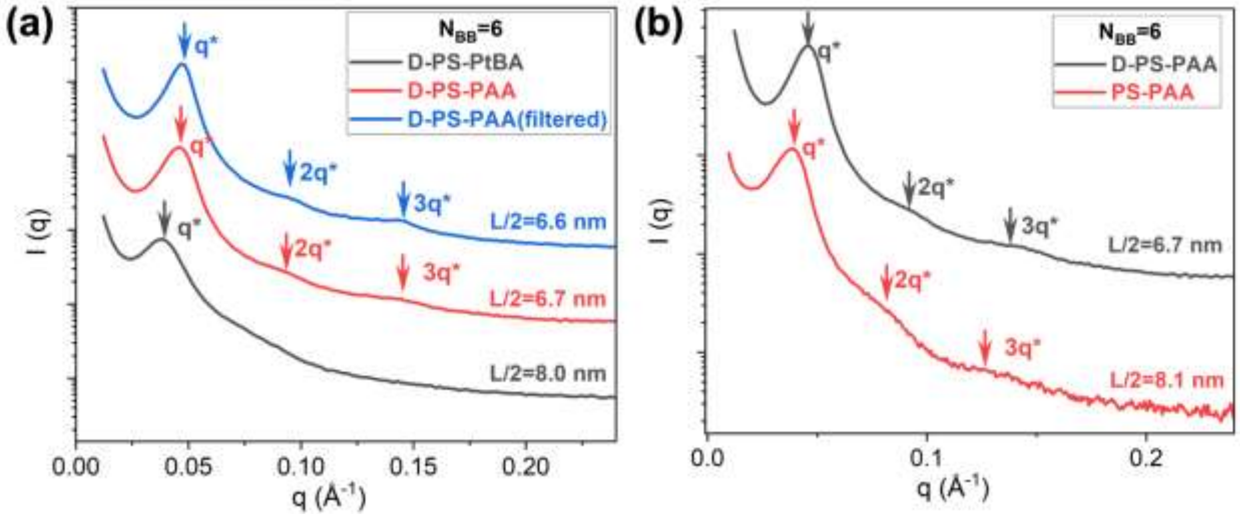


Figure S20. SAXS results of Janus bottlebrush copolymers at N_{BB}=6 in bulk. **(a)** Before conversion and after conversion of deuterated Janus bottlebrush copolymers. The filtered sample is prepared by filtering (D-PS-PAA)$_6$ in butyl acetate solution. **(b)** Comparison between deuterated and hydrogenated Janus bottlebrush copolymers with similar side chain length and N_{BB}=6. All samples are thermal annealed at 155 °C at vacuum overnight to reach equilibrium.

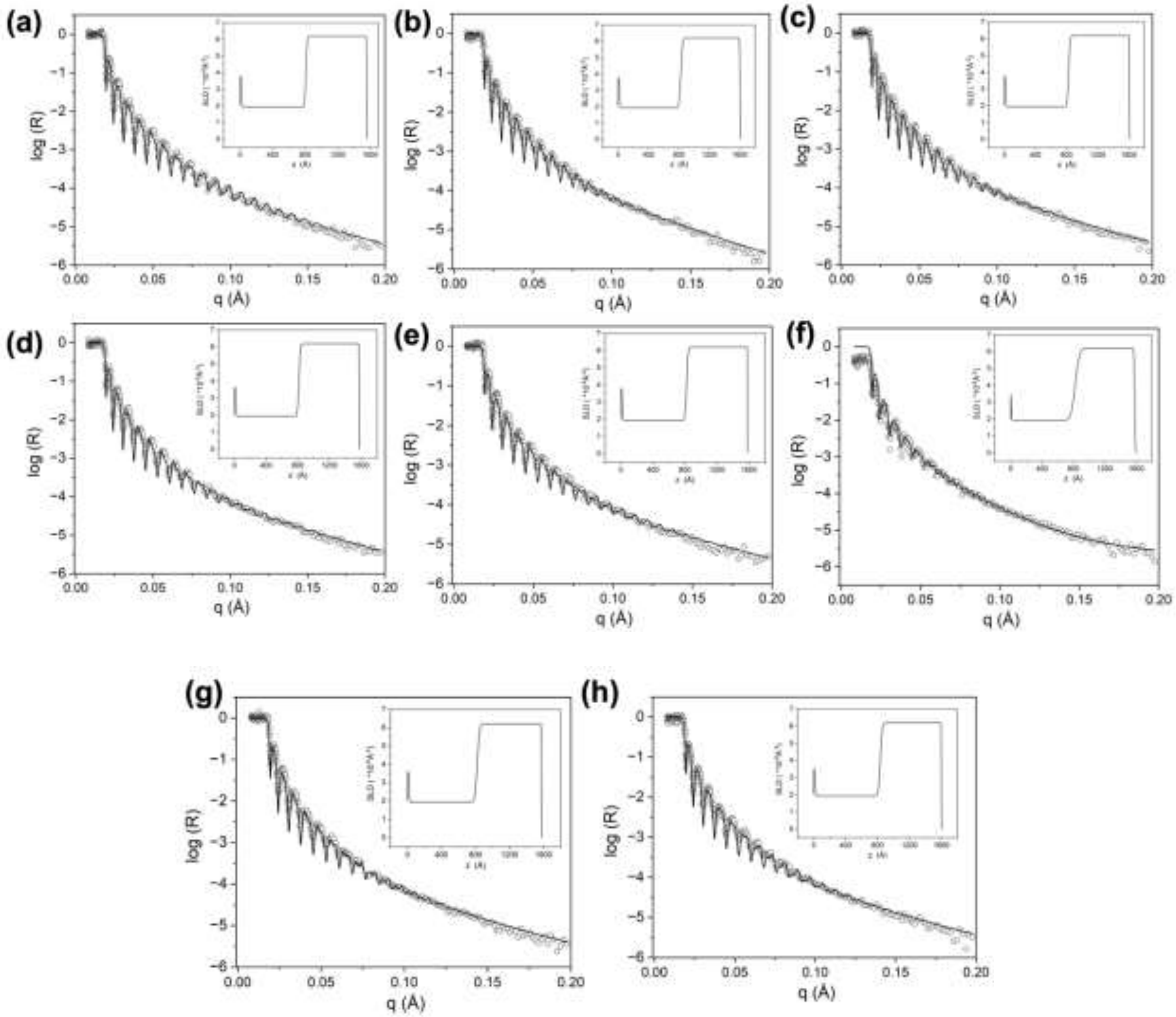


Figure S21. Neutron reflectivity of trilayer samples comprising DPS || (DPS-PAA)n || P2VP with variation of architectures. The open symbol is original data, the solid line is fitting, the corresponding SLD profile is embedded in the figure. **(a)** absence of BCPs. **(b)** N_{BB}=6. **(c)** N_{BB}=24. **(d)** N_{BB}=100, grafting density 100% **(e)** N_{BB}=250. **(f)** N_{BB}=100, grafting density 80%. **(g)** N_{BB}=100, grafting density 50%. **(h)** N_{BB}=100, grafting density 20%.

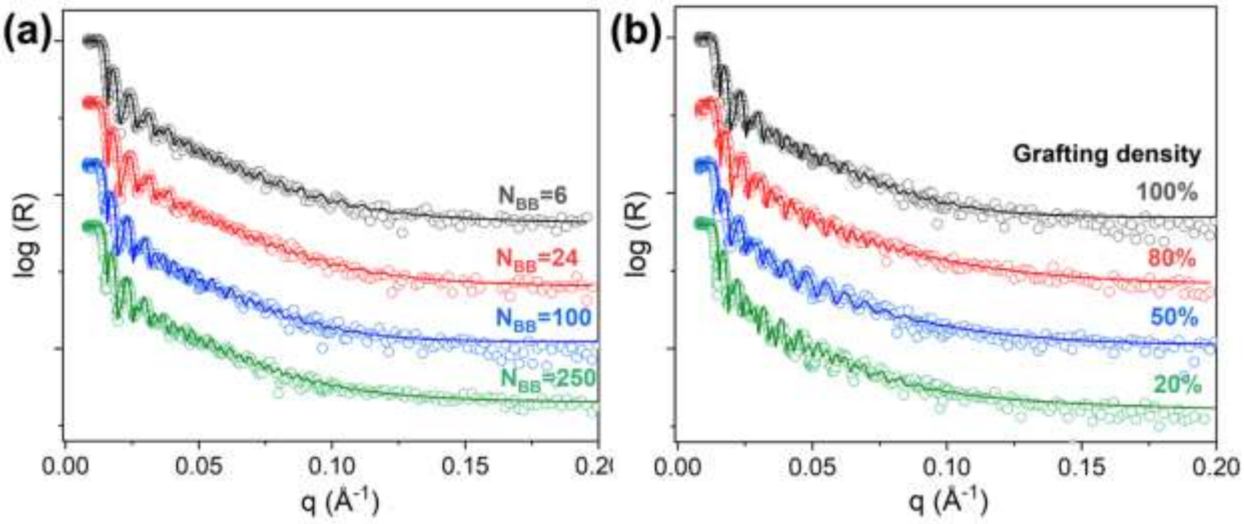


Figure S22. Neutron reflectivity of trilayer samples comprising PS || (DPS-PAA)n || DP2VP with variation of architectures. The open symbol is original data, the solid line is fitting. **(a)** With variation of N_{BB} at 100% grafting density. **(b)** With variation of grafting density at N_{BB}=100.

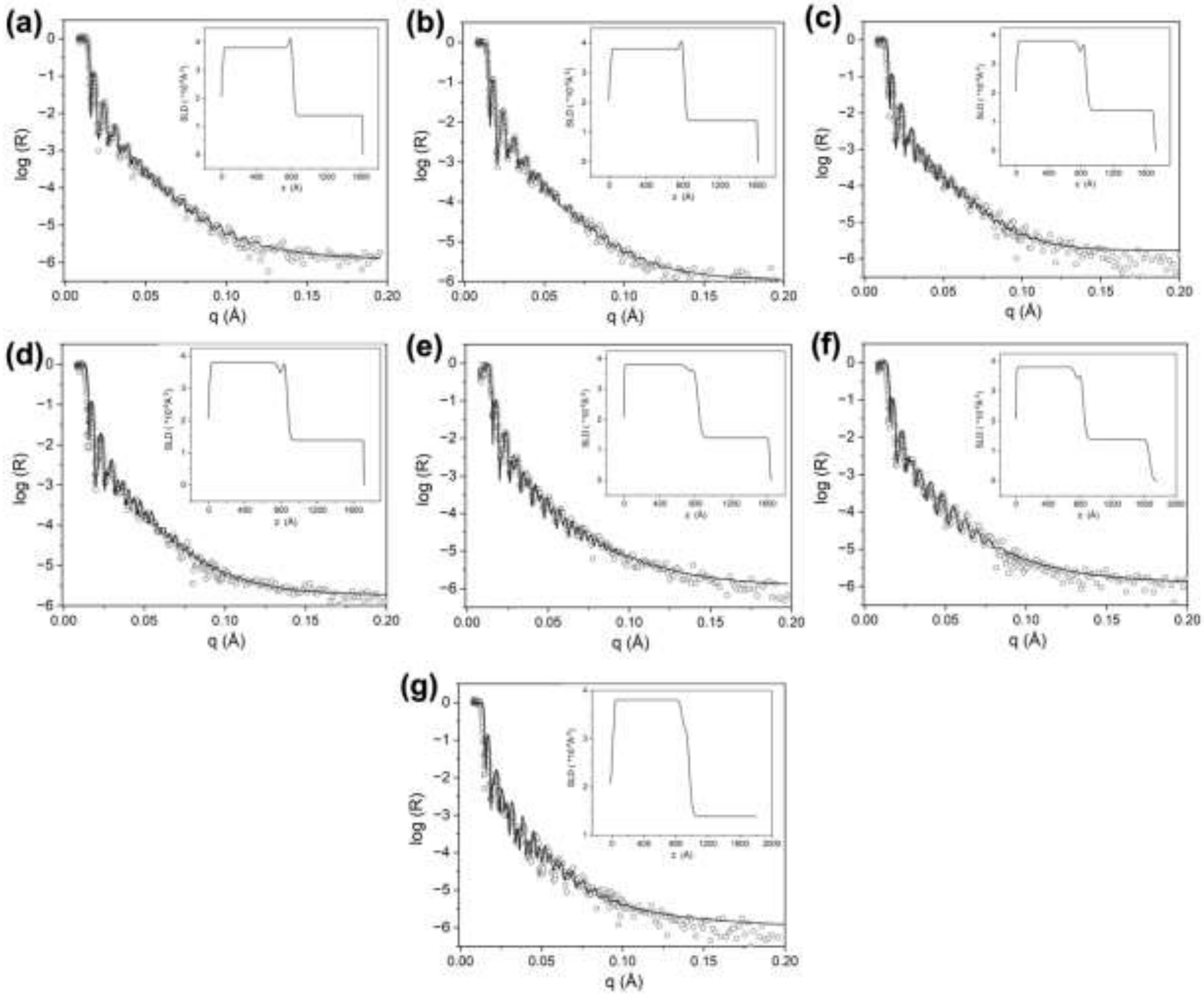


Figure S23. Neutron reflectivity of trilayer samples comprising PS || (DPS-PAA)n || DP2VP with variation of architectures. The open symbol is original data, the solid line is fitting, the corresponding SLD profile is embedded in the figure. **(a)** N_{BB}=6. **(b)** N_{BB}=24. **(c)** N_{BB}=100, grafting density 100% **(d)** N_{BB}=250. **(e)** N_{BB}=100, grafting density 80%. **(f)** N_{BB}=100, grafting density 50%. **(g)** N_{BB}=100, grafting density 20%.

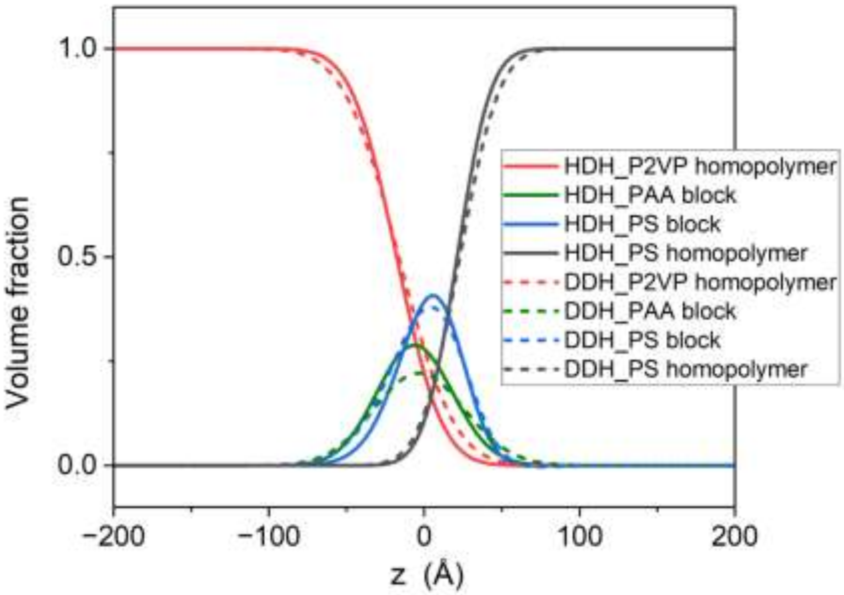


Figure S24. Comparison of segmental density distribution of N_{BB}=6 solved from two different deuterium contrasts. HDH: PS ‖ (DPS-PAA)n ‖ P2VP ; DDH: PS ‖ (DPS-PAA)n ‖ DP2VP .

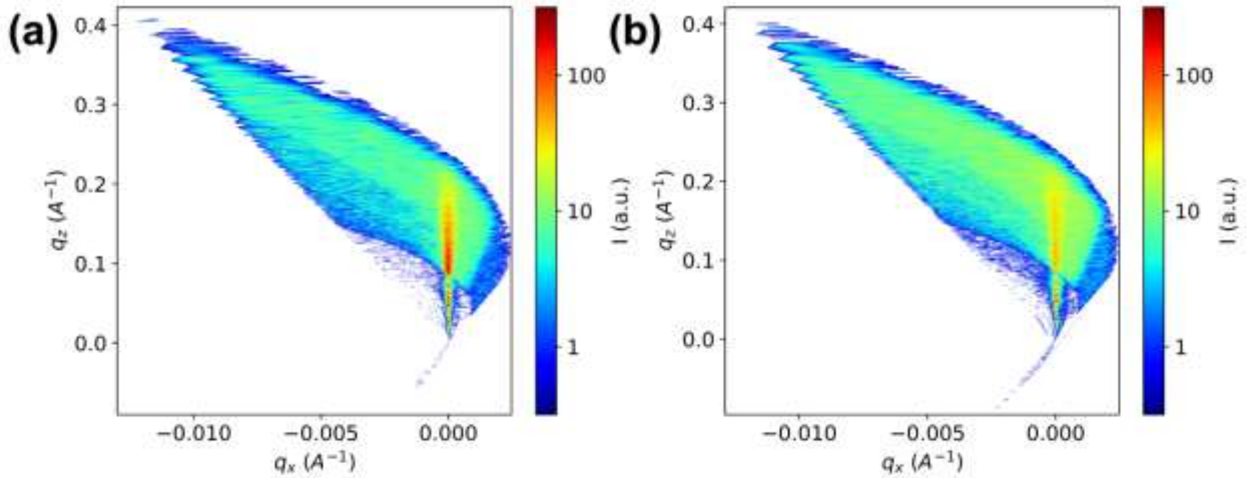


Figure S25. Off-specular neutron reflectivity of N_{BB}=6 for different deuterium contrasts. **(a)** DPS || (DPS-PAA)n || P2VP. **(b)** PS || (DPS-PAA)n || P2VP. Despite the efforts to solve off-specular reflection from 2D detector in LIQREF at ONRL SNS site, the detector height is limited, only giving q_x in highly narrow range. Consequently, only specular reflection was observed. The potential off-specular or in-plane interference may be answered by GISANS in the future.

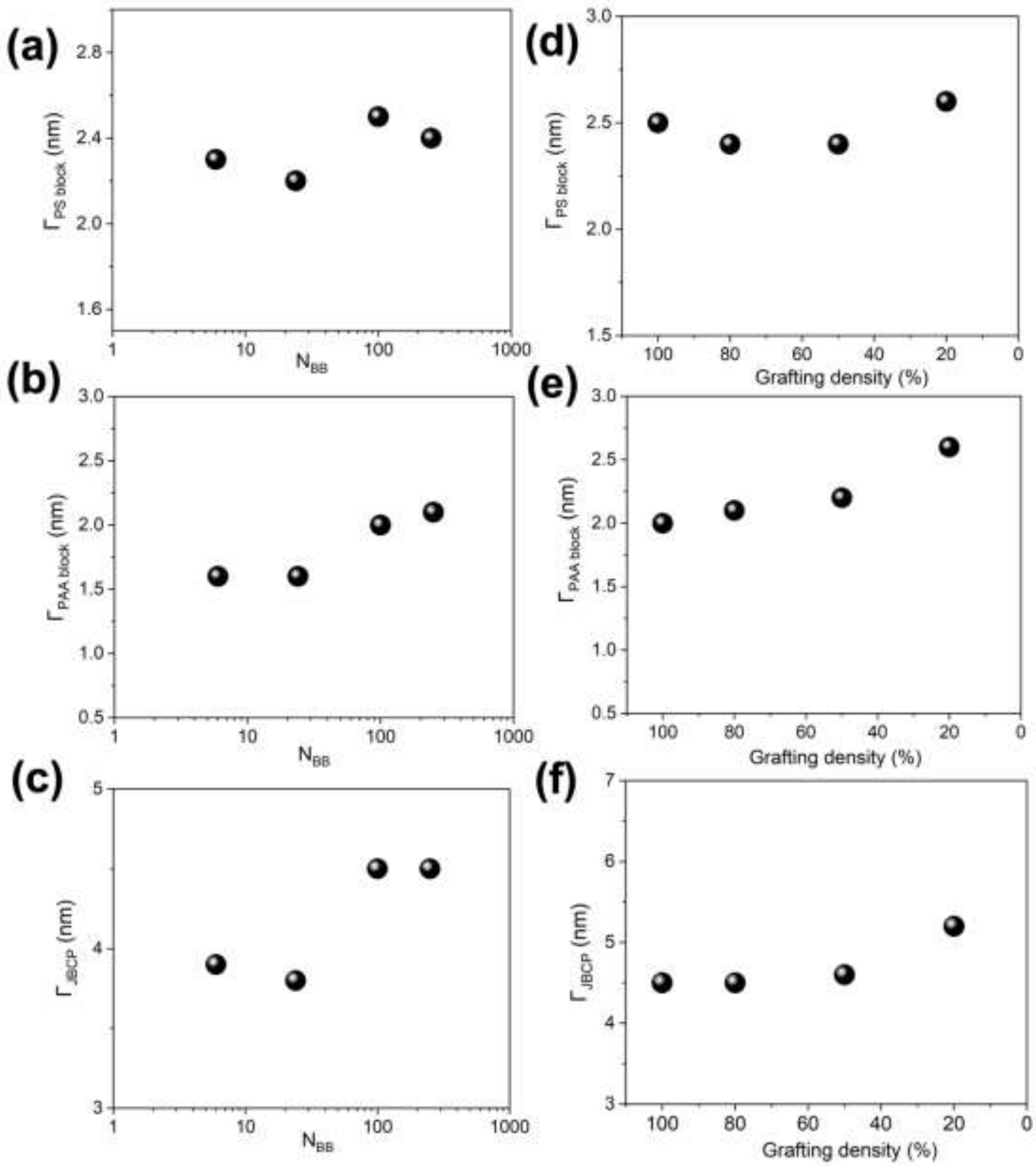


Figure S26. Surface excess (Γ) with variation of architectures, calculated from segmental density distribution using $\Gamma = \int_{-\infty}^{\infty} \Phi_{blocks} d_z$ or $\Gamma_{JBCP} = \int_{-\infty}^{\infty} (\Phi_{PS\ block} + \Phi_{PAA\ block}) d_z$. $\Gamma_{PS\ block}$ with varied **(a)**N_{BB}, **(d)**grafting density. $\Gamma_{PAA\ block}$ with varied **(b)**N_{BB}, **(e)**grafting density. Γ_{JBCP} with varied **(c)**N_{BB}, **(f)**grafting density.

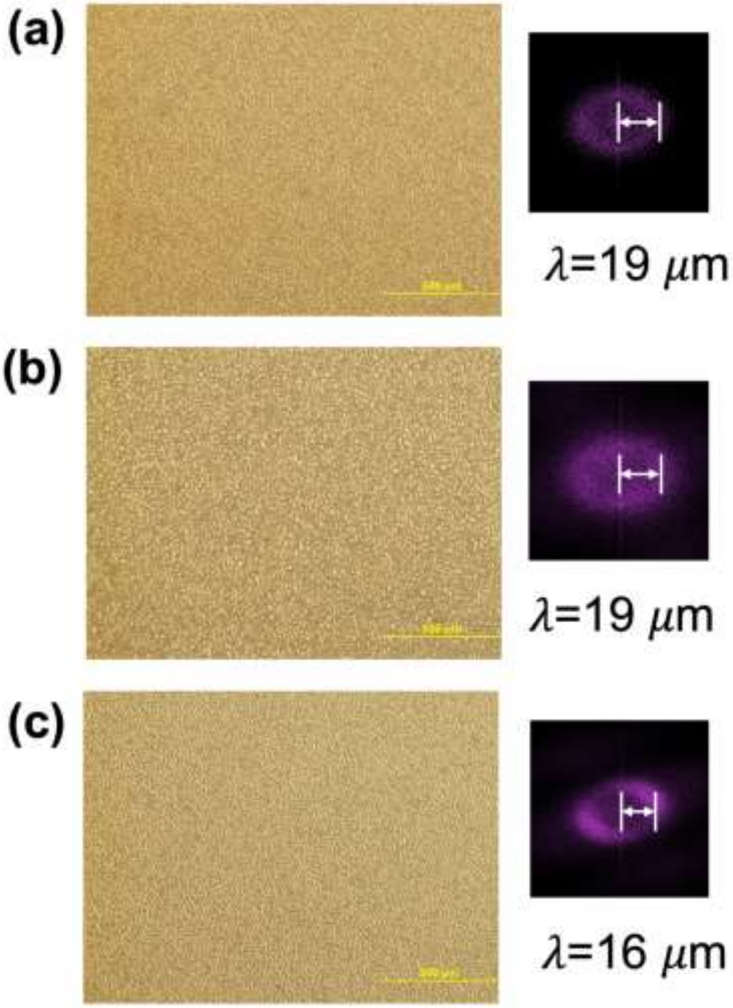


Figure S27. Representative POM images for thin films of blends with bicontinuous morphology. **(a)**N_{BB}=6. **(b)**N_{BB}=24 **(c)** N_{BB}=100, grafting density 80%. The embedded right images show the fast Fourier transform (FFT) results of POM with characteristic length.

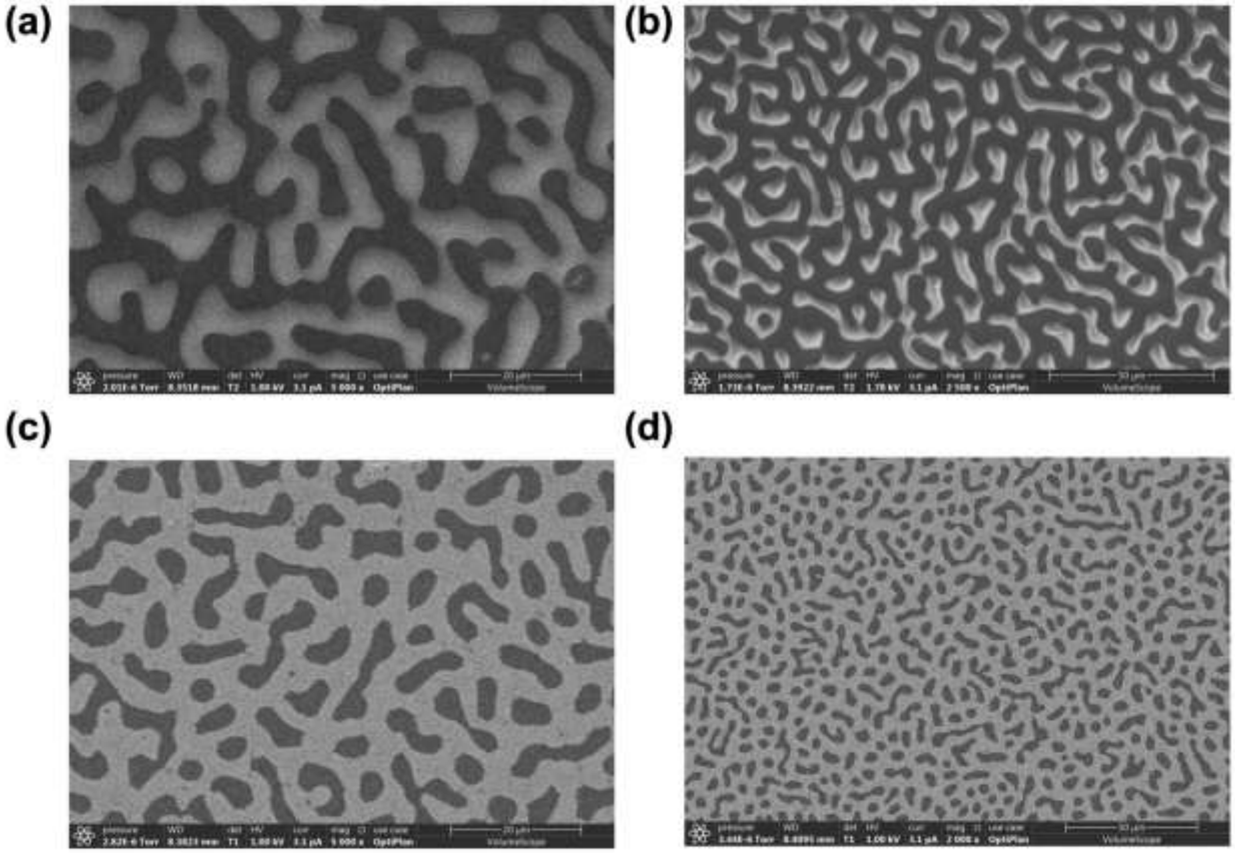


Figure S28. Representative SEM images for thin films of blends. **(a)-(b)** N_{BB}=6. **(c)-(d)** N_{BB}=100.

References

(1) H. -G. Seong, Z. Chen, T. Emrick, T. P. Russell, Reconfiguration and Reorganization of Bottlebrush Polymer Surfactants, *Angew. Chem. Int. Ed.* **2022**, 61, e202200530.

(2) H. -G. Seong, Z. Fink, Z. Chen, T. Emrick, T. P. Russell, Bottlebrush Polymers at Liquid Interfaces: Assembly Dynamics, Mechanical Properties, and All-Liquid Printed Constructs, *ACS Nano* **2023**, 17, 14731-14741.

(3) C. M. Bates, A. B. Chang, N. Momčilović, S. C. Jones, R. H. Grubbs, ABA Triblock Brush Polymers: Synthesis, Self-Assembly, Conductivity, and Rheological Properties, *Macromolecules* **2015**, 48, 14, 4967-4973.