Electronic Supplementary Information (ESI)

Synthesis of Core Cross-linked Star Polymers via Organocatalyzed Living Radical Polymerization

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1. Experimental Section

Materials. Methyl methacrylate (MMA) (>99.8%, Tokyo Chemical Industry (TCI), Japan), butyl acrylate (BA) (>99%, TCI), butyl methacrylate (BMA) (>99%, TCI), poly(ethylene glycol) methyl ether acrylate (PEGA) (average molecular weight = 480) (98%, Sigma-Aldrich, USA), ethylene glycol dimethacrylate (EGDMA) (98%, Sigma-Aldrich), di(ethylene glycol) diacrylate (DGDA) (75%, Sigma-Aldrich), 2-iodo-2-methylpropionitrile (CP–I) (>95%, TCI), tetrabutylammonium iodide (BNI) (>98%, TCI), tetrahydrofuran (THF) (>99.5%, VWR Chemicals, USA), diethylene glycol dimethyl ether (diglyme) (>99%, TCI), butyl acetate (>99%, TCI), *N*,*N*-dimethylformamide (DMF) (>99.5%, Kanto Chemical, Japan), toluene (99.5%, J.T.

Baker, USA), hexane (>99%, International Scientific, Singapore), and methanol (>99%, International Scientific) were used as received. Deionized water was generated from an EMD Millipore Milli-Q^{TM} Advantage A10 Water Purification System.

Measurements. The GPC analysis using THF as an eluent was performed on a Shimadzu i-Series Plus liquid chromatograph LC-2030c Plus (Kyoto, Japan) equipped with a Shodex (Japan) KF-804L mixed gel column (300 × 8.0 mm; bead size = 7 μm; pore size = 1500 Å) and a Shodex LF-804 mixed gel column (300 × 8.0 mm; bead size = 6 μm; pore size = 3000 Å). The flow rate was 0.7 mL/min (40 ^{o}C). The GPC analysis using DMF as an eluent was performed on a Shimadzu LC-2030c Plus equipped with two Shodex LF-804 mixed gel columns (300 × 8.0 mm; bead size = 6 μm; pore size = 3000 Å) and a Shodex KD-802 (300 × 8.0 mm; bead size = 6 μm; pore size = 150 Å). The flow rate was 0.34 mL/min (40 °C). The DMF eluent contained LiBr (10 mM). The GPC analysis using THF as an eluent was also performed on a Shimadzu LC-2030c Plus equipped with two Shodex KF-806L mixed gel columns (high molecular weight columns) (300 × 8.0 mm; bead size = 10 μm; pore size = 10000 Å) whose size exclusion limit is 20000000. The flow rate was 1.0 mL/min (40 ^{o}C). Sample detection was conducted using a Shimadzu differential refractometer RID-20A for all GPC measurements. The column systems were calibrated with standard poly(methyl methacrylate)s (PMMAs) for all GPC measurements.

The NMR spectra were recorded on a Bruker BBFO400 spectrometer (400 MHz) at ambient temperature. Chloroform-*d* ($CDCl_3$) (Cambridge Isotope Laboratories, USA) was used as the NMR solvent. The monomer conversion was calculated from the decay in the area of the vinyl peak of the monomer.

The DLS measurement was carried out on a Malvern Zetasizer Nano ZSP (Worcestershire, UK) at room temperature. The test angle for the DLS analysis was 173° (backscattering detection).

The static light scattering (SLS) measurement was carried out on a Malvern Zetasizer Nano ZSP (Worcestershire, UK) at room temperature. Pure toluene was used as the scattering standard. A sphere shape correction model was applied with $R_g = 0.774R_h$. The refractive index increment (dn/dc) values of the purified star polymers (Table 3) were determined using a refractive index (RI) detector (Shimadzu differential refractometer RID-20A) in a GPC system. The intensity of the RI detector (RI intensity) is given by equation (1):

$$\text{(RI intensity)} = K_{RI} \times (dn/dc) \times \text{(concentration of polymer)} \times \text{(injection volume)} \quad (1)$$

where K_{RI} is the RI detector constant. The K_{RI} value was determined using a PMMA homopolymer ($M_n = 30000$ and $Đ = 1.02$) (Agilent, USA) ($dn/dc = 0.0871$ mL/g in THF and $dn/dc = 0.0614$ mL/g in DMF) as a reference. The (dn/dc) values of the purified star polymers were determined according to equation (1).

Synthesis of PBA–I. A mixture of BA (14.0 g, 200 equiv), CP–I (107 mg, 1 equiv), and BNI (807 mg, 4 equiv) was heated in a Schlenk flask at 110 °C under argon atmosphere with magnetic stirring for 10 h. The monomer conversion was 37%. The mixture was cooled to room temperature, diluted with THF (10 mL), reprecipitated from 500 mL methanol/water (8/2 (v/v)) mixture (non-solvent) twice, and dried in vacuo to yield a purified PBA–I ($M_n = 12000$ and $Đ = 1.27$ after purification).

Synthesis of PMMA–I. A mixture of MMA (2.40 g, 100 equiv), CP–I (46.7 mg, 1 equiv), and BNI (44.3 mg, 0.5 equiv) was heated in a Schlenk flask at 70 °C under argon atmosphere with magnetic stirring for 0.5 h. The monomer conversion was 27%. The mixture was cooled to room temperature, diluted with THF (2 mL), reprecipitated from 50 mL hexane (non-solvent), and dried in vacuo to yield a purified PMMA–I (M_n = 3100 and $Đ$ = 1.25 after purification).

Synthesis of PMMA–PPEGA–I. A mixture of PEGA (20.2 g, 100 equiv), PMMA–I (M_n = 3100 and $Đ$ = 1.25, 1.05 g, 1 equiv), and BNI (1.24 g, 8 equiv) was heated in a Schlenk flask at 110 °C under argon atmosphere with magnetic stirring for 8 h. The monomer conversion was 23%. The mixture was cooled to room temperature, diluted with acetone (10 mL), reprecipitated from 600 mL hexane/diethyl ether (7/3 v/v) three times, and dried in vacuo to yield a purified PMMA–PPEGA–I (M_n = 12000 and $Đ$ = 1.19 after purification).

Synthesis of PMMA–PBA–I from PMMA–Y. A mixture of BA (1.50 g, 100 equiv), PMMA–Y (M_n = 3900 and $Đ$ = 1.67, 456 mg, 1 equiv), CP–I (22.8 mg, 1 equiv), and BNI (150 mg, 4 equiv) was heated in a Schlenk flask at 110 °C under argon atmosphere with magnetic stirring for 24 h. The monomer conversion was 85%. The mixture was cooled to room temperature, diluted with THF (3 mL), reprecipitated from 250 mL methanol/water (8/2 v/v) twice, and dried in vacuo to yield a purified PMMA–PBA–I (M_n = 15000 and $Đ$ = 1.81 after purification).

Synthesis of PBA star polymer with DGDA. A mixture of DGDA (188 mg, 30 equiv), PBA–I (M_n = 12000 and $Đ$ = 1.27, 350 mg, 1 equiv), BNI (21.5 mg, 2 equiv) and toluene (1.30 g, 70 wt%) was heated in a Schlenk flask at 110 °C under argon atmosphere with magnetic stirring for 48 h. An aliquot of the reaction mixture was taken out, diluted with THF, and analyzed with THF-GPC. Another aliquot of the mixture was taken out, diluted with $CDCl_3$, and analyzed with

^{1}H NMR. The rest of the mixture was diluted with THF (3 mL), reprecipitated in 100 mL methanol (non-solvent) twice, and dried in vacuo to yield a purified PBA star (M_n = 230000 and $Đ$ = 1.17 after purification).

Synthesis of PBA star polymer with EGDMA/BMA. A mixture of EGDMA (113 mg, 20 equiv), BMA (81.3 mg, 20 equiv), PBA–I (M_n = 12000 and $Đ$ = 1.27, 300 mg, 1 equiv), BNI (5.30 mg, 0.5 equiv), and butyl acetate (1.17 g, 70 wt%) was heated in a Schlenk flask at 110 °C under argon atmosphere with magnetic stirring for 24 h. An aliquot of the reaction mixture was taken out, diluted with THF, and analyzed with THF-GPC. Another aliquot of the mixture was taken out, diluted with $CDCl_3$, and analyzed with ^{1}H NMR.

Synthesis of PMMA–PPEGA star polymer. A mixture of DGDA (321 mg, 120 equiv), PMMA–PPEGA–I (M_n = 12000 and $Đ$ = 1.19, 150 mg, 1 equiv), BNI (18.5 mg, 4 equiv) and diglyme (1.14 g, 70 wt%) was heated in a Schlenk flask at 110 °C under argon atmosphere with magnetic stirring for 24 h. An aliquot of the reaction mixture was taken out, diluted with DMF, and analyzed with DMF-GPC. Another aliquot of the mixture was taken out, diluted with $CDCl_3$, and analyzed with ^{1}H NMR. The rest of the mixture was diluted with acetone (3 mL), reprecipitated in 100 mL diethyl ether (non-solvent) twice, and dried in vacuo to yield a purified PMMA–PPEGA star (M_n = 90000 and $Đ$ = 2.89 after purification).

Synthesis of PMMA–PBA star polymer. A mixture of DGDA (214 mg, 60 equiv), PMMA–PBA–I (M_n = 15000 and $Đ$ = 1.81, 250 mg, 1 equiv), BNI (12.3 mg, 2 equiv), and butyl acetate (1.11 g, 70 wt%) was heated in a Schlenk flask at 110 °C under argon atmosphere with magnetic stirring for 46 h. An aliquot of the reaction mixture was taken out, diluted with THF, and analyzed with THF-GPC. Another aliquot of the mixture was taken out, diluted with $CDCl_3$, and analyzed with ^{1}H NMR. The rest of the mixture was diluted with THF (3 mL), reprecipitated in

100 mL methanol (non-solvent) twice, and dried in vacuo to yield a purified PMMA–PBA star (M_n = 390000 and $Đ$ = 1.16 after purification).

One-pot synthesis of PBA star polymer. A mixture of BA (600 mg, 100 equiv), CP–I (9.10 mg, 1 equiv), and BNI (69.2 mg, 4 equiv) was heated in a Schlenk flask at 110 °C under argon atmosphere with magnetic stirring for 24 h. At 24 h, a mixture (purged with argon) of DGDA (501 mg, 50 equiv), DMF (19.7 mg, 0.5wt%) (internal standard), and toluene (3.89 g, 69.5 wt%) was added to the reaction mixture and was heated at 110 °C under argon atmosphere with magnetic stirring for another 46 h (in total 70 h). An aliquot of the reaction mixture was taken out, diluted with THF, and analyzed with THF-GPC. Another aliquot of the mixture was taken out, diluted with $CDCl_3$, and analyzed with ^1H NMR. The rest of the mixture was diluted with THF (3 mL), reprecipitated in 100 mL methanol (non-solvent) twice, and dried in vacuo to yield a purified PBA star (M_n = 230000 and $Đ$ = 1.42 after purification).

Chain extension test of PBA–I macroinitiator. A mixture of BA (1.20 g, 800 equiv), PBA–I (M_n = 12000 and $Đ$ = 1.27, 152 mg, 1 equiv), and BNI (69.2 mg, 16 equiv) was heated in a Schlenk flask at 110 °C under argon atmosphere with magnetic stirring for 40 h. An aliquot of the reaction mixture was taken out, diluted with THF, and analyzed with THF-GPC.

2. Peak resolution of GPC chromatograms.

Chain extension test of PBA–I macroinitiator. We carried out a chain extension test of the PBA–I obtained in Table 1 (entry 1). Namely, we carried out a polymerization of BA (800 equiv) with PBA–I (M_n = 12000 and $Đ$ = 1.27, 1 equiv) and BNI (16 equiv) at 110 °C for 40 h. Fig. S1 shows the chromatograms of the crude reaction mixture at t = 0 h (red solid line) and at t = 40 h (blue solid line). The chromatogram at 40 h (blue solid line) was resolved into the unreacted PBA–I (red dashed line) and the extended polymer (green dashed line). In the peak resolution, the chromatogram of the PBA–I is known and was subtracted from the chromatogram at 40 h to give the chromatogram of the extended polymer.

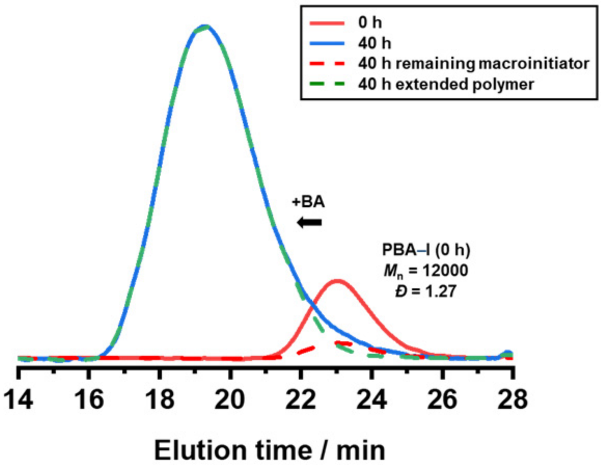

Fig. S1. GPC chromatograms for the chain extension of PBA–I (polymerization of BA (800 equiv) from PBA–I (1 equiv) using BNI (16 equiv) at 110 °C for 40 h). The synthetic details of the PBA–I is given in Table 1 (entry 1). The peak areas of the chromatograms of the crude reaction mixture at t = 0 h (red solid line) and at t = 40 h (blue solid line) are normalized by the monomer conversion. The chromatogram at 40 h (blue solid line) was resolved into the unreacted PBA–I (red dashed line) and the extended polymer (green dashed line). In the peak resolution, the chromatogram of the PBA–I is known and was subtracted from the chromatogram at 40 h to give the chromatogram of the extended polymer.

Synthesis of PBA star polymer using DGDA (Table 2 (entry 1)).

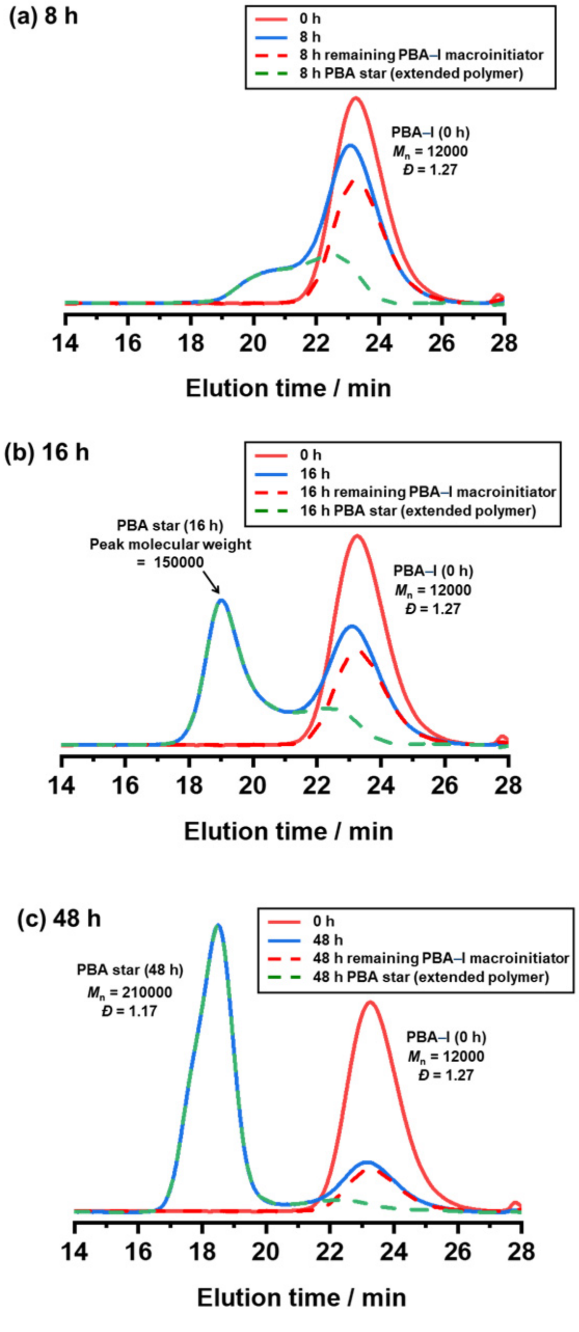

Fig. S2. GPC chromatograms for the synthesis of PBA star polymer for (a) 8 h, (b) 16 h, and (c) 48 h (Table 2, entry 1). The peak areas of the chromatograms of the crude reaction mixture at t = 0 h (red solid line) and at t = 8, 16, or 48 h (blue solid line) are normalized by the monomer conversion. The chromatogram at 8, 16, or 48 h (blue solid line) was resolved into the unreacted PBA–I (macroinitiator) (red dashed line) and the extended polymer (star polymer) (green dashed line). In the peak resolution, the chromatogram of the PBA–I is known and was subtracted from the chromatogram at 8, 16, or 48 h to give the chromatogram of the extended polymer.

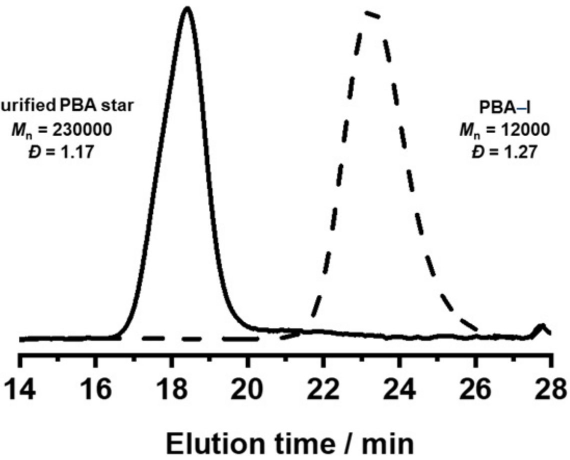

Fig. S3. GPC chromatograms of the purified PBA star polymer (solid line) (Table 2, entry 1, 48 h, and Table 3, entry 1) and the original PBA–I macroinitiator (dashed line).

Synthesis of PBA star polymer using EGDMA (Table 2 (entry 3)).

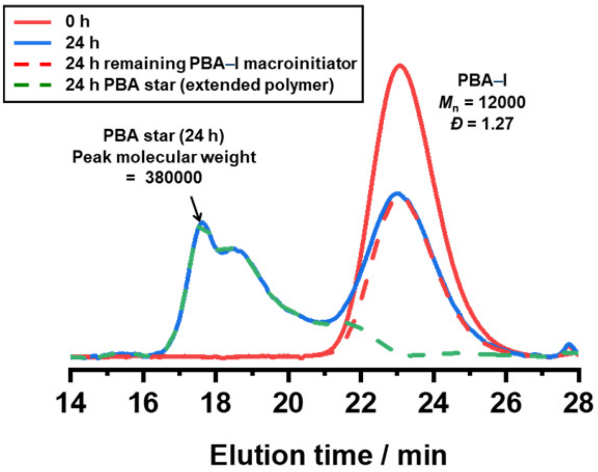

Fig. S4. GPC chromatograms for the synthesis of PBA star polymer for 24 h (Table 2, entry 3). The peak areas of the chromatograms of the crude reaction mixture at t = 0 h (red solid line) and at t = 24 h (blue solid line) are normalized by the monomer conversion. The chromatogram at 24 h (blue solid line) was resolved into the unreacted PBA–I (macroinitiator) (red dashed line) and the extended polymer (star polymer) (green dashed line). In the peak resolution, the chromatogram of the PBA–I is known and was subtracted from the chromatogram at 24 h to give the chromatogram of the extended polymer.

Synthesis of PBA star polymer using a mixture of EGDMA and BMA (Table 2 (entry 4)).

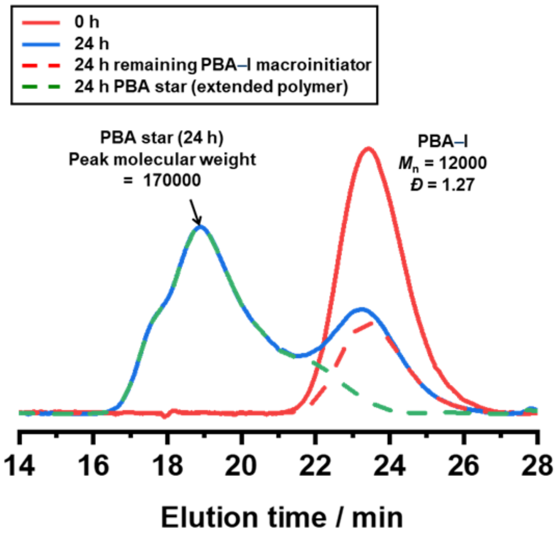

Fig. S5. GPC chromatograms for the synthesis of PBA star polymer for 24 h (Table 2, entry 4). The peak areas of the chromatograms of the crude reaction mixture at t = 0 h (red solid line) and at t = 24 h (blue solid line) are normalized by the monomer conversion. The chromatogram at 24 h (blue solid line) was resolved into the unreacted PBA–I (macroinitiator) (red dashed line) and the extended polymer (star polymer) (green dashed line). In the peak resolution, the chromatogram of the PBA–I is known and was subtracted from the chromatogram at 24 h to give the chromatogram of the extended polymer.

Synthesis of PMMA–PPEGA star polymer (Table 2 (entry 5)).

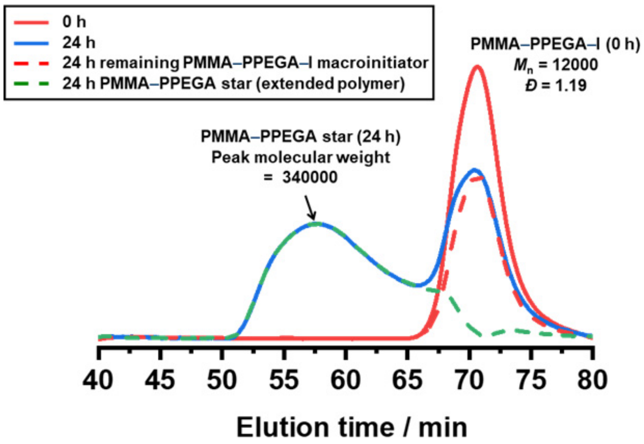

Fig. S6. GPC chromatograms for the synthesis of PMMA–PPEGA star polymer for 24 h (Table 2, entry 5). The peak areas of the chromatograms of the crude reaction mixture at *t* = 0 h (red solid line) and at *t* = 24 h (blue solid line) are normalized by the monomer conversion. The chromatogram at 24 h (blue solid line) was resolved into the unreacted PMMA–PPEGA–I (macroinitiator) (red dashed line) and the extended polymer (star polymer) (green dashed line). In the peak resolution, the chromatogram of the PMMA–PPEGA–I is known and was subtracted from the chromatogram at 24 h to give the chromatogram of the extended polymer.

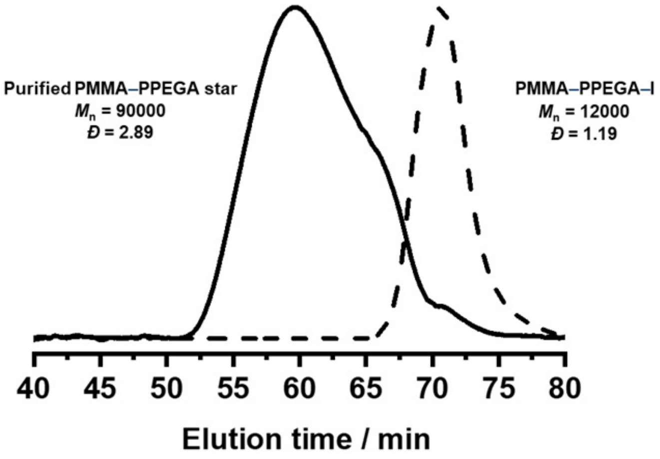

Fig. S7. GPC chromatograms of the purified PMMA–PPEGA star polymer (solid line) (Table 2, entry 5, 24 h, and Table 3, entry 2) and the original PMMA–PPEGA–I macroinitiator (dashed line).

Synthesis of PMMA–PBA star polymer from PMMA–Y (Table 4 (entry 2)).

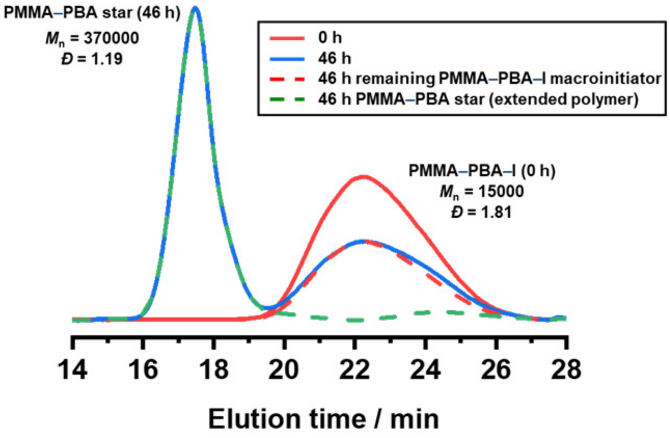

Fig. S8. GPC chromatograms for the synthesis of PMMA–PBA star polymer for 46 h (Table 4, entry 2). The peak areas of the chromatograms of the crude reaction mixture at t = 0 h (red solid line) and at t = 46 h (blue solid line) are normalized by the monomer conversion. The chromatogram at 46 h (blue solid line) was resolved into the unreacted PMMA–PBA–I (macroinitiator) (red dashed line) and the extended polymer (star polymer) (green dashed line). In the peak resolution, the chromatogram of the PMMA–PBA–I is known and was subtracted from the chromatogram at 46 h to give the chromatogram of the extended polymer.

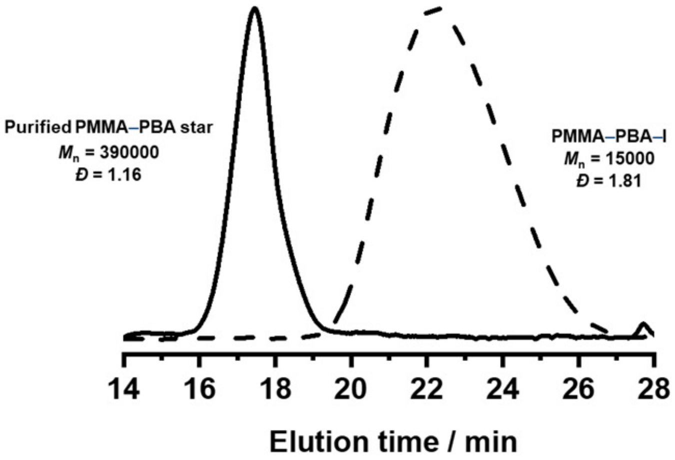

Fig. S9. GPC chromatograms of the purified PMMA–PBA star polymer (solid line) (Table 3, entry 3, and Table 4, entry 2, 46 h) and the original PMMA–PBA–I macroinitiator (dashed line).

One-pot synthesis of PBA star polymer (Table 5 (entry 1-2)).

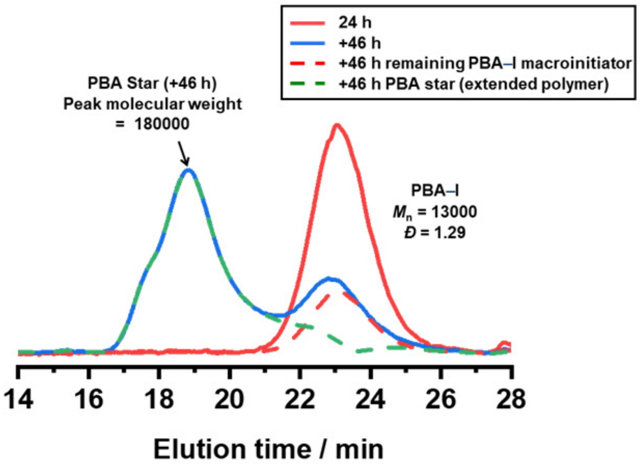

Fig. S10. GPC chromatograms for the one-pot synthesis of PBA star polymer for +46 h (70 h in total) (Table 5, entry 1-2). The peak areas of the chromatograms of the crude reaction mixture at t = 0 h (red solid line) and at t = +46 h (blue solid line) are normalized by the monomer conversion. The chromatogram at +46 h (blue solid line) was resolved into the unreacted PBA–I (macroinitiator) (red dashed line) and the extended polymer (star polymer) (green dashed line). In the peak resolution, the chromatogram of the PBA–I is known and was subtracted from the chromatogram at +46 h to give the chromatogram of the extended polymer.

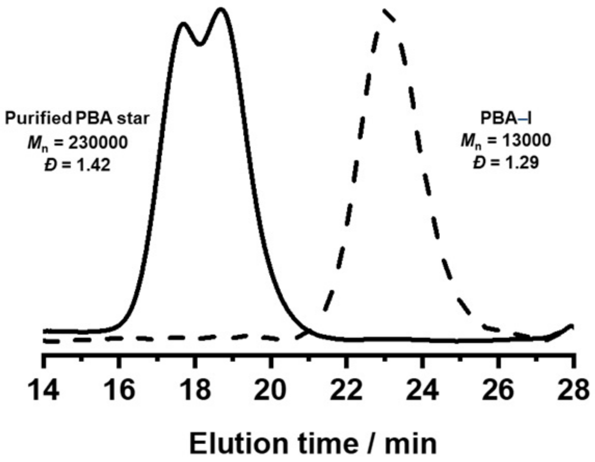

Fig. S11. GPC chromatograms of purified PBA star polymer (one-pot) (solid line) (Table 3, entry 4, and Table 5, entry 1-2, +46 h) and the original PBA–I macroinitiator (dashed line). For the purified PBA star polymer, a part of the star polymers with relatively low molecular weights were removed in the purification, and hence the shoulder peak appeared at approximately 17.5 min in Fig. S11 is more obvious in Fig. S10.