

Supporting Information

**Enhancing Mechanochemical Activation in the Bulk State by
Designing Polymer Architectures**

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Experimental details

Materials and Instruments

All solvents and reagents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Tokyo Chemical Industry, and Kanto Chemical and used as received, unless otherwise noted. Dihydroxy DABBF,¹ tetrahydroxy DABBF,² 5-hexynoyl chloride³, and 1,4-bis(phenylethenyl)benzene⁴ (PEB) were synthesized according to previously published methods. Copper (I) bromide (CuBr) was washed with glacial acetic acid and with ethanol and dried at 70 °C. Styrene and 1,3-dibromopropane were distilled under reduced pressure over calcium hydride before used. Prior to use for anionic polymerization, styrene was redistilled over di-*n*-butylmagnesium (Bu₂Mg) (~5 mol %) under reduced pressure. ¹H NMR spectroscopic measurements were carried out using 300 MHz Bruker spectrometer with tetramethylsilane (TMS) as internal standard in chloroform-*d* (CDCl₃). Analytical gel permeation chromatographic (GPC) measurements were carried out at 40 °C on TOSOH HLC-8320 GPC system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000, and 2500), a differential refractive index detector, and a UV-vis detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene (PS) standards ($M_n = 4430\text{--}3242000$; $M_w/M_n = 1.03\text{--}1.08$) were used to calibrate the GPC system. The absolute molecular weight of four-arm star polystyrenes with DABBF was measured on an Asahi Techneion AT-2002 equipped with a Viscotek TDA model 302 triple detector array using THF as a carrier solvent at a flow rate of 1.0 mL min⁻¹ at 30 °C. Three PS gel column (pore size (bead size)) were used: 650 Å (5 μm), 200 Å (5 μm), 75 Å (5 μm). Preparative GPC separating of the target polymers was run on JAI LC-9104 recycling preparative HPLC (JAIGEL 2.5H/3H column assembly) with chloroform as eluent.

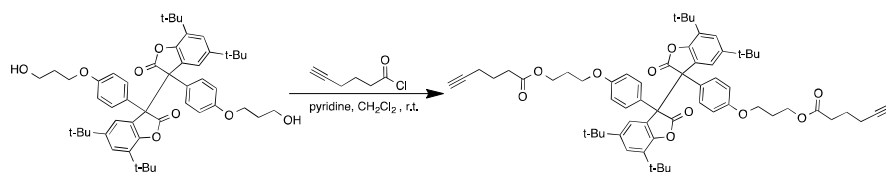
Grinding tests and electron paramagnetic resonance (EPR) spectroscopy

Grinding tests were performed on an auto-grinding machine, STM-D from ASONE. The mechanical energy was controlled by the rotational speed of the mortar. A powdered sample (100 mg) was placed in the mortar and ground for 10 min at 100 rpm. The ground sample was transferred into an EPR glass capillary, and the capillary was sealed after being degassed. EPR measurements were carried out on a JEOL JES-X320 X-band EPR spectrometer equipped with a JEOL DVT temperature controller. The spectra of ground samples were measured using a microwave power of 0.1 mW and a field modulation of 0.1 mT with a time constant of 0.03 s and a sweep rate of 0.25 mT/s at 25 °C. The concentration of the radicals formed from the cleavage of DABBF was determined by comparing the area of the observed integral spectrum with a 0.01 mM solution of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOL) in benzene under the same experimental conditions. The g value was calculated according to the following equation: $g = hv/\beta H$ where h is the Planck constant, ν is the microwave frequency, β is the Bohr magneton, and H is the magnetic field.

Variable-Temperature EPR spectroscopy

EPR measurements were carried out on a JEOL JES-X320 X-band EPR spectrometer equipped with a JEOL DVT temperature controller. The measured powdered samples were filled to 5 mm glass capillaries, and the capillaries were sealed after being degassed. Spectra were measured using microwave power of 0.1 mW and a field modulation of 0.1 mT with a time constant of 0.03 s and a sweep rate of 0.25 mTs⁻¹. The concentration of the radicals formed from cleaved DABBF was determined by comparing the area of the observed integral spectrum with that of 0.01 mM TEMPOL in benzene under the same experimental condition; the Mn²⁺ signal was used as an auxiliary standard.

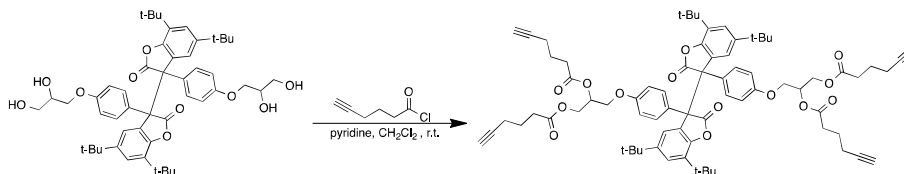
Synthesis of diarylbibenzofuranone-dialkyne derivative



Dihydroxy-DABBF (2.0 g, 2.5 mmol) was added to a flask. The flask was degassed and back-filled with nitrogen three times. CH_2Cl_2 (15 mL) and pyridine (2.5 mL, 30 mmol) were added to the flask under nitrogen flow. 5-hexynoyl chloride (1.2 mL, 10 mmol) was then added dropwise to the flask at 0 °C. The mixture was stirred at 0 °C for 1 h and at room temperature for 18.5 h. To stop the reaction, deionized water was added to the flask. The reaction mixture was extracted with CH_2Cl_2 three times. The organic layer was washed with water twice and brine once, dried over anhydrous MgSO_4 , and evaporated. The crude product was purified by silica gel column chromatography eluting with ethyl acetate/*n*-hexane (1/2). The desired compound was dried under vacuum (2.4 g, 96%). ^1H NMR spectrum of DABBF-dialkyne derivative was shown in Figure S1.

^1H NMR (300 MHz, CDCl_3): δ /ppm 1.16 (br, 18H, CH_3), 1.31 (br, 18H, CH_3), 1.85 (m, 4H, CH_2), 1.96 (t, 2H, CH), 2.13 (m, 4H, CH_2), 2.26 (m, 4H, CH_2), 2.47 (t, $J = 7.4$ Hz, 4H, CH_2), 4.07 (m, 4H, CH_2), 4.28 (t, 4H, CH_2), 6.82 (d, 6H, aromatic proton), 7.27 (br, 6H, aromatic proton). ^{13}C NMR: (75 MHz, CDCl_3): δ /ppm 17.72, 23.44, 29.57, 31.44, 34.26, 34.61, 61.11, 64.20, 69.17, 83.08, 113.03, 123.88, 132.19, 133.39, 145.58, 149.02, 158.73, 172.94.

Synthesis of diarylbibenzofuranone-tetraalkyne derivative

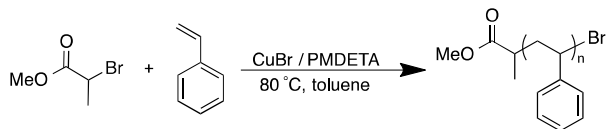


Tetrahydroxy-DABBF (2.0 g, 2.4 mmol) was added to a flask. The flask was degassed and back-filled with nitrogen three times. CH_2Cl_2 (20 mL) and pyridine (3.1 mL, 39 mmol) were added to the flask under nitrogen flow. 5-hexynoyl chloride (2.3 mL, 19 mmol) was

then added dropwise to the flask at 0 °C. The mixture was stirred at 0 °C for 1 h and at room temperature for 27.5 h. To stop the reaction, deionized water was added to the flask. The reaction mixture was extracted with CH₂Cl₂ three times. The organic layer was washed with water twice and brine once, dried over anhydrous MgSO₄, and evaporated. The crude product was purified by silica gel column chromatography eluting with ethyl acetate/*n*-hexane (1/4). The desired compound was dried under vacuum (2.5 g, 85%). ¹H NMR spectrum of DABBF-tetraalkyne derivative was shown in Figure S2.

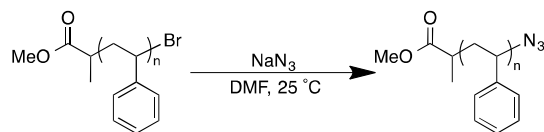
¹H NMR (300 MHz, CDCl₃): δ/ppm 1.17 (br, 18H, CH₃), 1.31 (br, 18H, CH₃), 1.84 (m, 8H, CH₂), 1.97 (m, 4H, CH), 2.27 (m, 8H, CH₂), 2.48 (m, 8H, CH₂), 4.13 (m, 4H, CH₂), 4.30 (m, 2H, CH₂), 4.47 (m, 2H, CH₂), 5.41 (m, 3H, CH), 6.82 (d, 6H, aromatic proton), 7.28 (br, 6H, aromatic proton). ¹³C NMR: (75 MHz, CDCl₃): δ/ppm 17.63, 17.65, 23.34, 23.39, 29.55, 31.43, 32.50, 32.70, 34.61, 62.32, 69.28, 69.41, 82.97, 113.13, 132.24, 133.47, 149.00, 158.20, 158.21, 172.21, 172.54.

Synthesis of bromine-terminated polystyrene⁴



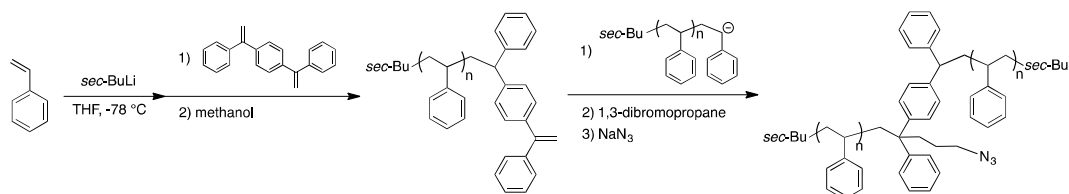
In a typical run, styrene (9.0 mL, 78 mmol), toluene (6.0 mL), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) (163 μL, 0.78 mmol), and methyl 2-bromopropionate (87 μL, 0.78 mmol) were added to a schlenk flask. The schlenk flask was degassed by means of three freeze-pump-thaw cycles and filled with nitrogen. The schlenk flask was carefully opened and CuBr (112 mg, 0.78 mmol) was quickly added, after which the schlenk flask was degassed again with three freeze-pump-thaw cycles, filled with nitrogen, sealed, and heated at 80 °C for 4.5 h. The reaction was stopped by opening the flask and exposing the catalyst to air. The mixture was diluted in tetrahydrofuran (THF) and passed through a neutral alumina column in order to remove the copper catalyst. The mixture was concentrated by rotary evaporation and subsequently precipitated in methanol. The precipitated bromine-terminated polystyrene was filtered and dried under vacuum at 40 °C to afford a white powder (3.0 g, 77% yield). The *M_n* and *M_w*/*M_n* values were determined by analytical GPC with polystyrene standards. *M_n* = 4900 g mol⁻¹, *M_w*/*M_n* = 1.20.

Synthesis of azide-terminated polystyrene⁵



In a typical run, bromine-terminated polystyrene (2.5 g, 0.50 mmol, 4900 g mol⁻¹), sodium azide (332 mg, 5.0 mmol), and DMF (25 mL) were added to a flask. The reaction mixture was stirred at 25 °C for 24 h. Then, the reaction mixture was precipitated in methanol, filtered, and dried under vacuum at 40 °C to afford a white azide-terminated polystyrene (2.5 g, 97 % yield). The substitution was verified by the signal shift of the methine proton neighboring the bromine in ¹H NMR spectra of the polymers before and after the reaction as shown in Figure S3.

Synthesis of in-chain azide-functionalized polystyrene



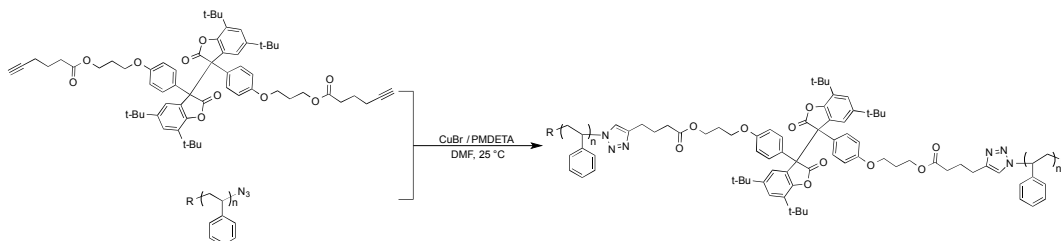
THF (40 mL) was transferred to a glass reactor equipped with stir bar and cooled to -78 °C. After 5 min, *sec*-BuLi was added until the color changed to slightly yellow. The reactor was removed from the cooling-bath and allowed to reach room temperature, upon which the solution became colorless. The reactor was cooled back to -78 °C, and 1.07 M *sec*-BuLi solution in hexane/cyclohexane (0.36 mmol) was added. After 5 min, styrene (4.5 mL, 39.2 mmol) was added to the reactor with vigorous stirring. After 10 min, PEB that had been dried under reduced pressure for several hours (0.13 g, 0.47 mmol) was dissolved in THF (5.0 mL) and transferred from the reservoir to the polymerization flask via syringe with vigorous stirring. The solution color changed deep blue. After 1 h at -78 °C, excess of methanol was added to the reactor to obtain the proton-terminated polymer. It was purified by reprecipitation twice from THF into

methanol and freeze-drying from its absolute benzene solution (3.91 g, 96%). ^1H NMR (300 MHz, CDCl_3): δ /ppm 0.74-0.87 (br, isobutyl), 1.18-2.16 (br, PS backbone), 5.40 (s, $\text{CH}_2=\text{C}$), 6.22-7.23 (br, PS). $M_n = 11200 \text{ g mol}^{-1}$

A THF solution (20.0 mL) of ω -chain-ended DPE-functionalized PS (3.80 g, 0.34 mmol, $M_n = 11\,200$) pre-cooled at $-78\text{ }^\circ\text{C}$, was added to prior prepared the living polystyrene (0.40 mmol, $M_n = 9\,600 \text{ g mol}^{-1}$) at $-78\text{ }^\circ\text{C}$ for 10 min. The reaction mixture was allowed to stand at $-78\text{ }^\circ\text{C}$ for 3 h. Then, the resulting in-chain anion reacted with 1,3-dibromopropane (0.83 g, 3.40 mmol) in THF (3.0 mL) at $-78\text{ }^\circ\text{C}$ for 3 h. The reaction mixture was terminated by a small amount of degassed methanol and poured into a large amount of methanol to precipitate the polymer. The objective in-chain bromo-functionalized polystyrenes was isolated by fractional precipitation using cyclohexane and hexane mixtures in 83% yield. ^1H NMR (300 MHz, CDCl_3): δ /ppm 0.74-0.87 (br, isobutyl), 1.18-2.16 (br, PS backbone), 3.22 (br, Br-CH_2-), 6.22-7.23 (br, PS). $M_n = 20200 \text{ g mol}^{-1}$.

The bromo function of polymer (6.00 g, 0.29 mmol) was converted to the azide group by reacted with sodium azide (0.18 g, 2.90 mmol) in the same manner as mentioned above (5.72 g, 97%). ^1H NMR (300 MHz, CDCl_3): δ /ppm 0.74-0.87 (br, isobutyl), 1.18-2.16 (br, PS backbone), 2.86 (br, $\text{N}_3\text{-CH}_2-$), 6.22-7.23 (br, PS).

Synthesis of linear polystyrene with diarylbibenzofuranone functionality in the center of polymer chain⁵

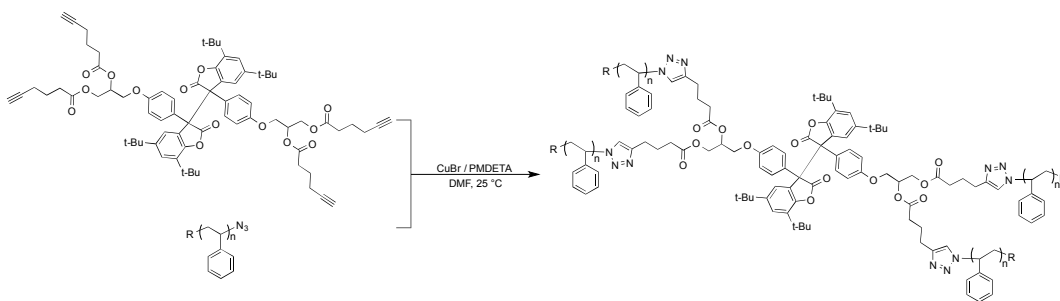


In a typical run, azide-terminated polystyrene (1.3 g, 0.26 mmol, 4900 g mol^{-1}), DABBF-dialkyne derivative (127 mg, 0.13 mmol), DMF (13 mL), and PMDETA (54 μL , 0.26 mmol) were added to a flask. The flask was capped with a septum and the mixture was bubbled with nitrogen for 20 min. The flask was carefully opened and CuBr (37 mg, 0.26 mmol) was quickly added, after which the flask was filled with nitrogen and sealed. The mixture was stirred

at 25 °C for 24 h. The reaction was stopped by opening the flask and exposing the catalyst to air. The mixture was diluted in THF, passed through a neutral alumina column in order to remove the copper catalyst, concentrated, and subsequently precipitated in methanol. The precipitated polymer was filtered and dried under vacuum at 40 °C. The target linear polymer was isolated by preparative GPC, fractional precipitation using cyclohexane/hexane, and precipitation in methanol, and dried under vacuum at 40 °C to afford a white powder (0.61 g, 50 % yield). ¹H NMR spectrum of the linear polymer was shown in Figure S4. The M_n and M_w/M_n values were determined by analytical GPC with polystyrene standards (Figure S5). $M_n = 13100 \text{ g mol}^{-1}$, $M_w/M_n = 1.05$.

¹H NMR (300 MHz, CDCl₃): δ /ppm 0.81-0.94 (br, -CHCH₃), 1.13 (br, ^tBu), 1.19-2.15 (br, PS backbone), 2.25 (br, CH₂), 2.59 (br, CH₂), 3.42 (br, -OCH₃), 4.02 (br, CH₂), 4.22 (br, CH₂), 5.04 (br, -CHPh), 6.17-7.23 (br, PS).

Synthesis of four-arm star polystyrene with diarylbibenzofuranone functionality at the core

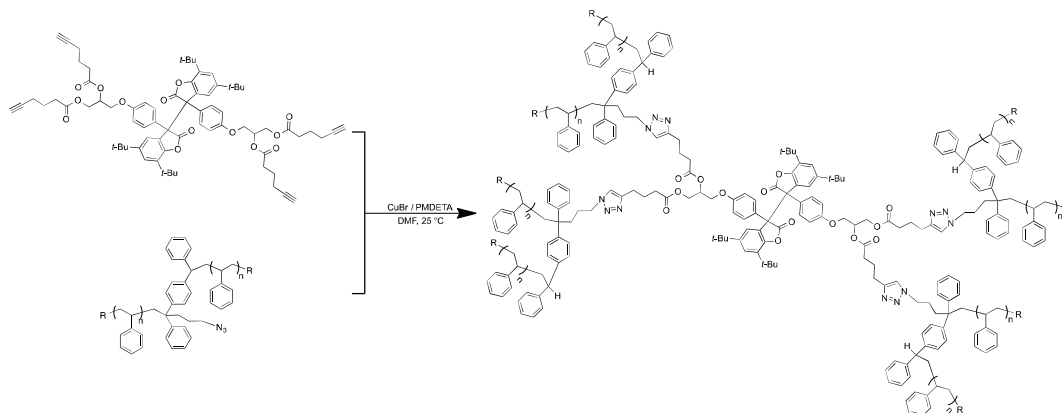


Azide-terminated polystyrene (2.0 g, 0.17 mmol, 11600 g mol⁻¹), DABBF-tetraalkyne derivative (41 mg, 0.034 mmol), DMF (15 mL), and PMDETA (36 μ L, 0.17 mmol) were added to a flask. The flask was capped with a septum and the mixture was bubbled with nitrogen for 20 min. The flask was carefully opened and CuBr (25 mg, 0.17 mmol) was quickly added, after which the flask was filled with nitrogen and sealed. The mixture was stirred at 25 °C for 24 h. The reaction was stopped by opening the flask and exposing the catalyst to air. The mixture was diluted in THF, passed through a neutral alumina column in order to remove the copper catalyst, concentrated, and subsequently precipitated in methanol. The precipitated polymer was filtered and dried under vacuum at 40 °C. The target star polymer was isolated by fractional precipitation using cyclohexane/hexane and then

precipitation in methanol, and dried under vacuum at 40 °C to afford a white powder (0.68 g, 45 % yield). The M_n and M_w/M_n values were estimated by analytical GPC with polystyrene standards. $M_n = 38600 \text{ g mol}^{-1}$, $M_w/M_n = 1.05$. The absolute M_n value was estimated by GPC equipped with RI, viscometer, and right angle laser light scattering (RALLS) detection. M_n (GPC-RALLS) = 44200 g mol^{-1} .

^1H NMR (300 MHz, CDCl_3): δ /ppm 0.80-0.94 (br, $-\text{CHCH}_3$), 1.14 (br, ^tBu), 1.19-2.16 (br, PS backbone), 2.26 (br, CH_2), 2.58 (br, CH_2), 3.41 (br, $-\text{OCH}_3$), 4.04 (br, CH_2), 4.23 (br, CH_2), 5.05 (br, $-\text{CHPh}$), 6.16-7.25 (br, PS).

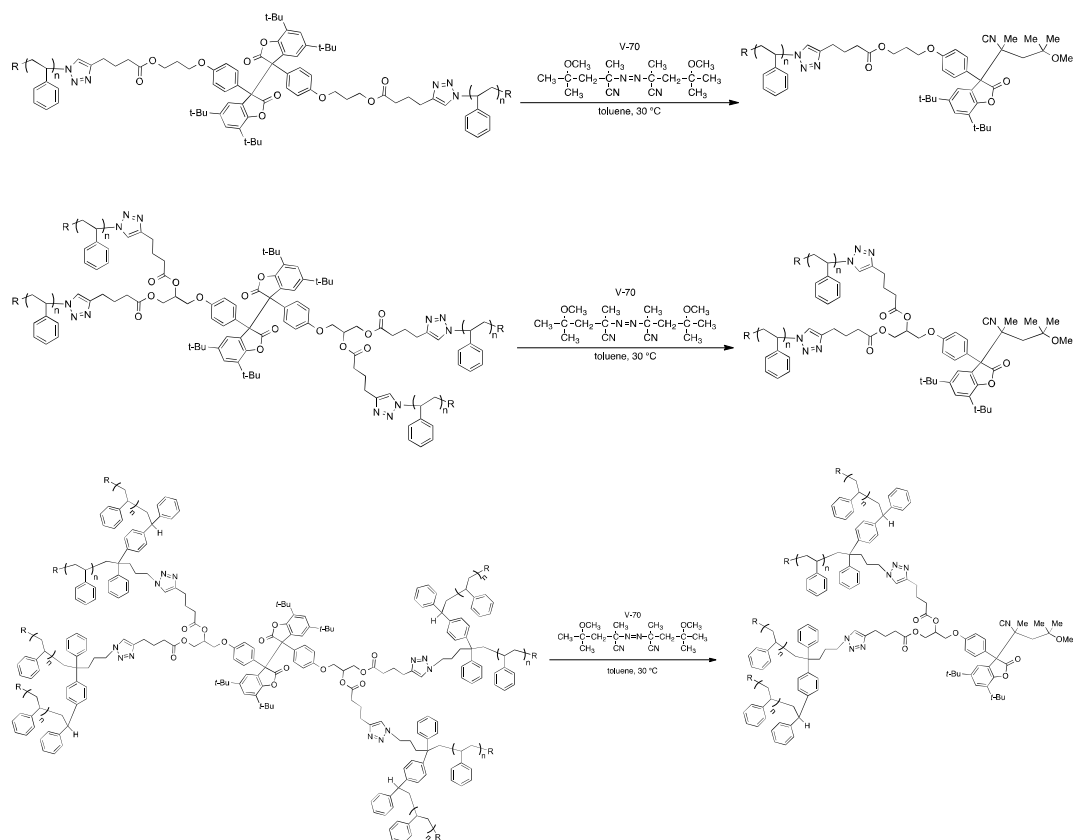
Synthesis of eight-arm star polystyrene with diarylbibenzofuranone functionality at the core



Eight-arm star polystyrene with diarylbibenzofuranone functionality at the core was synthesized by click reaction as similar manner using in-chain azide-functionalized polystyrene (5.0 g, 0.24 mmol), DABBF-tetraalkyne derivative (64 mg, 0.054 mmol), DMF (45 mL), CuBr (34.4 mg, 0.24 mmol), and PMDETA (51 μL , 0.24 mmol). The target star polymer was isolated by fractional precipitation (1.98 g, 44 % yield). The absolute M_n value was estimated by GPC equipped with RI, viscometer, and right angle laser light scattering (RALLS) detection. M_n (GPC-RALLS) = 81600 g mol^{-1} .

^1H NMR (300 MHz, CDCl_3): δ /ppm 0.71-0.87 (br, isobutyl), 0.88-0.94 (br, $-\text{CHCH}_3$), 1.14 (br, ^tBu), 1.18-2.42 (br, PS backbone and CH_2), 2.62 (br, CH_2), 4.12 (br, CH_2), 4.25 (br, CH_2), 6.16-7.25 (br, PS).

Selective Scission of DABBF units in the center of polymer structure



Linear polystyrene with DABBF in the center of polymer chain (50 mg, $3.8 \mu\text{mol}$, 11600 g mol^{-1}) and toluene (3.8 mL) were added to a test tube. The reaction vessel was capped with a septum and the mixture was bubbled with nitrogen for 20 min. 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (24 mg, 0.077 mmol) was added to the reaction vessel and the mixture was bubbled with nitrogen for 20 min. The reaction was carried out at 30 °C and traced by GPC. After 24 h, the reaction mixture was precipitated in methanol and the precipitated polymer was filtered and dried under vacuum (46 mg, 92% yield). The M_n and M_w/M_n values were estimated by analytical GPC with polystyrene standards (Figure S6). $M_n = 6700 \text{ g mol}^{-1}$, $M_w/M_n = 1.06$. The selective scission reaction condition of DABBF units in the star polymers ($M_{n\text{GPC}} = 38600$, 52100 g mol^{-1}) were similar to that mentioned above (over 90 % yield). The M_n and M_w/M_n values were estimated by analytical GPC with polystyrene standards (Figure S7,8). Four-arm star polystyrene: $M_n = 22000 \text{ g mol}^{-1}$, $M_w/M_n = 1.06$. Eight-arm star polystyrene: $M_n = 34600 \text{ g mol}^{-1}$, $M_w/M_n = 1.04$.

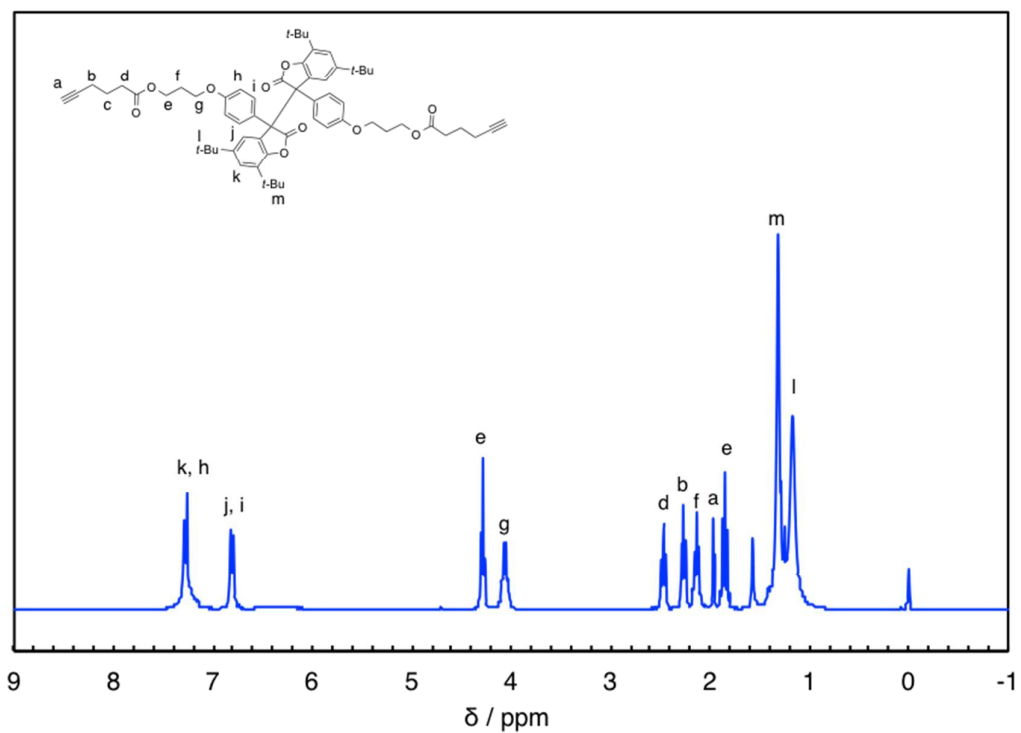


Figure S1. ¹H NMR spectrum of DABBF-dialkyne derivative.

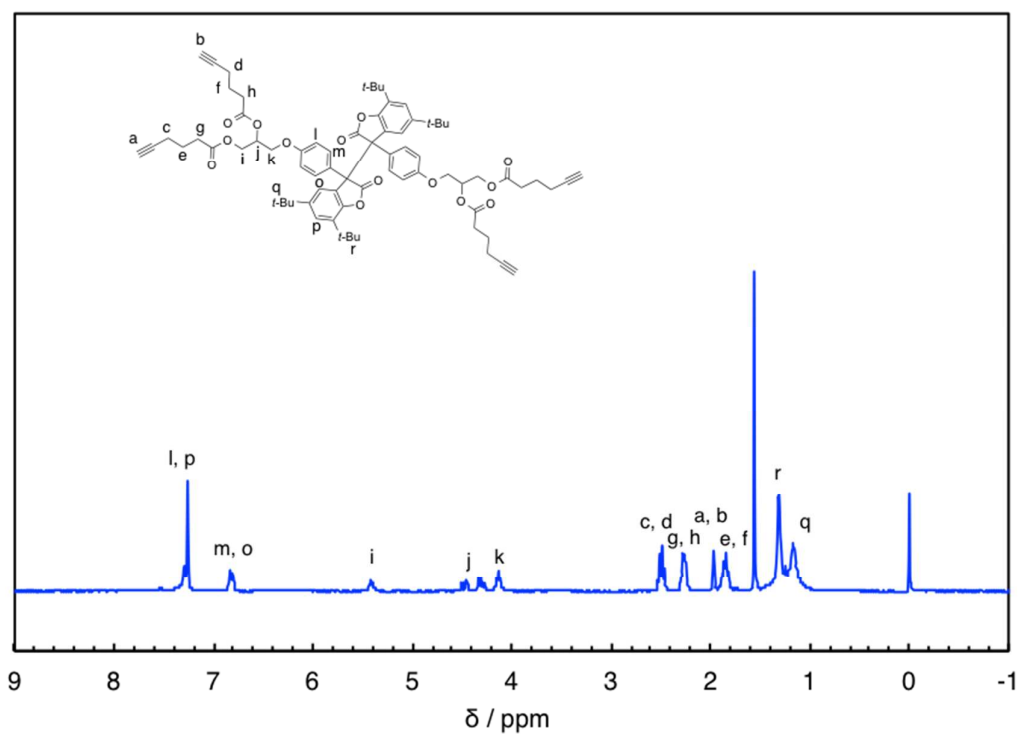


Figure S2. ¹H NMR spectrum of DABBF-tetraalkyne derivative.

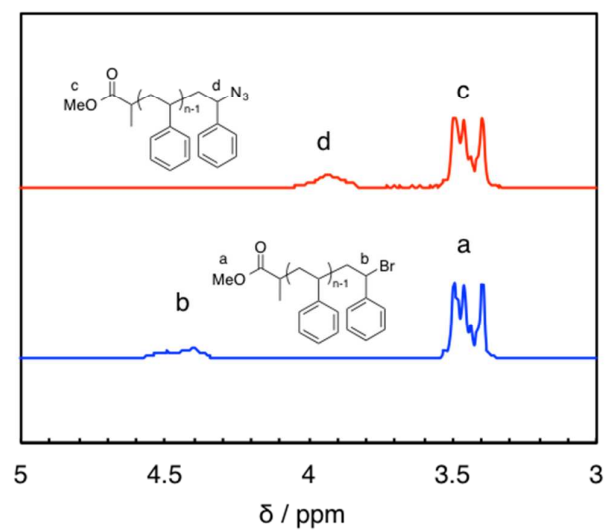


Figure S3. ^1H NMR spectra of bromine-terminated polystyrene ($M_n = 4900$) (blue) and azide-terminated polystyrene ($M_n = 4900$) (red) in the chemical shift range from 3.0 to 6.0 ppm.

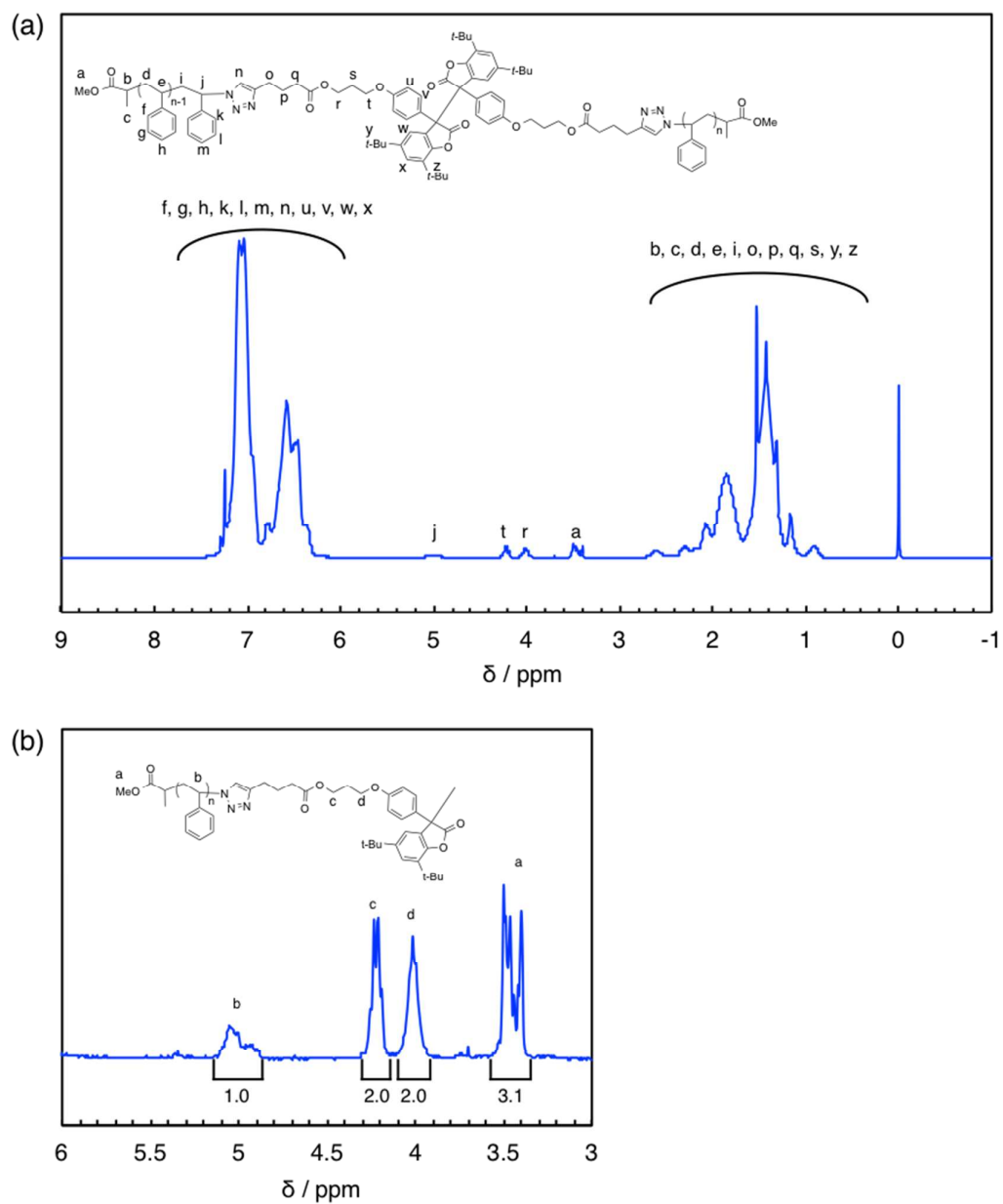


Figure S4. (a) ^1H NMR spectrum of linear polystyrene with DABBF in the center of polymer chain ($M_n = 13100$), and (b) the extended figure in the chemical shift range from 3.0 to 6.0 ppm.

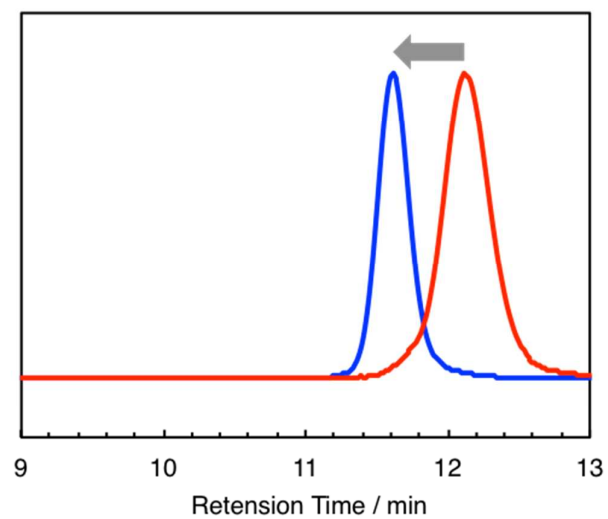


Figure S5. GPC profiles of azide-terminated polystyrene ($M_n = 4900$) (red) and DABBF mid-functionalized linear polystyrene ($M_n = 13100$) (blue).

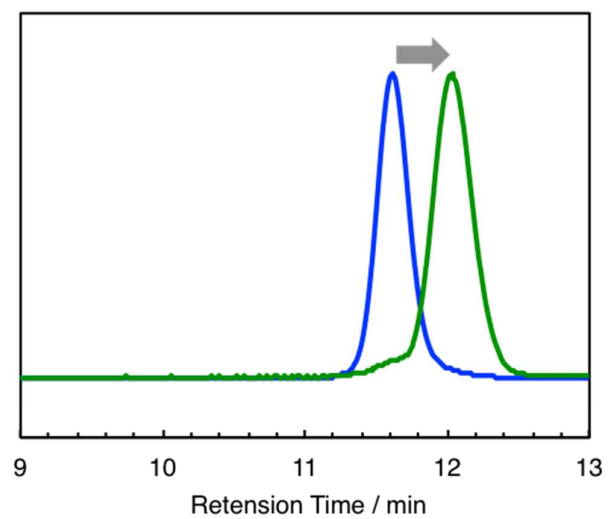


Figure S6. GPC profiles of linear polystyrene with DABBF in the center of polymer chain ($M_n = 13100$) before (blue) and after (green) treatment with a radical generator (V-70) ($M_n = 6700$).

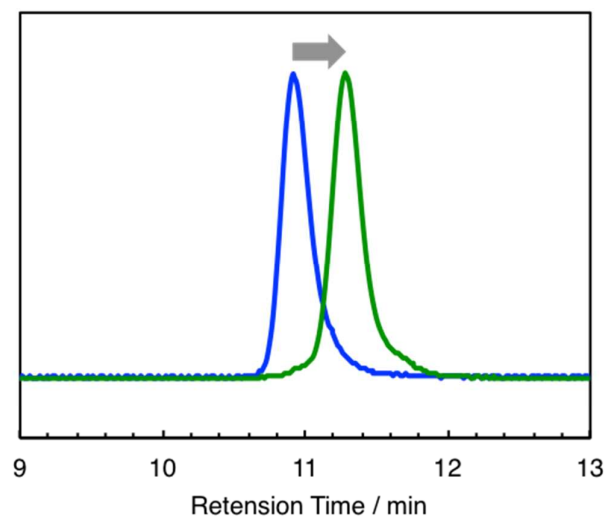


Figure S7. GPC profiles of star polystyrene with DABBF in the core of polymer structure ($M_n = 38600$) before (blue) and after (green) treatment with a radical generator (V-70) ($M_n = 22000$).

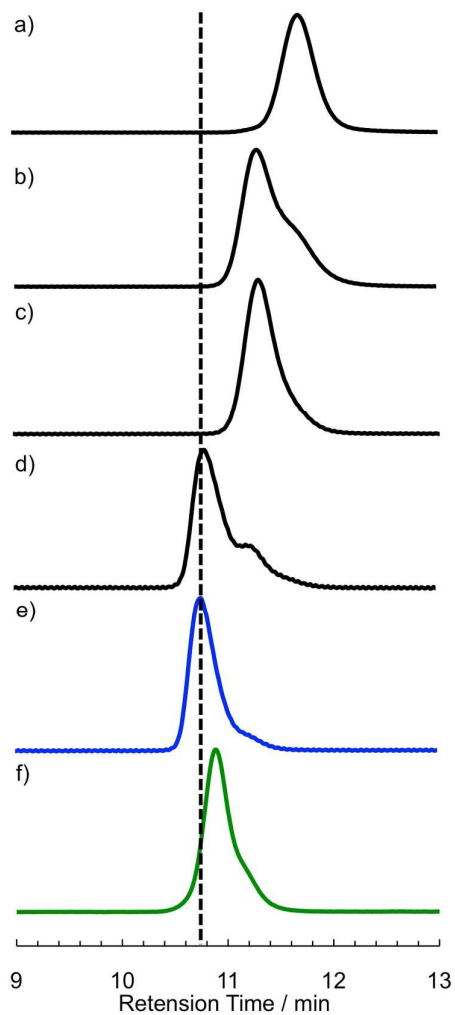


Figure S8. GPC profiles of a) chain-end diphenylethylene-functionalized polystyrene (PS-DPE), b) after addition reaction of PS-DPE and living polystyrene, c) in-chain-azide-functionalized polystyrenes (PS-(N₃)-PS), d) after click reaction of PS-(N₃)-PS and DABBF-dialkyne, e) eight-arm star polystyrene with DABBF in the core of polymer structure (blue), and f) after treatment with a radical generator (V-70) (green).

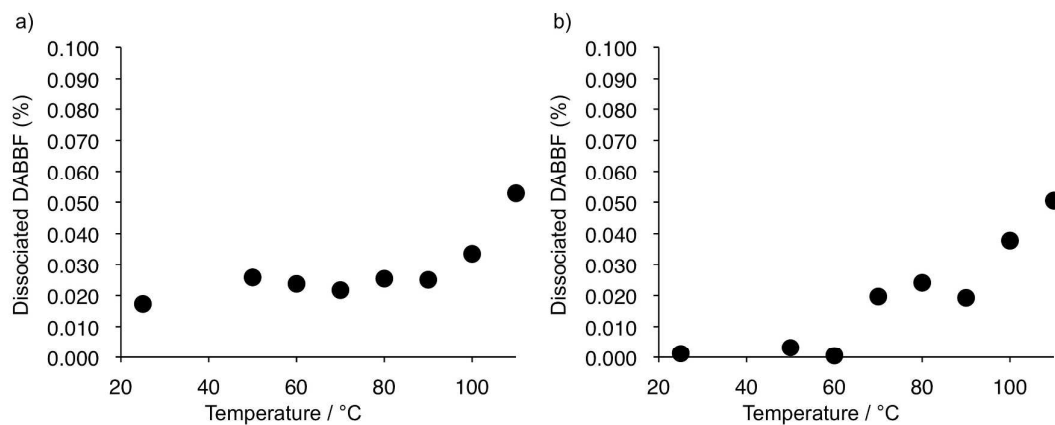


Figure S9. The ratio of dissociated DABBF in a) linear PS2 ($M_n = 24700 \text{ g mol}^{-1}$) and b) eight-arm star PS ($M_n = 81600 \text{ g mol}^{-1}$) during the heating process from 25 to 110 °C.

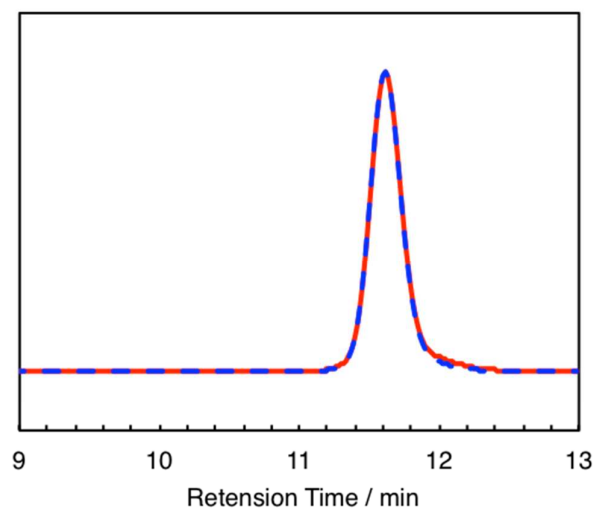


Figure S10. GPC profiles of linear polystyrene with DABBF in the center of polymer chain ($M_n = 13100$) before (red solid) and after (blue dashed) grinding ($M_n = 13100$).

References

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