Electronic Supplementary Information (ESI)

One-Pot Synthesis of Core-Crosslinked Star Polymers from Poly(methyl methacrylate) with Unsaturated Chain End and Encapsulation of UV Absorbing Molecule

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1. Experimental Section

Materials. Butyl acrylate (BA) (>99%, Tokyo Chemical Industry (TCI), Japan), styrene (St) (>99%, TCI), 2-methoxyethyl acrylate (MEA) (>98%, TCI), tetrahydrofurfuryl acrylate (THFA) (>98%, TCI), poly(ethylene glycol) methyl ether acrylate (PEGA) (average molecular weight = 480) (98%, Sigma-Aldrich, USA), di(ethylene glycol) diacrylate (DGDA) (75%, Sigma-Aldrich), 2-iodo-2-methylpropionitrile (CP–I) (>95%, TCI), tetrabutylammonium iodide (BNI) (>98%, TCI), 2-(2-hydroxy-5-methylphenyl)benzotriazole (>97%, Sigma), poly(methyl methacrylate) (PMMA) (M_n = 26000 and $Đ$ = 1.02, Agilent, USA), PMMA (M_n = 51000 and $Đ$ = 1.88, Mitsubishi Chemical, Japan), tetrahydrofuran (THF) (>99.5%, VWR Chemicals, USA),

N,*N*-dimethylformamide (DMF) (>99.5%, Kanto Chemical, Japan), diethylene glycol dimethyl ether (diglyme) (>99%, TCI), butyl acetate (BuAc) (>99%, TCI), 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. PMMA bearing an unsaturated C=C group at the chain end (PMMA–Y with Y = $CH_2CH(═CH_2)COOCH_3$) was synthesized, as reported previously.[1]

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 ºC). 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). Sample detection was conducted using a Shimadzu differential refractometer RID-20A for all GPC measurements. The column systems were calibrated with standard 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 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*) of the purified star polymers (**Table 3**) was 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 = 26000 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).

The transmission electron microscopy (TEM) images were obtained with a JEOL TEM-1400 transmission electron microscope operated at 100 kV. The TEM grid was carbon-coated on 200 mesh (copper (Cu)) (Ted Pella, Redding, US).

The UV measurement was carried out on a Shimadzu UV-3600 (Kyoto, Japan) at room temperature. For liquids, quartz cuvettes with a path length of 1 cm were used.

Synthesis of PMMA–P_A–I block copolymers from PMMA–Y. In a typical run, a mixture of BA (3.00 g, 200 equiv), PMMA–Y (M_n = 3900 and $Đ$ = 1.67, 456 mg, 1 equiv), CP–I (22.8 mg,

1 equiv), and BNI (346 mg, 8 equiv) was heated in a Schlenk flask at 110 °C under argon atmosphere with magnetic stirring for 24 h (**Table 1** (entry 1)). The mixture was cooled to room temperature, diluted with THF (3 mL), reprecipitated from a methanol/water (8/2 v/v) mixed solvent (non-solvent) (250 mL) twice, and dried in vacuo to yield a purified PMMA–PBA–I (M_n = 22000 and $Đ$ = 2.28 after purification).

Synthesis of PMMA–P$_A$ star polymer. In a typical run, a mixture of DGDA (171 mg, 40 equiv), PMMA–PBA–I (M_n = 22000 and $Đ$ = 2.28, 400 mg, 1 equiv), BNI (57.1 mg, 8 equiv), and BuAc (1.47 g, 70 wt%) was heated in a Schlenk flask at 110 °C under argon atmosphere with magnetic stirring for 24 h (**Table 2** (entry 1)). 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 mixture was cooled to room temperature, diluted with THF (2 mL), reprecipitated from methanol (non-solvent) (50 mL) twice, and dried in vacuo to yield a purified PMMA–PBA star.

One-pot synthesis of PMMA–P$_A$ star from PMMA–Y. In a typical run, a mixture of BA (600 mg, 200 equiv), CP–I (4.56 mg, 1 equiv), PMMA–Y (M_n = 3900 and $Đ$ = 1.67, 91.3 mg, 1 equiv.), and BNI (69.2 mg, 8 equiv) was heated in a Schlenk flask at 110 °C under argon atmosphere with magnetic stirring for 24 h (**Table 4** (entry 1-1)). After 24 h, a mixture (purged with argon) of DGDA (201 mg, 40 equiv) and BuAc (1.87 g, 70 wt% of BuAc and 30 wt% of the initial BA and added DGDA in total) was added to the reaction mixture and was heated at 110 °C under argon atmosphere with magnetic stirring for another 48 h (in total 72 h) (**Table 4** (entry 1-2)). 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 mixture was cooled to room temperature, diluted with THF (2 mL), reprecipitated from methanol (non-solvent) (50 mL) twice, and dried in vacuo to yield a purified star polymer.

Encapsulation of UV absorber (UVA) in PMMA–PTHFA star polymer. The purified PMMA–PTHFA star polymer (**Table 5** (entry 1-2)) (1.96 g) was dissolved in THF (13.9 g) at 50 ^{o}C, to which 2-(2-hydroxy-5-methylphenyl)benzotriazole (UV absorber (UVA)) was added until the UVA (3.50 g) was saturated in the solution. The solution was stirred for 2 h to allow the diffusion of UVA into the star polymer. To this solution, hexane, which is a non-solvent for the star polymer, was added dropwise to slowly precipitate the UVA-encapsulated star polymer. Hexane is a poor solvent of the UVA but still had a sufficient solubility of the UVA for this separation.

Preparation of PMMA films with and without UVA (Table 6). Three stock solutions were prepared by dissolving PMMA (M_n = 51000 and $Đ$ = 1.88, Mitsubishi Chemical, Japan), non-encapsulated UVA, and UVA-encapsulated PMMA–PTHFA star polymer (**Table 5** (entry 1-2)) in BuAc. The PMMA solution was used to prepare a PMMA film without UVA (**Table 6** (entry 1)). The PMMA and non-encapsulated UVA solutions were combined to prepare a PMMA film with non-encapsulated UVA (**Table 6** (entry 2)). The PMMA and encapsulated UVA solutions were combined to prepare a PMMA film with encapsulated UVA (**Table 6** (entry 3)). The solutions were casted in moulds and dried at room temperature for 12 h, giving approximately 100 μm thick films.

2. ^{1}H NMR spectra

^{1}H NMR analysis (**Fig. S1**) showed that, after the polymerization, the unsaturated chain end protons (*a* and *b*) of PMMA nearly completely disappeared. The ^{1}H NMR analysis also showed that the generated PBA–Y with an unsaturated chain end (P_A–Y shown in **Scheme 1**) (protons *c* and *d*)[1] was also largely consumed as a macromonomer and incorporated in the PMMA–PBA block copolymer.

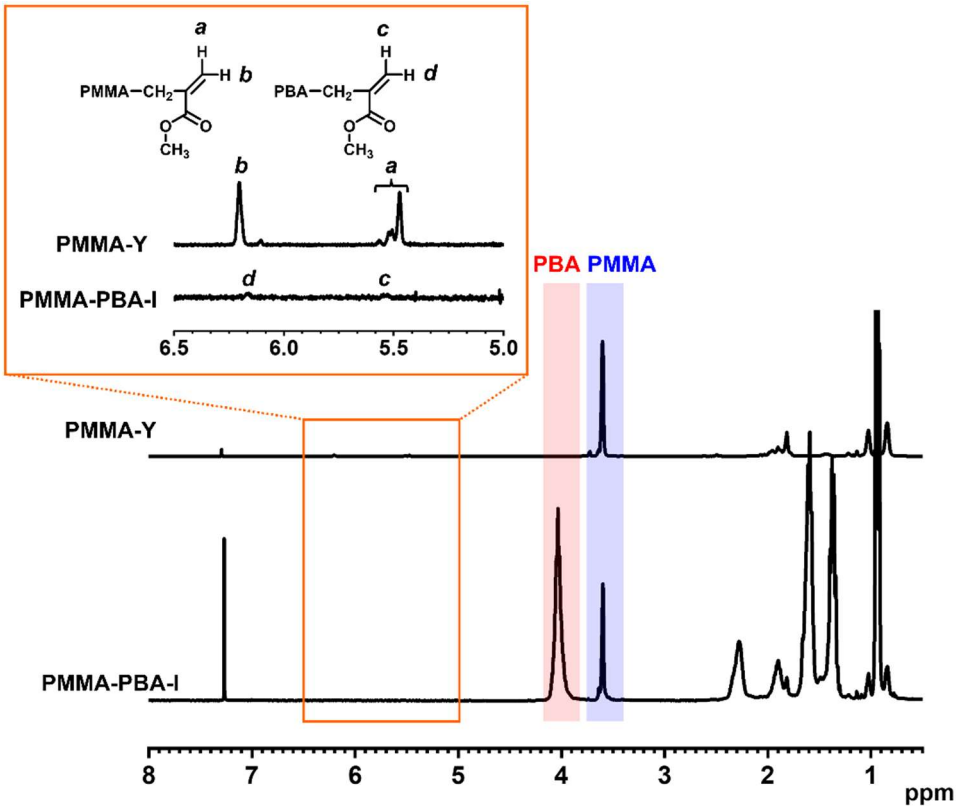

Fig. S1. ^{1}H NMR spectra ($CDCl_3$) of the original PMMA–Y (M_n = 3900) and the obtained PMMA–PBA–I macroinitiator after purification (**Table 1** (entry 1)).

2. Peak resolution of GPC chromatograms and TEM image

Two-pot synthesis of PMMA–PBA star polymer from PMMA–Y (M_n = 3900) (Table 2 (entry 1)).

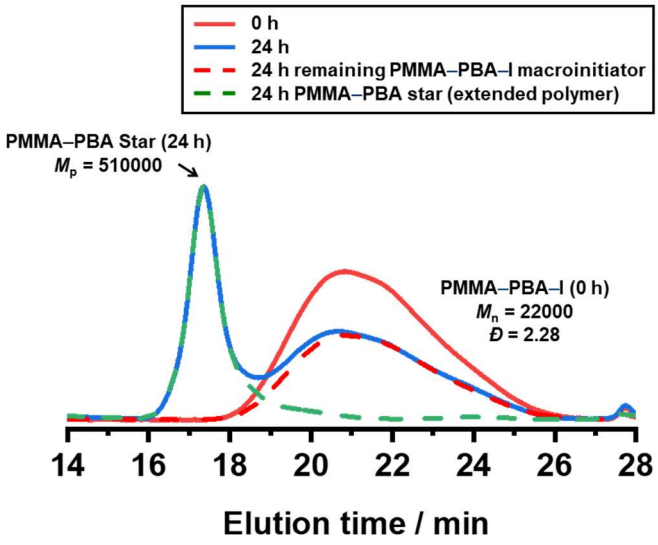

Fig. S2. GPC chromatograms for the synthesis of PMMA–PBA star polymer for 24 h (**Table 2** (entry 1)). The peak areas of the chromatograms of the crude reaction mixture at t = 0 h (red solid line) and at t = 24 h (blue solid line) are normalized by the monomer conversion. The chromatogram at 24 h (blue solid line) was resolved into the unreacted PMMA–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 24 h to give the chromatogram of the extended polymer.

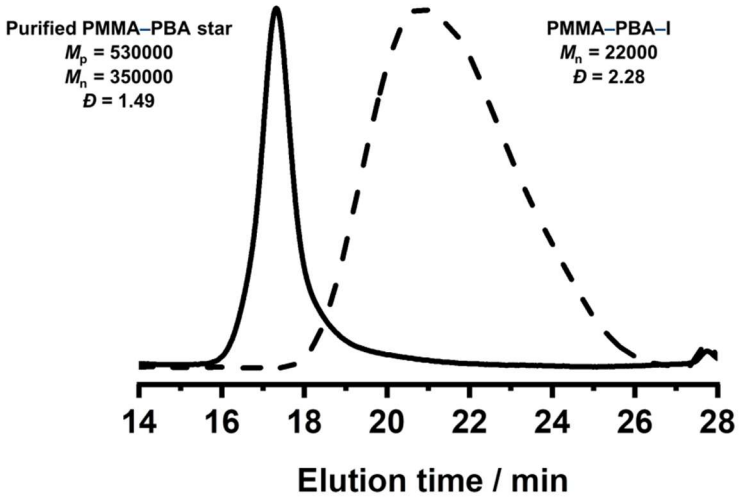

Fig. S3. GPC chromatograms of the purified PMMA–PBA star polymer (solid line) (**Table 2** (entry 1)), and the original PMMA–PBA–I macroinitiator (dashed line) (**Table 1** (entry 1)).

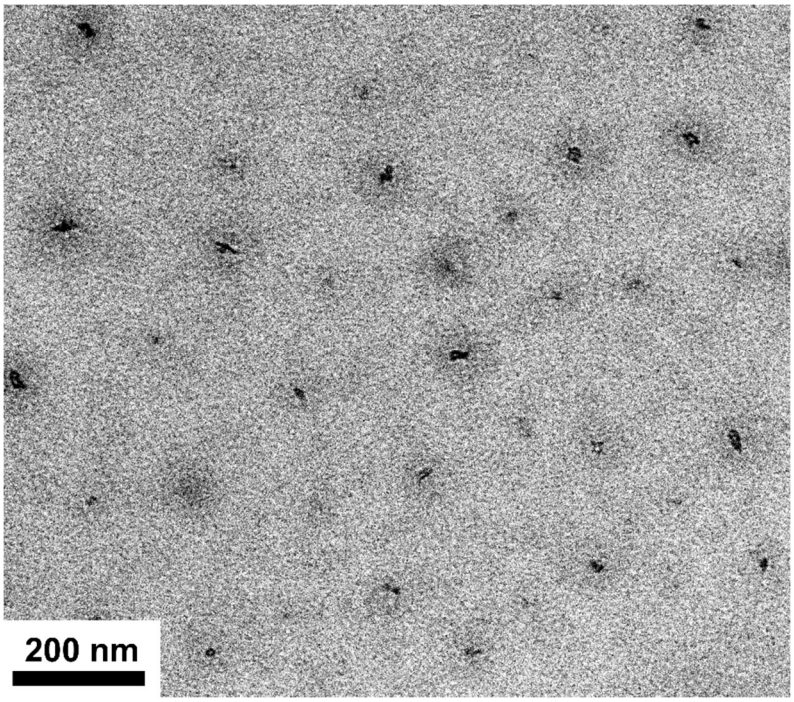

Fig. S4. TEM image of the purified PMMA–PBA star polymer (solid line) (**Table 2** (entry 1)).

Two-pot synthesis of PMMA–PBA star polymer from PMMA–Y (M_n = 12000) (Table 2 (entry 2)).

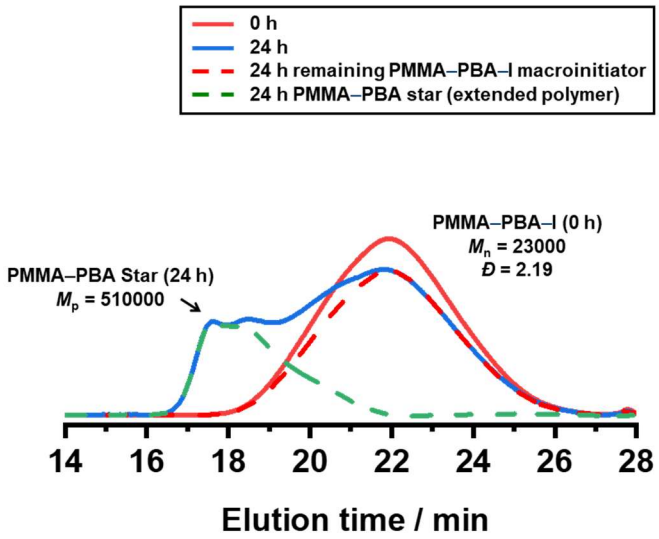

Fig. S5. GPC chromatograms for the synthesis of PMMA–PBA star polymer for 24 h (**Table 2** (entry 2)). The peak areas of the chromatograms of the crude reaction mixture at t = 0 h (red solid line) and at t = 24 h (blue solid line) are normalized by the monomer conversion. The chromatogram at 24 h (blue solid line) was resolved into the unreacted PMMA–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 24 h to give the chromatogram of the extended polymer.

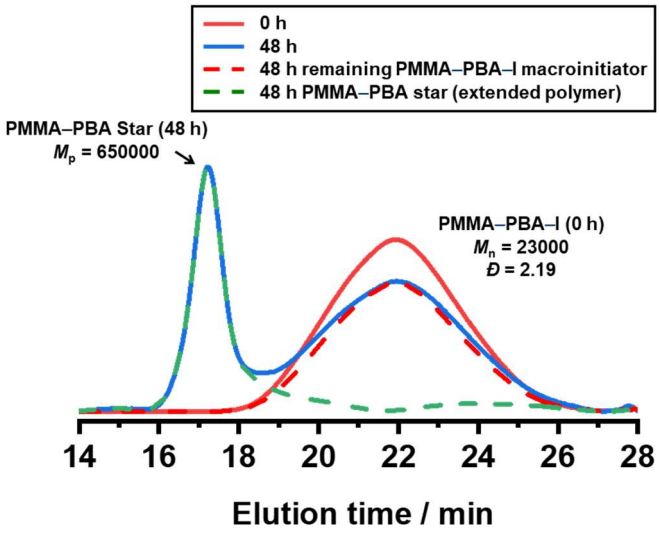

Fig. S6. GPC chromatograms for the synthesis of PMMA–PBA star polymer for 48 h (**Table 2** (entry 2)). The peak areas of the chromatograms of the crude reaction mixture at t = 0 h (red solid line) and at t = 48 h (blue solid line) are normalized by the monomer conversion. The chromatogram at 48 h (blue 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 48 h to give the chromatogram of the extended polymer.

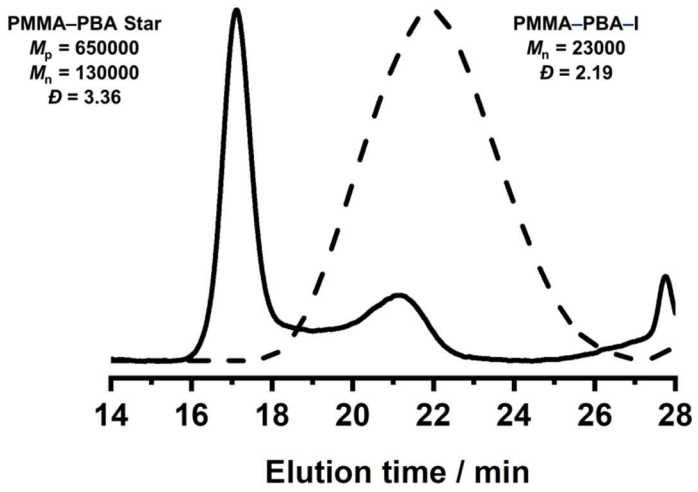

Fig. S7. GPC chromatograms of the purified PMMA–PBA star polymer (solid line) (**Table 2** (entry 2)), and the original PMMA–PBA–I macroinitiator (dashed line) (**Table 1** (entry 2)).

Two-pot synthesis of PMMA–PMEA star polymer from PMMA–Y (M_n = 3900) (Table 2 (entry 3)).

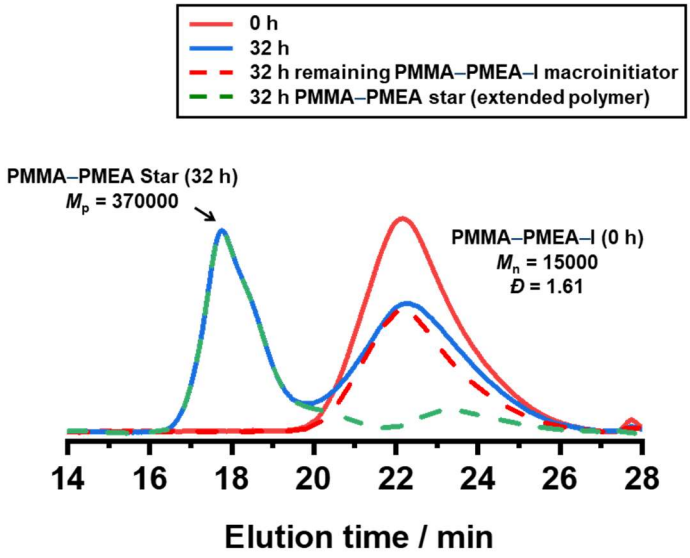

Fig. S8. GPC chromatograms for the synthesis of PMMA–PMEA star polymer for 32 h (**Table 2** (entry 3)). The peak areas of the chromatograms of the crude reaction mixture at t = 0 h (red solid line) and at t = 32 h (blue solid line) are normalized by the monomer conversion. The chromatogram at 32 h (blue solid line) was resolved into the unreacted PMMA–PMEA–I (macroinitiator) (red dashed line) and the extended polymer (star polymer) (green dashed line). In the peak resolution, the chromatogram of the PMMA–PMEA–I is known and was subtracted from the chromatogram at 32 h to give the chromatogram of the extended polymer.

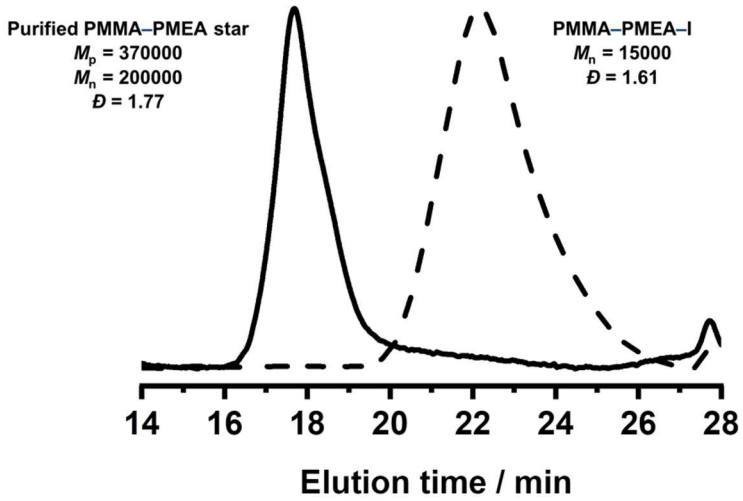

Fig. S9. GPC chromatograms of the purified PMMA–PMEA star polymer (solid line) (**Table 2** (entry 3)), and the original PMMA–PMEA–I macroinitiator (dashed line) (**Table 1** (entry 3)).

Two-pot synthesis of PMMA–PSt star polymer from PMMA–Y (M_n = 3900) (Table 2 (entry 4)).

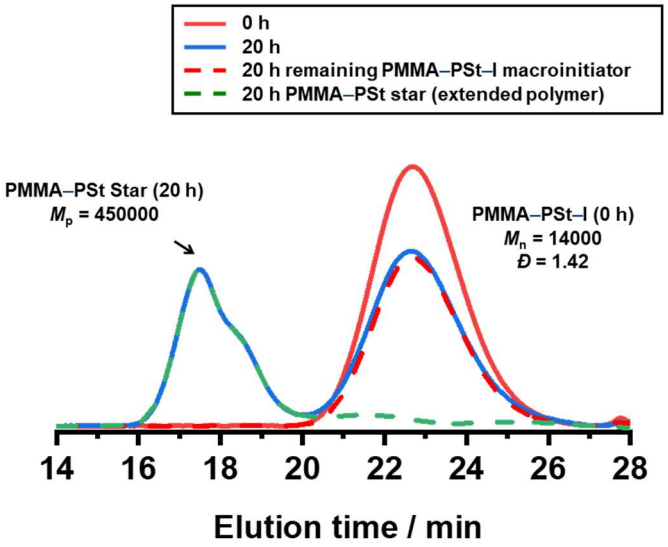

Fig. S10. GPC chromatograms for the synthesis of PMMA–PSt star polymer for 20 h (**Table 2** (entry 4)). The peak areas of the chromatograms of the crude reaction mixture at t = 0 h (red solid line) and at t = 20 h (blue solid line) are normalized by the monomer conversion. The chromatogram at 20 h (blue solid line) was resolved into the unreacted PMMA–PSt–I (macroinitiator) (red dashed line) and the extended polymer (star polymer) (green dashed line). In the peak resolution, the chromatogram of the PMMA–PSt–I is known and was subtracted from the chromatogram at 20 h to give the chromatogram of the extended polymer.

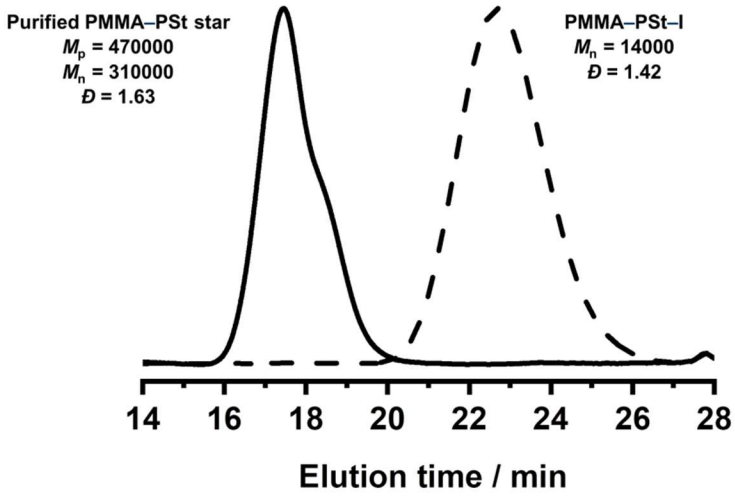

Fig. S11. GPC chromatograms of the purified PMMA–PSt star polymer (solid line) (**Table 2** (entry 4)), and the original PMMA–PSt–I macroinitiator (dashed line) (**Table 1** (entry 4)).

Two-pot synthesis of PMMA–PTHFA star polymer from PMMA–Y (M_n = 3900) (Table 2 (entry 5)).

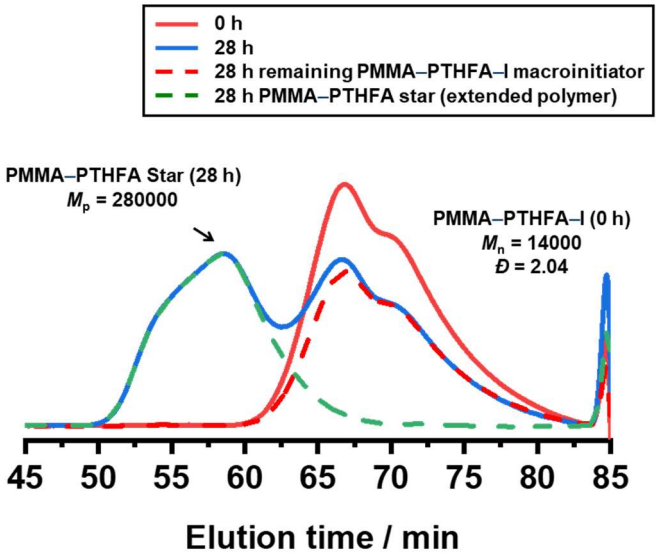

Fig. S12. GPC chromatograms for the synthesis of PMMA–PTHFA star polymer for 28 h (**Table 2** (entry 5)). The peak areas of the chromatograms of the crude reaction mixture at t = 0 h (red solid line) and at t = 28 h (blue solid line) are normalized by the monomer conversion. The chromatogram at 28 h (blue solid line) was resolved into the unreacted PMMA–PTHFA–I (macroinitiator) (red dashed line) and the extended polymer (star polymer) (green dashed line). In the peak resolution, the chromatogram of the PMMA–PTHFA–I is known and was subtracted from the chromatogram at 28 h to give the chromatogram of the extended polymer.

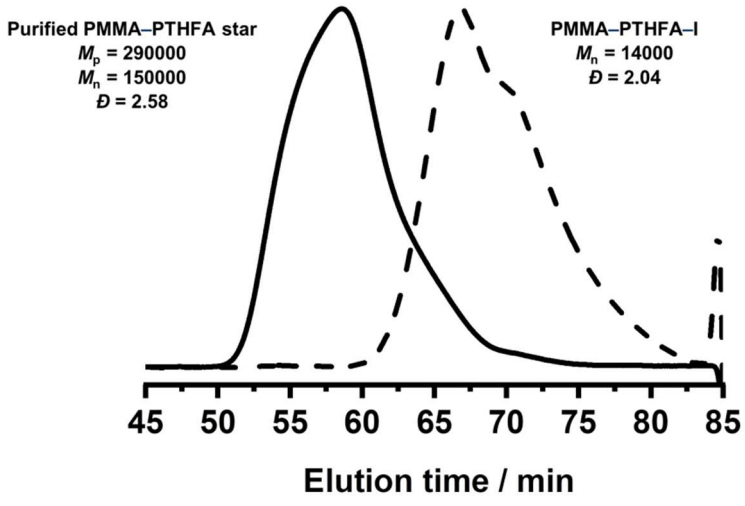

Fig. S13. GPC chromatograms of the purified PMMA–PTHFA star polymer (solid line) (**Table 2** (entry 5)), and the original PMMA–PTHFA–I macroinitiator (dashed line) (**Table 1** (entry 5)).

Two-pot synthesis of PMMA–PPEGA star polymer from PMMA–Y (M_n = 3900) (Table 2 (entry 6)).

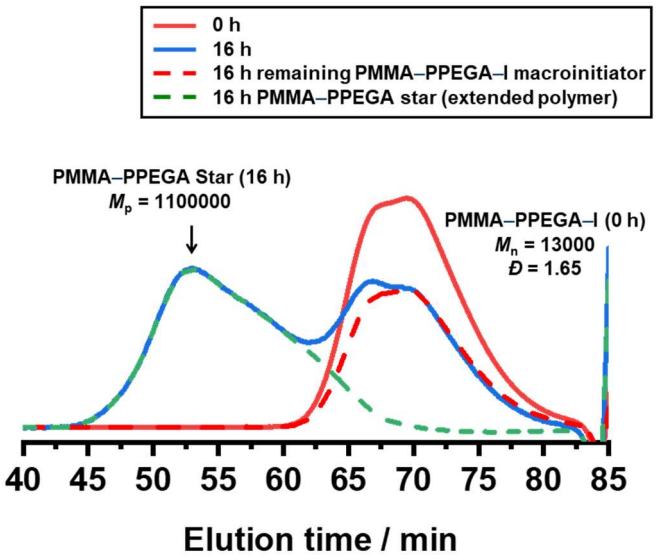

Fig. S14. GPC chromatograms for the synthesis of PMMA–PPEGA star polymer for 16 h (**Table 2** (entry 6)). The peak areas of the chromatograms of the crude reaction mixture at t = 0 h (red solid line) and at t = 16 h (blue solid line) are normalized by the monomer conversion. The chromatogram at 16 h (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 16 h to give the chromatogram of the extended polymer.

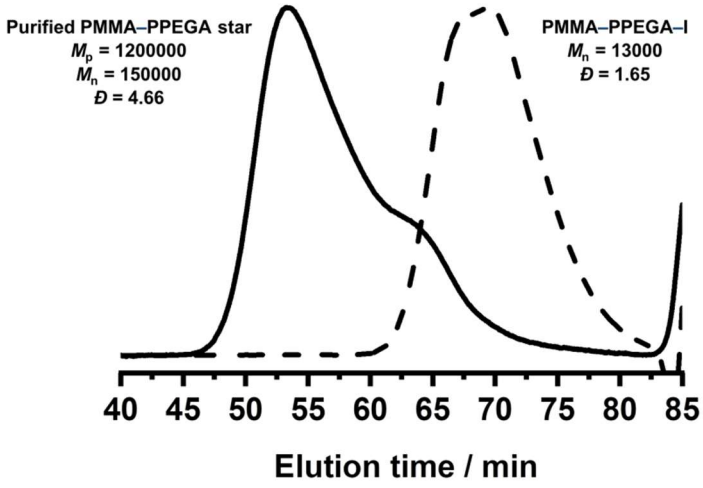

Fig. S15. GPC chromatograms of the purified PMMA–PPEGA star polymer (solid line) (**Table 2** (entry 6)), and the original PMMA–PPEGA–I macroinitiator (dashed line) (**Table 1** (entry 6)).

DLS size distribution (by intensity) of the various isolated star polymers (Table 2 (entries 3-6))

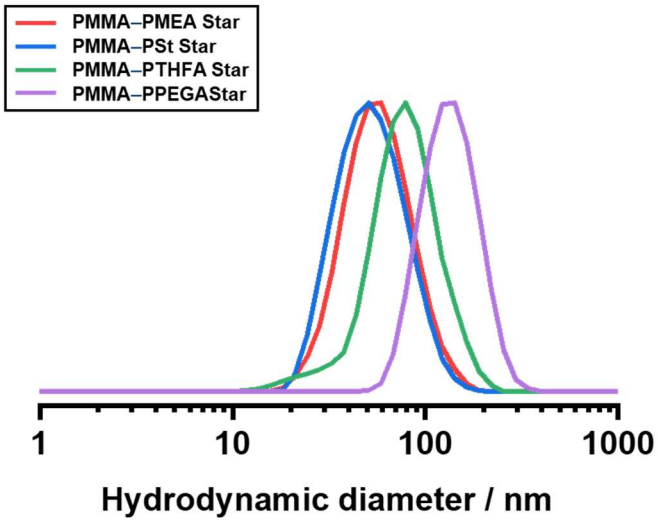

Fig. S16. DLS size distribution curves (by intensity) of the purified PMMA–PMEA star (red line) (**Table 2** (entry 3)), PMMA–PSt star (blue line) (**Table 2** (entry 4)), PMMA–PTHFA star (green line) (**Table 2** (entry 5)), and PMMA–PPEGA star (purple line) (**Table 2** (entry 6)).

One-pot synthesis of PMMA–PBA star polymer from PMMA–Y (M_n = 3900) (Table 4 (entry 1-2)).

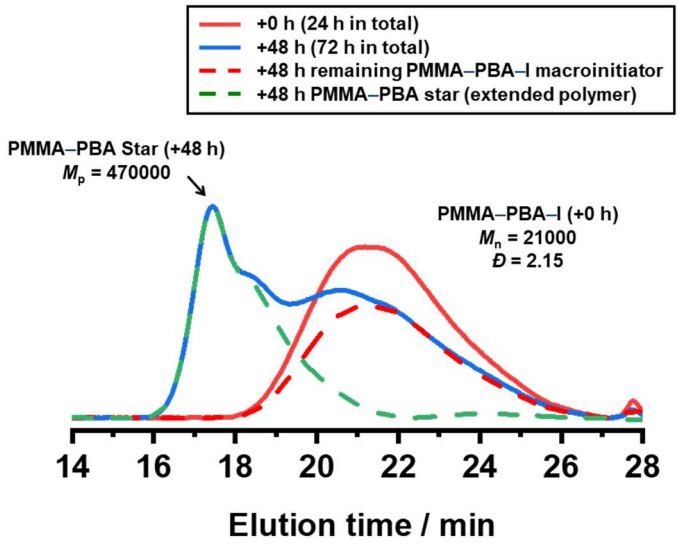

Fig. S17. GPC chromatograms for the one-pot synthesis of PMMA–PBA star polymer for +48 h (72 h in total) (**Table 4** (entry 1-2)). The peak areas of the chromatograms of the crude reaction mixture at t = +0 h (24 h in total) (red solid line) and at t = +48 h (72 h in total) (blue solid line) are normalized by the monomer conversion. The chromatogram at +48 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 +48 h to give the chromatogram of the extended polymer.

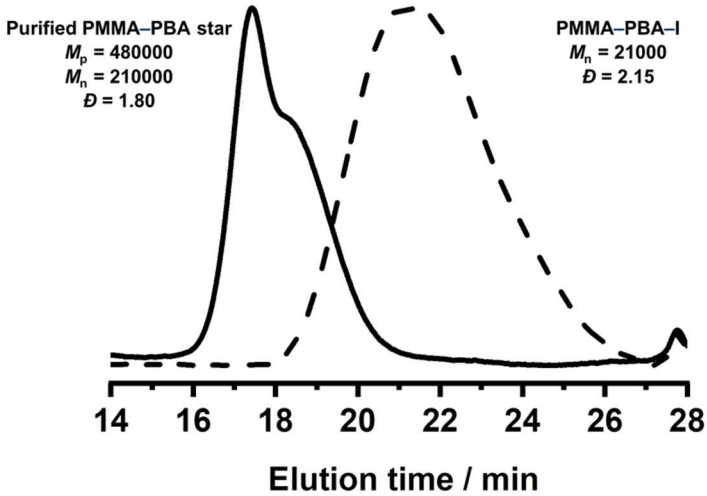

Fig. S18. GPC chromatograms of the purified PMMA–PBA star polymer (solid line) (**Table 4** (entry 1-2)), and the original PMMA–PBA–I macroinitiator at +0 h (24 h in total) (dashed line) (**Table 4** (entry 1-1)).

One-pot synthesis of PMMA–PBA star polymer from PMMA–Y (M_n = 3900) (Table 4 (entry 2-2)).

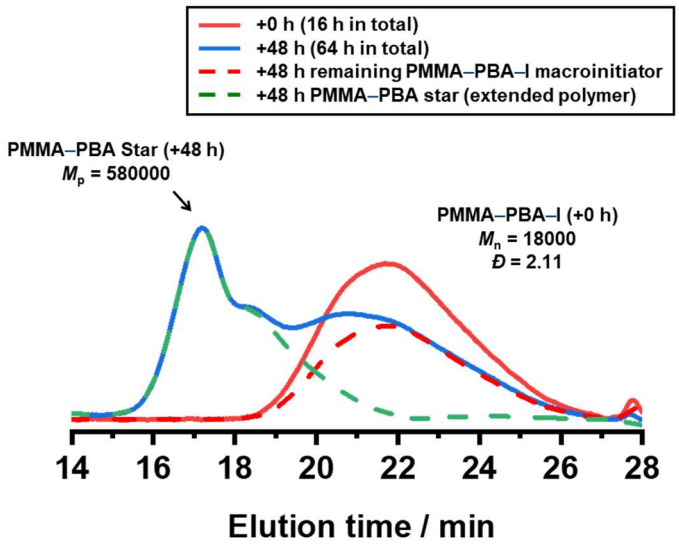

Fig. S19. GPC chromatograms for the one-pot synthesis of PMMA–PBA star polymer for +48 h (64 h in total) (**Table 4** (entry 2-2)). The peak areas of the chromatograms of the crude reaction mixture at t = +0 h (16 h in total) (red solid line) and at t = +48 h (64 h in total) (blue solid line) are normalized by the monomer conversion. The chromatogram at +48 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 +48 h to give the chromatogram of the extended polymer.

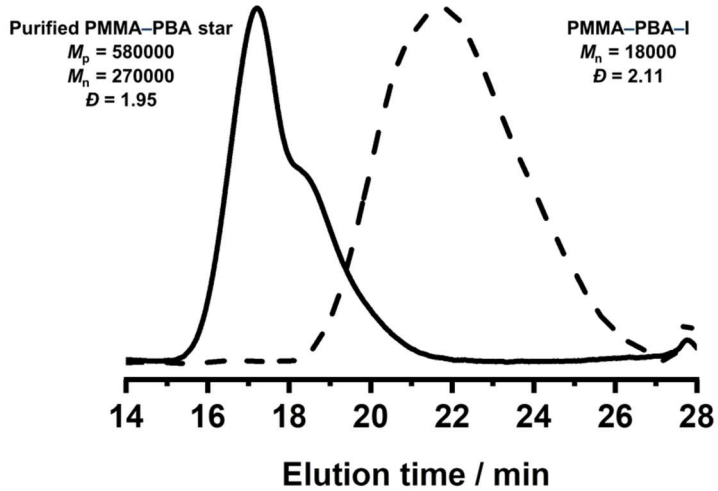

Fig. S20. GPC chromatograms of the purified PMMA–PBA star polymer (solid line) (**Table 4** (entry 2-2)), and the original PMMA–PBA–I macroinitiator at +0 h (16 h in total) (dashed line) (**Table 4** (entry 2-1)).

One-pot synthesis of PMMA–PTHFA star polymer from PMMA–Y (M_n = 3900) (Table 5 (entry 1-2)).

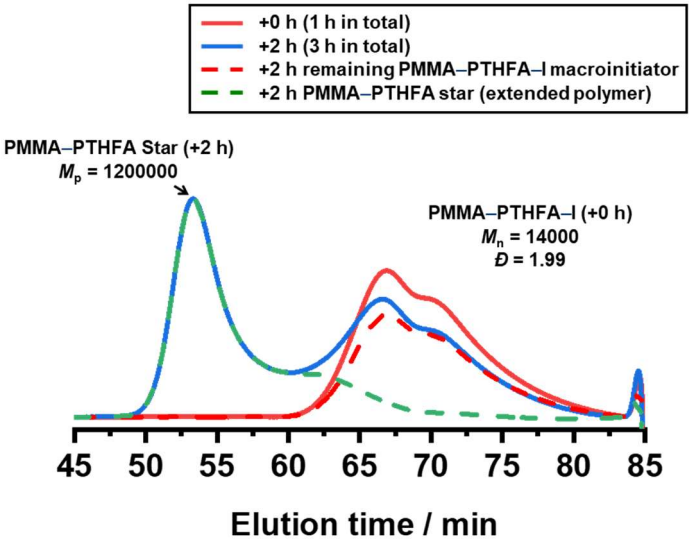

Fig. S21. GPC chromatograms for the one-pot synthesis of PMMA–PTHFA star polymer for +2 h (3 h in total) (**Table 5** (entry 1-2)). The peak areas of the chromatograms of the crude reaction mixture at t = +0 h (1 h in total) (red solid line) and at t = +2 h (3 h in total) (blue solid line) are normalized by the monomer conversion. The chromatogram at +2 h (blue solid line) was resolved into the unreacted PMMA–PTHFA–I (macroinitiator) (red dashed line) and the extended polymer (star polymer) (green dashed line). In the peak resolution, the chromatogram of the PMMA–PTHFA–I is known and was subtracted from the chromatogram at +2 h to give the chromatogram of the extended polymer.

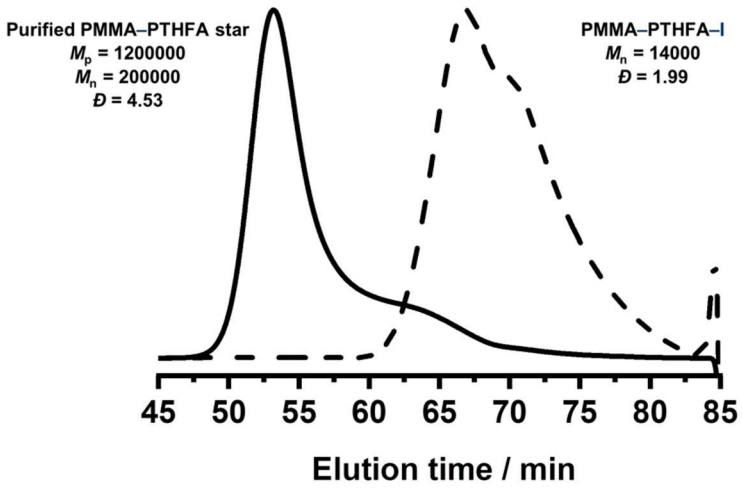

Fig. S22. GPC chromatograms of the purified PMMA–PTHFA star polymer (solid line) (**Table 5** (entry 1-2)), and the original PMMA–PTHFA–I macroinitiator at +0 h (1 h in total) (dashed line) (**Table 5** (entry 1-1)).

3. Encapsulation of UV absorber (UVA) in PMMA–PTHFA star polymers

Table S1. Preparation of UVA encapsulated PMMA–PTHFA star polymers at 50 °C.

Entry	Star polymer	Mass of star polymer (g)	Mass of THF (g)	Mass of UVA (g)	Mass of star polymer after encapsulation (g)	Encapsulation efficiency[c] (wt%)
1	PMMA–PTHFA (one-pot)[a]	1.96	13.9	3.50	3.25	40
2	PMMA–PTHFA (two-pot)[b]	0.478	2.40	0.502	0.548	13

[a] Purified PMMA–PTHFA (M_n = 200000, $Đ$ = 4.53) from one-pot synthesis (**Table 5** (entry 1-2)). [b]Purified PMMA–PTHFA (M_n = 150000, $Đ$ = 2.58) from two-pot synthesis (**Table 2** (entry 5)). [c] Encapsulation efficiency (%) = [(mass of star polymer after encapsulation) – (mass of star polymer before encapsulation)]/(mass of star polymer after encapsulation).

4. Determination of the amount of UV absorber (UVA) from films

The PMMA films with non-encapsulated UVA (**Table 6** (entry 2)) and encapsulated UVA (**Table 6** (entry 3)) were heated in an oven at 150 ºC for 3 h. After cooling to room temperature, the films were immersed in methanol for 30 min to dissolve the leached UVA in methanol. The absorbance of the UVA present in the methanol solution was determined at 336 nm using UV absorption spectroscopy (**Fig. S23**). From the absorbance, we determined the amount of the leached UVA and hence the fraction of the leached UVA from the originally embedded UVA (**Table S2**). The same procedure was conducted repeatedly in three cycles (**Table S2**).

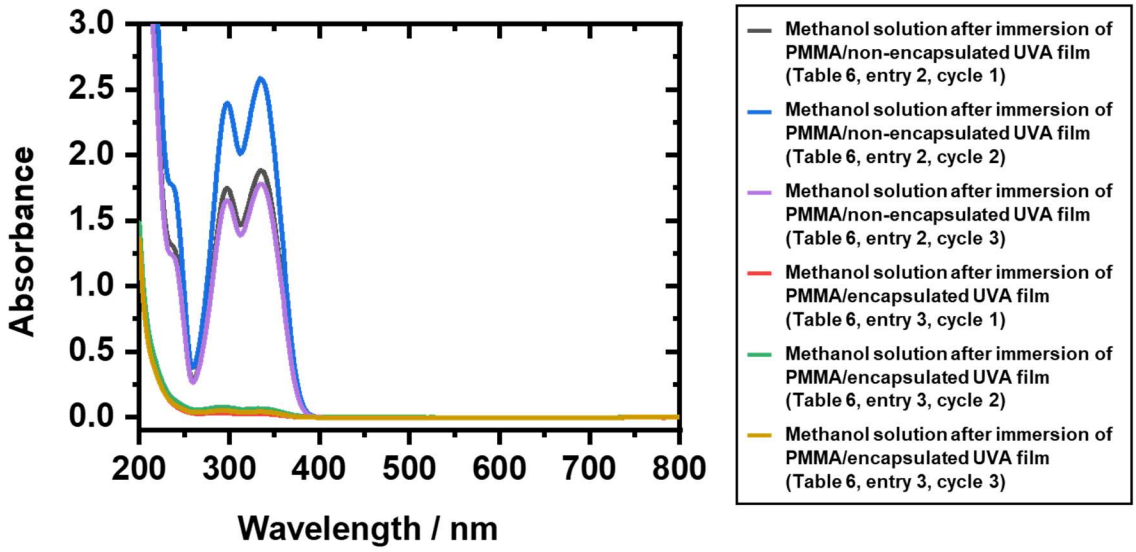

Fig. S23. Absorption spectra of the UVA in the methanol solution after immersion of PMMA films with non-encapsulated UVA (**Table 6** (entry 2)) and encapsulated UVA (**Table 6** (entry 3)) in three heating cycles. The film was heated at 150 ºC for 3 h for each cycle. The absorption spectra are normalized in 5 g methanol solution after immersion of 100 mg of film.

Table S2. Amount of UVA leached from films.

Entry	Star polymer	Cycle	Normalized absorbance at 336 nm in 5 g methanol solution after immersion of 100 mg of film	Amount of UVA leached from 100 mg of film (i.e., embedded 7 mg of UVA)	Fraction of leached UVA from original amount of UVA (%)
1	PMMA film with non-encapsulated UVA (**Table 6** (entry 2))	1	1.881	0.1775	2.54
		2	2.584	0.2438	3.48
		3	1.781	0.1681	2.40
		Total	NA	0.5894	8.42
2	PMMA film with encapsulated UVA (**Table 6** (entry 3))	1	0.028	0.0026	0.04
		2	0.066	0.0062	0.09
		3	0.043	0.0041	0.06
		Total	NA	0.0129	0.19

Reference

1. J. J. Chang, L. Xiao, C. -G. Wang, H. Niino, S. Chatani, A. Goto, *Polym. Chem.*, 2018, **9**, 4848-4855.