Electronic supplementary information

Using the Dynamic Behavior of Macrocyclic Monomers with a Bis(hindered amino)disulfide Linker for the Preparation of End-functionalized Polymers

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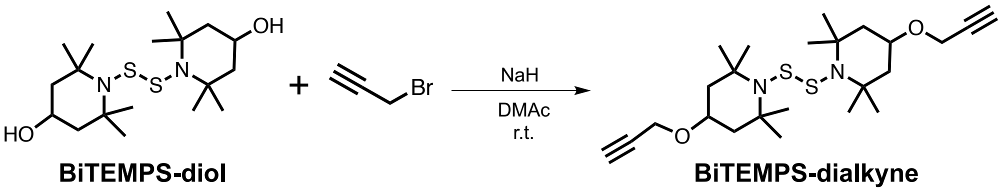
Table of Contents

1. Synthetic procedure

1.1. BiTEMPS-dialkyne



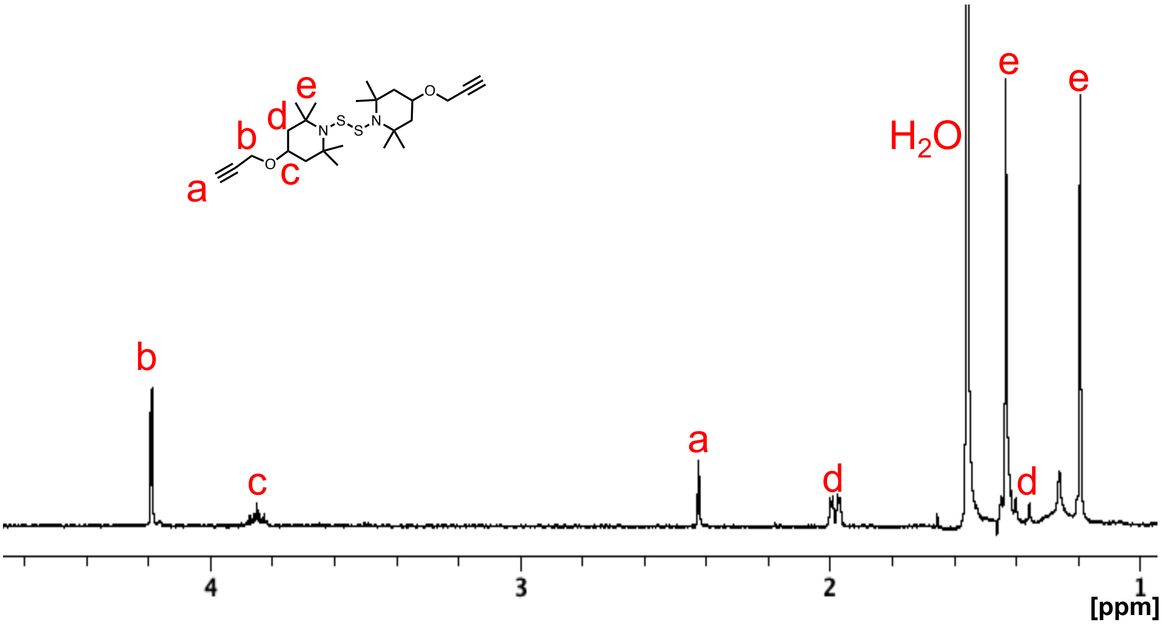
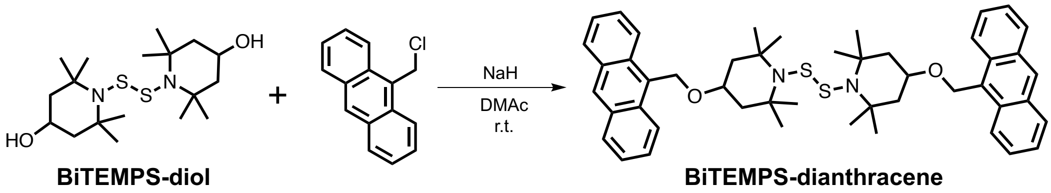


Figure S1. ^{1}H NMR spectrum of **BiTEMPS-dialkyne** (500 MHz, 25 °C, $CDCl_3$).

1.2. BiTEMPS-dianthracene



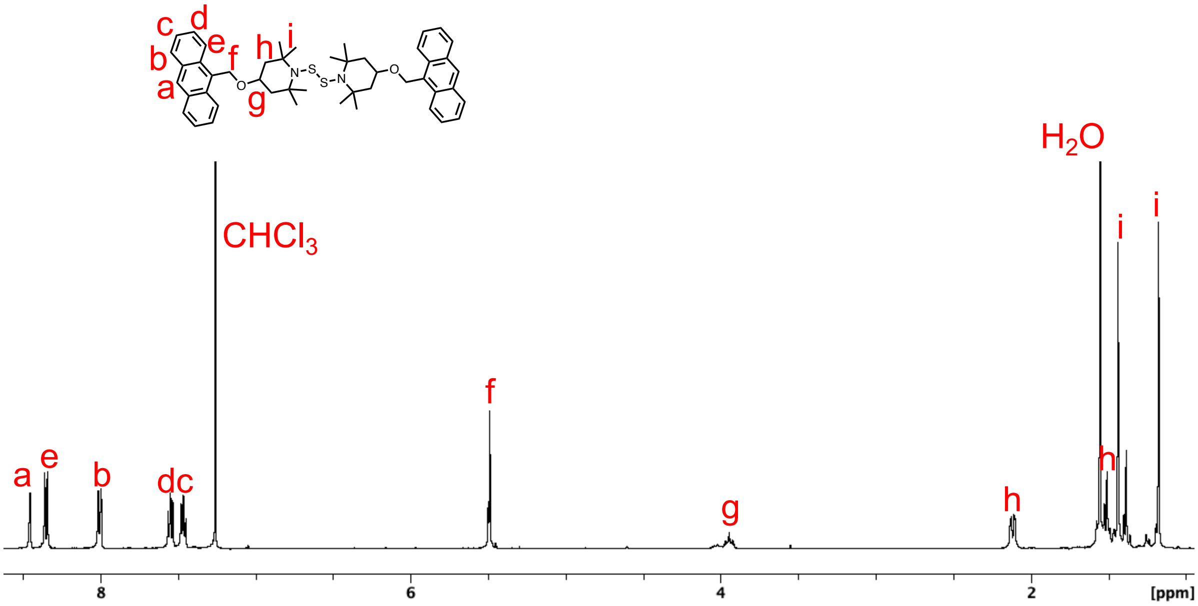
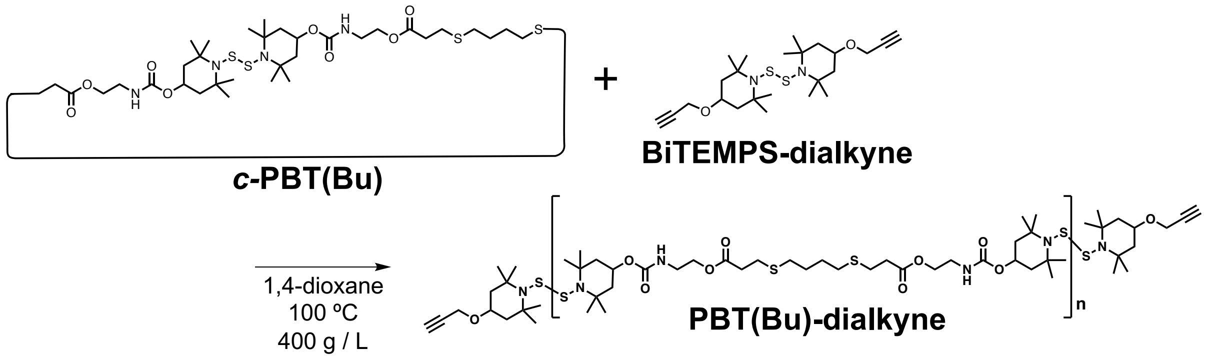


Figure S2. ^{1}H NMR spectrum of **BiTEMPS-dianthracene** (500 MHz, 25 °C, $CDCl_3$).

1.3. PBT(Bu)-dialkyne



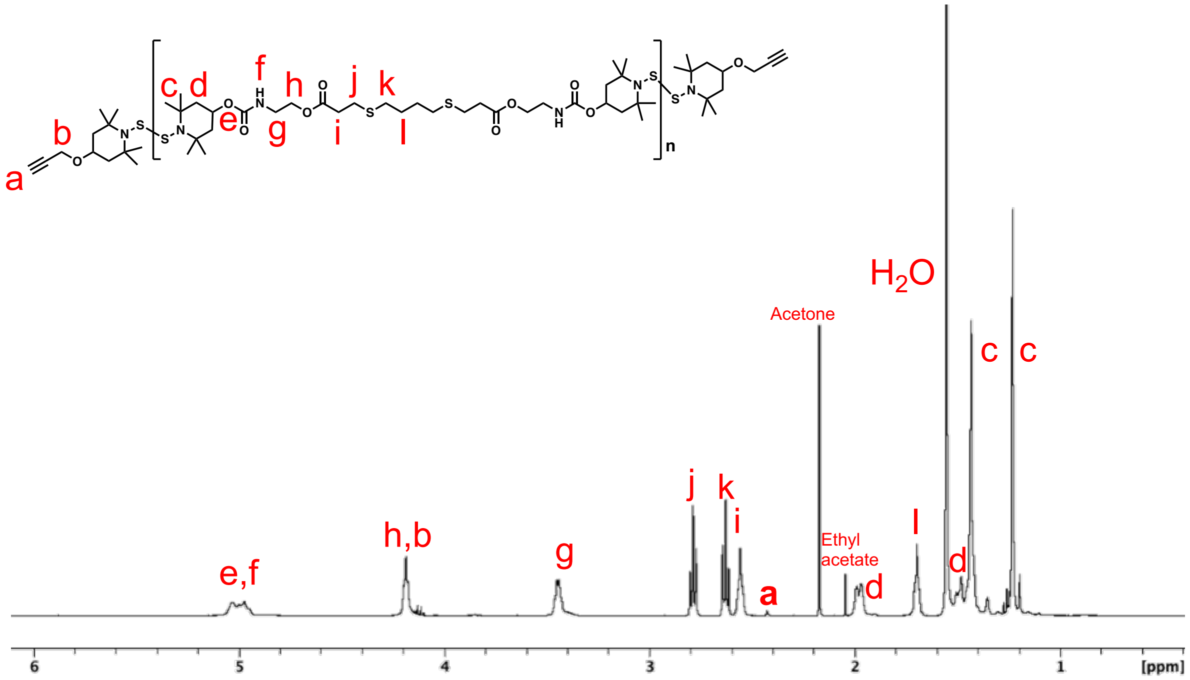
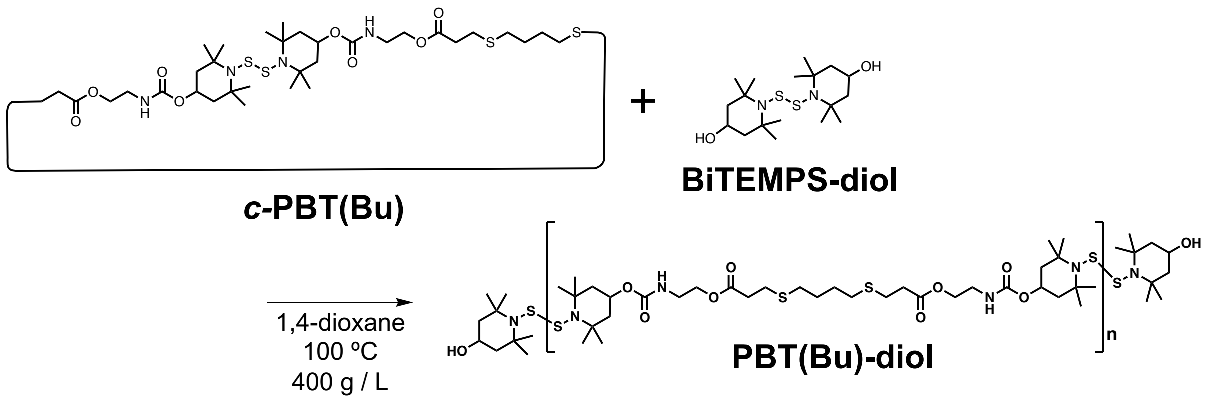


Figure S3. ^{1}H NMR spectrum of **PBT(Bu)-dialkyne** (500 MHz, 25 °C, $CDCl_3$).

1.4. PBT(Bu)-diol



In a 20 mL test tube, 1,4-dioxane (0.5 mL) was added to the mixture of ***c*-PBT(Bu)** (200 mg, 256 μmol) and **BiTEMPS-diol** (19.3 mg, 51.2 μmol). Then, it was stirred at 100 °C for 6 hours. After the reaction, the reaction mixture was poured into 50 mL of methanol. Since a little monomer component remained, it was poured into 50 mL of methanol again to afford **PBT(Bu)-diol** (127 mg, 57.9%).

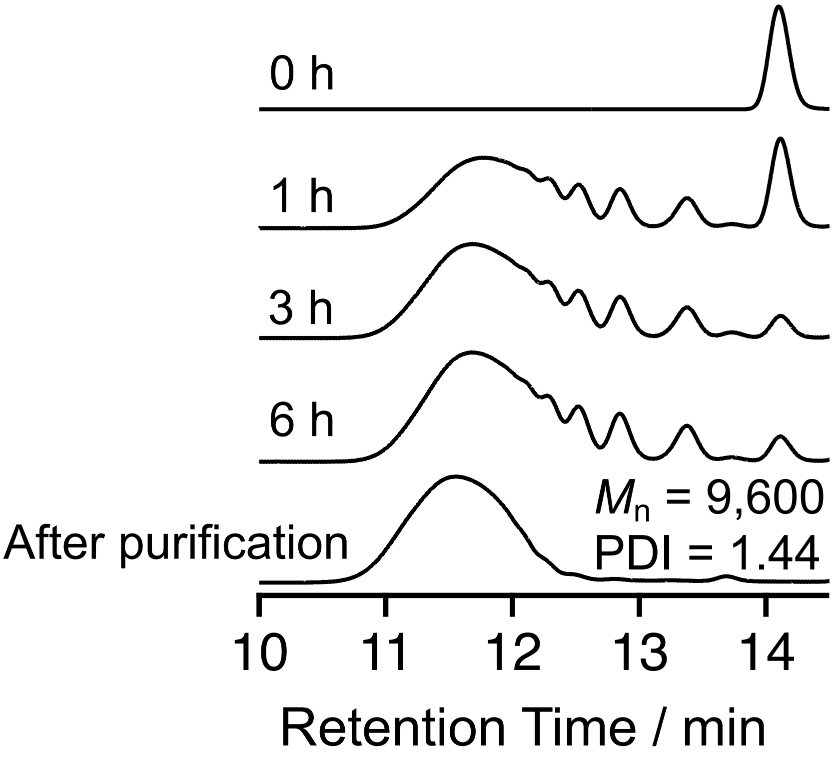


Figure S4. Change in GPC profiles in polymerization of ***c*-PBT(Bu)** in the presence of **BiTEMPS-diol** at 100 °C in 1,4-dioxane. (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI).

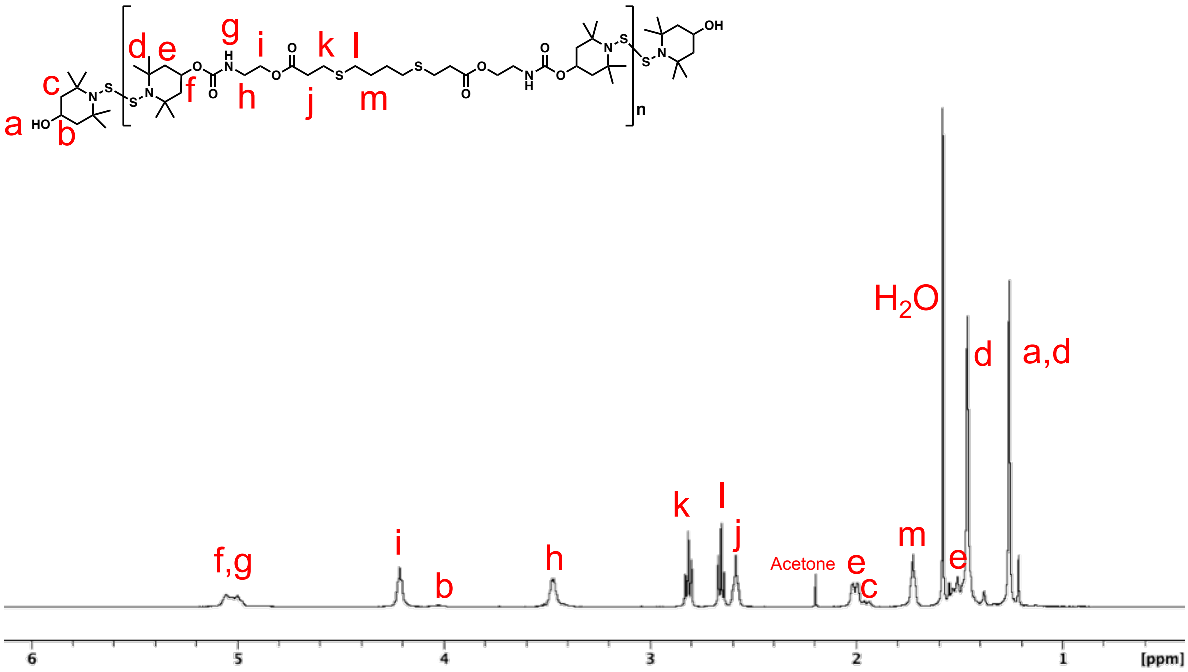


Figure S5. ^{1}H NMR spectrum of **PBT(Bu)-diol** (500 MHz, 25 °C, CDCl$_3$).

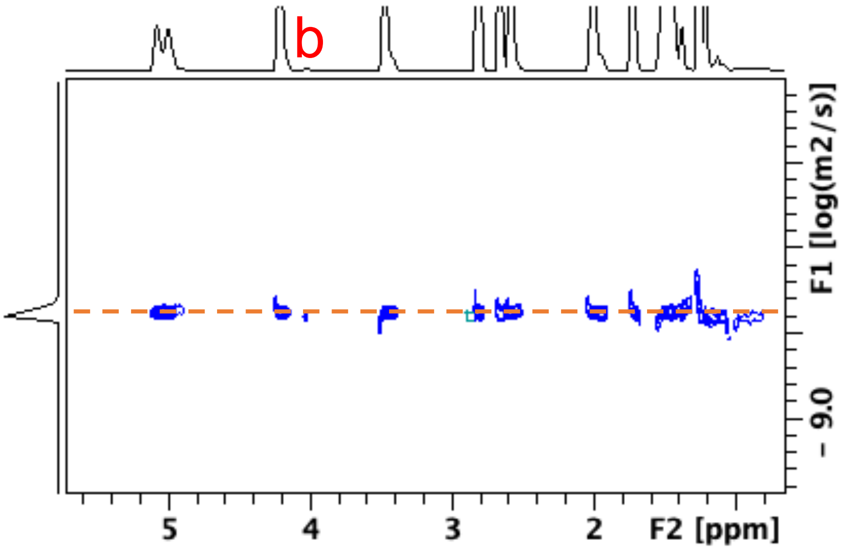
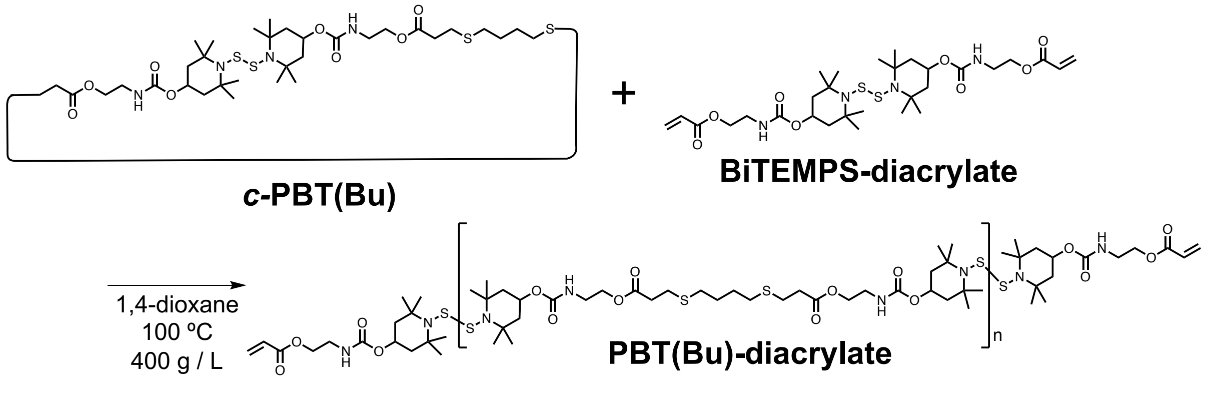


Figure S6. DOSY NMR spectrum of **PBT(Bu)-diol** (500 MHz, 25 °C, CDCl$_3$).

1.5. PBT(Bu)-diacrylate



In a 20 mL test tube, 1,4-dioxane (0.5 mL) was added to the mixture of ***c*-PBT(Bu)** (200 mg, 256 µmol) and **BiTEMPS-diacrylate** (16.9 mg, 25.6 µmol). Then, it was stirred at 100 °C for 6 hours. After the reaction, the reaction mixture was poured into 50 mL of methanol to afford **PBT(Bu)-diacrylate** (185 mg, 85.3%). Since a little monomer component remained, it was poured into 50 mL of methanol again to afford **PBT(Bu)-diacrylate** (148 mg, 68.2%).

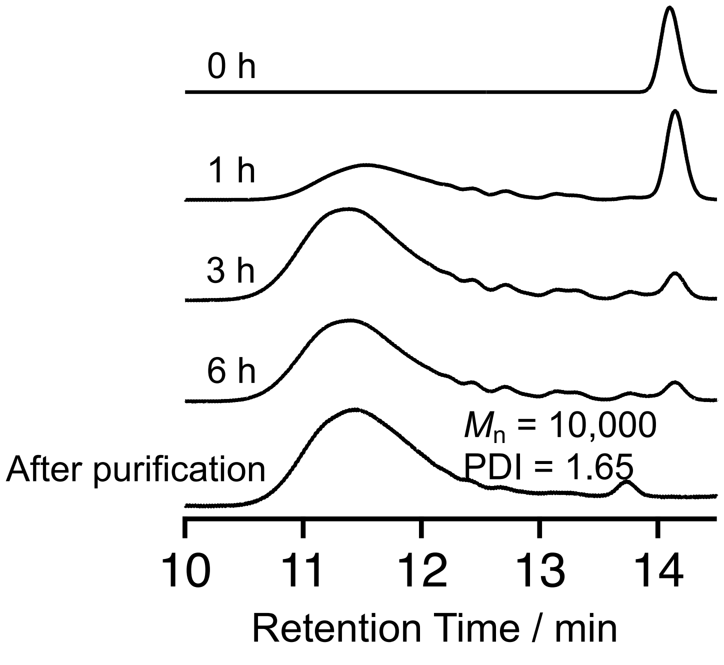


Figure S7. Change in GPC profiles in polymerization of ***c*-PBT(Bu)** in the presence of **BiTEMPS-diacrylate** at 100 °C in 1,4-dioxane. (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI).

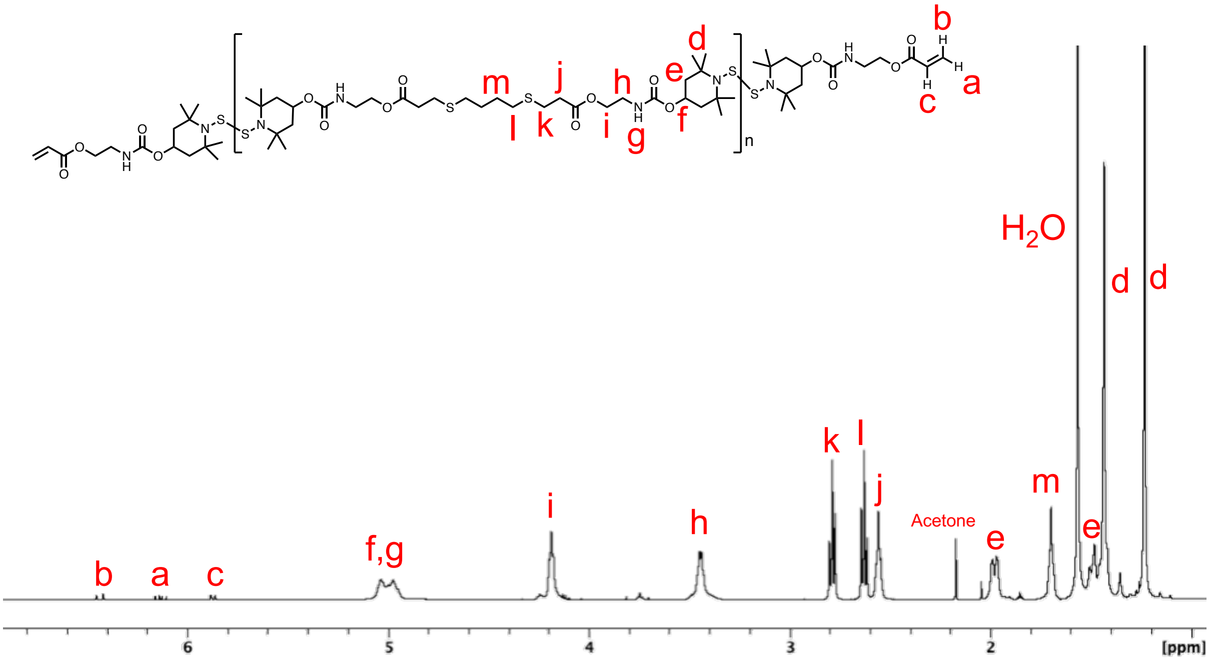


Figure S8. ^{1}H NMR spectrum of **PBT(Bu)-diacrylate** (500 MHz, 25 °C, $CDCl_3$).

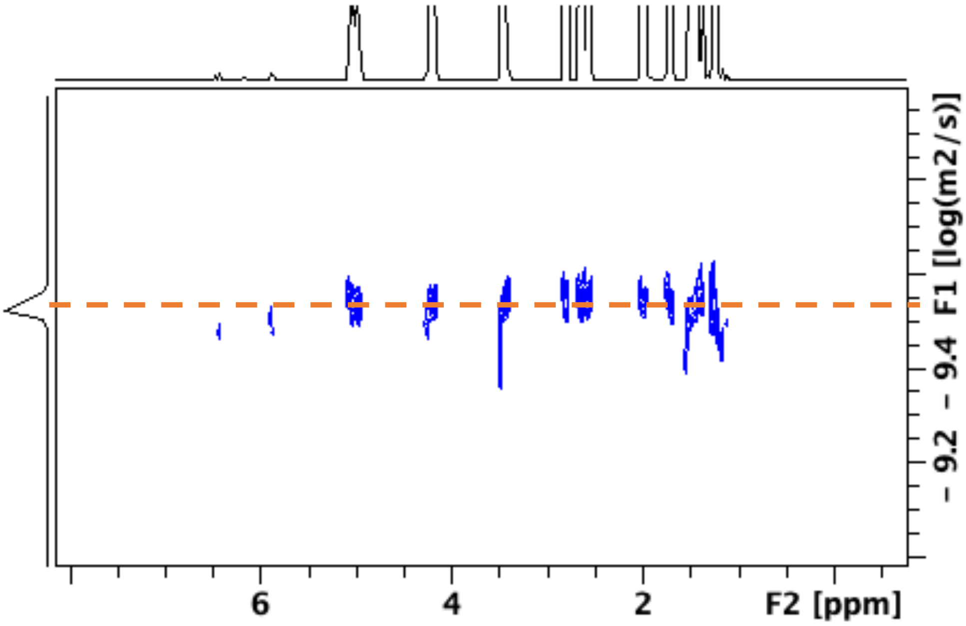
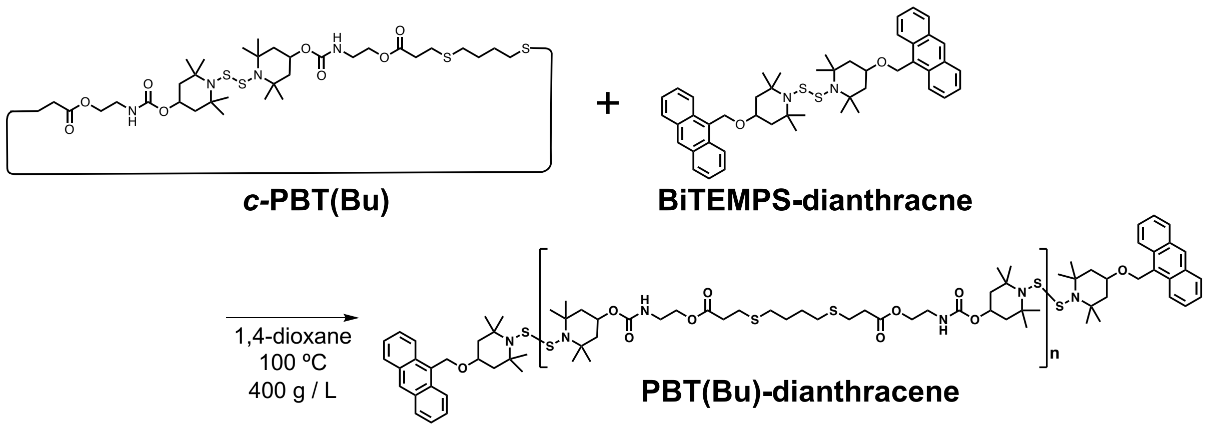


Figure S9. DOSY NMR spectrum of **PBT(Bu)-diacrylate** (500 MHz, 25 °C, $CDCl_3$).

1.6. PBT(Bu)-dianthracene



In a 20 mL test tube, 1,4-dioxane (0.5 mL) was added to the mixture of ***c*-PBT(Bu)** (200 mg, 256 μmol) and **BiTEMPS-dianthracene** (19.4 mg, 25.6 μmol). Then, it was stirred at 100 °C for 6 hours. After the reaction, the reaction mixture was poured into 50 mL of methanol to afford **PBT(Bu)-dianthracene** (159 mg, 72.5%).

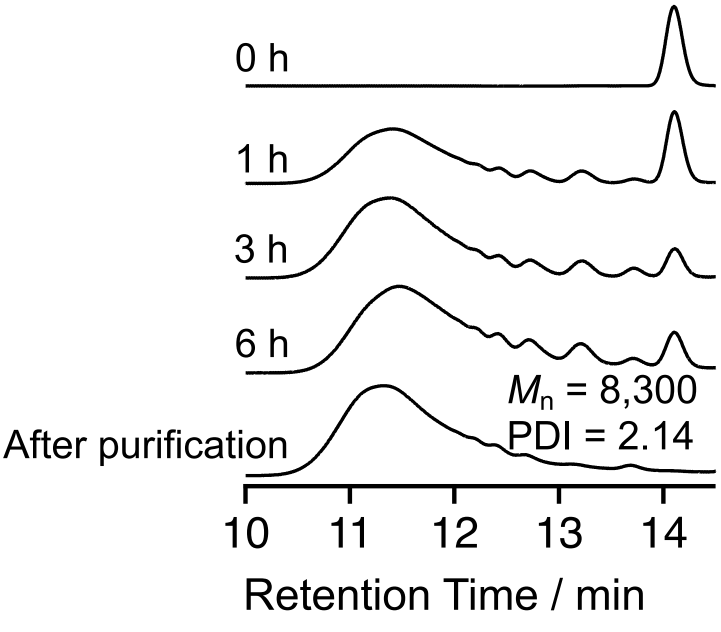


Figure S10. Change in GPC profiles in polymerization of ***c*-PBT(Bu)** in the presence of **BiTEMPS-dianthracene** at 100 °C in 1,4-dioxane. (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI).

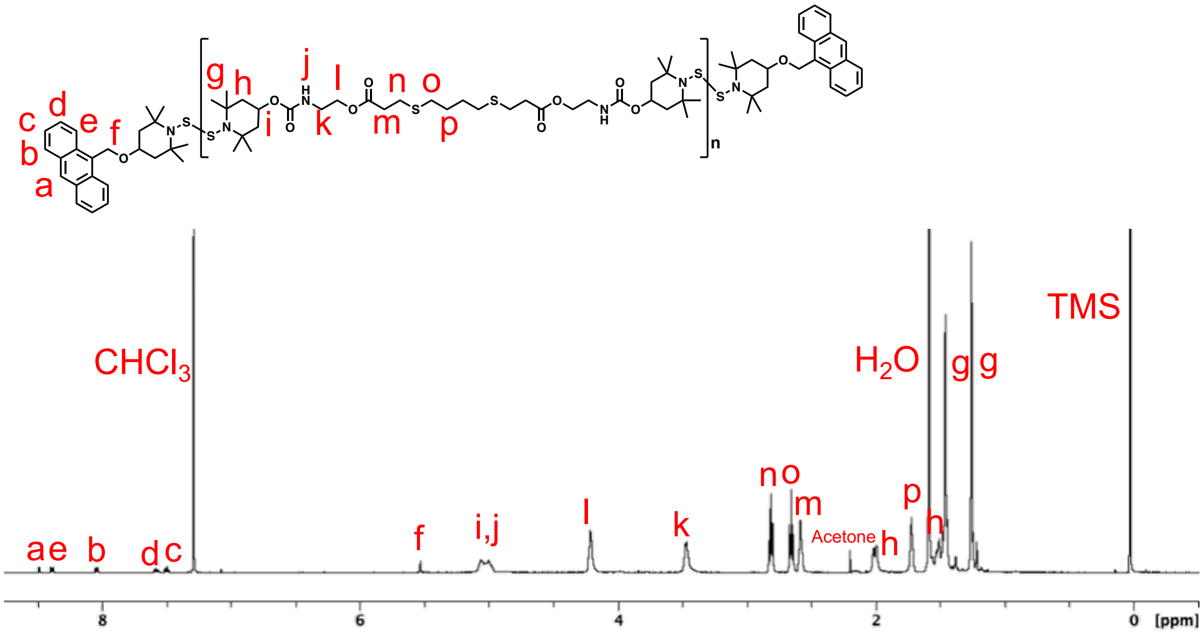


Figure S11. ^{1}H NMR spectrum of **PBT(Bu)-dianthracene** (500 MHz, 25 °C, CDCl$_3$).

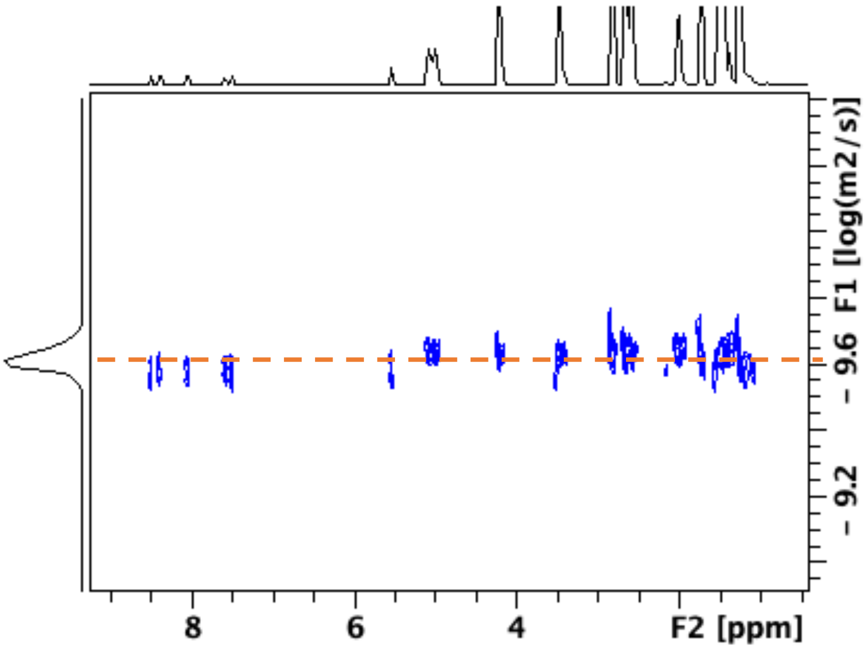
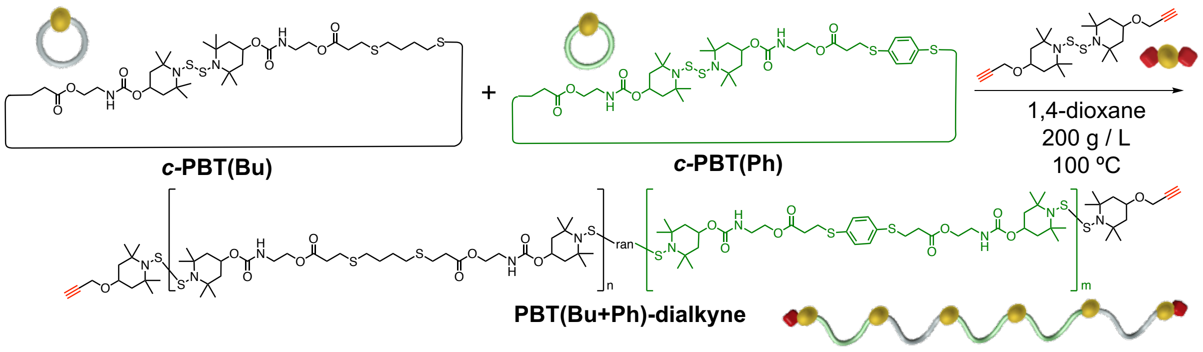


Figure S12. DOSY NMR spectrum of **PBT(Bu)-dianthracene** (500 MHz, 25 °C, CDCl$_3$).

1.7. PBT(Bu+Ph)-dialkyne



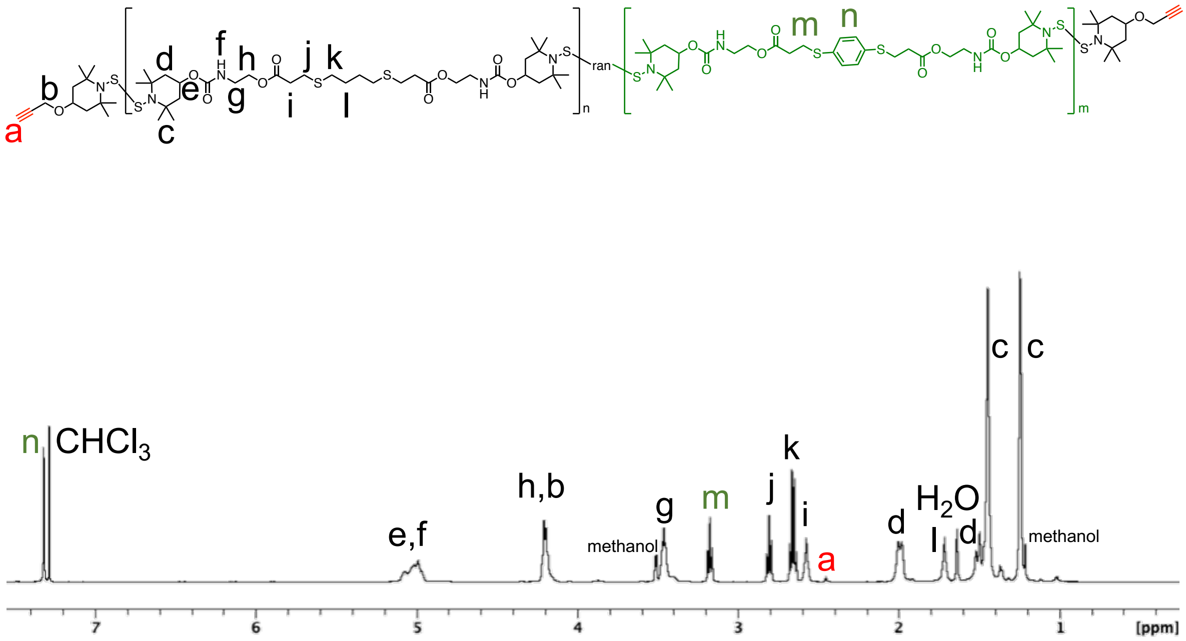
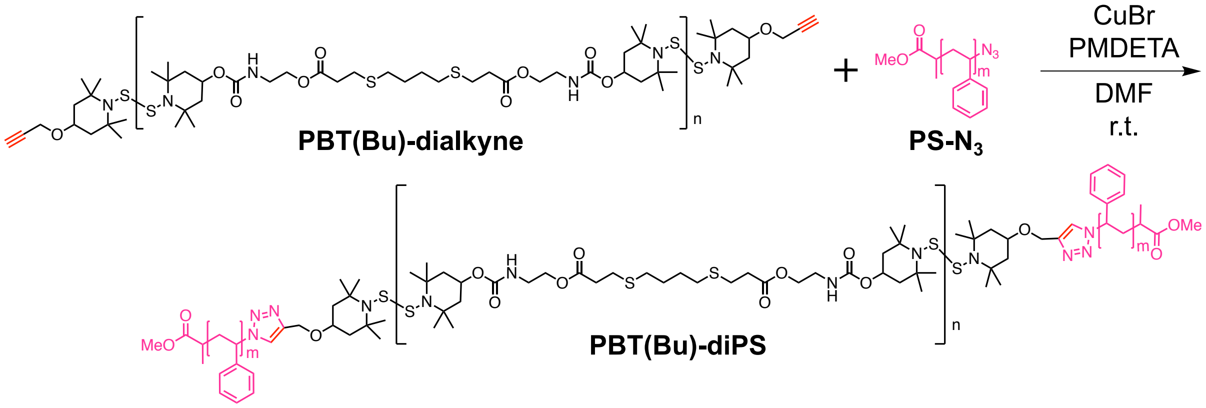


Figure S13. ^{1}H NMR spectrum of **PBT(Bu+Ph)-dialkyne** (500 MHz, 25 °C, $CDCl_3$).

1.8. PBT(Bu)-diPS



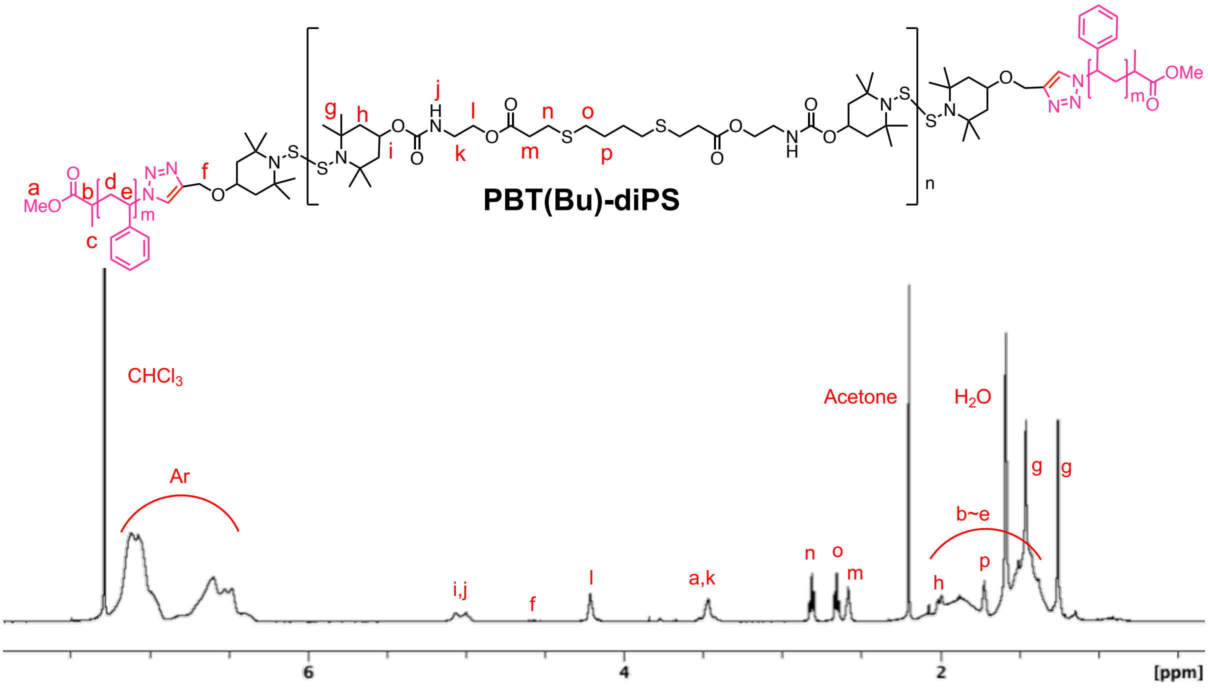
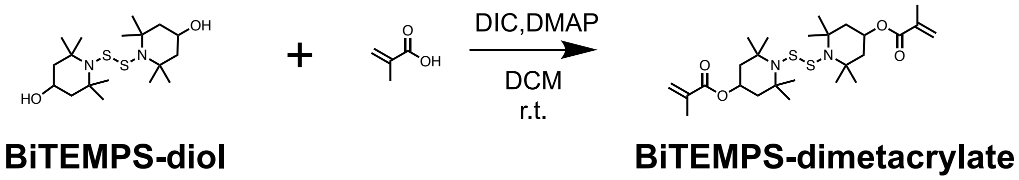


Figure S14. ^{1}H NMR spectrum of **PBT(Bu)-diPS** (500 MHz, 25 °C, CDCl$_3$).

1.9. BiTEMPS-dimetacrylate



N,*N*'-diisopropylcarbodiimide (105 mL, 674 mmol) and methacrylic acid (55.0 mL, 559 mmol) were dissolved in DCM (1.00 mL) and the mixture was stirred for 15 min at room temperature. Then DMAP (32.5 mg, 266 mmol) was added to this solution and the mixture was stirred for 30 min at room temperature. Then, BiTEMPS-diol (100 mg, 266 mmol) was added to this solution and the mixture was stirred for 6 hours at room temperature. The resulting solution was filtered and further purification was carried out by flash column chromatography with hexane/ethyl acetate mixture (8/2, v/v) to afford **BiTEMPS-dimetacryate** as white solid (47.4 mg, 34.8%). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 6.08 (s, 2H, $C\mathit{H}_2$C-), 5.55 (s, 2H, $C\mathit{H}_2$C-), 5.15 (t, *J* = 12.0 Hz, 2H, –$C(CH_3)_2CH_2\mathit{CH}$<), 2.00 (d, *J* = 11.7 Hz, 4H, –$C(CH_3)_2\mathit{CH_2}CH$<), 1.60-1.40 (m, 16H, –$C(\mathit{CH_3})_2CH_2CH$<, –$C(CH_3)_2\mathit{CH_2}CH$<), 1.26 (s, 12H, –$C(\mathit{CH_3})_2CH_2CH$<); ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 167.03, 136.62, 125.33, 67.36, 59.60, 45.58, 34.83, 26.72, 18.32 ; FT-IR (KBr, cm^{-1}): 2974, 2369, 2343, 1714, 1635, 1546, 1462, 1379, 1327, 1239, 1163, 1012, 918, 816, 486, 414; FAB-MS (m/z): calcd for $C_{26}H_{44}N_2O_4S_2$, 512.2743; found, 512.2743.

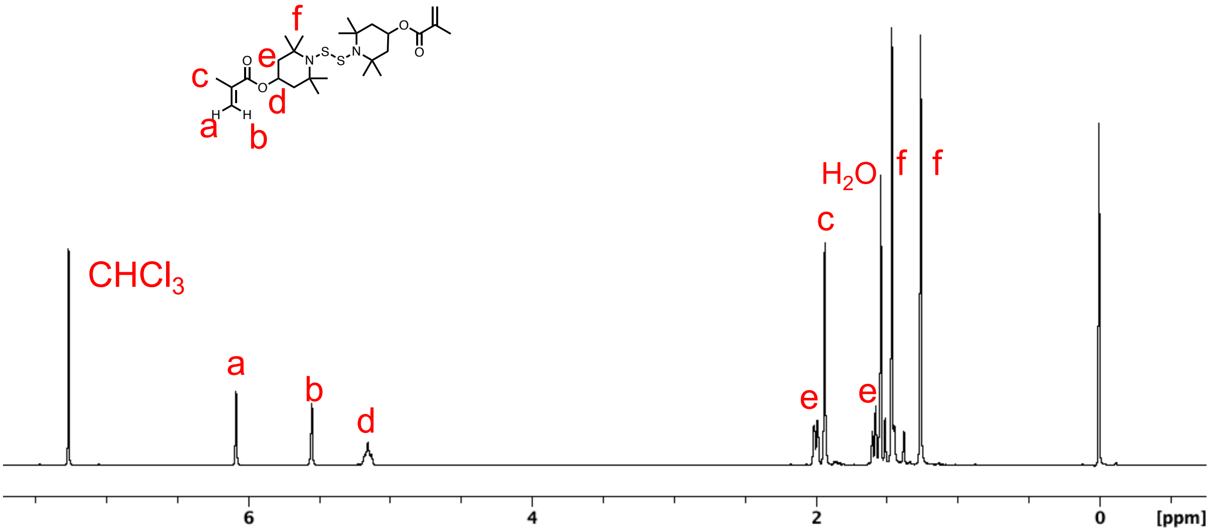
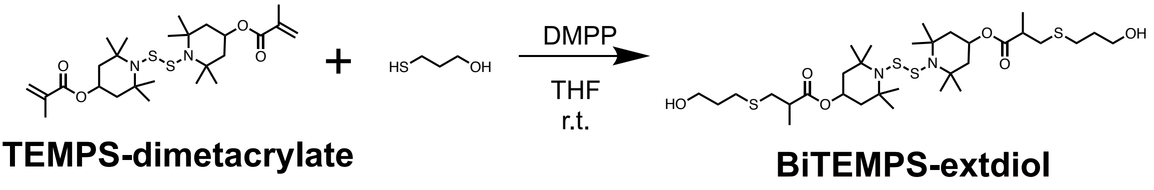


Figure S15. ^{1}H NMR spectrum of **BiTEMPS-dimetacrylate** (500 MHz, 25 °C, $CDCl_3$).

1.10. BiTEMPS-extdiol.



BiTEMPS-dimetacrylate (3.15 g, 6.14 mmol) and 3-mercapto-1-propanol (8.00 mL, 92.6 mmol) were dissolved in THF (15.0 mL). Then, dimethylphenylphosphine (DMPP) (350 µL, 2.54 mmol) was added to this solution and the mixture was stirred for 24 h at room temperature. The reaction mixture was poured into 500 ml of water. Further purification was carried out by silica gel chromatography with hexane / ethyl acetate (v/v = 3/7) to afford **BiTEMPS-extdiol** (1.45 g, 33.9%). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 5.12 (m, 2H, $–C(CH_3)_2CH_2\mathit{CH}<$), 3.76 (q, *J* = 5.68 Hz, 4H, $-O\mathit{CH_2}CH_2$), 2.83 (dd, *J* = 6.72 Hz, 2H, $-S\mathit{CH_2}CH<$), 2.69-2.56 (m, 8H, $-S\mathit{CH_2}CH_2-$, $-S\mathit{CH_2}CH<$, $-OCO\mathit{CH}<$), 1.95 (m, 4H, $–C(CH_3)_2\mathit{CH_2}CH<$), 1.85 (m, 4H, $-OCH_2\mathit{CH_2}CH_2-$), 1.65-1.48 (m, 12H, $-O\mathit{H}$, $–C(CH_3)_2\mathit{CH_2}CH<$, $\mathit{CH_3}CH<$), 1.45 (s, 12H, $-C(\mathit{CH_3})_2CH_2CH<$), 1.26 (d, 12H, $–C(\mathit{CH_3})_2CH_2CH<$); ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 174.79, 67.35, 61.58, 59.55, 45.49, 40.32, 35.40, 34.81, 31.84, 29.23, 26.72, 17.00 ; FT-IR (KBr, cm^{-1}): 3423, 2972, 2934, 1730, 1460, 1380, 1365, 1239, 1207, 1165, 1121, 1060, 1005, 984, 959, 912, 824, 758, 529; FAB-MS (m/z): calcd for $C_{32}H_{60}N_2O_6S_4Na$, 719.3232; found, 719.3234.

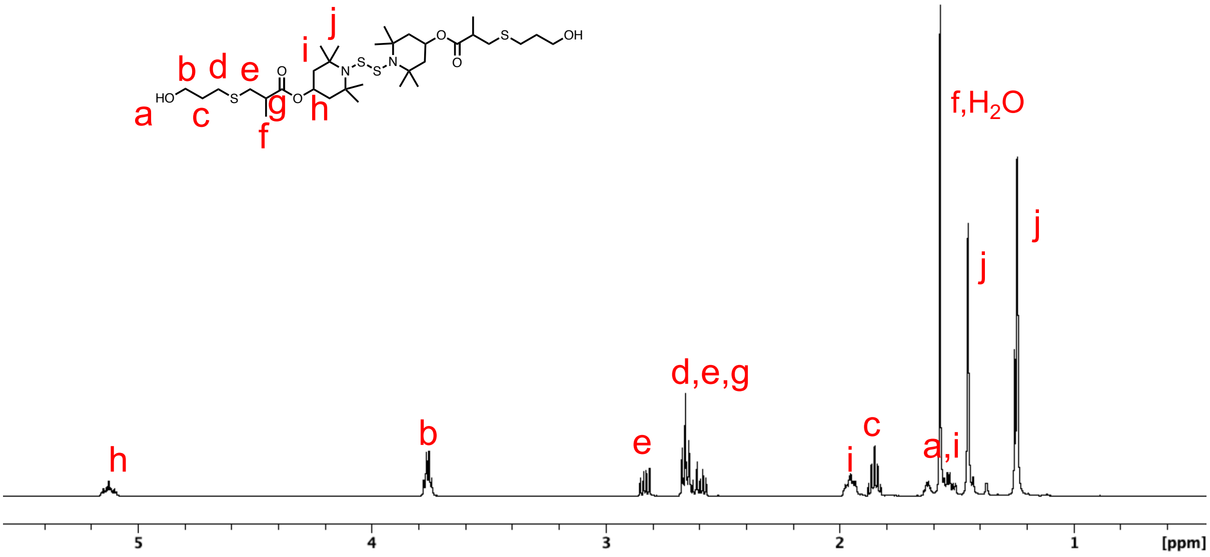
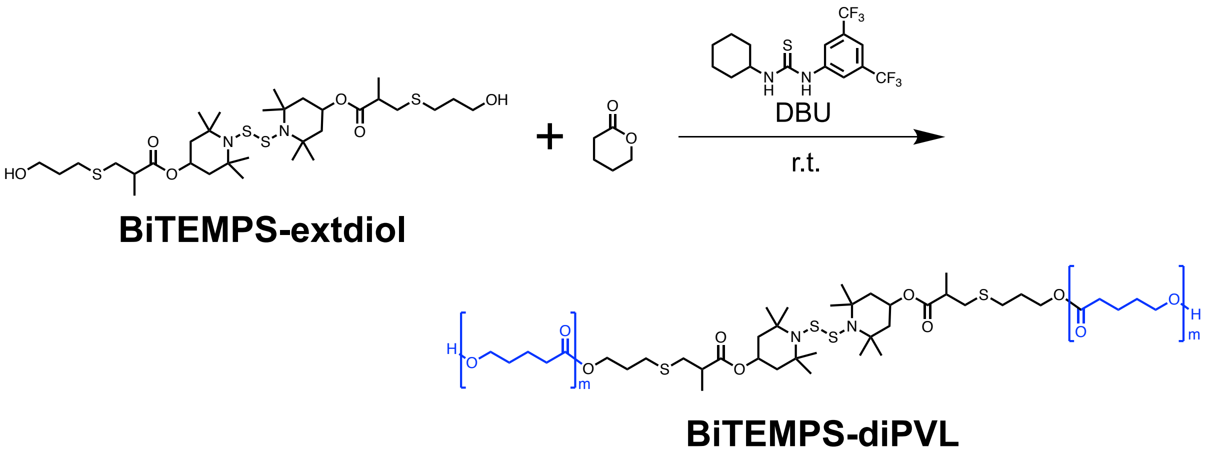


Figure S16. ^{1}H NMR spectrum of **BiTEMPS-extdiol** (500 MHz, 25 °C, $CDCl_3$).

1.11. BiTEMPS-diPVL.[1]



In a test tube, **BiTEMPS-extdiol** (100 mg, 149 μmol) and 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (122 mg, 329 μmol) were freeze-dried three times using 1,4-dioxane and then kept under nitrogen atmosphere. δ-Valerolactone (1.00 mL, 415 mmol) and DBU (50.0 mg, 329 μmol) was added to this mixture and stirred at room temperature overnight. The reaction mixture was poured into methanol to afford **BiTEMPS-diPVL** (M_n = 7300 g/mol, M_w/M_n = 1.15, 970 mg, 82.8%).

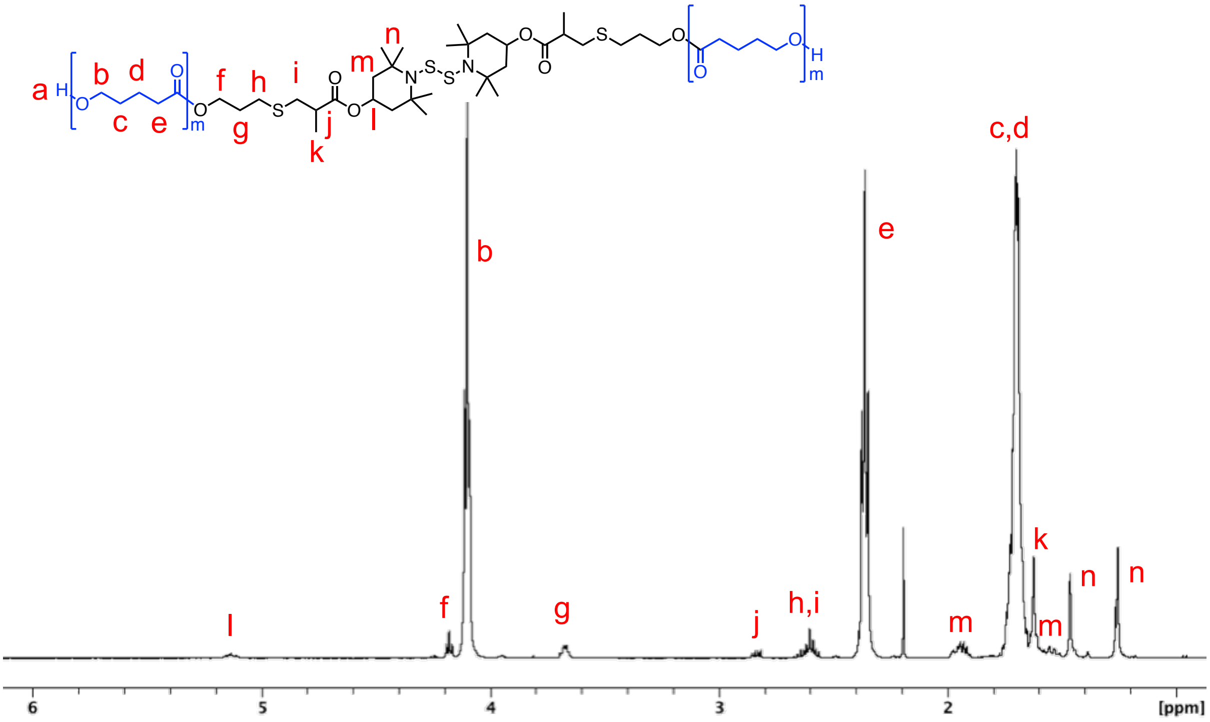


Figure S17. ^{1}H NMR spectrum of **BiTEMPS-diPVL** (500 MHz, 25 °C, CDCl$_3$).

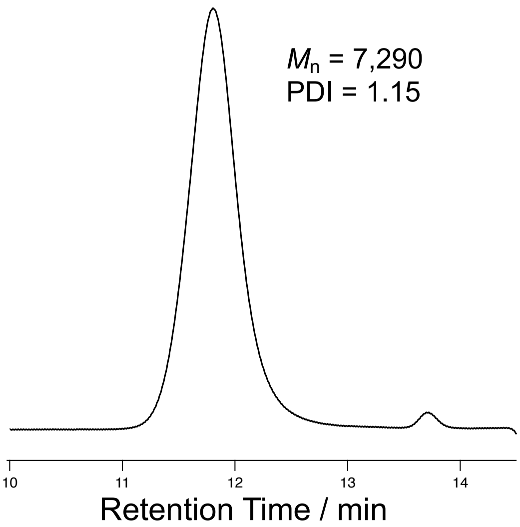


Figure S18. GPC profile of **BiTEMPS-diPVL**. (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI).

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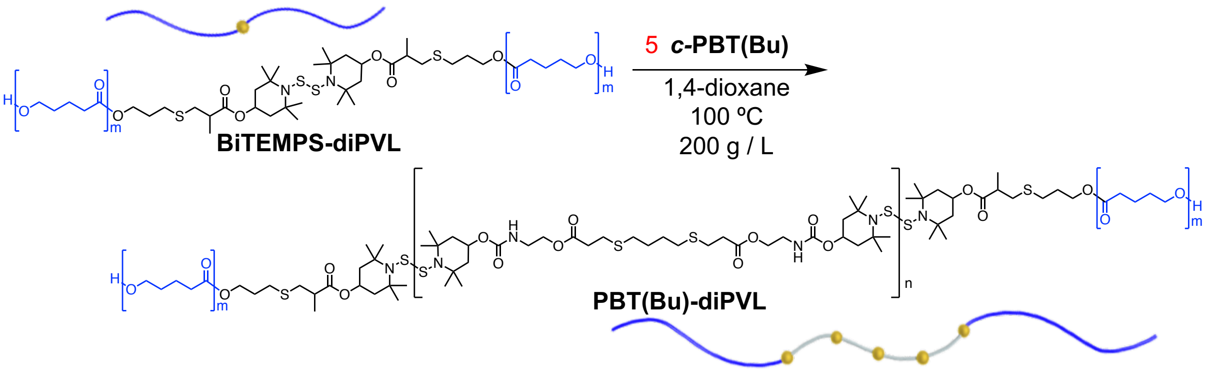
1.12. PBT(Bu)-diPVL.



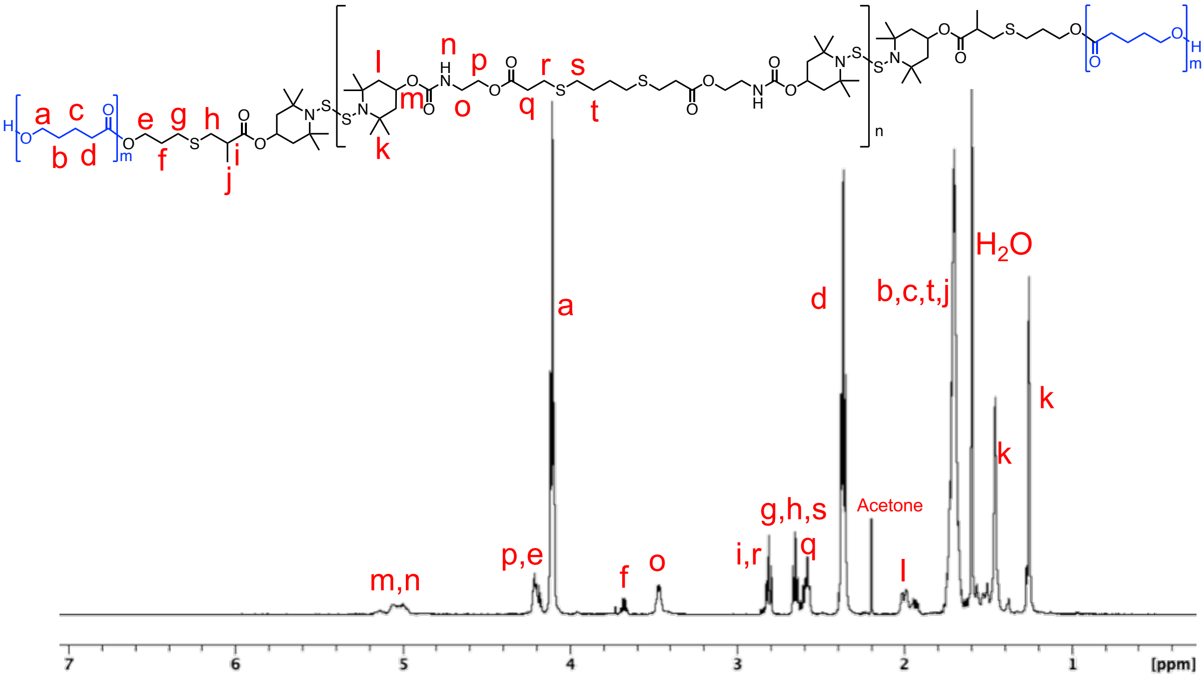
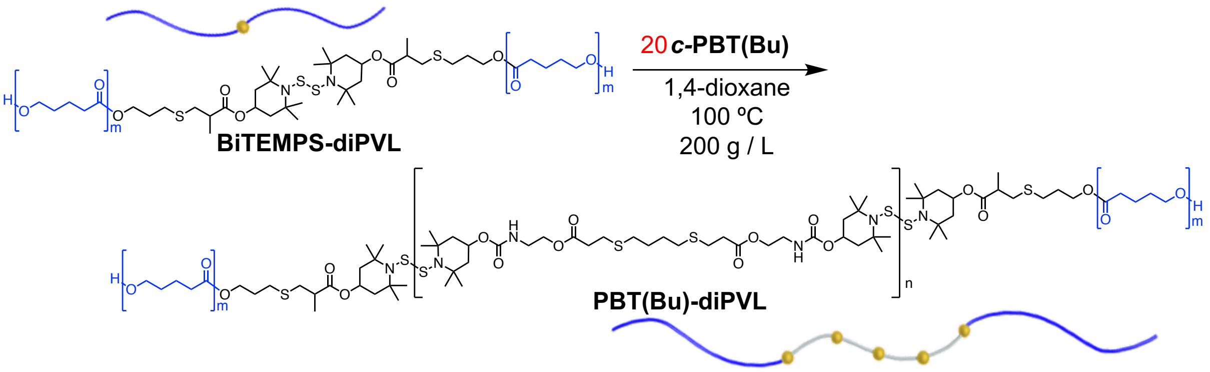


Figure S19. ^{1}H NMR spectrum of **PBT(Bu)-diPVL** (500 MHz, 25 °C, CDCl$_3$).

1.13. Synthesis of PBT(Bu)-diPVL(20/1).



In a 20 mL test tube, 1,4-dioxane (0.5 mL) was added to ***c*-PBT(Bu)** (100 mg, 128 μmol) and **BiTEMPS-diPVL** (M_n = 7,300 g/mol, M_w/M_n = 1.15, 53.6 mg, 6.40 μmol). Then, it was stirred at 100 °C for 6 hours. After the reaction, the solvent was removed by freeze drying. The reaction mixture was poured into 100 mL of methanol to afford **PBT(Bu)-diPVL(20/1)** (M_n = 19000 g/mol, M_w/M_n = 1.38, 117 mg, 76.2%).

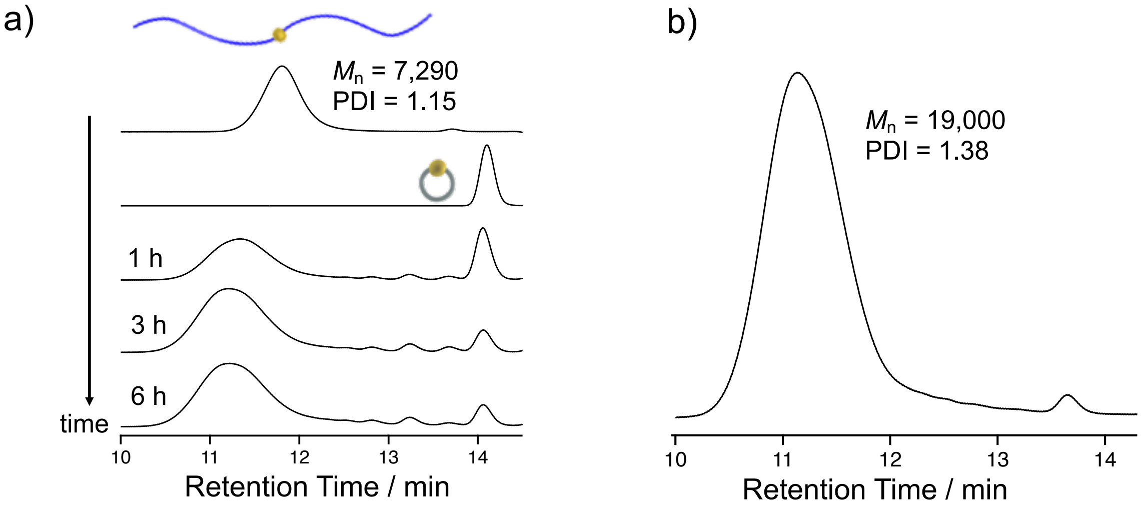


Figure S20. (a) Change in GPC profiles of synthesis **PBT(Bu)-diPVL(20/1)** and (b) GPC profile of **PBT(Bu)-diPVL(20/1)** after purification (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI).

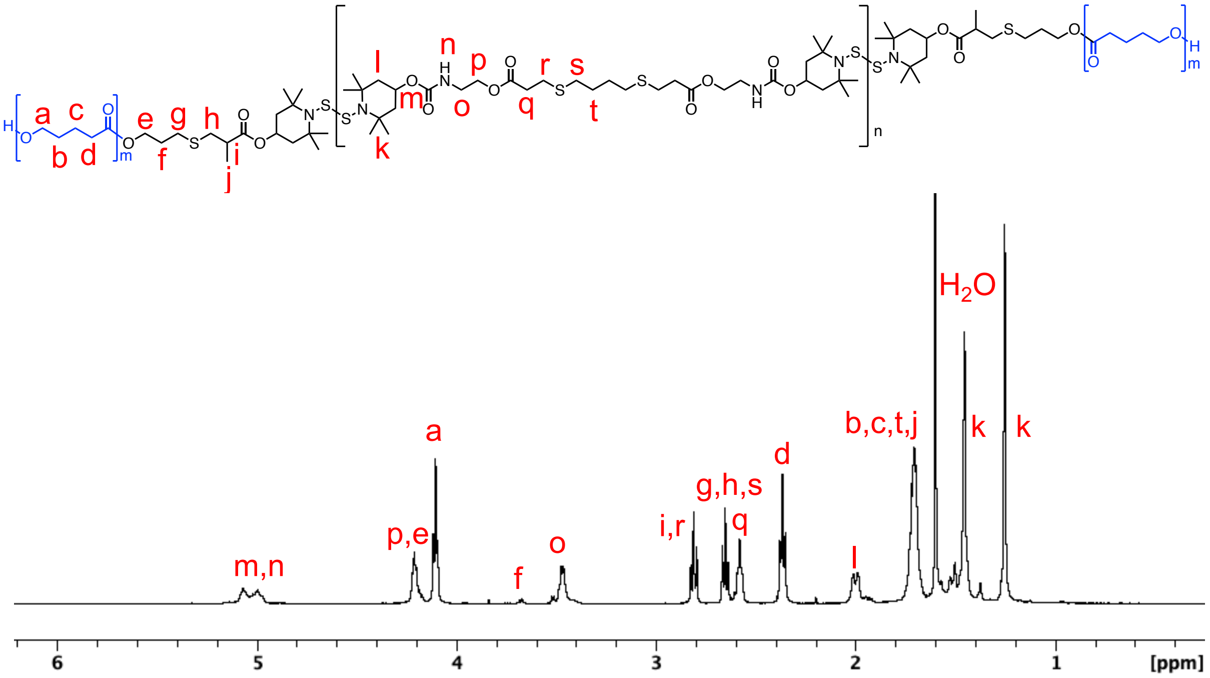


Figure S21. ^{1}H NMR spectrum of **PBT(Bu)-diPVL(20/1)** (500 MHz, 25 °C, CDCl$_3$).

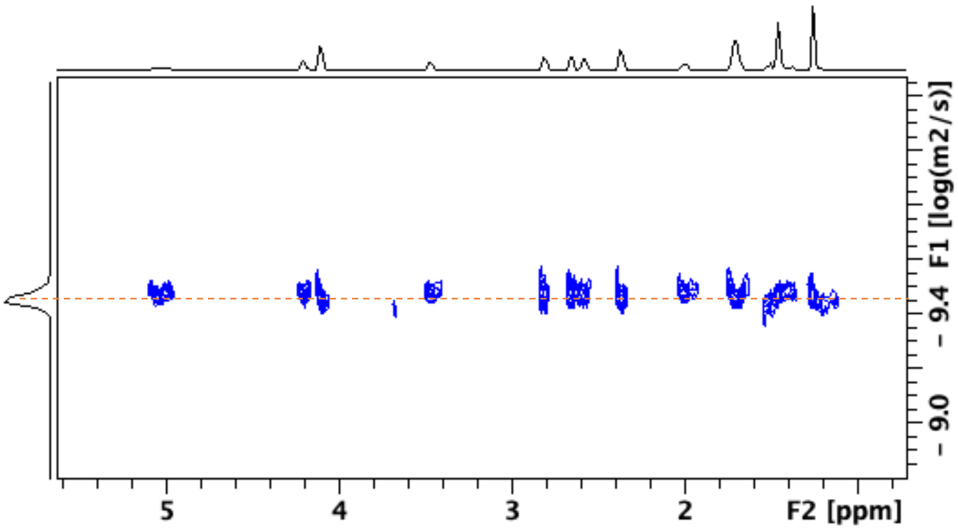


Figure S22. DOSY spectrum of **PBT(Bu)-diPVL(20/1)** (500 MHz, 25 °C, CDCl$_3$).

2. Relation between time and concentration

Macrocyclic compounds need concentrated conditions to obtain the corresponding linear polymers. The degree of change in a linear polymer varies depending on the concentration of the macrocyclic compounds. From the production ratio of the polymer at each concentration, the macrocyclic compound concentration is appropriate in 200 g/L or more, and the reaction proceeds sufficiently by heating for 6 hours.

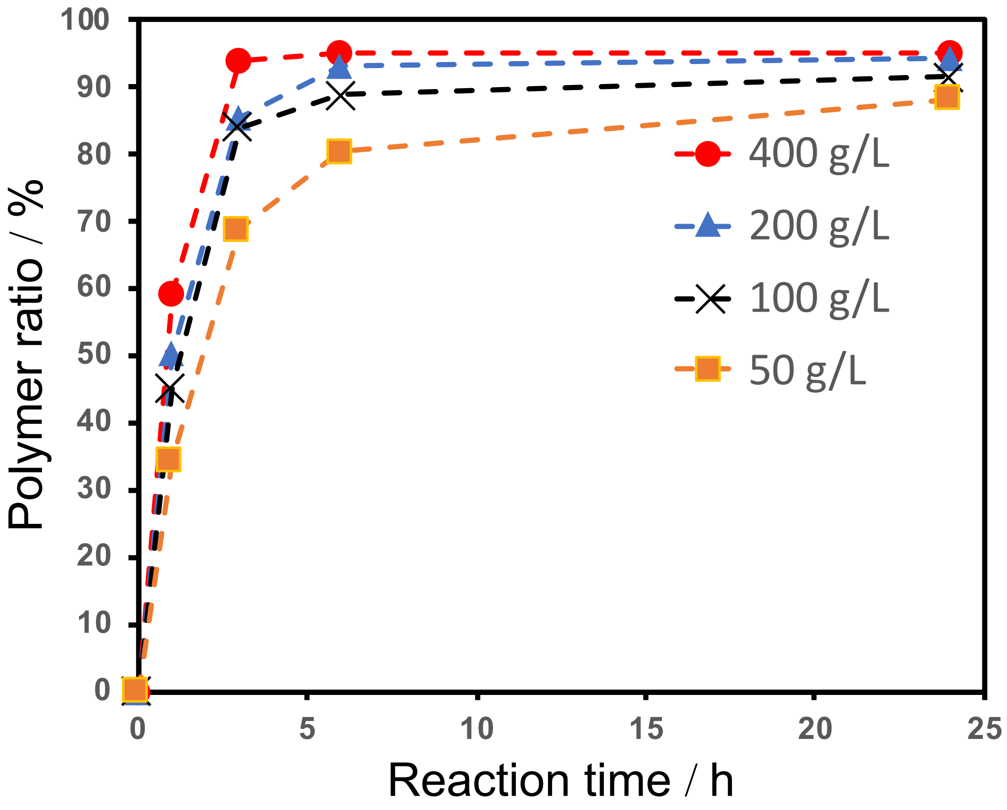


Figure S23. Difference in reaction rate depending on concentration.

3. Conversion of *c*-PBT(Bu) and *c*-PBT(Ph)

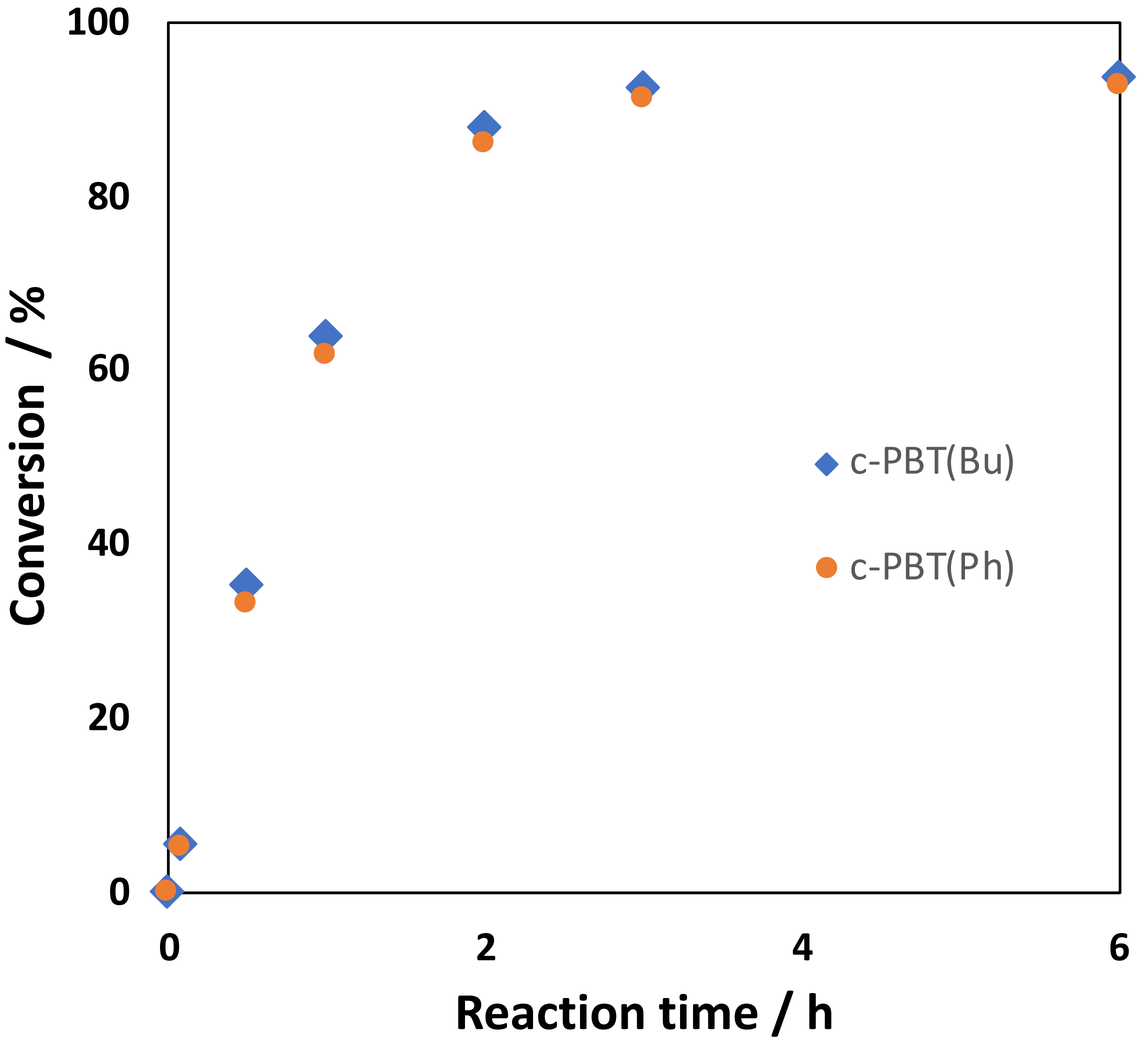


Figure S24. Conversion rate of ***c*-PBT(Bu)** and ***c*-PBT(Ph).** The conversion of each monomer was calculated from the area ratio of GPC detected by RI and overwritten in the same figure.

4. UV absorption evaluation by anthracene

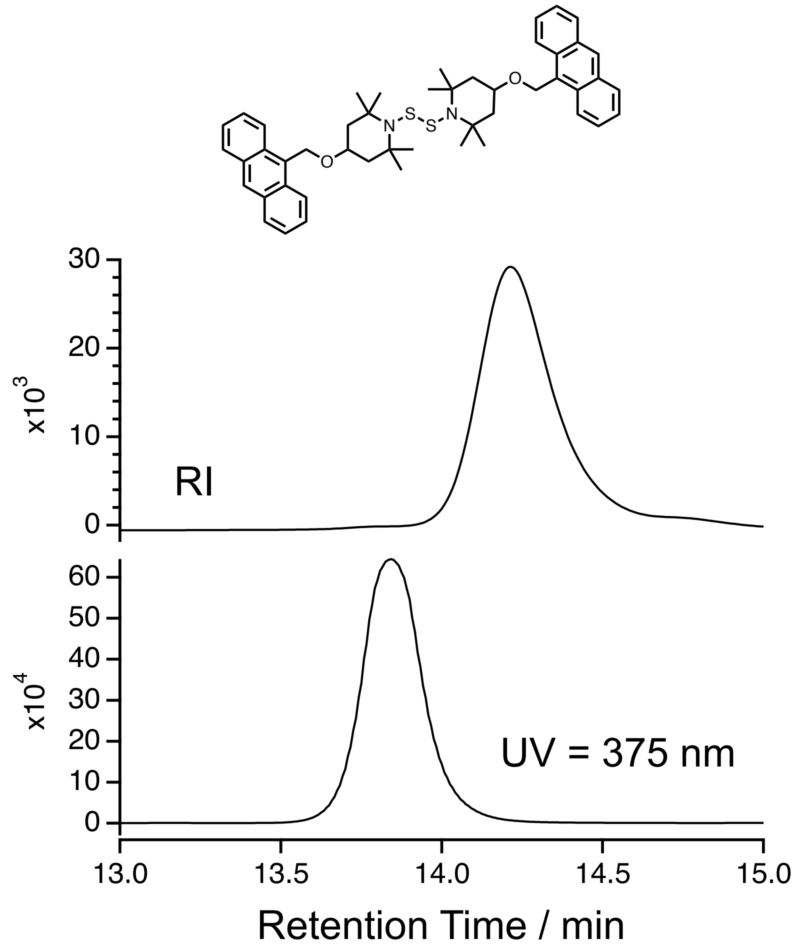


Figure S25. GPC profiles of **BiTEMPS-dianthracene**. Note that there is time difference between RI detector and UV detector. (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI and UV in 375 nm).

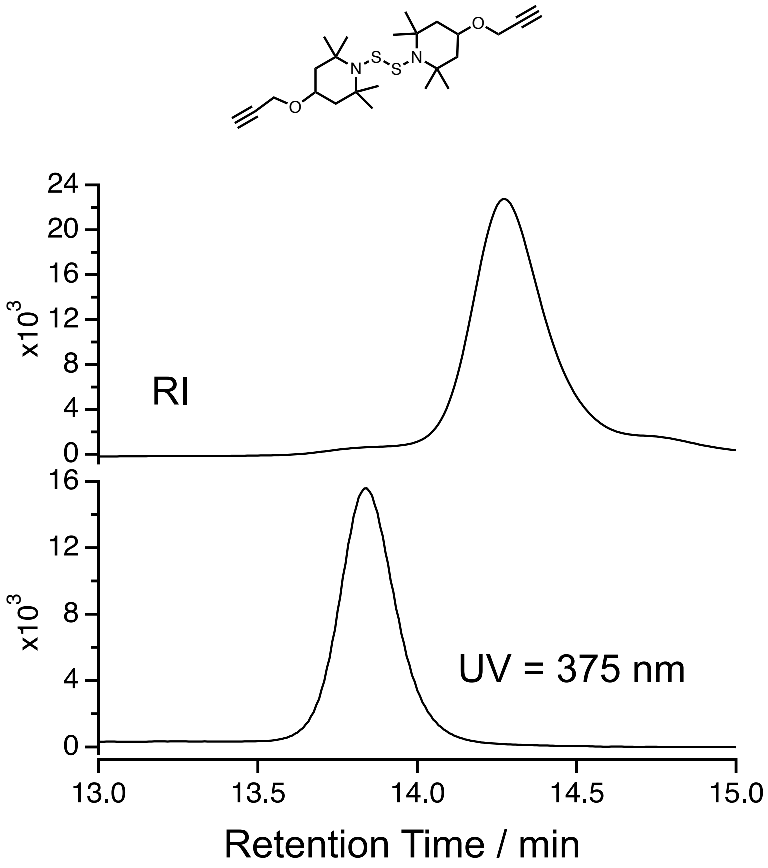


Figure S26. GPC profiles of **BiTEMPS-dialkyne**. Note that there is time difference between RI detector and UV detector. (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI and UV in 375 nm).

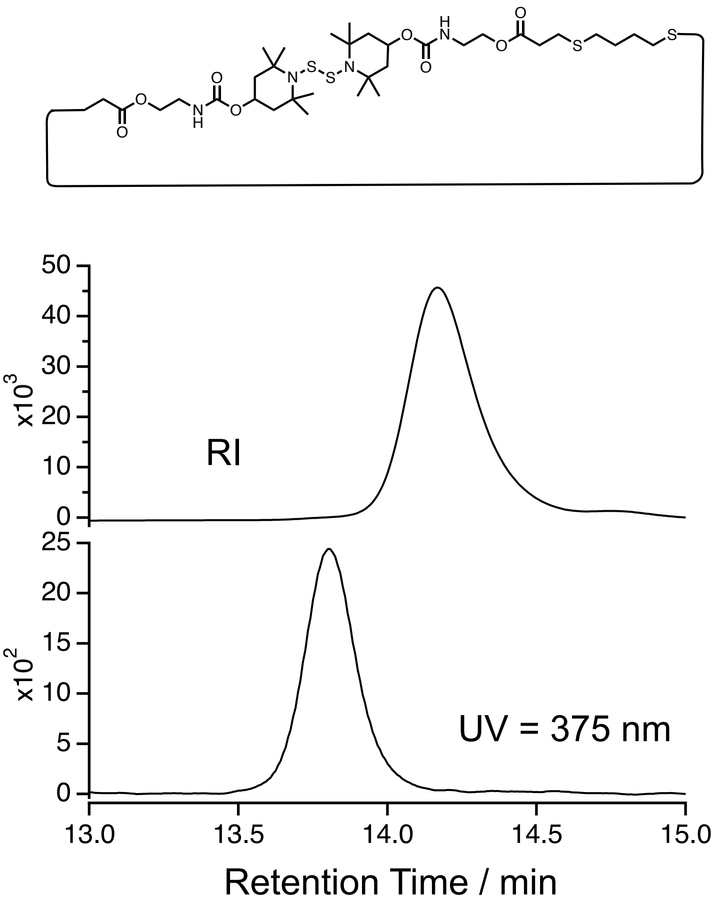


Figure S27. GPC profiles of ***c*-PBT(Bu)**. Note that there is time difference between RI detector and UV detector. (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI and UV in 375 nm).

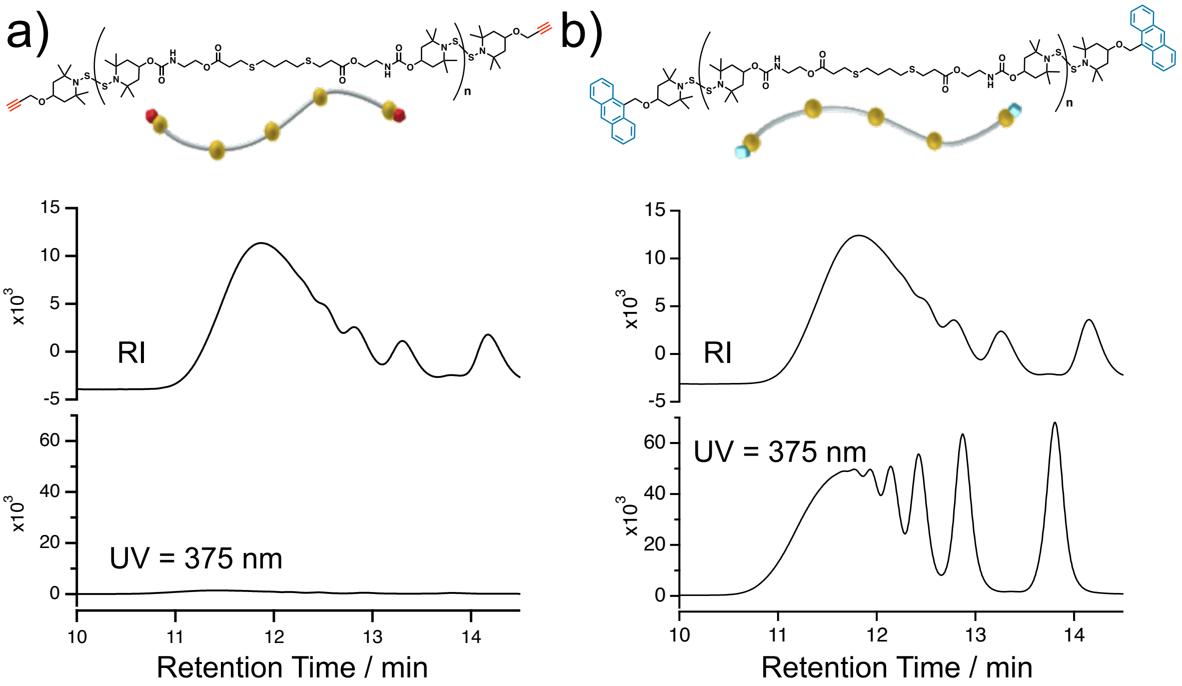


Figure S28. (a) GPC profiles of **PBT(Bu)-dialkyne**. (b) GPC profiles of **PBT(Bu)-dianthracene**. (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI and UV). Note that there is time difference between RI detector and UV detector.

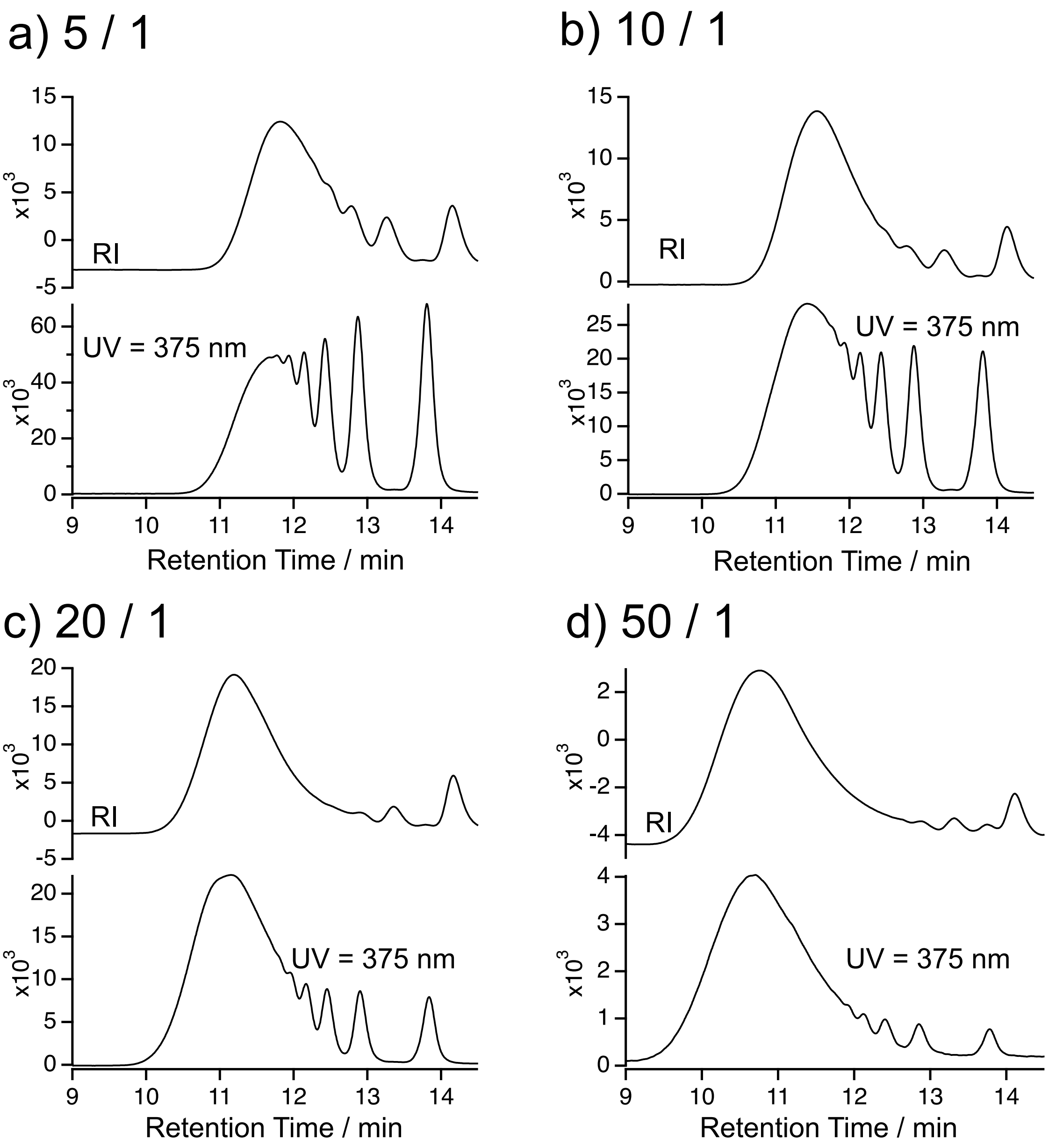


Figure S29. GPC profiles of synthesized **PBT(Bu)-dianthracene** by changing feed ratio (***c*-PBT(Bu)** / **BiTEMPS-dianthracene** = (a) 5, (b) 10, (c) 20, and (d) 50). Note that there is time difference between RI detector and UV detector. (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI and UV in 375 nm).

The residual ratio of monomers peaked around 14 min, was roughly calculated as about 5% of the whole in GPC analysis detected by RI. However, the peak around 14 min overlapped with macrocyclic compounds and terminal structure (acyclic BiTEMPS derivative). On the other hand, the residual ratio of only **BiTEMPS-dianthracene** can be calculated from the area ratio of the peak at around 14 min in the UV-detected profile (375 nm), which is summarized as “Experimental Value” in **Table S-1**.

The theoretical value of the remaining ratio of **BiTEMPS-dianthracene** can be calculated by theoretical equations as follows.

First, we supposed that all BiTEMPS units dissociate and reconnect at the same probability, and considered the case of mixing macrocyclic compounds and terminal structure. The ratio of macrocyclic compounds to terminal structure is noted as x.

The probability that the terminal structure is connected to the macrocyclic compound can be expressed in equation 1.

$$\frac{x}{x+1} \quad \ldots(1)$$

The probability that the terminal structure is connected to themselves can be expressed in equation 2.

$$\frac{1}{x+1} \quad \ldots(2)$$

Therefore, the probability of the terminal structure connected to oligomerized *n*-mer macrocyclic compounds can be determined by equation 3.

$$a_n = \frac{1}{x+1}\left(\frac{x}{x+1}\right)^n \quad \ldots(3)$$

From equation 3, the existence ratio of the terminal structure can be calculated by substituting *n* into 0. The theoretical values calculated from this equation are summarized in **Table S-1**. As shown in **Table S-1**, the measured values in GPC profiles are close to the theoretical values. From the above, this system is considered to be consistent with simple probability calculations which is provided as the theoretical formula of polycondensation.

Table S-1. Existence ratio of terminal structure (**BiTEMPS-dianthracene**)

***c*-PBT(Bu)/BiTEMPS-dianthracene**	5/1	10/1	20/1	50/1
Experimental value (%)	16.6	10.5	5.07	2.40
Theoretical value (%)	16.7	9.09	4.76	1.96

5. SI references

1 B. G. G. Lohmeijer, R. C. Pratt, F. Leibfarth, J. W. Logan, D. A. Long, A. P. Dove, F. Nederberg, J. Choi, C. Wade, R. M. Waymouth and J. L. Hedrick, *Macromolecules*, 2006, **39**, 8574–8583.