Supporting Information

Rapid and Versatile Polymer-Polymer Coupling *via* Iodide-Thiol Substitution Click Chemistry

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KEYWORDS

Polymer-polymer coupling, iodide-terminated polymers, dithiol linkers, block copolymers, star copolymers.

1. Experimental.

MATERIALS

Butyl acrylate (BA, >99%, Tokyo Chemical Industry (TCI), Japan), 2-iodo-2-methylpropionitrile (CP–I, >95%, TCI), tetrabutylammonium iodide (BNI, >98%, TCI), ethyl *α*-bromoisobutyrate (EBiB, 98%, Sigma-Aldrich, USA), copper (II) bromide (Cu(II)Br_2, 99%, Sigma-Aldrich), *tris*-(2-(dimethylamino)ethyl)amine (Me_6TREN, Sigma-Aldrich), tetramethylguanidine (TMG, 99%, Sigma-Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, >98%, Sigma-Aldrich), *N*-ethyldiisopropylamine (EDPA, ≥98%, Sigma-Aldrich), *tris*(2-pyridylmethyl) amine (TPMA, >98%, TCI), 1,8-octanedithiol (ODT, >97%, Sigma-Aldrich), 1,16-hexadecanedithiol (HDDT, 99%, Sigma-Aldrich), trimethylolpropane *tris*(3-mercaptopropionate) (TMPT, ≥95%, Sigma-Aldrich), pentaerythritol *tetrakis*(3-mercaptopropionate) (PATM, ≥95%, Sigma-Aldrich), benzyl mercaptan (BMC, 99%, Sigma-Aldrich), 1-phenylethyl mercaptan (PEMC, Aldrich^{CPR}, Sigma-Aldrich), 2-(Boc-amino)ethanethiol (Boc-SH, 97%, Sigma-Aldrich), glutathione (GLT, pharmaceutical secondary standard, Sigma-Aldrich) poly(ethylene glycol) methyl ether thiol (PEG_{2k}-SH, Sigma-Aldrich), poly(ethylene glycol) dithiol (PEG_{1k}-2SH and $PEG_{1.5k}$-2SH, Sigma-Aldrich), 4arm poly(ethylene glycol)-SH (PEG_{5k}-4SH and PEG_{10k}-4SH, Sigma-Aldrich), dimethyl sulfoxide (DMSO, ≥99.7%, Sigma-Aldrich), *N*,*N*-dimethylformamide (DMF) (>99.5%, Kanto Chemical, Japan) *N*,*N*-dimethylacetamide (DMAc, ≥98%, Sigma-Aldrich), tetrahydrofuran (THF) (≥99.8%, Fisher Chemical, USA), toluene (≥99.5%, Sigma-Aldrich), and Cyrene (≥98.5%, Sigma-Aldrich) were used as received.

CHARACTERIZATIONS

NMR: The proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at ambient temperature on a Bruker (Germany) BBFO400 spectrometer (400 MHz). Chloroform-*d* ($CDCl_3$, Cambridge Isotope Laboratories, USA) or acetone-d_6 (Cambridge Isotope Laboratories) was used as the NMR solvent. The residual non-deuterated solvents and tetramethylsilane (TMS) were used as the internal standards for ^{1}H NMR analysis (calibration of chemical shift).

GPC: The gel permeation chromatography (GPC) analysis was performed on a Shimadzu LC-2030C Plus liquid chromatography (Tokyo, Japan) equipped with a Shodex (Tokyo, Japan) LF-804 mixed gel column (300 × 8.0 mm; bead size = 6 μm; pore size = 3000 Å) and a Shodex KF-804L mixed gel column (300 × 8.0 mm; bead size = 7 μm; pore size = 1500 Å). The eluent was THF at a flow rate of 0.7 mL/min (40 °C). Sample detection was conducted using a Shimadzu differential refractometer RID-20A. The column system was calibrated with standard poly(methyl methacrylate)s (PMMAs).

TGA: The thermal gravimetric analysis (TGA) curves were recorded with TGA Q500 model device (TA instrument, New Castle, US). The TGA analysis was carried out in platinum pans under flowing nitrogen at a flow rate of 60 mL/min with a heating rate of 10 °C/min at a temperature range of 25–600 °C.

DSC: The differential scanning calorimetry (DSC) curves were recorded with QSeries DSC Q50 model device (TA instrument). The DSC analysis was conducted using aluminium sample pans under nitrogen flow at a flow rate of 50 mL/min. The samples were cooled down to –60 °C and heated up to 150 °C with a heating rate of 10 °C/min.

TEM: The transmission electron microscopy (TEM) images were obtained on a JEM-1400 transmission electron microscope (JEOL, Tokyo, Japan) operated at 100 kV. A polymer (~0.01 mg) was dissolved into 10 mL of THF/I_2 solution (5wt% of I_2), and the aliquots (5 μL) were drop-casted on carbon-coated grids (200 mesh, supplied by Ted Pella, Redding, US) and dried at room temperature.

Rheometer: The rheometer analysis was performed on Anton Paar (Graz, Austria) MCR 702e rheometer equipped with a PP12 configuration (plate to plate diameter of 12 mm). The data were analysed and processed using the RheoCompass software.

SYNTHETIC PROCEDURE

General Procedures for Synthesis of PBA–I. In a typical run (synthesis of PBA_{22}–I), a mixture of BA (1.29 mL, 30 equiv), CP–I (58.5 mg, 1 equiv), and BNI (111 mg, 1 equiv) was heated in a Schlenk tube at 110 °C under argon atmosphere with magnetic stirring. After 18 h, the mixture was cooled to room temperature. An aliquot (0.1 mL) was diluted with $CDCl_3$ and analyzed with ^{1}H NMR for determining the monomer conversion. Another aliquot (0.1 mL) was diluted with THF and analyzed using GPC. The polymer (rest of the mixture) was purified by precipitation in water/methanol (1/6 (v/v)) mixture (non-solvent). The polymer was dried under the vacuum.

Synthesis of PBA–Br.[1] A mixture of BA (2.15 mL, 30 equiv), EBiB (73.4 μL, 1 equiv), Cu(II)Br_2 (2.25 mg, 0.02 equiv), Me_6TREN (16 μL, 0.12 equiv), and DMSO (2 mL) were added to a septum sealed vial and deoxygenated by purging with argon for 15 min. The polymerization

was conducted under UV box (UVP Cross-linker, Analytik Jena, Germany) (λ_{max} ~ 365 nm) for 18 h. An aliquot (0.1 mL) was diluted with $CDCl_3$ and analyzed with ^1H NMR for determining the monomer conversion. Another aliquot (0.1 mL) was diluted with THF, passed through neutral alumina for removal of copper salts, and analyzed using GPC. The polymer (rest of the mixture) was purified by precipitation in water/methanol (1/6 (v/v)) mixture (non-solvent). The polymer was dried under the vacuum.

General Procedures for Halogen-Thiol Substitution In a typical run, a solution of PBA_{22}–I (50 mg, 2 equiv), ODT (1.21μL, 1 equiv), TMG (8.3 μL, 10 equiv), and DMF (0.5 mL) (**Table 1** (entry 13)) was magnetically stirred in a 4 mL glass vial at room temperature under dark for 2.5 h. After the reaction, the solution was diluted with THF and analyzed using GPC. In some cases, the product was purified via reprecipitation in water or a water/methanol mixture (non-solvent) for subsequent NMR, thermal, and rheological analysis. The polymer was dried under the vacuum.

2. Synthetic, Coupling, Thermal, NMR, GPC, TGA, DSC, and Viscoelastic Data

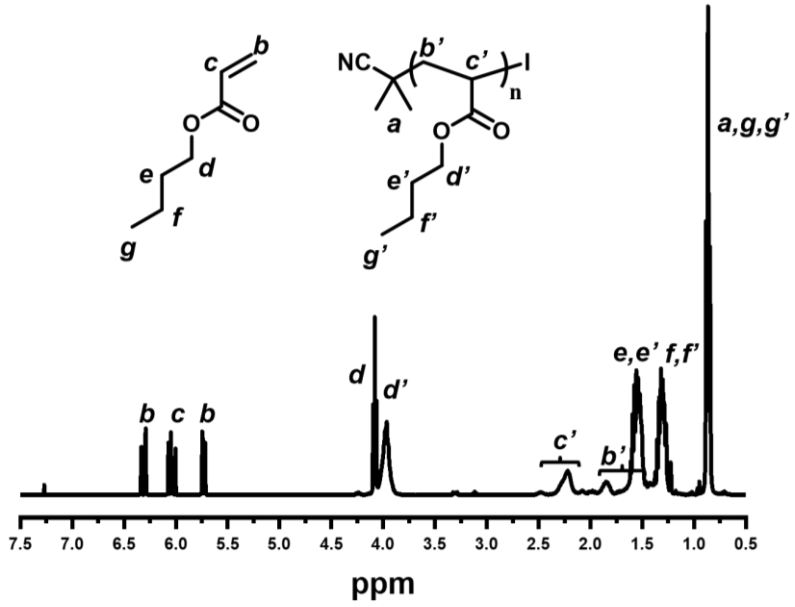

Fig. S1.[1]H NMR spectrum ($CDCl_3$) of the reaction mixture for the synthesis of PBA–I after the reaction (**Table S1** (entry 1) in Supporting Information). The monomer (BA) conversion was determined from the peak areas of the C*H*$_2$O protons in the monomer (peak *d*) and polymer (peak *d'*).

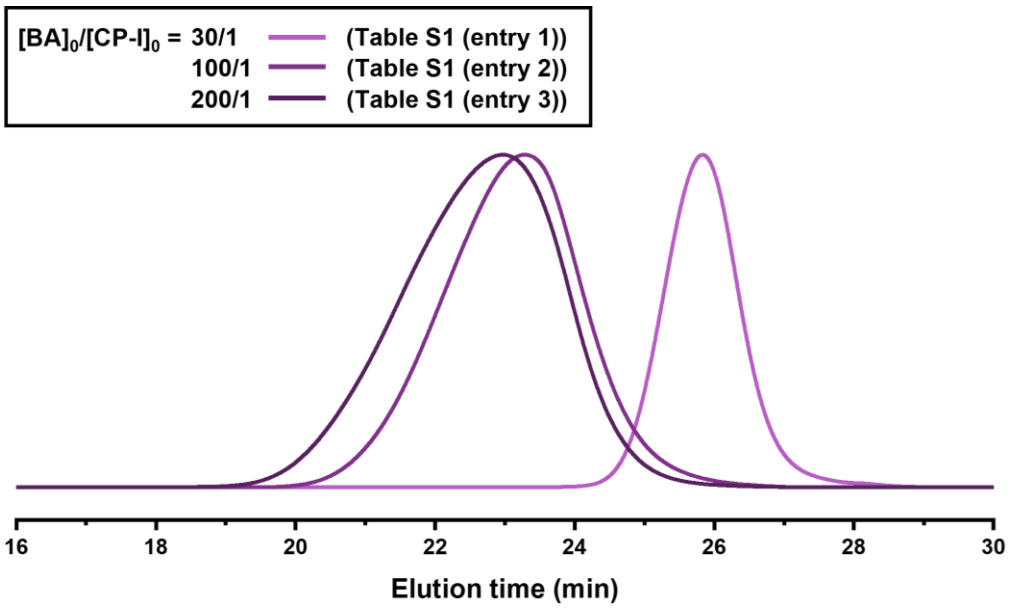

Fig. S2. GPC chromatograms of PBA–I (**Table S1** (entries 1–3) in Supporting Information) after purification (reprecipitation).

Table S1. Synthesis of PBA–I *via* RCMP and PBA–Br *via* Copper-Catalyzed ATRP.

Entry	R–X	Catalyst	$[BA]_0/[R–X]_0/[catalyst]_0$	Monomer conversion[a] (%)	Before purification		After purification		$DP_{n,theo}$[d]	Polymer
					M_n[b] ($M_{n,theo}$[c]) (g/mol)	$Đ$[b]	M_n[b] (g/mol)	$Đ$[b]		
1	CP–I	BNI	30/1/1[e]	72	3700 (3000)	1.14	3800	1.12	22	PBA_{22}–I
2	CP–I	BNI	100/1/1[e]	79	11000 (10500)	1.41	15000	1.29	79	PBA_{79}–I
3	CP–I	BNI	200/1/1[e]	78	19000 (20000)	1.34	22000	1.34	156	PBA_{156}–I
C1	EBiB	$CuBr_2$[f]	30/1/0.02[f]	97	4800 (3900)	1.10	4900	1.10	29	PBA_{29}–Br

[a] Monomer conversion determined using ^{1}H NMR. [b] PMMA-calibrated GPC values (THF) of polymer [c] Theoretical M_n value calculated according to ($[BA]_0/[R–X]_0$)×(monomer conversion)×(molecular weight of BA) + (molecular weight of R–X). [d] Theoretical number-average degree of polymerization calculated according to $[BA]_0/[R–X]_0$×(monomer conversion). In the present work, the DP value was estimated from the $[BA]_0/[CP–I]_0$ ratio multiplied by the monomer (BA) conversion. This DP is not an absolute value but should be viewed as an estimate for classifying short to long chains. (The quantitative estimate of the DP value using ^{1}H NMR was difficult because of ^{1}H NMR peak overlapping.) [e] The polymerization was conducted at 110 °C for 18 h for entries 1–3. [f] The catalyst was $CuBr_2$/Me_6TREN complex (0.02/0.12 equiv). The polymerization was conducted at an ambient temperature for 18 h under UV light (λ = 365 nm) for entry C1. $CuBr_2$ was in situ reduced to CuBr by an excess amount of Me_6TREN under light.

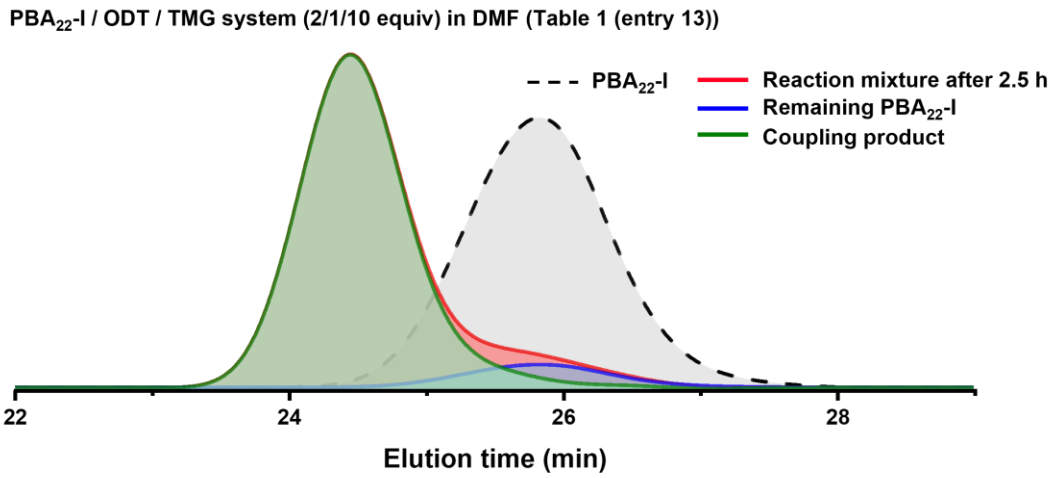

Fig. S3. GPC chromatograms of the original PBA_{22}–I (black dashed line) and the reaction mixtures of PBA_{22}–I (2 equiv), ODT (1 equiv), TMG (10 equiv), and DMF at ambient temperature for 2.5 h (red solid line) (**Table 1** (entry 13)). The chromatogram of the reaction mixture (red solid line) was resolved into the unreacted PBA_{22}–I (blue solid line) and the coupling product (green solid line). In the peak resolution, (the shape of) the chromatogram of PBA_{22}–I is known. Thus, the chromatogram of PBA_{22}–I (blue solid line) was subtracted from the chromatogram of the reaction mixture (red solid line) to give the chromatogram of the coupling product (green solid line).

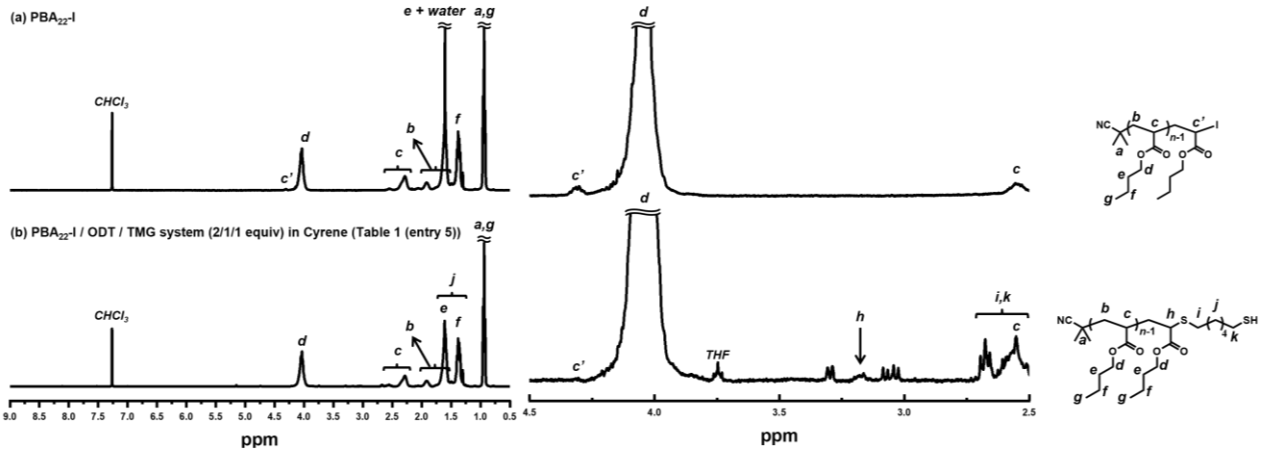

Fig. S4. ^1H NMR spectra ($CDCl_3$) of (**a**) the original PBA_{22}–I and (**b**) the purified polymer after the reaction of PBA_{22}–I (2 equiv), ODT (1 equiv), TMG (1 equiv), and Cyrene at ambient temperature for 2.5 h (**Table 1** (entry 5)).

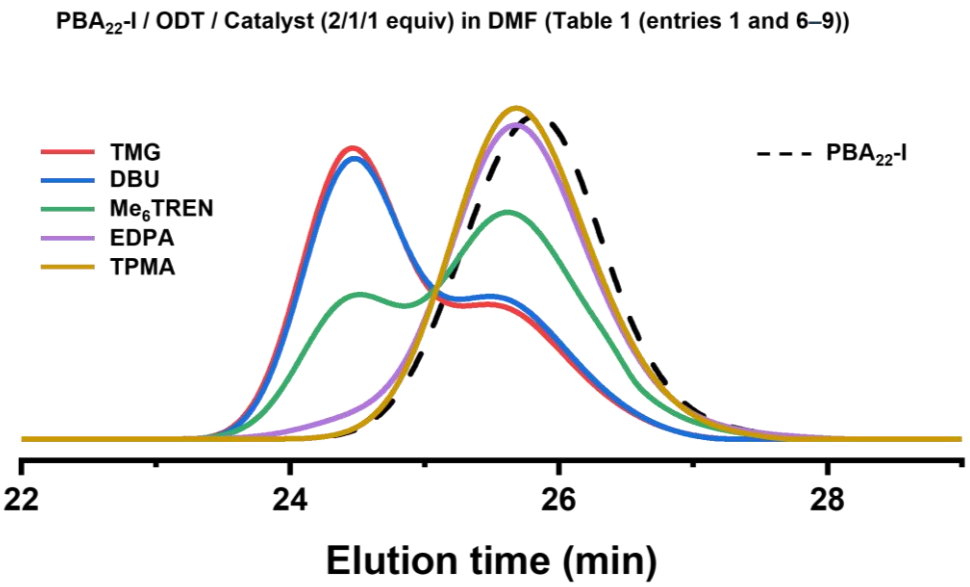

Fig. S5. GPC chromatograms of the original PBA_{22}–I (black dashed line) and the reaction mixtures of PBA_{22}–I (2 equiv), ODT (1 equiv), catalyst (1 equiv), and DMF at ambient temperature for 2.5 h (**Table 1** (entries 1 and 6–9)). The catalysts are indicated in the figure.

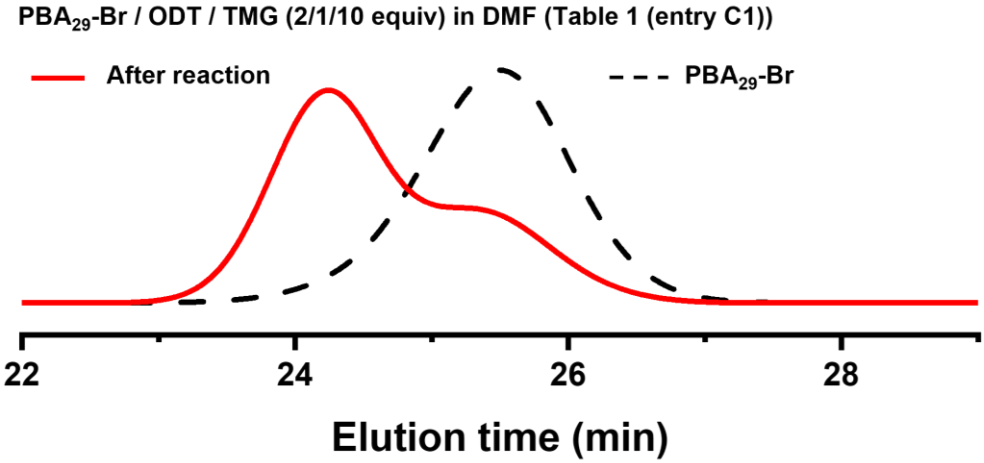

Fig. S6. GPC chromatograms of the original PBA_{29}–Br (black dashed line) and the reaction mixtures of PBA_{29}–Br (2 equiv), ODT (1 equiv), TMG (10 equiv), and DMF at ambient temperature for 2.5 h (red solid line) (**Table 1** (entry C1)).

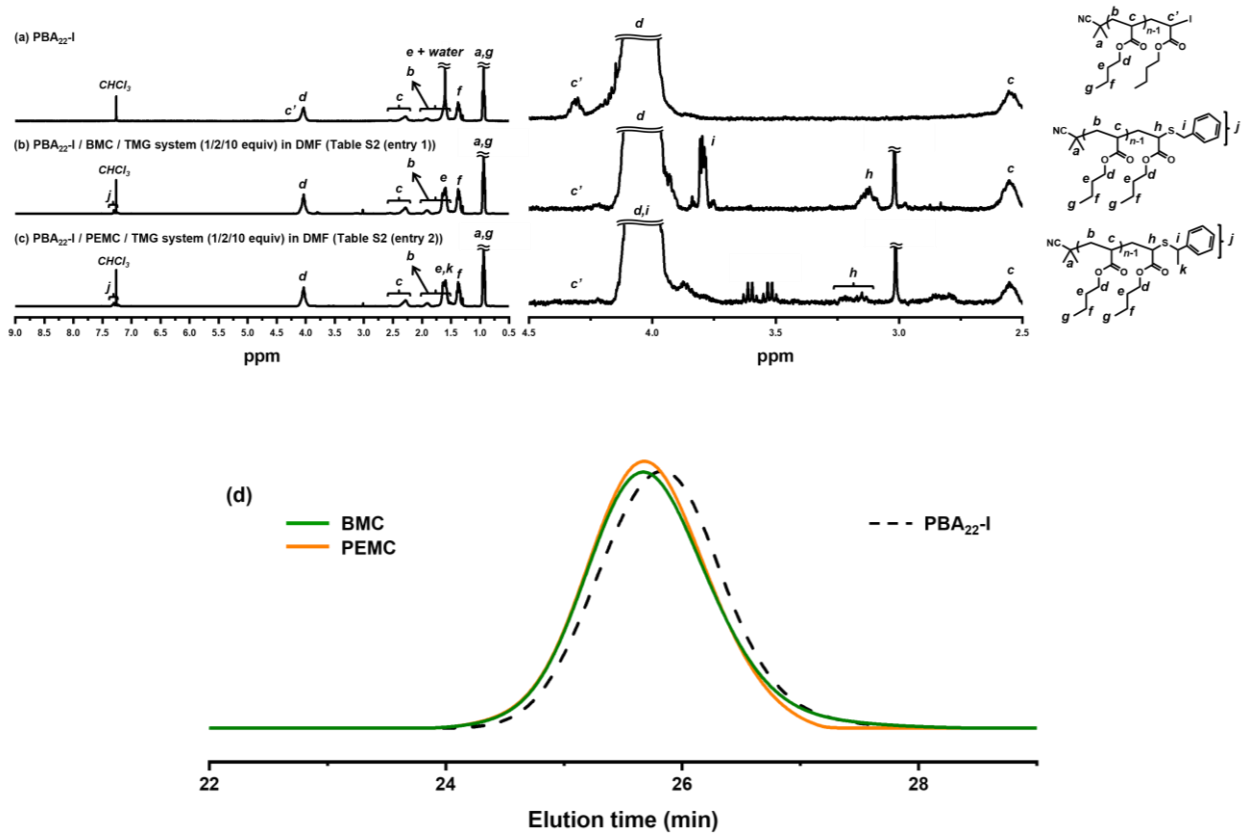

Fig. S7. ^{1}H NMR spectra ($CDCl_3$) of (**a**) the original PBA_{22}–I, and the purified products after the reaction of PBA_{22}–I (1 equiv), monothiol (2 equiv), catalyst (10 equiv), and DMF at ambient temperature for 2.5 h, where the monothiol was (**b**) BMC and (**c**) PEMC (**Table S2** (entries 1 and 2) in Supporting Information). (**d**) GPC chromatograms of the original PBA_{22}–I (black dashed line) and the reaction mixtures after the reaction (solid lines) (**Table S2** (entries 1 and 2) in Supporting Information). The monothiols are indicated in the figure.

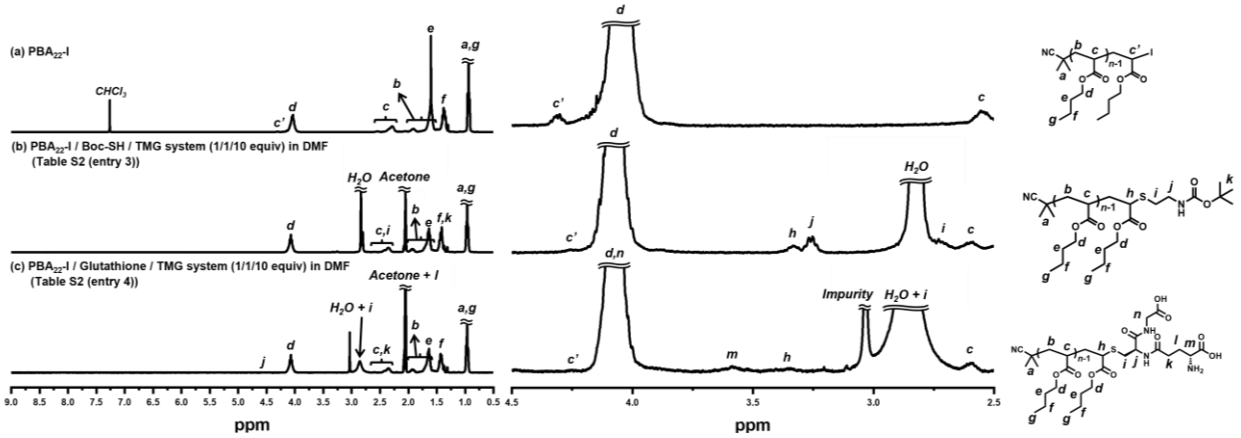

Fig. S8. ^{1}H NMR spectra (acetone-d_6) of (**a**) the original PBA_{22}–I, and the purified products after the reaction of PBA_{22}–I (1 equiv), monothiol (1 equiv), catalyst (10 equiv), and DMF at ambient temperature for 2.5 h, where the monothiol was (**b**) Boc-SH and (**c**) Glutatione (**Table S2** (entries 3and 4) in Supporting Information).

Table S2. Substitution of PBA–I with Monothiols (Small Molecular and Biological Thiol-Containing Compounds).

Entry	Monothiol	$[PBA_{22}–I^{a}]_0/[monothiol]_0/[TMG]_0$ [b]	M_p [c] (g/mol) of substituted product	M_n [c] (g/mol) of the entire reaction mixture	$Đ$ [c] of the entire reaction mixture	Substitution yield [d] (%)
1	BMC	1/2/10	4600	4100	1.10	>90
2	PEMC	1/2/10	4600	4300	1.08	>90
3	Boc-SH	1/1/10	4700	4200	1.11	70
4	Glutatione	1/1/10	4800	5200	1.59	55

[a] M_n = 3800 g/mol and M_p = 4200 g/mol determined using PMMA-calibrated GPC (THF eluent) (**Table S1** (entry 1)). M_p is the GPC peak-top molecular weight. [b] PBA_{22}–I was 10 wt% and DMF (solvent) was 90 wt%. The reaction mixture was stirred under dark at room temperature for 2.5 h. [c] Determined with PMMA-calibrated GPC (THF eluent). [d] The substitution yield was determined using ^{1}H NMR.

Table S3. Substitution of PBA–I with PEG_{2k}–SH (Monothiol) to Generate PBA-*b*-PEG Diblock Copolymer.

Entry	PBA–I	$[PBA–I]_0/[PEG_{2k}–SH^b]_0/[TMG]_0$	M_p[c] (g/mol) of substituited product	M_n[c] (g/mol) of the entire reaction mixture	$Đ$[c] of the entire reaction mixture	Substitution yield[d] (%)
1	PBA_{22}–I (M_p = 4200 g/mol)[a] (M_n = 3800 g/mol)[a]	1/1/10	8100	7200	1.08	85
2	PBA_{79}–I (M_p = 16000 g/mol)[a] (M_n = 15000 g/mol)[a]	1/1/10	21000	18000	1.27	NA[e]
3	PBA_{156}–I (M_p = 24000 g/mol)[a] (M_n = 22000 g/mol)[a]	1/1/10	36000	20000[f]	1.98	NA[e]

[a] Determined using PMMA-calibrated GPC (THF eluent) (**Table S1** (entries 1–3)). M_p is the GPC peak-top molecular weight. [b] PBA–I was 10 wt% and DMF (solvent) was 90 wt%. The reaction mixture was stirred under dark at room temperature for 2.5 h. PEG_{2k}–SH contained dimer of PEG_{2k}–SH (~9%) and non-SH-terminated (H-terminated) PEG (~4%) according to the supplier (Aldrich). [c] Determined with PMMA-calibrated GPC (THF eluent). M_n includes the remaining (unreacted PEG_{2k}–SH). M_p is the GPC peak-top molecular weight. [d] The substitution yield was determined from GPC peak areas of the substituted product and the original PBA–I. [e] The substitution yield was not able to determine because of the overlapped chromatograms of the substituted product and the original PBA–I. [f] M_n appeared to be slightly lowered from the original PBA_{156}–I after the substitution reaction because of the inclusion of the unreacted PEG_{2k}–SH.

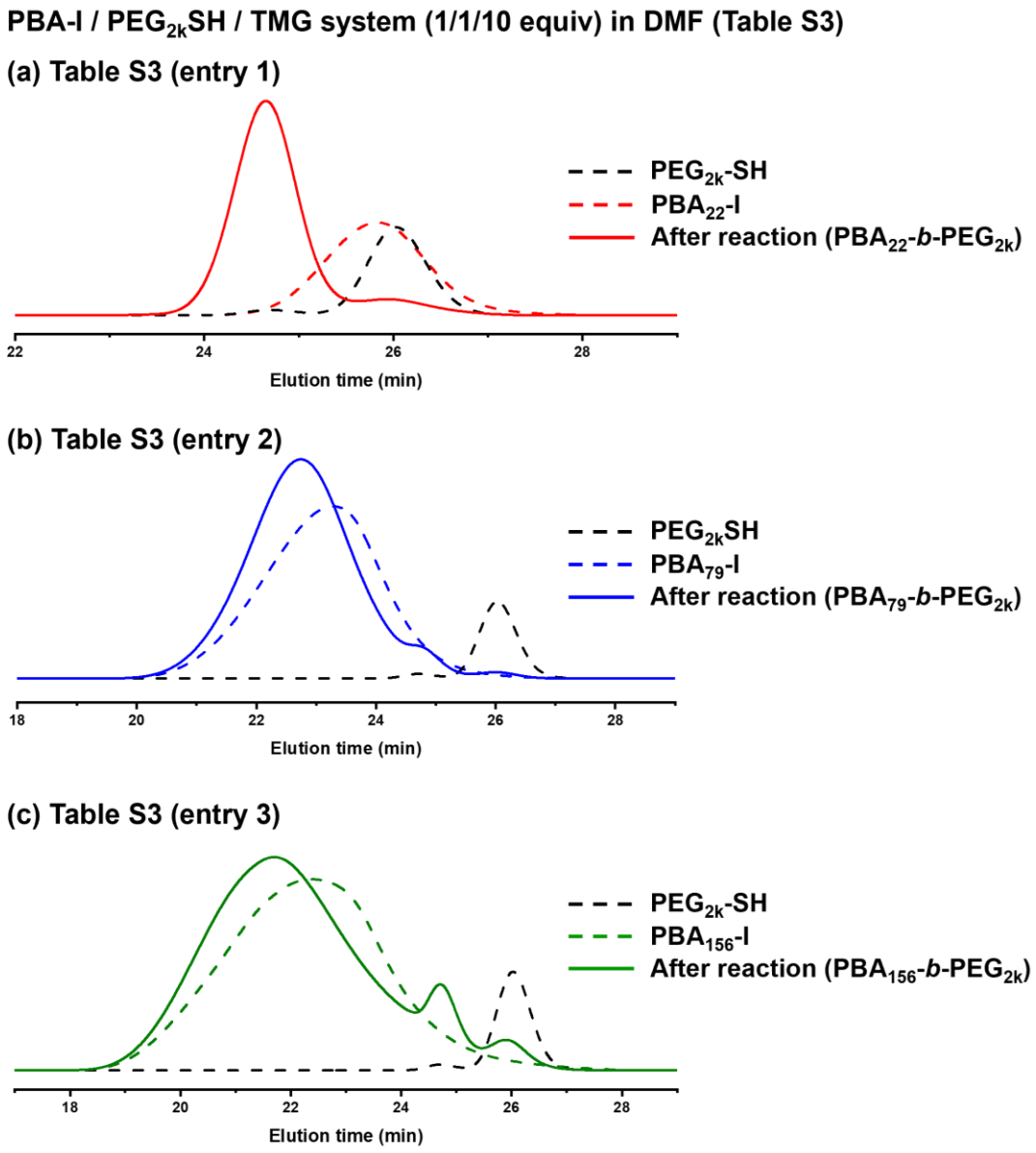

Fig. S9. GPC chromatograms of the original PEG_{2k}–SH (black dashed lines), the original PBA–I (coloured dashed lines), and the reaction mixtures of PBA–I (1 equiv), PEG_{2k}-SH (1 equiv), TMG (10 equiv), and DMF at ambient temperature for 2.5 h (coloured solid lines), where PBA–I is (**a**) PBA_{22}–I (**Table S3** (entry 1) in Supporting Information), (**b**) PBA_{79}–I (**Table S3** (entry 2)), and (**c**) PBA_{156}–I (**Table S3** (entry 3)).

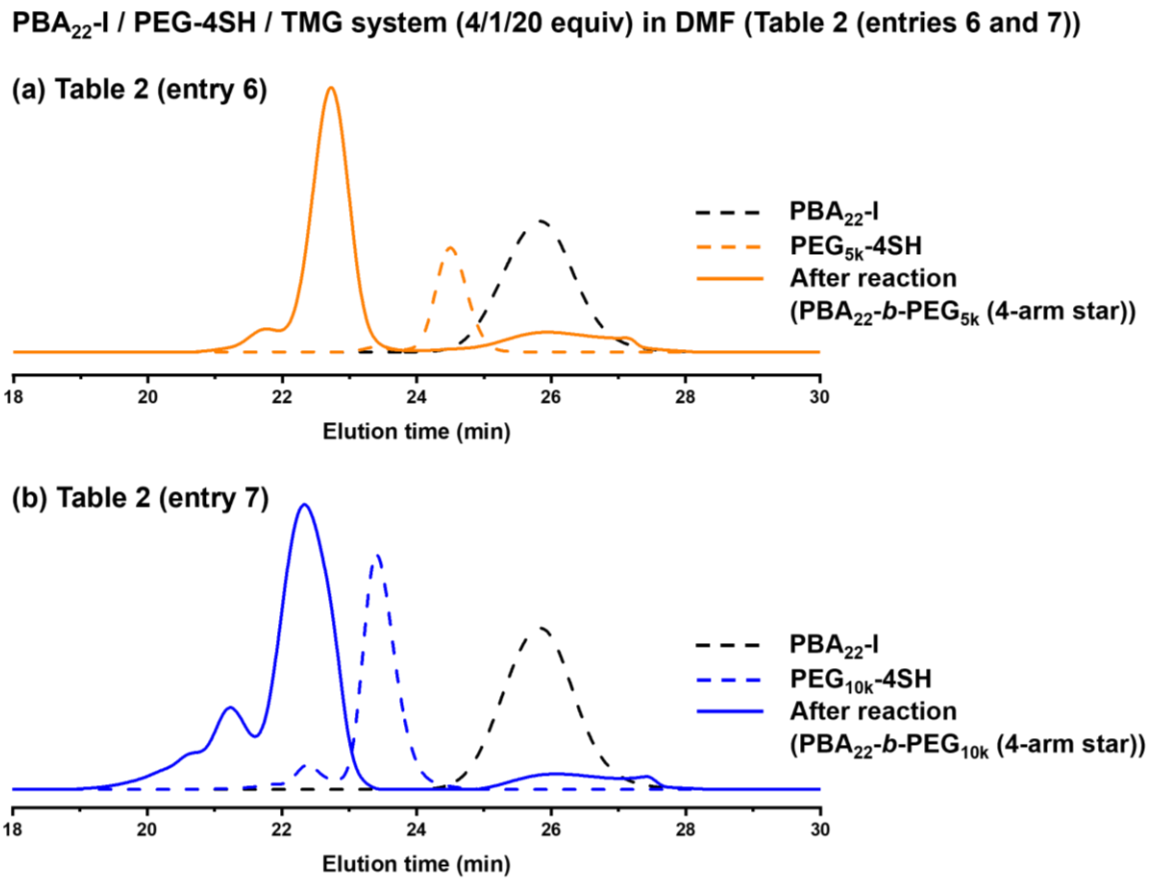

Fig. S10. GPC chromatograms of the original PBA_{22}–I (black dashed line), the original PEG–4SH (coloured dashed lines), and the reaction mixtures of PBA_{22}–I (4 equiv), PEG–4SH (1 equiv), TMG (20 equiv), and DMF at ambient temperature for 2.5 h (coloured solid lines), where PEG–4SH is (**a**) PEG_{5k}–4SH (**Table 2** (entry 6)) and (**b**) PEG_{10k}–4SH (**Table 2** (entry 7)).

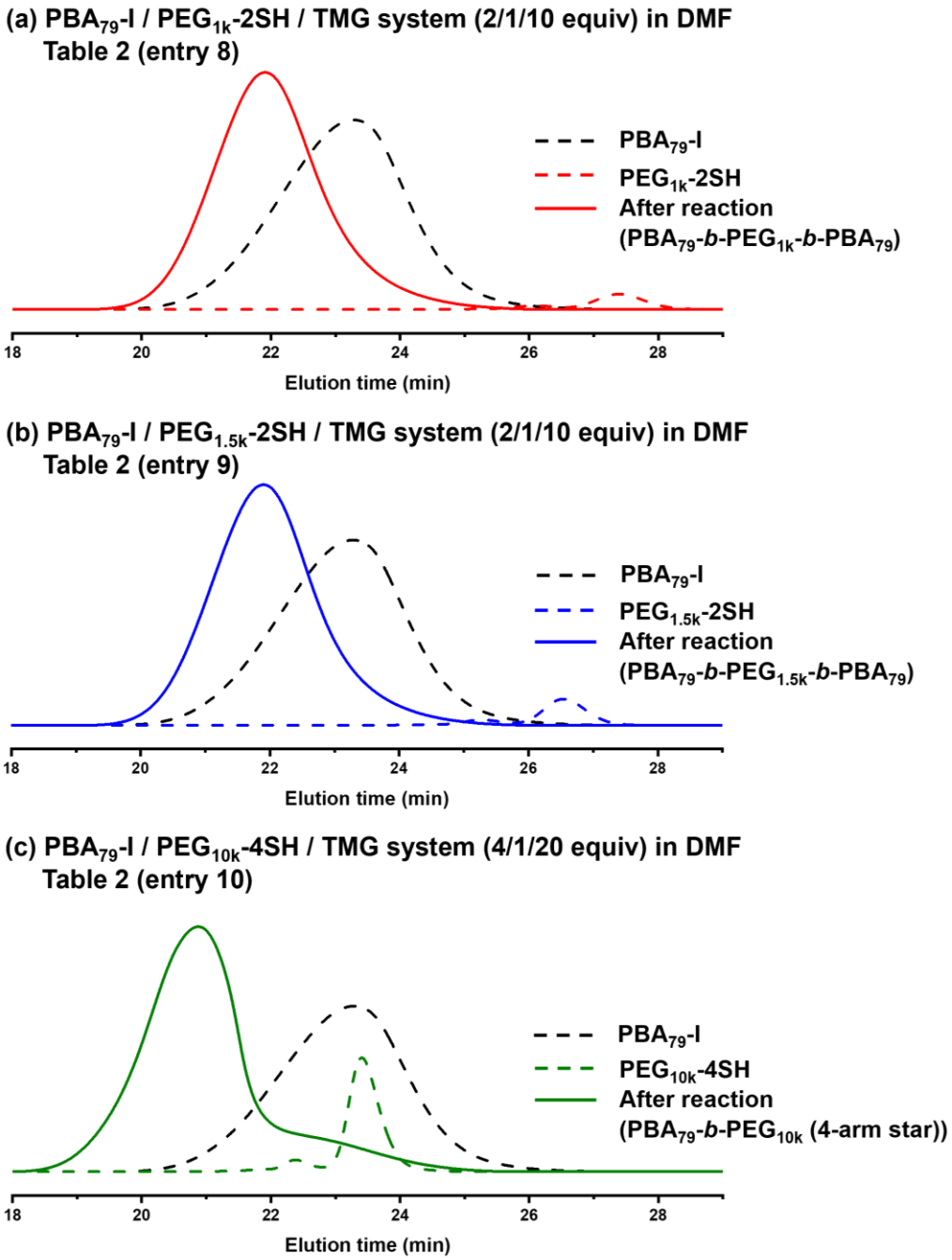

Fig. S11 (continued). GPC chromatograms of the original PBA–I (black dashed line), the original PEG-containing thiol (coloured dashed lines), and the reaction mixtures of PBA–I (2 or 4 equiv), PEG-containing thiol (1 equiv), TMG (10 or 20 equiv), and DMF at ambient temperature for 2.5 h (coloured solid lines), where PBA–I and PEG-containing thiol are (**a**) PBA_{79}–I and PEG_{1k}–2SH (**Table 2** (entry 8)), (**b**) PBA_{79}–I and $PEG_{1.5k}$–2SH (**Table 2** (entry 9)), and (**c**) PBA_{79}–I and PEG_{10k}–4SH (**Table 2** (entry 10)), (**d**) PBA_{156}–I and PEG_{1k}–2SH (**Table 2** (entry 11)), (**e**) PBA_{156}–I and $PEG_{1.5k}$–2SH (**Table 2** (entry 12)), and (**f**) PBA_{156}–I and PEG_{10k}–4SH (**Table 2** (entry 13)), respectively.

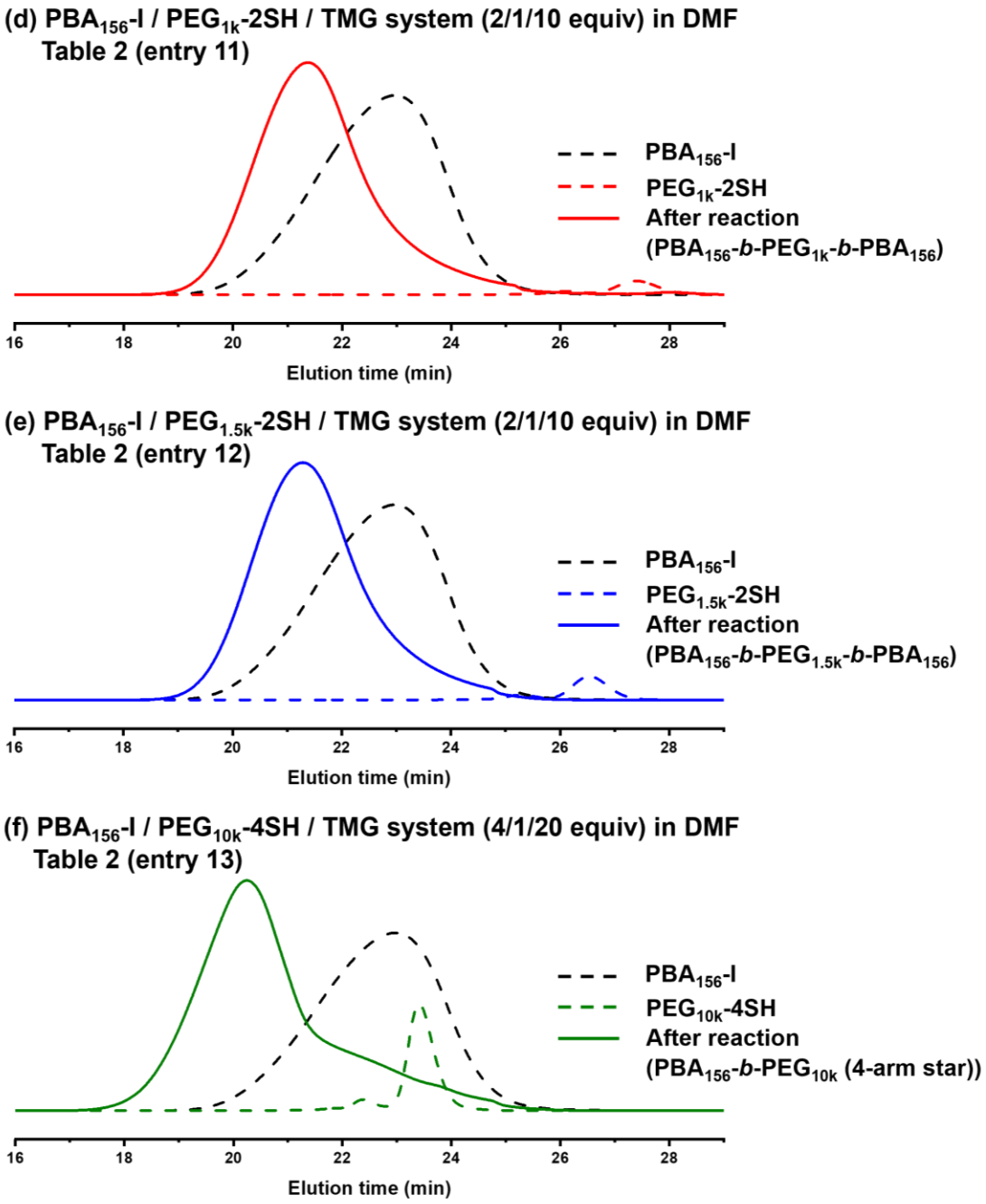

Fig. S11. GPC chromatograms of the original PBA–I (black dashed line), the original PEG-containing thiol (coloured dashed lines), and the reaction mixtures of PBA–I (2 or 4 equiv), PEG-containing thiol (1 equiv), TMG (10 or 20 equiv), and DMF at ambient temperature for 2.5 h (coloured solid lines), where PBA–I and PEG-containing thiol are (**a**) PBA_{79}–I and PEG_{1k}–2SH (**Table 2** (entry 8)), (**b**) PBA_{79}–I and $PEG_{1.5k}$–2SH (**Table 2** (entry 9)), and (**c**) PBA_{79}–I and PEG_{10k}–4SH (**Table 2** (entry 10)), (**d**) PBA_{156}–I and PEG_{1k}–2SH (**Table 2** (entry 11)), (**e**) PBA_{156}–I and $PEG_{1.5k}$–2SH (**Table 2** (entry 12)), and (**f**) PBA_{156}–I and PEG_{10k}–4SH (**Table 2** (entry 13)), respectively.

Table S4. $T_{d,5\%}$, T_g, and T_m values of Block Copolymers, Original PEG thiols, and Original PBA–I.

Entry	Polymer	Synthetic condition	$T_{d,5\%}$ (°C)	T_g (°C)	T_m (°C)
1	PBA_{22}-*b*-PEG_{2k} (diblock)	**Table S3** (entry 1)	334	–50	39
2	PBA_{22}-*b*-$PEG_{1.5k}$-*b*-PBA_{22} (triblock)	**Table 2** (entry 3)	335	–58	NA[b]
3	PBA_{22}-*b*-PEG_{10k} (4 arm star)	**Table 2** (entry 7)	343	–47	40
4	PBA_{79}-*b*-PEG_{2k} (diblock)	**Table S3** (entry 2)	301	–47	36
5	PBA_{79}-*b*-$PEG_{1.5k}$-*b*-PBA_{79} (triblock)	**Table 2** (entry 9)	317	–50	NA[b]
6	PBA_{79}-*b*-PEG_{10k} (4 arm star)	**Table 2** (entry 10)	303	–47	37
7	PBA_{156}-*b*-PEG_{2k} (diblock)	**Table S3** (entry 3)	302	–47	36
8	PBA_{156}-*b*-$PEG_{1.5k}$-*b*-PBA_{156} (triblock)	**Table 2** (entry 12)	311	–49	NA[b]
9	PBA_{156}-*b*-PEG_{10k} (4 arm star)	**Table 2** (entry 13)	342	–48	40
C1	PEG_{2k}–SH (monothiol)	NA[a]	330	NA[b]	58
C2	$PEG_{1.5k}$–2SH (dithiol)	NA[a]	331	NA[b]	52
C3	PEG_{10k}–4SH (tetrathiol)	NA[a]	312	NA[b]	58
C4	PBA_{156}–I	**Table S1 (**entry 3)	315	–50	NA[b]

[a] Purchased from Sigma-Aldrich. [b] Not clearly observed.

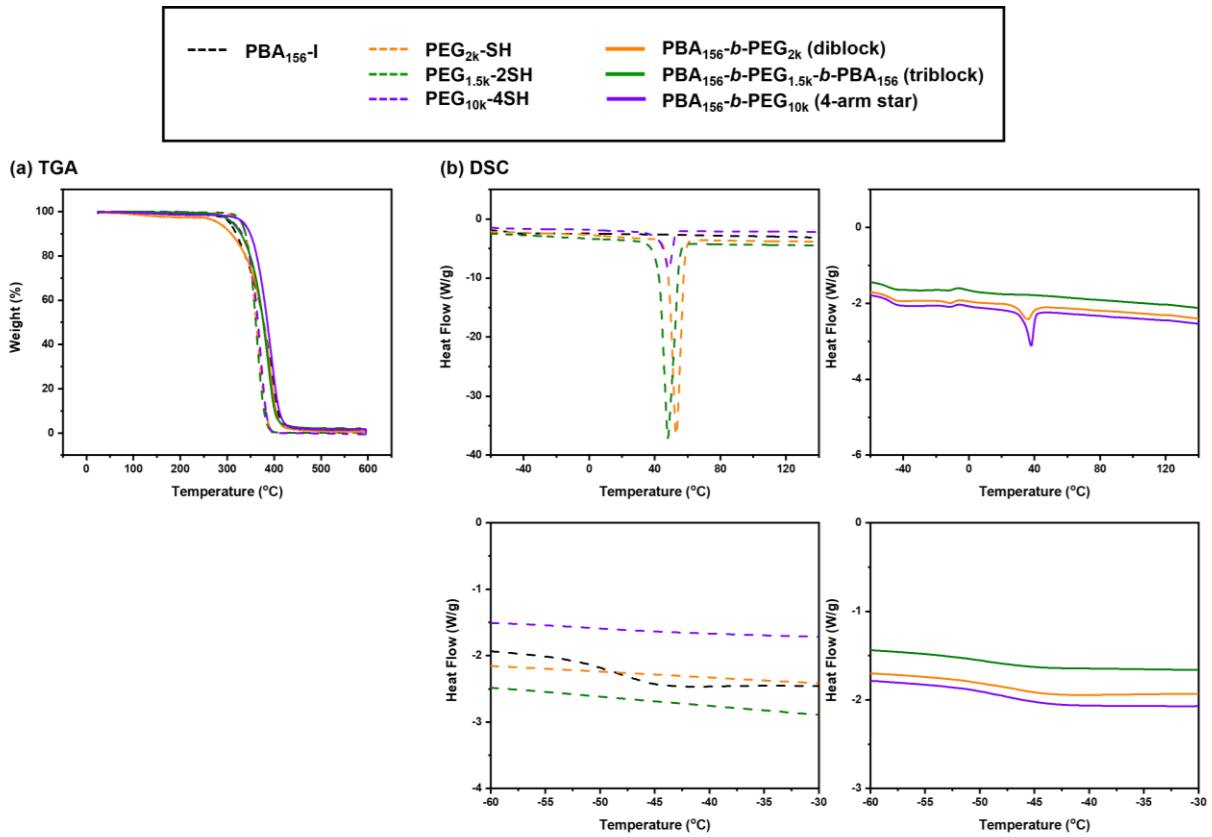

Fig. S12. (**a**) TGA and (**b**) DSC curves of the original PBA_{156}–I (black dashed lines) and the original PEG-based thiols (PEG_{2k}–SH, $PEG_{1.5k}$–2SH, and PEG_{10k}–4SH) (coloured dashed lines), and the block copolymers (PBA_{156}-*b*-PEG_{2k} (diblock) (**Table S3** (entry 3) in Supporting Information), PBA_{156}-*b*-$PEG_{1.5k}$-*b*-PBA_{156} (triblock) (**Table 2** (entry 12)), and PBA_{156}-*b*-PEG_{10k} (4 arm star) (**Table 2** (entry 13))) (coloured solid lines). The thiols and block copolymers are indicated in the figure.

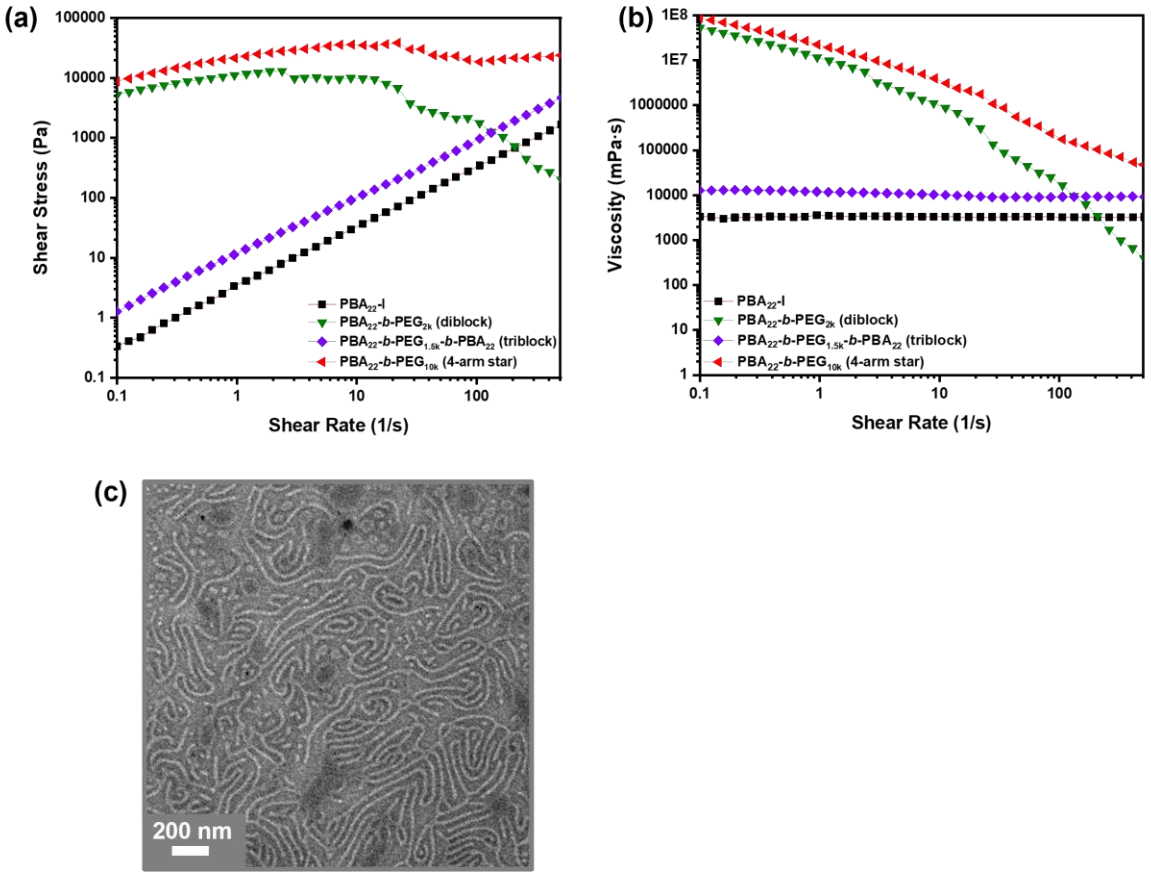

Fig. S13. Plots of (**a**) shear stress and (**b**) viscosity vs shear rate for PBA_{22}–I, and PBA_{22}-*b*-PEG_{2k} (diblock), PBA_{22}-*b*-$PEG_{1.5k}$-*b*-PBA_{22} (triblock), and PBA_{22}-*b*-PEG_{10k} (4-arm star) at 25 ^{o}C. (**c**) TEM image of drop-cast film of PBA_{22}-*b*-PEG_{10k} (4-arm star).

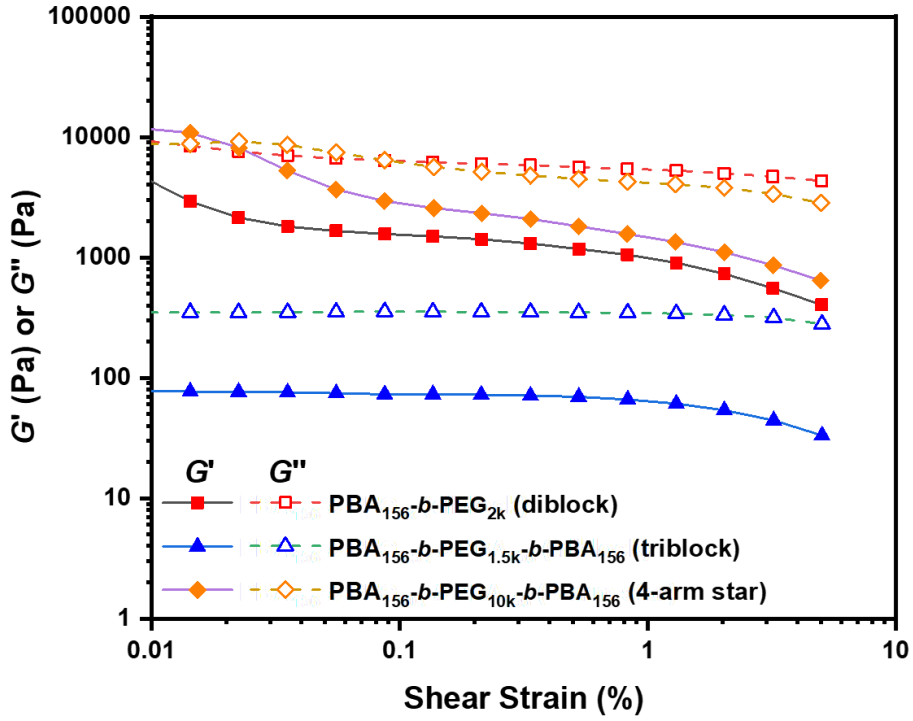

Fig. S14. Plots of *G*' (filled symbols) and *G*" (open symbols) vs shear strain at 25 °C at a constant frequency of ω = 10 rad/s (amplitude sweep experiment) for PBA_{156}-*b*-PEG_{2k} (diblock), PBA_{156}-*b*-$PEG_{1.5k}$-*b*-PBA_{156} (triblock), and PBA_{156}-*b*-PEG_{10k} (4-arm star). The polymers are indicated in the figure.

3. Determination of Coupling and Substitution Yields

Determination of Coupling Yield Using GPC Chromatogram. An example of the GPC peak resolution is given in **Figure S3** in Supporting Information. The coupling yield was determined from GPC peak areas of the coupling product and the unreacted original PBA–I (or PBA–Br) according to **Equation S1**.

$$\text{Coupling yield} = \left[1 - \frac{(\text{area of remaining PBA} - \text{I})}{(\text{areas of coupling product}) + (\text{area of remaining PBA} - \text{I})}\right] \times 100\%$$

(Equation S1)

Determination of Substitution Yield Using NMR Spectrum. For monothiols (BMC, PEMC, Boc-SH, and Glutathione) (**Table S2** in Supporting Information), the substitution yield was determined using ^{1}H NMR. For example, the substitution yield for the BMC system (**Table S2** (entry 1) in Supporting Information) was determined as follows. For the original PBA–I (**Figure S7a** in Supporting Information), the C*H* proton (*c*') adjacent to iodide at the terminal unit of PBA appeared at 4.30 ppm. After the substitution reaction (**Figure S7b** in Supporting Information), the signal for the proton *c*' decayed and a new signal for the C*H* proton (*h*)[2] adjacent to sulfur at the terminal unit of PBA appeared at 3.12 ppm. The substitution yield was determined according to **Equation S2**.

$$\text{Substitution Yield (\%)} = \frac{(\text{peak area of proton } h)}{(\text{peak area of proton } c') + (\text{peak area of proton } h)} \times 100\%$$

(**Equation S2**)

REFERENCES

1 A. Anastasaki, V. Nikolaou, Q. Zhang, J. Burns, S. R. Samanta, C. Waldron, A. J. Haddleton, R. McHale, D. Fox, V. Percec, P. Wilson, D. M. Haddleton, *J. Am. Chem. Soc.* 2014, **136**, 1141-1149.

2 X. M. Sim, C. Chen, A. Goto, *ACS Appl. Mater. Interface*. 2021, **13**, 24183-24193.